Assessing the Fate and Significance of Microconstituents and Pathogens in Sewage Biosolids

Update of the 2001 WEAO Report on Fate and Significance

Water Environment Association of Ontario

Final Report
May 2010

FOREWORD

This literature review was prepared for the Water Environment Association of Ontario by Hydromantis, Dr. Mel Webber of Webber Environmental, and Dr. Wayne Parker of the University of Waterloo with the support of a Technical Steering Committee.

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A number of experts across North America were asked to review the document

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The report has been supported by funds from the Ontario Ministry of the Environment. The review represents an update of the scientific data available since the report of 2001 (Fate and Significance of Contaminants in Sewage Biosolids Applied to Agricultural Land Through Literature Review and Consultation with Stakeholder Groups).

Every attempt has been made to access the latest scientific data: to review and synthesize; and to provide direction as to new substances of interest and areas for future research.

EXECUTIVE SUMMARY

ES.1 Introduction

The application of wastewater biosolids to agricultural land is an important management option in Ontario. Although the considerable fertilizer and soil conditioning values of biosolids are well established, concerns related to environmental and health issues of land-applied biosolids have been expressed by citizens and non-governmental organizations.

In 2001, the Water Environment Association of Ontario (WEAO) issued a report entitled "Fate and Significance of Contaminants in Sewage Biosolids Applied to Agricultural Land Through Literature Review and Consultation with Stakeholder Groups". The report summarized the state of knowledge of contaminants in wastewater biosolids at that time.

Based on the findings of and agreement from the Technical Steering Committee of the first review, the contaminants were allocated to two groups: Group I - no additional studies recommended; and Group II – additional studies required. The Group I contaminants included: regulated metals, volatile organic contaminants (VOCs), polychlorinated biphenyls (PCBs), polynuclear aromatic hydrocarbons (PAHs), pesticides, linear alkylbenzene sulphonate (LAS) and alkylphenol (APs) surfactants, dioxins and furans (PCDD/Fs), radionuclides, nitrogen and phosphorous. The Group II contaminants included: unregulated metals, pathogens, estrogenic hormones and pharmaceuticals.

Since the 2001 WEAO report was issued, considerable Ontario, national and international research has been conducted on land application of sewage biosolids and in particular on pharmaceuticals and personal care products (PPCPs) and pathogens. Moreover, significant advances in analytical protocols have occurred, enabling researchers to analyze biosolids and sludges for contaminants at concentrations that were not previously possible.

WEAO decided that there is a need to update the 2001 report to reflect recent research findings; and to determine if a new focus is required for future research. This report responds to that need.

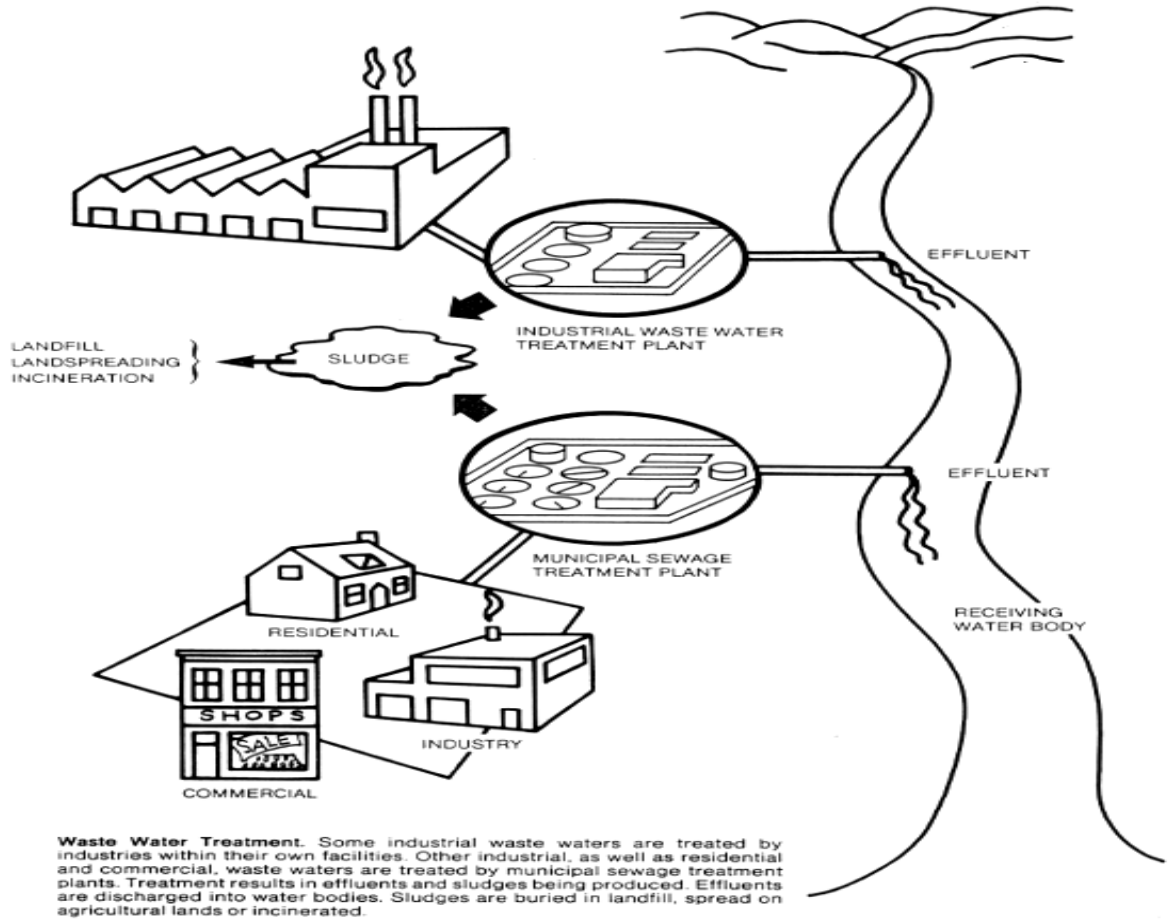
A key fact that the Ontario public should be aware of, is that there are different regulatory regimes in Ontario, the other provinces and the United States. This becomes important when reporting and trying to compare biosolids related activities between Canada and the United States. For instance, reference to Class A and Class B biosolids apply to the United States, not Ontario. Reference to Group I and Group II substances are the result of the findings of the first review and have been used only to categorize substances for future research.

This report focuses on the results of studies of the Group II contaminants - in particular PPCPs - identified in the previous WEAO report as requiring additional research. However, it also includes recent results of Group I contaminants and some contaminants not identified in the previous WEAO report.

The Technical Steering Committee for this review felt it important to provide context to assist the public in better understanding the role of each of us in contributing to the content of biosolids, and to provide some relevent examples of our use of substances versus the levels of those substances found in biosolids.

It is important to understand how the products we use in our everyday lives (at home, at work, in industry) move into the sewers and wastewater treatment plants, are treated and the end products discharged as liquid effluents to surface waters, or as solids for land application, incineration or landfilling.

There are a wide variety of compounds and chemicals found in the substances we consume or use everyday in our households and work places. Throughout their lifespan from use to treatment to final disposal or beneficial use these substances may remain unchanged, transform or degrade. Based on the products chemistry they may breakdown to innocuous forms, simple substances with no potential harmful effects, or into more harmful substances. They may partition into solids, air, or water. The initial literature review in 2001 identified some of these substances, and this review builds on that study and addresses new substances. This study focuses on our current knowledge of those substances and identifies potential research gaps that need to be addressed.



Waste Water Treatment. Some industrial waste waters are treated by industries within their own facilities. Other industrial, as well as residential and commercial, waste waters are treated by municipal sewage treatment plants. Treatment results in effluents and sludges being produced. Effluents are discharged into water bodies. Sludges are buried in landfill, spread on agricultural lands or incinerated.

Note: the terminology used in Canada is “biosolids” not “sludges”

ES.2 Review Objectives

The 2010 study focuses on the following objectives:

1. Review of the technical literature to identify research that has addressed recommendations arising from the 2001 report;
2. Review and identify other research that is applicable to the recommendations of the 2001 report or provide insight for developing projects as part of a next phase for WEAO.
3. Identify potential stakeholders and their contact information so that they can be contacted as needed to complete this updated review. The suggested list will include, but is not limited to, government and non-government personnel, national associations, and the farming, academic and regulatory communities.
4. Produce a comprehensive final report that:
    a. documents research undertaken since 2001 that is germane to the 2001 report recommendations;
    b. provides names and contact information of researchers and other knowledgeable personnel;
    c. documents the issues addressed in the new review, and the results thereof;
    d. identifies the knowledge "gaps" remaining; and
    e. provides recommendations for future work and identifies relevant research partners.

ES.3 Literature Search and Identification

In May 2009, a computerised literature search was executed by Dr. Wayne Parker at the University of Waterloo with the objective of identifying citations pertaining to contaminants in sewage biosolids and the fate and transport of contaminants in terrestrial systems following biosolids land application. More than 200 papers were identified and reviewed as to relevance to the project objectives. The primary focus of the literature review was to identify technical documents published since 2001 related to the Group II contaminants described above, as well as what may be variously termed emerging contaminants (ECs), compounds of emerging concern (CECs), micro-pollutants (MPs) or micro-constituents (MCs). Included in the umbrella term of emerging contaminants are pharmaceutical and personal care products (PPCPs), hormones and other endocrine disrupting compounds (EDCs), and industrial chemicals such as plasticizers, flame retardants and perfluorinated organic compounds used in stain-repellent and non-stick applications.

The computerised literature search was supplemented with telephone calls to experts on the topic of emerging contaminants (ECs) in biosolids. Contact information for these and other experts identified in this study appear in Appendix A of this report, while responses of a number of experts to a series of research questions are provided in Appendix B. In addition, many helpful references were obtained from members of the draft report review committee of this project.

The review was complicated by the imprecision of the terms "sludge" and "biosolids" used in the various papers examined. Many papers failed to distinguish between the two terms. For the purpose of this review the terms as defined by WEAO (2009) are as follows:

"Municipal Sewage Sludge": Municipal sewage sludge is a mixture of solids and water that is generated from the treatment of municipal wastewater.

"Biosolids": Biosolids are municipal sewage sludge that has been treated by physical, chemical and/or biological processes to reduce pathogen and vector attraction potential, and that meet quality criteria such as metals and pathogens concentrations. In Ontario, the quality criteria for biosolids and standards for their application to agricultural land are set out in the Province's Nutrient Management Regulation 267/03.

The major categories of Group I and II substances identified in the literature review include:

- Industrial chemicals (plasticizers, pesticides, perfluorinated organic compounds, linear alkylbenzene sulfonates, etc.)
- Alkylphenols and their ethoxylates
- Flame retardants
- Hormones, steroids and sterols
- Pharmaceuticals
- Personal Care Products
- Certain metals (arsenic, silver, selenium, mercury, etc.)
- Other (e.g. polyaromatic hydrocarbons, polychlorinated dioxins and furans)
- Pathogens

The substances within the categories have been selected because we know they are present in products used on a daily basis; the analytical capability now exists to detect them; the environmental fate and significance is not known, or well known; and some of them, depending on their chemistry, can partition to different media requiring management of that media (e.g. biosolids, water, animal issues).

For consistency, concentrations of chemical contaminants in biosolids are reported in units of mass per g of total solids on a dry weight basis (e.g., ng/g TS dw), unless otherwise specified. Concentrations of the chemical contaminants in environmental matrices (soils, plant matter, and animal tissue) are expressed in units of mass per gram of dry matter (e.g., ng/g DM).

ES.4 Literature Results

Pharmaceuticals

This class of micro-constituents in sludges and biosolids includes many different sub-classes with different therapeutic uses. Since these substances are designed to have a physiological effect on humans, concern about pharmaceuticals in biosolids is centred around the potential for subtle, detrimental, multi-generational effects on non-target terrestrial and aquatic organisms and ecosystems. The literature review revealed that there is a wide range of data available for the different pharmaceuticals that may be present in sludges and biosolids. Some compounds like

carbamazepine have been widely characterized, while others have only one or two references (e.g. beta-blockers, alimentary tract pharmaceuticals) in the literature. With the exception of data on the presence of a limited number of pharmaceuticals in tile drainage or surface runoff, there are few studies documenting the fate and transport of these compounds in the terrestrial environment.

Antibiotics themselves (e.g. penicillin) can be naturally occurring substances. As an example of the use of pharmaceuticals by humans and the levels found in biosolids, we can consider a 100 kg person taking two tablets (600 mg/100 kg) of ibuprofen for a headache. By the time the ibuprofen is found in biosolids it has been reduced to 6000 ng/gm, a number considerably below what we put into our mouths.

Virtually all of the considerable quantity of pharmaceutical information for sewage biosolids reported here has been generated since the WEAO (2001) report was published. Much of the information is very recent because as late as 2005 there was some pharmaceutical information available for municipal wastewaters but very little for sewage biosolids (Webber and Sidhwa 2005). The several Ontario studies reported here were a direct result of the WEAO (2001) report recommendations suggesting they are in Group II and require more research. Overall, the data characterizing the fate, persistence, mobility, and bioaccumulation of all classes of pharmaceuticals are sparse, and thus can be considered as research gaps. Consequently, it is recommended that pharmaceuticals in sewage biosolids be classified as Group II compounds requiring additional research.

Alkylphenols and Their Ethoxylates

Alkylphenol ethoxylates (APEs) are among the most commonly used surfactants (surface active agents) worldwide. The predominant uses of APEs are in pulp and paper production, textile manufacturing and in the production of crop protection chemicals. The primary concern related to the presence of alkylphenols (APs) in the environment is the endocrine disrupting potential of these compounds (they are weak estrogen hormone mimics). From the literature review, it was determined that nonylphenol (NP) has been well characterized in biosolids and in soils. The ethoxylates of nonylphenol or other alkylphenols are less well characterized. There appear to be differences in APE and AP concentrations between biosolids samples collected from different countries, possibly due to different regulations for detergent product formulation. Of the biosolids treatment processes examined, anaerobic digestion consistently results in the highest concentrations of 4-NP because anaerobic biotransformation processes convert mono- and di-ethoxylate species to the non-substituted AP. With a half-life in the range of 10 to 25 days, nonylphenol is not persistent in soil, and thus does not bioaccumulate to any extent in soil biota such as earthworms. Nonylphenol is not readily mobile in the soil column. Most of the nonylphenol subject to biotransformation in the soil remains in the soil in some form, as opposed to mineralization, leaching through the soil column or being taken up by plants.

Considerable research on the fate and significance of alkylphenols and their ethoxylates in biosolids and soils has been done since publication of the WEAO (2001) report, however the findings and conclusions are consistent with those stated in the 2001. As a result of the considerable body of work provided in the WEAO (2001) report, and identified in this review, it

is recommended that the alkylphenols and their ethoxylates continue to be classified as Group I contaminants.

Linear Alkylbenzene Sulphonate Surfactants (LAS)

Linear alkylbenzene sulphonates (LAS) are a class of surfactants widely used in commercial products, but especially in detergent formulations. Possible adverse effects when applied to land in biosolids include the potential to dissolve biomembranes of soil microbes and invertebrates, and also the potential to increase the mobilization of other hydrophobic contaminants in the soil, resulting in higher concentrations of the contaminants in leachate and drainage water.
Based on the literature review, linear alkylbenzene sulphonates are present at higher concentrations (e.g. mg/kg TS dw level) in biosolids than are many of the other microconstituents. The compounds do not appear to be persistent in soil, with reported half-lives of 7 to 9 days. Mineralization of LAS was reduced in a coarse sandy soil as the degree of water saturation of the soil was increased – presumably due to reduced soil oxygen. No studies of mobility through soils to groundwater or in runoff to surface waters were identified in this review. No studies of bioaccumulation of LAS were observed, although with a short half-life of less than 10 days, little bioaccumulation would be expected.

The above findings for LAS are similar to those contained in the WEAO (2001) report, Evidence in this and the WEAO (2001) report indicate that LAS degrades rapidly in aerobic soils. Since agricultural crop production requires aerobic soils, it can be assumed that LAS does not persist in biosolids treated Ontario soils. No data were identified in the current literature review that supported the potential concerns about biomembrane dissolution or enhanced mobility of other hydrophobic contaminants. Based on the evidence in this review and the WEAO (2001) report, it is recommended that linear alkylbenzene sulfonates (LAS) continue to be classified as Group I contaminants. The need to obtain the above-mentioned soil data, as recommended in the WEAO (2001) report, is considered to be of secondary importance relative to characterization of other contaminants in soils.

Brominated Flame Retardants

Polybrominated diphenyl ethers (PBDEs) are compounds used as flame retardants in a wide variety of applications. The environmental and health concerns with PBDEs centre on their persistence, potential toxicity and ability to bioaccumulate. From the literature review, it was determined that there are apparent differences in concentrations of PBDE isomers in North America, and other countries (e.g., Europe, Kuwait, and Australia) in which the concentrations in biosolids are lower. The isomer decabromo DPE (BDE 209) was observed in the biosolids samples at the highest concentration of any of the isomers, followed by the penta BDE99 and tetra BDE47. Because of their high hydrophobicity, when applied to land in biosolids, PBDEs are not likely to migrate downward through the soil column. Concentrations of PBDEs in soils exhibited a wide variability from 0.01 ng/g to 658 ng/g DM, possibly due to differences in biosolids concentrations and application rates in different countries. Bioaccumulation factors of PBDEs for earthworms growing on biosolids amended sites ranged up to 34, compared to a range of 4 to 8 in control fields. No published data were found for transport of PBDEs in surface runoff or leachate, studies of mineralization in soils, or any studies of either plant uptake or toxicity. These are knowledge gaps that future research may address.

The WEAO (2001) report contained no information about PBDEs because they were not identified as compounds of concern in sewage biosolids when that report was prepared. However, they are structurally akin to PCBs and other polyhalogenated compounds, consisting of two halogenated aromatic rings and so are likely to be subject to similar concerns as were the PCBs.

PBDEs have been used in a wide array of products, including building materials, electronics, furnishings, motor vehicles, airplanes, plastics, polyurethane foams, and textiles. People are exposed to them domestically because of their prevalence in common household items. Studies in Canada have found significant concentrations in common fatty foods such as salmon, ground beef, butter, cheese and high concentrations in indoor dust. Increasing PBDE levels have been detected in the blood of marine mammals such as harbor seals.

Given the high levels of exposure to PBDEs in the domestic environment it is unlikely that the low concentrations of these compounds in soils observed as a result of soil amendment with biosolids represent a significant human health hazard. However, their fate, transport and effects in the environment are unknown and warrant further study. For this reason, they are recommended for classification as Group II compounds requiring additional research.

Plasticizers and their Metabolites

Plasticizers are added to polymeric materials to increase flexibility and suppleness. Phthalate and adipate esters are two common classes of plasticizers. A main health concern appears to be the potential for harm to developing male reproductive organs. Review of the literature indicated that most of the biosolids characterization and fate data are centred on bis(2-ethylhexyl) phthalate (BEHP), with much less data available for other plasticizer compounds. Concentrations of (BEHP) are the highest among the phthalate esters in biosolids, at concentrations typically in the range of 2,000 – 200,000 ng/g TS dw. Mineralization of BEHP in soil is slow, however, it appears to be tightly bound to the soil, with little opportunity for leaching. BEHP does not appear to bioaccumulate in biota in biosolids-amended soils. No studies were identified that investigated plant uptake of phthalate esters or related compounds from biosolids-amended soils; thus this lack of studies constitutes a knowledge gap.

Concentration data for phthalates in biosolids are similar in this and the WEAO (2001) report. Phthalates were considered to be organics of secondary importance in the WEAO (2001) report Except for data showing that BEHP may be more persistent in soils than was previously thought, evidence in this and the WEAO (2001) report are in agreement. The data in this review, that of Smith (2009), the Norwegian Scientific Committee for Food Safety - Panel on Contaminants (VKM, 2009), and the WEAO (2001) all indicate that phthalates, including BEHP, in land-applied sewage biosolids do not present significant human or environmental health risks. Based on the above, it is recommended that phthalates including BEHP be considered as Group I compounds.

Bisphenol A

Bisphenol A (BPA) is mostly used in manufacture of polycarbonate plastics and epoxy resins. Uses of the compound are for food and beverage storage, and in sealants in canned food products. The primary concerns with BPA relate to food and drink packaging relate to possible harmful effects on the brain, behaviour and prostate gland of foetuses, infants and children. Use of BPA

in polycarbonate baby bottles was restricted by the Canadian government in 2008 (Health Canada, 2008).

Based on this review, concentrations of BPA in biosolids and sludges have been well documented in the literature, at concentrations typically in the range of 100 to 10,000 ng/g TS dw. However, there are few data available regarding the fate of BPA in the terrestrial environment following land application of biosolids. One review indicated that bisphenols (which includes BPA) have short half-lives of a few days in soil. One study indicated that BPA did not bioaccumulate in earthworms. No studies were identified investigating BPA mobility in percolation water, surface runoff, dissipation, mineralization or accumulation in soils or plants grown on biosolids-amended soils; thus this lack of information constitutes a knowledge gap.

BPA was not identified as an organic compound of concern in sewage biosolids applied on agricultural land and was not assessed in the WEAO (2001) report. Because of its wide use in polycarbonate plastics for food and beverage storage, and in sealants in canned food products it seems reasonable to conclude that human health risks associated with these domestic uses substantially outweigh those associated with health risks from BPA in agricultural land amended with biosolids. There are, however, only sparse data on the fate, mobility and potential bioaccumulation in the terrestrial environment as a result of land application of biosolids. Consequently, it is recommended that BPA be considered a Group II contaminant.

Perfluorinated Organic Acid and Derivative Compounds

Perfluorinated organic compounds (PFOCs) and derivative products have been used as stain repellents for fabrics, and as constituents of non-stick cookware and food wrappers, personal care products and fire-fighting foams. Environment Canada has determined that human exposure to perfluorinated substances is below levels that would cause adverse health effects. Environment Canada has determined however, that accumulation of compounds, such as perfluorooctane sulphonate (PFOS) and perfluorooctanoic acid (PFOA), may have adverse effects in species at risk, such as polar bears and birds.

From the literature, it was determined that concentrations of PFOS and PFOA are typically the highest identified for this category of contaminants, ranging from approximately 1 to 100 ng/g TS dw. Perfluoroalkyl phosphoric acid diesters have been identified as additional perfluorinated compounds that can accumulate in biosolids, but the data are limited to one recent study (D'Eon *et al*., 2009). The fate, transport and bioaccumulation of perfluoroalkyl compounds in the terrestrial environment are virtually unknown. The lack of information on the fate and transport of these compounds in the terrestrial environment represents a knowledge gap.

Perfluorinated organic acid and derivative compounds were not identified as organics of concern in sewage biosolids applied on agricultural land prior to 2001 and hence were not assessed in the WEAO (2001) report. The lack of data on the fate, transport and bioaccumulation potential of these compounds in the terrestrial environment represents a knowledge gap, and it is recommended that they be considered as Group II contaminants.

Synthetic Fragrance Compounds

The two main classes of fragrance compounds used in consumer and commercial products (e.g., detergents, fabric softeners, fabric conditioners, cleaning agents, air fresheners, and cosmetics such as soaps, shampoos and perfumes) are the nitro musks and the polycyclic musks. However, health and environmental persistence concerns about nitro musks have resulted in a preference for use of polycyclic musks. The health concerns regarding synthetic musks include estrogenic activity and accumulation in human adipose tissue and breast milk.

Based on the review of the literature, polycyclic musks are present at higher concentrations in sludges and biosolids than nitro musks. The predominant polycyclic musks are designated by acronyms HHCB and AHTN followed by ATII. The two main nitro musks identified in sludge samples were musk ketone and musk xylene. Polycyclic musks are present at higher concentrations in sludges and biosolids (e.g., 5,000 – 50,000 ng/g TS dw) than nitro musks (e.g., 25 – 150 ng/g TS dw). Concentrations of individual fragrance compounds in biosolids-amended soils can range up to 3,000 ng/g TS dw. Full-scale anaerobic digestion does not appear to reduce concentrations of polycyclic musks in sludges, as concentrations in the digested sludges have been found to be higher than in the raw sludge. Bioaccumulation factors (determined as the ratio of the concentration of the contaminant in the organism to that in the soil, both on a dry matter basis) of synthetic fragrance compounds in earthworms inhabiting biosolids-amended soils were low (bioaccumulation factor 6 or less). Low but detectable concentrations of the compound AHTN were observed 6 months after amendment of a soil with biosolids. Because of their high hydrophobicity, fragrance compounds are not expected to be mobile in soil. No studies on percolation or surface run-off, dissipation, mineralization or plant uptake of fragrance compounds were noted in this review; thus this lack of knowledge constitutes a knowledge gap.

Synthetic musk compounds were not identified as organics of concern in sewage biosolids applied on agricultural land prior to 2001, and were not assessed in the WEAO (2001) report. Because the almost complete lack of data on the fate, transport and bioaccumulation potential of these compounds in the terrestrial environment represents a knowledge gap, it is recommended that this class of compounds be considered Group II contaminants.

Antimicrobials

Triclosan and triclocarban are compounds that display antimicrobial activity and are used in an array of consumer products such as soaps, detergents and cosmetics. Hexachlorophene is used as a topical anti-bacterial agent in soaps and some toothpastes. As of October 2008, the U.S. EPA determined that triclosan did not pose a human health hazard when used in personal care products as intended. Although it is anticipated to be immobile in soils, the EPA expressed concern that triclosan could bioaccumulate in aquatic organisms to levels posing a concern. Hexachlorophene is acutely toxic to aquatic organisms, and bioaccumulation in the food chain can be expected.

As determined by this review, concentrations of triclosan in biosolids are well characterized, with a typical range of 1,000 to 40,000 ng/g TS dw. Triclocarban is not as well characterized in biosolids, but available data indicate a similar concentration range to triclosan. Data from one publication indicated that hexachlorophene concentrations in biosolids are lower than those of triclosan by up to an order of magnitude. Triclosan appears to be less persistent in soils than

triclocarban, with half-lives on the order of 18 and 108 days, respectively. Triclosan may be biotransformed in soils to methyl-triclosan and may be more mobile in soil columns than triclocarban. It was released to surface runoff faster than triclocarban. Triclocarban is more mobile in sandy soils than fine-textured soils. The bioaccumulation factor for triclosan ranged from 11 to 27 in earthworms from biosolids-amended soils; a similar value was determined for triclocarban. The accumulation of triclocarban by Bahia grass grown on biosolids-amended soil was very small. The persistence, fate, mobility and bioaccumulation of hexachlorophene in the terrestrial environment are poorly documented.

Triclosan and triclocarban were not identified as organics compounds of concern in sewage biosolids applied on agricultural land and were not assessed in the WEAO (2001) report. Much new data on the fate, transport and effects of triclocarban in the terrestrial environment were documented by Snyder (2009). Data for triclosan is somewhat more scattered through the literature, but in general results are similar to those provided for triclocarban. Although both triclosan and triclocarban are bioaccumulative in earthworms (data on accumulation in other species was not identified); the effects of this bioaccumulation are unknown. Based on the lack of information about bioaccumulative effects, concern regarding soil microbial health recently expressed by Smith (2009), and the lack of any data for hexachlorophene, it is recommended that antimicrobial compounds be considered as Group II contaminants.

Other Personal Care Products

Included within this class are products such as fluorescent whitening agents, used to enhance the appearance of textiles and papers; quaternary ammonium compounds (QACs), an important class of cationic surface-active agents used in a variety of commercial products such as disinfectants and sanitizing agents; siloxanes, organic silicon polymers used as additives that improve the properties of personal care products, paper coatings and textiles; and UV filters, used as sunscreens to help to reduce potential ageing of skin and cancers.

Based on the literature review, concentrations of these compounds in biosolids are generally poorly characterized. No concentration data for fluorescent whitening agents and siloxanes in biosolids were found. Concentrations of quaternary ammonium compounds in biosolids are in the range of 20,000 to 100,000 ng/g TS dw. Concentrations of UV filters in biosolids are in the range of 100 to 30,000 ng/g TS dw.

Fluorescent whitening agents, quaternary ammonium compounds, siloxanes and UV filters were not yet identified by the industry as organic compounds of concern in sewage biosolids applied on agricultural land, and therefore were not assessed in the WEAO (2001) report. The sparse data show that these various types of organic compounds are poorly characterized in biosolids, particularly siloxanes and fluorescent whitening agents. Further, there are virtually no published data encountered concerning the fate, transport, bioaccumulation or environmental effect of these compounds in the terrestrial environment. Consequently, it is recommended that the classes of compounds included in this Section be categorized as Group II compounds.

Hormones and Sterols

Compounds in this category include both natural and synthetic estrogens and androgens, all of which can affect the human endocrine system. The synthetic estrogens, used for birth control and

hormone replacement therapies, and the natural estrogens and androgens are excreted on a daily basis to sewage. Phytosterols are naturally occurring alcohols of steroids, and are present in vegetable oils used in cooking and salads. These can be ingested and excreted, or end up in household grey water during dish washing. The presence of animal sterols in receiving waters is typically viewed as a marker for sewage contamination. Environmental concerns arising from this group of compounds is mostly focused on the synthetic estrogens, which have potency orders of magnitude higher than the natural estrogens.

Based on the literature review, 17α-ethinylestradiol (EE2), estrone (E1) and 17β-estradiol (E2) are among the most frequently characterized hormones in sludges and biosolids, and of these, estrone (E1) exhibits the highest concentrations. Of the natural hormones, progesterone exhibited the highest concentrations, with a median value of 139 ng/g TS dw. Concentrations of androgens in biosolids were reported less frequently than estrogens, with median values for three androgens from the EPA sludge survey ranging from 85 to 158 ng/g TS dw. Concentrations of plant sterols in sludges and biosolids were among the highest observed in this literature review, with values in the tens of thousands of ng/g TS dw. Concentrations of the animal sterols reported in sludges varied substantially from one reference or source to the next, but as for plant sterols they were among the highest observed in this review. Removal efficiencies up to 85% were recorded for both 17α-ethinylestradiol (EE2) and a mixture of estrone (E1) and 17β-estradiol (E2) resulting from both thermophilic and mesophilic anaerobic sludge digestion. Removal efficiency data for hormones and sterols resulting from other biosolids treatment processes are scarce. Human hormones in biosolids disappear rapidly (less than 96 hours) when incorporated into soils, with estimated half-lives of 1 to 7 days. Testosterone is mineralized in soil to a greater extent (30-45%) than 17β-estradiol (E2) (2-10%). Approximately 50-60% of ^{14}C-labelled testosterone added to three soils was mineralized to CO_2 within 265 days. Human hormones were not taken up by turf grass grown on biosolids-amended soils in one study.

Hormones and sterols were not identified as organic compounds of concern in sewage biosolids applied on agricultural land and were not assessed in the WEAO (2001) report. The weight of data examined in this review indicates the human hormones (estrogens and androgens) have short half-lives in soil. One review indicates there is no accumulation by plant matter from biosolids-amended soils. Animal and plant sterols, although among the highest concentrations in biosolids, are naturally-occurring compounds that can be found at concentrations of similar magnitude in both non-amended and biosolids-amended soils. It is recommended that these compounds be considered as Group I contaminants.

Metals

Concentrations of metals in sludges and biosolids have been of concern for decades because of the use of biosolids as a soil amendment in agriculture and silviculture. Concerns regarding metals in biosolids are related to their potential toxicity to or uptake by, agricultural crops or foraging animals.

The present literature review determined that the recent concentration database for metals and metalloids is limited because little research has been conducted since publication of the WEAO (2001) report. However, limited research has been completed in Ontario to determine the concentrations of non-regulated metals in biosolids. Study data indicated that after iron and

aluminum, the non-regulated metals of highest concentration were barium and titanium. There are few data characterizing concentrations of elements such as silver, thallium, antimony, vanadium, yttrium and others in biosolids. The lack of information found in this review on the fate, transport and bioaccumulation of these non-regulated metals in the terrestrial environment due to land application of biosolids constitutes a knowledge gap.

Since recent evidence indicates no increase in regulated metal concentrations in Ontario sewage biosolids, it can be concluded that the WEAO (2001) conclusions concerning these metals remain valid. The recent concentration data for non-regulated metal concentrations in Ontario sewage biosolids were obtained in response to the WEAO (2001) recommendation for further research concerning concentrations of these metals in biosolids. There is good agreement among these and the previous 2001 data, with current levels at or lower than the concentrations reported in the 2001 report. It may be assumed, therefore, as was concluded previously, that loadings of unregulated metals in land applied sewage biosolids are unlikely to exceed the soil metal concentration standards as set out in Ontario' Record of Site Condition Regulation 153/04. The WEAO (2001) conclusions concerning these unregulated metals remain valid and unchanged. Based on the knowledge gap identified above on the fate, transport and bioaccumulation of the unregulated metals in the terrestrial environment resulting from biosolids applications to soil, it is recommended that the unregulated metals be categorized as Group II contaminants. Work undertaken in Québec has shown that source control has been working to reduce metals entering into the sewer systems to the wastewater treatment plant and into the final effluents and biosolids (Marc Hébert, personal communication, 2010).

Radionuclides

Radionuclides in sludges and biosolids are also of concern and very limited information for them was included in the (WEAO 2001) report. Based on a major survey of U.S. sludges (ISCORS, 2003), radionuclide levels in municipal sludge (or by extension in biosolids) are generally comparable to what is found in other media (e.g. soil and fertilizer), and do not represent a widespread or nationwide public health concern.

The conclusions based on the U.S. study (ISCORS, 2003) and contained in the WEAO (2001) report regarding radionuclides are essentially the same, although their derivations are different. The U.S. conclusion was based on extensive sampling, analysis and risk assessment, whereas the WEAO (2001) conclusion that radionuclides are "Group I contaminants for which no further study is necessary at this time" was based on the facts that medically used radionuclides are short-lived and that Ontario sewer use by-laws prohibit discharge of long-lived radionuclides into municipal sewer systems. In the absence of any recent data that characterize radionuclide concentrations in Ontario or other Canadian biosolids, it is probable that the concentrations of radionuclides reported in the broad U.S. sludge survey, using mostly similar approaches, would be representative of the Canadian situation.

The results of the U.S. study would thus support the WEAO (2001) assumption of low radionuclide levels that are not a detriment for biosolids land application. It is recommended that radionuclides be categorized as Group I contaminants, as they were in the WEAO (2001) report.

Polyaromatic Hydrocarbons (PAHs)

PAHs are a product of carbon combustion, and enter the environment from volcanoes, forest fires, residential wood burning, and exhaust from automobiles and trucks. Health concerns related to the PAH and polychlorinated polyaromatic classes of compounds are their potential human carcinogenic properties.

From the literature review, it was determined that the upper range of concentrations of naphthalene, methylnaphthalene isomers and benzo(a)anthracene in sludges and biosolids were at or above 100,000 ng/g TS dw in the literature review of Harrison *et al*. (2006), although a survey of Canadian sludges revealed median concentrations typically in the range of 100 to 2,700 ng/g TS dw. The simplest PAHs, naphthalene and phenanthrene, consisting of two and three fused benzene rings, respectively, have the highest median concentrations (e.g., 1,500 to 2,700 ng/g TS dw), but not the highest maximum levels, of all of the PAHs in the Canadian survey. The fate of PAHs in the terrestrial environment is not well documented, often with only one representative compound tested. For example, a high degree of soil water saturation exhibited a detrimental effect on the mineralization of pyrene, which occurred slowly (only 2-5% mineralization after two months) in several different soil types.

Concentration data for PAHs in sludges are similar in this and the WEAO (2001) report. PAHs were considered to be organics of secondary importance in the WEAO (2001).

Benzo(a)pyrene, however, was identified as a compound of concern by the screening methodology used by the US EPA during development of Reg. 503 (US EPA, 1993). Despite this concern there has not been a strong research focus on benzo(a)pyrene and although sparse, recent information provides no evidence for heightened concern.

There were no studies identified in this current review that examined percolation of the compounds through soil, or mobilization in surface runoff, or uptake by plants; however most of these concerns were addressed in the 2001 report, and thus the lack of recent information is not considered to constitute a knowledge gap.

Thus, evidence in this current review and the WEAO (2001) report are in agreement and indicate that PAHs, and particularly benzo(a)pyrene in land applied sewage sludges do not present significant human or environmental health risks. As a result, it is recommended that the contaminants remain as Group I contaminants.

Polychlorinated Polyaromatic Compounds

Polychlorinated biphenyls (PCBs) were widely used in a variety of products such as electrical transformer fluids, but their import, manufacture and sale in Canada was banned in 1977. Polychlorinated dibenzodioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) are not manufactured or used, but result from combustion of products consisting of chlorinated organics. (e.g. polyvinyl chloride plastics) and as a by-product of pentachlorophenol production. Atmospheric deposition of these chlorinated substances is likely a major contributor in wastewater treatment.

For the literature surveyed, the range and mean concentrations of the PCDDs and PCDFs reported in biosolids from different countries appear to be very similar, with mean values in the range of 0.020 ng toxic equivalents (TEQ)/g TS dw. Concentrations of total PCBs listed in Canadian sludge samples appeared to be higher than corresponding sludge samples from Europe. Concentrations of PCBs in soils may be elevated by 2 to 10 times the background concentrations as a result of biosolids amendment. Bioaccumulation factors for one PCB congener (PCB149) in earthworms on control and biosolids-amended soils generally ranged from 3 to 7, but for PCB149 in one biosolids amended clay soil, they ranged up to 18. Fate and transport of these compounds through the terrestrial environment is not well documented.

Concentration data for dioxins/furans and PCBs in sludges are similar in this and the WEAO (2001) report. Evidence to date indicates that PCBs in land-applied sewage sludge have not been associated with significant human or environmental health hazard. Moreover, given the consistently low (<3000 ng/g) concentrations of total PCBs in Canadian sludges and the fact that use of these compounds has been banned in Canada since the mid-1970s, there is no reason to believe that they will become significant hazards in the future.

Dioxins and furans were identified as organics of concern in land-applied sludge, and they received special attention in the WEAO (2001) report. Although there were no Ontario dioxin/furan guidelines or standards related to sludge use on agricultural land, it was calculated that, at the maximum (sludge) application rate of 8 dry tonnes/hectare/5 years, and assuming no degradation of dioxins and furans in soil, biosolids containing median concentrations of dioxins and furans could be applied repeatedly to the same field 66 times or (for) 330 years before the "Effects Based" soil concentration would be reached (see Table 9.6, WEAO, 2001). The WEAO (2001) report concluded "Thus they are Group I contaminants for which no further study is necessary, at this time." This conclusion was supported by the EPA (2003) final decision not to regulate dioxins in land-applied sewage sludge (EPA did not differentiate between sludge and biosolids). After five years of study, including outside peer review, the Agency determined that dioxins in sludge did not pose a significant risk to human health or the environment.

Based on the above discussion, and on the absence of new evidence of adverse effects to the terrestrial environment from these compounds as a result of application of biosolids to land, it is recommended that the polychlorinated dioxins, furans and PCBs remain as Group I contaminants, as was recommended in the WEAO (2001) report.

Pathogens

The presence of pathogens in biosolids has been one of the major concerns about land application of biosolids due to the potential for infection from food crops or livestock raised on biosolids-amended soils, or from transfer to surface or groundwater and bioaerosol transport off-site during land application. Much new information has been published in the technical literature since the 2001 WEAO report.

Based on the literature, regrowth of *E. coli* and *Salmonella* spp. was observed in some cases when dewatered anaerobically digested biosolids were centrifuged, stored or rewetted. Select pathogens such as *Listeria* and *Salmonella* have been detected frequently in biosolids~~. The~~ published data on occurrence of other bacterial pathogens in biosolids, such as *Campylobacter*,

Yersinia, and Helicobacter are scarce, although work is being done by Agriculture Canada in Ottawa and Lethbridge on *Helicobacter* and campylobacters in manure and biosolids. Data on concentrations of the parasites *Cryptosporidium* and *Giardia* in biosolids or biosolids-amended soils were limited, possibly due to inadequate analytical procedures. Geometric mean densities of target indicators and pathogenic bacteria in biosolids can range from 10^6-10^7 (e.g., fecal coliforms, *Enterococci* spp and *C. perfringens*) to lower than 1 MPN/g TS dw (e.g., *L. monocytogenes* and *Salmonella* spp.).

Microbial risk assessments indicate that when biosolids are incorporated into soil at regulated rates in Europe or North America, there appears to be only a very small risk of infection from ingesting soil amended with the biosolids. The risk of infection to communities from bioaerosols resulting from land application appears to be very slight, although occupational exposure appears to offer a slightly higher risk, particularly for infection from the enterovirus coxsackievirus A21. The work of Pepper and others indicates there is negligible risk of infection from *Staphylococcus aureus* resulting from biosolids applied to land or in biosolids aerosols.

Pathogens can enter surface water either as a result of surface runoff or tile drainage. Although tile drainage appears to contribute to pathogen loadings more regularly than surface runoff, heavy precipitation events can cause pathogen concentrations in runoff to rise to the levels higher than found in tile drainage. Different types of pathogens survive in soils and plants for different durations; protozoa from biosolids can survive in soils for a period measured in days or weeks while helminth ova can survive for several years. Survival times of pathogens associated with plants following application of biosolids are shorter than the survival times of the same pathogens in soil. One soil column study indicated that bacterial pathogens are tightly bound to soils following biosolids application. Because viruses can be transported in groundwater, they may pose more of a risk to human health than the larger pathogens which tend to be bound tightly to the soil. Transport of all pathogens through soil is aided by the presence of macropores, such as cracks in soils with high clay content, worm holes and roots.

There is no evidence of the presence of prions in municipal biosolids or in soils amended with biosolids; however improved analytical techniques for detection of these substances are needed. Published data on recent influenza-like viruses (e.g., H1N1, H5N1, H5N2) in biosolids and soils amended with biosolids are lacking but during the recent pandemic biosolids were not considered by health agencies as pathways for spreading of the viruses. Improved analytical methods are needed for identifying the number and viability of pathogens such as *Cryptosporidium* in biosolids and soils.

The Stakeholder Advisory Group consulted during preparation of the WEAO (2001) report expressed a high level of concern about the potential for disease transmission resulting from land application of sewage biosolids. Based on that concern and limited available study information, it was concluded that pathogens in land applied sewage biosolids are Group II contaminants requiring additional research.

Limited published literature was identified in this new review with respect to addressing the recommendation that a sampling survey of biosolids across Ontario be conducted to develop a more comprehensive database of pathogen occurrence and concentration data. There are current

research efforts by MOE and Agriculture and Agri-Food Canada to quantify select pathogens in biosolids.

In addition there are still data gaps in available analytical microbiological methods for achieving effective recovery and enumeration of pathogens in environmental samples, particularly in biosolids and soils, and even bigger gaps in acquiring relevant data on the viability and human infectivity of organisms such as *Giardia, Cryptosporidium, Campylobacter*, and others (Flemming, 2009b).

New literature regarding the fate and transport of pathogens (particularly bacteria) in the terrestrial environment has been published since the 2001 WEAO report that appears to address many of the issues of the second recommendation for field plot studies. A substantial body of this research has occurred in Ontario, conducted and/or funded by federal and provincial ministries. Agencies involved in the research include Agriculture and Agri-Food Canada, the Ontario Ministry of the Environment and Ontario Ministry of Agriculture, Food and Rural Affairs. Diverse studies have been published on the fate and transport of pathogens in surface runoff and tile drainage resulting from applications of liquid and dewatered biosolids to field plots.

The growing body of data from Canadian and international researchers appears to indicate that concerns regarding the transfer of pathogens in biosolids to soils have been or are being addressed. A number of research gaps or concerns remain, however, including development of adequate analytical procedures for pathogens in biosolids, viability and infectivity of identified pathogens; occurrence and fate of identified pathogens such as *Helicobacter, Campylobacter* and *Yersinia*, occurrence and fate of newer pathogens (e.g. influenza viruses such as H1N1, H5N1 and H5 N2); and the potential human health risks from transport of viruses through ground water and into surface water via runoff. Consequently, it is recommended that pathogens as a class be categorized as Group II contaminants requiring additional research, as they were in the WEAO (2001) report.

ES.5 Data Review Summary

Compared to the classes of contaminants reviewed in the WEAO (2001) report, the number of classes of contaminants that have been reviewed herein has grown substantially. Due to the relatively short timeframe of this interim, the ability of the scientific community to define and document publically all aspects of the different contaminant classes with respect to biosolids application to soils would clearly represent an enormous task. This review has identified that the attention awarded to and the understanding of the contaminants identified herein is very uneven. Some classes of compounds have been studied in detail for many years, such as nonylphenol and its ethoxylates and linear alkylbenzene sulfonates (LAS). Knowledge of the effect of other contaminants in soils, such as pharmaceuticals, polybrominated diphenyl ethers (PBDEs), perfluorinated organic compounds and Bisphenol A is very limited. For example, in the cases of fluoroquinolone antibiotics and PBDEs, the literature may show that they are persistent and even accumulate in the soil, but it is uncertain whether these observations represent an environmental health concern. Similarly, in this review, bioaccumulation factors (principally in earthworms) were often identified as greater than 1, (e.g., triclosan BAF value was 27, and for PBDEs was up

to 20), indicating biomagnification by the organism; the environmental significance of BAF values greater than 1 has not been documented.

In the main body of the report, at the conclusion of each section on contaminants, the main points of knowledge were summarized and then put in context with the conclusions of the WEAO (2001) report. Lastly, in each section on contaminants, a recommendation was provided for categorizing the compounds in a manner similar to the 2001 report, namely as Group I compounds for which research and data were deemed sufficient, and the Group II contaminants for which additional research was recommended.

The contaminants or classes of contaminants were summarized according to their recommended Group I or Group II designations with the specific knowledge gaps summarized for each and a priority ranking for research provided. There are insufficient research funds available to address all knowledge gaps identified, so the effort should be focused on addressing the data lacking for the Group II contaminants. Within the Group II contaminants, it is impossible to assign a ranking of priority, as this must be based on risk assessments which have not been conducted.

Knowledge gaps and research requirement were identified in the responses received from experts on biosolids applied to land, found tabulated in Appendix B. These knowledge gaps and research recommendations have been summarized. In general, the major research focuses can be summarized as the fate of pathogens in the environment following biosolids application, ecotoxicity and bioaccumulation studies of the micro-constituents in biosolids applied to soil, and occurrence and analytical methods for micro-constituents in biosolids and soils. The same experts are pursuing research in the coming year to address these knowledge gaps.

Other knowledge gaps that may be addressed include the type of biosolids applied (e.g., lime-stabilized vs. anaerobic vs. compost) vs. mobility in soil, and the effect of soil structure (% sand and clay, pH, OC content, possibly cation exchange capacity) on the persistence and mobility of contaminants.

This review identified on-going research by a number of organizations or agencies, much of which has overlap with the current interests of this review. These organizations and agencies included the Canadian Council of Ministers of the Environment, Environment Canada, Agriculture and Agri-food Canada, the U.S. National Biosolids Partnership and the Water Environment Research Federation. Contact should be made with these organizations to promote common research goals and to prevent unnecessary duplication of research efforts.

ES.6 Recommendations

Recommendations based on identified knowledge gaps include the following:

- Because the data characterizing the fate, persistence, mobility, and bioaccumulation of all classes of pharmaceuticals are sparse, studies are needed to further the scientific understanding of these compounds when applied to soils in biosolids.

- The transport of PBDEs in surface runoff or leachate, mineralization of PBDEs in soils, and studies of plant uptake and toxicity of PBDEs are poorly documented and studies on these issues are recommended.

- Because there are only sparse data on the fate, mobility and potential bioaccumulation of Bisphenol A (BPA), perfluorinated organic compounds (PFOCs), synthetic fragrances and the antimicrobial hexachlorophene in the terrestrial environment as a result of land application of biosolids, research should be initiated to address these knowledge gaps.

- The lack of knowledge of bioaccumulative effects resulting from the antimicrobial triclosan in biosolids, and the concern regarding the effects of triclosan on soil microbial health, warrants additional research.

- A wide variety of compounds used in personal care products, such as fluorescent whitening agents, quaternary ammonium compounds, siloxanes and UV filters are poorly characterized in biosolids, and there are virtually no published data that describe the fate, transport, bioaccumulation and environmental effects of these compounds in the terrestrial environment. Research studies are needed to respond to these diverse knowledge gaps.

- Recommendations from the WEAO (2001) report for studies on the mobility and effects of unregulated metals in biosolids applied to Ontario soils have not been addressed and should be a research focus.

- In addition to addressing the knowledge gaps of individual contaminants in biosolids when applied to soils, complementary investigations of potential ecotoxicological effects of biosolids on plants and animals in soils should be conducted.

- The importance of the magnitude of bioaccumulation factors in soil fauna and flora is not well understood and needs to be investigated.

- With respect to pathogens, studies to elucidate the following are recommended:
  - development of adequate analytical procedures for pathogens in biosolids, including viability of identified pathogens;
  - occurrence and fate of known pathogens such as *Helicobacter, Campylobacter* and *Yersinia*, and of newer pathogens (e.g. influenza viruses such as H1N1, H5N1 and H5 N2); and
  - the potential human health risks from transport of viruses and other pathogens in surface water runoff and in groundwater.

Other recommendations resulting from this review include:

- Much new data are being published in the literature as of this date, and so the review should be updated again in approximately 5 years.

- WEAO should attempt to leverage biosolids research results by coordinating with other organizations or agencies that are active in biosolids research, such as the

Canadian Council of Ministers of the Environment, the U.S. National Biosolids Partnership, and the Water Environment Research Foundation.

Prioritization of the research requirements is properly accomplished by comparing risks associated with the various contaminants in biosolids applied to land. Since the risk assessments have not been completed, the prioritization must be based on professional judgement involving subjective interpretation of the collected information.

Because the Biosolids Steering Committee has requested prioritization of research requirements for contaminants in land applied biosolids, it seems reasonable to seek data for those contaminants for which there is little or no information. Using this approach, research efforts should be directed toward determining the occurrence and concentrations in biosolids, and the fate, transport, accumulation and environmental effects of the following biosolids constituents, not listed in order of preference:

- perfluorinated organic compounds;
- the myriad personal care products including, but not limited to fluorescent whitening agents, quaternary ammonium compounds, siloxanes and UV filters;
- concentrations and viability of protozoans such as *Cryptosporidium* in biosolids and soils receiving biosolids applications;
- pathogens of recent concern such as H1N1 virus (swine influenza) and H5N1 and H5N2 viruses (avian influenza).

The above short list of contaminants is proposed based on the assumption that adequate analytical procedures exist to accomplish the research goals. If the analytical procedures do not exist, the greatest priority must be in the method development so that the research priorities identified can then be carried out.

It should also be stated that costs to continue to address single substances is prohibitative and efforts should be made to address mixures, their fate and significance to the environment and human health.

TABLE OF CONTENTS

LIST OF TABLES

1. INTRODUCTION

1.1 Rationale for Literature Review

The application of sewage-derived biosolids to agricultural land is an important management option in Ontario. Of the estimated 300,000 tonnes of dry wastewater solids produced in the Province of Ontario each year, approximately 40 % is applied to agricultural land (Meerveld, 2007). Although the considerable fertilizer and soil conditioning values of biosolids is well established, concerns related to environmental and health issues of land-applied biosolids have been expressed by citizens and non-governmental organizations.

In 2001, the Water Environment Association of Ontario (WEAO) issued a report entitled "Fate and Significance of Contaminants in Sewage Biosolids applied to Agricultural Land Through Literature Review and Consultation with Stakeholder Groups". The report summarized the state of knowledge of contaminants in biosolids at that time.

Based on the findings of extensive literature review and agreement from the Technical Steering Committee, the contaminants were allocated to two groups: Group I - no additional studies recommended; and Group II – additional studies required.

The Group I contaminants included; regulated metals, volatile organic contaminants (VOCs), polychlorinated biphenyls (PCBs), polynuclear aromatic hydrocarbons (PAHs), pesticides; linear alkylbenzene sulphonate (LAS) and alkylphenol (APs), surfactants, dioxins and furans (PCDD/Fs), radionuclides, nitrogen and phosphorous.

The Group II contaminants included; unregulated metals, pathogens, estrogenic hormones and pharmaceuticals.

Since the 2001 WEAO report was issued, considerable Ontario, national and international research has been conducted on land application of sewage biosolids and in particular on pharmaceuticals and personal care products (PPCPs) and pathogens. Moreover, significant advances in analytical protocols have occurred, enabling researchers to analyze biosolids and sludges for contaminants and concentrations that were not previously possible.

WEAO decided that there is a need to update the 2001 report to reflect recent research findings; to try to clarify differences between United States' regulation and that in Ontario; and to determine if a new focus is required for future research. The Ministry of the Environment provided financial support to this initiative. This report responds to that need.

A key fact that the Ontario public should be aware of, is that there is a different regulatory regime in Ontario from some of the other provinces and the United States. This becomes very important when reporting and trying to compare biosolids related activities between Canada and the United States. For instance, reference to Class A and Class B biosolids apply to the United States, not Ontario. Reference to Group I and Group II substances are the result of the findings of the first review (2001) and have been used only to categorize substances for future research.

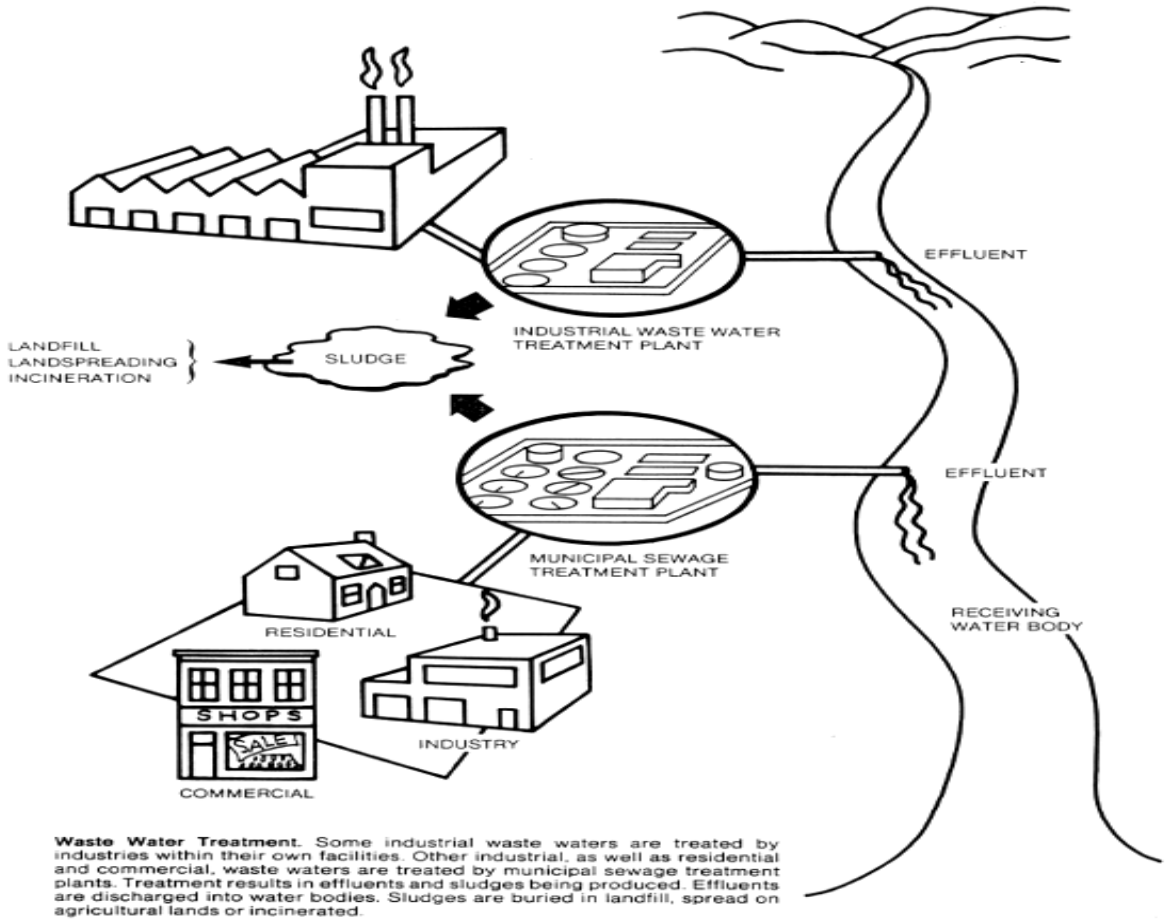
This report focuses on the results of studies of the Group II contaminants - in particular PPCPs - identified in the previous WEAO report as requiring additional research. However, it also includes recent results of Group I contaminants and some contaminants not identified in the previous WEAO report.

It was also recognized that the review had to be completed by a set time, therefore any papers published in late 2009 or early 2010 (research was underway when the review occurred) were not included in this report. WEAO recognizes that this type of document should be updated on a regular basis to account for ongoing research.

The Technical Steering Committee for this review felt it important to provide context to assist in better understanding the role of each of us in contributing to the content of biosolids, and providing some relative examples of our use of substance versus the levels found in biosolids.

The following graphic shows how the products we use in our everyday lives (at home, at work, in industry) move into the sewers and wastewater treatment plant, are treated and the end products discharged as liquid effluents to surface waters, or as solids to land, incineration or landfills.

At each stage, the substances initially used in household or industrial/commercial operations are converted into different forms. Based on the products chemistry they may breakdown to less innocuous forms and partition into solids, air, water or animals. The substances found in products we use may be reduced to simple substances with no potential harmful effects, or into more harmful substances. The initial literature review in 2001 identified some of these substances, and this review builds on that to address new substances. Overall, we then understand which substances in daily use should be of more interest to us in how they are managed.



Waste Water Treatment. Some industrial waste waters are treated by industries within their own facilities. Other industrial, as well as residential and commercial, waste waters are treated by municipal sewage treatment plants. Treatment results in effluents and sludges being produced. Effluents are discharged into water bodies. Sludges are buried in landfill, spread on agricultural lands or incinerated.

1.2 Review Objectives

Based on the Statement of Work provided in the Solicitation, the following objectives have been identified:

1. Following review of the 2001 report recommendations, review the technical literature to identify research that has addressed recommendations arising from the 2001 report;
2. Review and identify other research that is applicable to the recommendations of the 2001 report or provides insight for developing projects as part of a next phase for WEAO.
3. Identify potential stakeholders and their contact information so that they can be contacted as needed to complete this updated review. The suggested list will include, but is not limited to, government and non-government personnel, national associations, and the farming, academic and regulatory communities.
4. Produce a comprehensive final report that:
    a. documents research undertaken since 2001 that is germane to the 2001 report recommendations;
    b. provides names and contact information of researchers and other knowledgeable personnel;
    c. documents the issues addressed in the new review, and the results thereof;
    d. identifies the knowledge "gaps" remaining; and

e. provides recommendations for future work and identifies relevant research partners.

2.0 METHODOLOGY OF REVIEW

2.1 Literature Search and Identification

In May 2009, a computerised literature search was executed by Dr. Wayne Parker at the University of Waterloo with the objective of identifying citations pertaining to contaminants in sewage biosolids and the fate and transport of contaminants in terrestrial systems following biosolids land application. More than 200 papers identified and reviewed as to relevance to the project objectives. The primary focus of the literature review was to identify technical documents published since 2001 related to the Group II contaminants described above, as well as what may be variously termed emerging contaminants (ECs), compounds of emerging concern (CECs), micro-pollutants (MPs) or micro-constituents (MCs). Included in the umbrella term of emerging contaminants are pharmaceutical and personal care products, hormones and other endocrine disrupting compounds (EDCs), and industrial chemicals such as plasticizers, flame retardants and perfluorinated organic compounds used in stain-repellent and non-stick applications.

The computerised literature search was supplemented with telephone calls to experts on the topic of emerging contaminants (ECs) in biosolids. Telephone discussions or email responses to identify status of research, knowledge gaps and to identify relevant publications were held with:

- Drs. Ian Pepper, Charles Gerba and Rolf Halden of Arizona State University;
- Dr. Thomas Granato, Metropolitan Water Reclamation District of Greater Chicago;
- Dr. Robert Hale and Dr. Mark LaGuardia of the Virginia Institute of Marine Science, The College of William and Mary, Gloucester Point, VA;
- Dr. John Brooks, U.S. Department of Agriculture
- Dr. George O'Connor of the Dept. of Soil and Water Science, the University of Florida at Gainesville;
- Dr. Sally Brown of the University of Washington;
- Dr. Lynda McCarthy of Ryerson University, Toronto;
- Mr. Alan Hais, Project Manager, Water Environment Research Foundation (WERF), Alexandria, VA;
- Mr. Robert Bastian, U.S. Environmental Protection Agency EPA), Washington, D.C.;
- Ms. Shirley Anne Smyth, Environment Canada, Burlington, ON;
- Dr. Kang Xia, Mississippi State University

Contact information for these and other experts identified in this study appear in Appendix A. Summaries of correspondence are provided in Appendix B.

2.2 Literature Compilation

A citation review template was created in MS-Excel to capture the relevant data extracted from each citation. An initial data review session with Hydromantis and Dr. Parker assessed the nature and quality of the information extracted. Two major categories were identified for the concentration data provided, namely for "occurrence" purposes, and for "fate and transport" purposes. Occurrence data were those in treated biosolids streams which had not been adjusted in any manner, such as by spiking to elevate concentrations. Fate and transport data included both laboratory and field studies on biosolids-amended soils which encompassed a number of research objectives such as dissipation over time, migration through soil columns, transport to subsurface leachate or surface runoff, volatilization from the soil:air interface, and uptake by animal or plant biota. The scale of the tests was identified to allow assessment of possible differences between laboratory or pilot-scale and full-scale studies.

The review was complicated by the imprecision of the terms "sludge and "biosolids" used in the various papers examined. Many papers failed to distinguish between the two terms. For the purpose of this review the terms as defined by WEAO (2009) are as follows:

"Municipal Sewage Sludge": Municipal sewage sludge is a mixture of solids and water that is generated from the treatment of municipal wastewater.

"Biosolids": Biosolids are municipal sewage sludge that has been treated by physical, chemical and/or biological processes to reduce pathogen and vector attraction potential, and that meet quality criteria such as metals and pathogens concentration. In Ontario, the quality criteria for biosolids and standards for their application to agricultural land are set out in the Nutrient Management Regulation (O.Reg 267/03).

Due to imprecision of the use of the terms in many of the reviewed papers, material that might meet the definition of "biosolids" above were classified as sludges. Less frequently, material that should rightly be termed "sewage sludge" might be included under the umbrella term biosolids. Because of a lack of description of how the material was generated, it was not possible to determine the appropriate classifications.

Consistency in the reported use of units of concentration also represented a complexity in the review. The units of measurement were variously reported on a volumetric liquid basis (e.g., ng/L), a solids mass basis (e.g., ng/g dry solids), or in other units such as ng/g of organic carbon. For consistency in this review, concentrations of chemical contaminants in biosolids or sludges are reported in units of mass per g of total solids on a dry weight basis (e.g., ng/g TS dw), unless otherwise specified. Concentrations of the chemical contaminants in environmental matrices (soils, plant matter, and animal tissue) are expressed in units of mass per gram of dry matter (e.g., ng/g DM).

The reporting (or not) of contaminants in sludges and biosolids is highly dependent on inter-actions between the target compound, the matrix to be analysed, the analytical procedure, and

analytical equipment used. Analytical techniques continue to be refined, reducing limits of quantitation to ever lower levels. As a consequence, certain compounds reported as non-detectable as little as five to ten years previously can now be observed at reportable concentrations in the technical literature. Even as the detection limits become lower, however, there can be a significant range in detection limits between compounds in the same major contaminant category. For example, in the same analytical procedure, the detection limit of the analgesic compound acetaminophen is several orders of magnitude higher than an antibiotic such as erythromycin. Lastly, there are still some target compounds for which methods may not have been adequately developed when dealing with complex matrices such as sludges and biosolids.

The way in which data were to be presented in this review, as summarized from the original data in the technical publication, required another decision. Mean or median values were entered in the spreadsheet if reported in the original citations. When several concentrations within a category were documented within the same citation, a range could be reported (e.g. 2-20 ng/L).

2.3 Classification of Substances

The major categories of substances identified in the literature review include:

- Industrial chemicals (plasticizers, pesticides, perfluorinated organic compounds, solvents)
- Alkylphenols and their ethoxylates
- Flame retardants
- Hormones, steroids and sterols
- Pharmaceuticals
- Personal Care Products
- Certain metals (arsenic, silver, selenium, mercury, etc.)
- Other (e.g. polyaromatic hydrocarbons, polychlorinated dioxins and furans)
- Pathogens

The choice of categories of substances included in this paper offers an update of the 2001 report which identified two Groups of substances, Group I not requiring additional research at that time; and Group II as those that required more scientific study.

The substances within the categories have been selected because we know they are present in products used on a daily basis; the analytical capability now exists to detect them; the environmental fate and significance is not known, or well known; and some of them, depending on their chemistry, can partition to different media requiring management of that media (e.g. sludge, water, animal issues).

3. LITERATURE REVIEW

3.1 Overview of Literature Review

The land application of biosolids literature is diverse and studies have been conducted for a variety of purposes. In very general terms, the contaminant studies reported here can be categorized as follows:

- Effects of individual sewage treatment plant biosolids processes on micro-constituent fate
- Biosolids surveys
- Environmental exposure studies (i.e. establishing fate and effects in soils)
- Environmental transport studies (i.e. transport in tile drains and surface runoff)
- Environmental accumulation studies (bioaccumulation[1] in plant and animal biota growing in biosolids-amended soils).

Due to the diverse nature of these studies, the database is somewhat fragmented with regards to:

- Types of substances and concentrations (variable units) reported
- Detail provided on sludge/biosolids composition and/or origin
- Geography, climate, soil type

The fragmented nature of the literature presented challenges for data consolidation and formulating conclusions. Thus, emphasis was placed on presenting available information and identifying information gaps.

3.2 Pharmaceuticals

3.2.1 Introduction

This class of micro-constituents in sludges and biosolids includes many different sub-classes with different therapeutic uses. Consistent with the report by Hydromantis *et al* (2009), this review will follow to a great extent the classification used by Gielen (2007). The classes of pharmaceuticals investigated and reported herein are provided in Table 1. By far, the most compounds identified belonged to the general categories of antibiotics.

3.2.2 Antibiotics

Antibiotic pharmaceuticals consist of many classes of compounds applied to inhibit or kill pathogenic bacteria.

Table 1. Categories and Pharmaceuticals Identified in this Review

[1] Note that throughout the report any reference to bioaccumulation does not necessarily imply causation of an environmental effect. Environmental effect can be used synonymously with environmental impacts or ecotoxicity.

Antibiotics		Nervous system	Analgesic	Blood
sulfonamides	macrolides	anti-epileptic	Acetaminophen	anti-lipid
Sulfadimethoxine	Clarithromycin	Primidone	NSAID	Bezafibrate
Sulfamethazine	Erythromycin	Carbamazepine	Diclofenac	Clofibric Acid
Sulfamerazine	Azithromycin	anti-depressant	Naproxen	Gemfibrozil
Sulfametazine	Ormetoprim	fluoxetine	Ibuprofen	Anti-coagulant
Sulfadiazine	Virginiamycin	anti-psychotic	Indometacin	Warfarin
Sulfisoxazole	Tylosin	Chlorpromazine	Mefenamic acid	
Sulfachloro-pyridazine	Roxithromycin	Thioridazine	Ketoprofen	**Other**
Sulfanilamide	tetracyclines	anti-anxiety		anti-parasitic
Sulfadimidine	Doxycycline	Diazepam	**Alimentary**	Thiabendazole
Sulfonamide	Chlortetracycline	Amitriptyline	gastric	Carbadox
Sulfamethizole	Minocycline	Paroxetine	Cimetidine	Anti-fungal
fluoroquinolones	Oxytetracycline	stimulants	Ranitidine	Miconazole
Norfloxacin	Demeclocycline	Methamphetamine	Famotidine	Other
Enrofloxacin	beta-lactams	Amphetamine	Omeprazole	Digoxigenin
Lomefloxacin	Cloxacillin	Caffeine	Diabetic	Cotinine
Sarafloxacin	Oxacillin	1,7-Dimethylxanthine	Glibenclamide	Norgestimate
Flumequine	Penicillin G		Metformin (hydrochloride)	Salicylic Acid
Ciprofloxacin	Penicillin V	**Respiratory/allergy**		
Ofloxacin	Dicloxacillin	anti-histamine	**Cardiac**	
Clinafloxacin	bacteriostats	Diphenylhydramine	Digoxin	Atenolol
lincosamides	Triclosan	Diphenhydramine	Hydrochlorothiazide	Propranolol
Clindamycin,	Triclocarban	Loratidine	Chlorpromazine	Diltiazem
Lincomycin	Trimethoprim	anti-bronchospasm	Thioridazine	
	Chloramphenicol	Albuterol		

3.2.2.1 Occurrence of Antibiotics in Biosolids

Tetracycline Antibiotics

Data on the occurrence of tetracycline compounds in sludge and biosolids are sparse. The recent U.S. EPA Targeted National Sewage Sludge Survey (TNSSS) (U. S. EPA, 2009a) provides one of the most complete pictures of the compounds, as indicated in Table 2. Tetracycline and its metabolite 4-epitetracycline, doxycycline and minocycline were found in the highest concentrations. The literature review of Harrison *et al*. (2006) reported a range of doxycycline concentrations from <1200 to 1500 ng/g TS on a dry weight (dw) basis.

Table 2. Concentrations of Tetracycline Antibiotics in Sludges and Biosolids

Tetracycline Compound	Concentration (ng/g TS dw)	
	Sludge or biosolids not differentiated (sludge survey)	Sludge or biosolids not differentiated (literature survey)
Tetracycline	1278 (630) [a]	
4-ETC	1135 (620)	
4-Epianhydro-tetracycline	251 (140)	
Anhydrotetracycline	263 (153)	
Chlortetracycline	55.1 (39.7)	
4-Epichlortetracycline	119 (100)	
4-Epianhydrochlortetracycline	421 (397)	
Anhydrochlortetracycline	126 (105)	
Isochlortetracycline	83.4 (39.6)	
Oxytetracycline	57.9 (43.2)	
4-Epioxytetracycline	45.3 (41.5)	
Demeclocycline	106 (99.2)	
Doxycycline	877 (424)	<1200–1500
Minocycline	660 (432)	
Reference	U.S. EPA (2009a)	Harrison *et al*. (2006)

[a] mean (median) TS DW = total solids dry weight basis

Sulfonamide Antibiotics

Occurrence data for the sulphonamide class of drugs is sparse in the technical literature, with the exception of sulfamethoxazole. Concentrations reported on a dry matter basis are in a relatively narrow range, with mean values of 10 to 20 ng/g TS dw. The most complete data set is documented in the U.S. EPA's TNSSS, in which sulfanilamide was detected at the highest concentration, approximately one to two orders of magnitude higher than the remaining drugs in this class (Table 3). In the literature survey by Jones-Lepp and Stevens (2007), maximum concentrations of sulfametazine and sulfapyridine were 160 and 197 ng/g TS, respectively.

Many of the sulphonamide class tested by Spongberg and Witter (2008) were beneath the limit of quantitation.

Table 3. Concentrations of Sulfonamide Antibiotics in Sludges and Biosolids

Sulfonamide Compound	Concentration (ng/g TS dw)							
	Survey of biosolids	biosolids before land application	dewatered biosolids	Unknown sludge (An urban WWTP)	Biosolids class A + sludge	Anaerobic digested sludge	Primary Sludge	Anaerobic Sludge
Sulfadiazine	13.6 (9.8) [a]							
Sulfachloropyridazine	12.0 (9,8)							
Sulfadimethoxine	3.57 (2.01)			< 2.04 - 8.15				
Sulfamethazine	7.38 (4.0)			<3.58 - 26.7	nd-160			
Sulfamethizole	4.72 (3.97)			<2.91				
Sulfamethoxazole	21.59 (4.32)	12.4 ± 1.6	15				10±10[b]	5 ±5
Sulfanilamide	536 (99.2)							
Sulfathiazole	10.7 (9.8)			<6.74				
Sulfapyridine		<4			nd-197	1,000±100		
Sulfisoxazole				<4.07 - 21.9				
Sulfadimidine								
Sulfonamide								
Reference	U.S. EPA (2009a)	Sabourin *et al* (2009)	Edwards *et al* (2009)	Spongberg and Witter (2008)	Jones-Lepp and Stevens (2007)	Göbel *et al*. (2005)	Radjenovic *et al*. (2009)	

[a] mean (median) [b] mean ± standard deviation nd = not detected

Fluoroquinolone and Quinoline Antibiotics

Concentrations of the three main identified fluoroquinolones in raw and digested sludge samples are summarized in Table 4. The drugs found at the highest levels in the U.S. TNSSS were ciprofloxacin and ofloxacin, at median concentrations of 5,370 and 3,110 ng/g TS dw, respectively. These two fluoroquinolones have been identified most frequently in the literature, along with norfloxacin.

Table 4. Concentrations of Three Fluoroquinolones in Sludge and Biosolids

Sludge Type	Source	Concentration (ng/g TS dw)			Reference
		Ciprofloxacin	Norfloxacin	Ofloxacin	
	Sludge Survey	10,500 (5,370)[a]	275 (109)	8,570 (3,110)	U.S. EPA (2009a)
Anaerobic digestion (n=5 WWTPs)		1,400-4,800	900–4,200	<LOQ–2,000	Lindberg *et al*. (2005)
Aerobic digestion (n=1 WWTP)		500-900	100-400	100-700	
	Literature Review	50-4,800	10–4,200	<10–2,000	Harrison *et al*. (2006)
Unknown sludge (An urban WWTP)		<5.62-46.3			Spongberg and Witter (2008)
Unknown sludge (A rural WWTP)		8.3			
Raw sludge to digester		6,600	5,100		Lindberg *et al*. (2006)
Digested sludge		6,000	7,000		
Dewatered digested sludge		10,600	9,800		
Dried biosolids (Pellets)		2,600	3,400		
Raw sludge	WWTP1	1,400 ± 120[b]	1,540 ± 30		Golet *et al*. (2002)
	WWTP2	2,030 ± 200	1,960 ± 150		
Digested sludge	WWTP3	2,420 ± 60	2,370 ± 70		
	WWTP2	2,720 ± 200	2,130 ± 190		
Raw sludge		2,200± 400	2,100 ± 200		Golet *et al*. (2003)
Anaerobic digested sludge		3,100 ± 400	2,900 ± 400		
Raw sludge		1,000-2,000	1,500–2,000		Jones-Lepp and Stevens (2007)
Digested sludge		2,300–2,400	2,100–2,400		
Digested sludge		3,100-5970	2,900-6970		Heidler and Halden (2008)
Primary Sludge				190±280	Radjenović *et al*. (2009)
Anaerobic Digested				80 ±30	

[a] mean (median) [b] mean ± standard deviation

Many of the publications reviewed indicate that the concentrations of ciprofloxacin and norfloxacin in the sludge samples are similar in magnitude on the order of 2,000 to 6,000 ng/g TS dw. Lindberg *et al*. (2005) tracked the concentrations of ciprofloxacin and norfloxacin through

the residual solids stream of a wastewater treatment plant in Umea, Sweden. The concentrations increased as the sludge was combined, digested and dewatered, but then dropped significantly after drying by pelletization. It appears that these fluoroquinolone compounds are relatively unaffected by the anaerobic digestion process (Golet *et al*., 2002, 2003). There is some possibility that aerobic sludge digestion may result in lower concentrations of this class of antibiotics than does anaerobic digestion from the study by Lindberg *et al.* (2005), but with only one aerobically digested sludge location for reference, additional study is required to confirm the hypothesis.

The most complete identification of other fluoroquinolone compounds in biosolids comes from the U.S. EPA TNSSS (Table 5). In that survey, median concentrations of the antibiotics were under 50 ng/g TS dw.

Table 5. Concentrations of Other Fluoroquinolones in Sludge and Biosolids (U.S. EPA, 2009a)

Fluoroquinoline/ Quinoline	Concentration (ng/g TS dw)
Clinafloxacin	75.6 (40.4)[a]
Enrofloxacin	27.9 (19.8)
Flumequine	10.6 (9.87)
Lomefloxacin	22.9 (19.8)
Oxolinic acid	4.7 (4.0)
Sarafloxacin	294 (91.9)

[a] mean (median)

Macrolide Antibiotics

In Table 6, the data generated by the U.S. EPA's TNSSS suggest that azithromycin, tylosin and virginiamycin are present at the highest concentrations of the macrolide antibiotics, with mean values of 831, 269 and 138 ng/g TS, respectively. Concentration data from an anaerobically digested sludge by Gobel *et al*. (2005) exhibited some of the highest concentrations of this class of antibiotics. Otherwise, concentration data for this class of antibiotics were sparse.

Beta-Lactam Antibiotics

This class of antibiotics contains the well-recognized penicillin and similar drugs. Few data were identified for these compounds, with only the U.S. EPA's TNSSS providing any information on occurrence in sludges and biosolids (Table 7). Penicillin V at 41 ng/g TS dw was detected at approximately twice the concentration of the other types of beta-lactams.

Lincosamide Antibiotics

Only limited occurrence data in biosolids or sludges were found for this class of compounds (Table 8). In the EPA's TNSSS (U.S. EPA, 2009a), lincomycin and clindamycin were found at median concentrations of 19.9 and 13.4 ng/g TS, respectively. In Ohio, clindamycin in sludges of three urban treatment plants ranged from 3.7 to 154 ng/g TS, while in sludge from a rural treatment facility, the concentration was18.2 ng/g TS (Spongberg and Witter, 2008).

Table 6. Concentrations of Macrolide Antibiotics in Sludges and Biosolids

Sludge Type	Concentration (ng/g TS dw)						Reference
	Azithro-mycin	Clarithro-mycin	Erythro-mycin	Roxithro-mycin	Virginia-mycin	Tylosin	
Not specified (sludge survey)	831 (278)[a]	41.58 (13.4)	36 (19)	8.1 (4.7)	138 (73.3)	269 (128)	U.S. EPA (2009a)
Activated and digested	1.3-158	0.3-63		nd-131			Jones-Lepp and Stevens (2007)
Anaerobic digestion	2,500± 1,000[b]	700 ± 400					Göbel *et al*. (2005)
Unknown sludge (urban WWTP)		<1.39 - 30.2					Spongberg and Wittmer (2008)
Unknown sludge (rural WWTP)		<1.39					
Primary sludge			105±50				Radjenović *et al*. (2009)
Anaerobically digested			70 ±30				
Not specified (2 plants)				<7 – 1,800		300 – 4,000	Nieto *et al*. (2007a)

[a] mean (median) [b] mean ± standard deviation
LOQ = limit of quantitation nd = not detected

Table 7. Concentrations of Beta-Lactam Antibiotics in Sludges and Biosolids (U.S. EPA, 2009a)

Beta-lactam	Concentration (ng/g TS dw)
Cloxacillin	26.4 (19.9)[a]
Oxacillin	20.8 (19.8)
Penicillin G	20.8 (19.8)
Penicillin V	41.4 (39.6)

[a] mean (median)

Table 8. Concentrations of Lincosamide Antibiotics in Sludges and Biosolids

Sludge Type	Concentration (ng/g TS dw)		
	Lincomycin	Clindamycin	Reference
Not Specified (sludge survey)	30.2 (19.9) [a]	41.58 (13.4)	U.S. EPA (2009a)
Unknown sludge (3 urban WWTP)		3.7 - 154	Spongberg and Witter (2008)
Unknown sludge (A rural WWTP)		18.2	

[a] mean (median)

3.2.2.2 Fate and Transport of Antibiotics in the Terrestrial Environment

Properties Affecting Fate and Transport

According to Thiele-Brun (2003), properties affecting antibiotic fate include soil pH, organic matter and aerobic conditions. Photodecomposition was not a major mechanism, however more recently, Chee-Sanford *et al.* (2009) indicated that quinolones and tetracyclines in soils amended

with livestock manure are susceptible to photodecomposition, but that sulfonamides are not. Hydrolysis of antibiotics, including beta-lactams, macrolides and sulfonamides, in soil following manure application was reported by Chee-Sandford *et al*. (2009) to be an important removal pathway. The sorption of antibiotics to soil organic matter and mineral exchange sites is more dependent on charge transfer, ionic interactions and hydrogen bonding than on dependency of hydrophobic properties, according to both Thiele-Brun (2003) and Chee-Sandford *et al.* (2009). Many antibiotics have water solubilities greater than 1 g/L, and thus are relatively hydrophilic. Soil solution pH is important in the mobility of the antibiotics because many have acid dissociation constants in the range of soil pH (Chee-Sandford *et al*., 2009), wherein dissociation of the compounds from non-ionized to ionized forms can cause differences with the electrostatic binding properties of the soil components (clays, organic matter, etc.).

Surface Runoff

Concentrations of sulfamethoxazole in surface runoff samples following application of liquid biosolids are summarized in Table 9. Both studies involved simulated rainfall events for the runoff collection. In the study with liquid biosolids, the highest concentration was observed immediately after the biosolids application (day 1), declining to non-detectable concentrations by the 36th day after application. With dewatered biosolids, the rate of dissipation was much slower, with detectable concentrations reported 36 days after biosolids application.

Table 9. Concentration of Sulfamethoxazole in Tile Drainage Water Following Biosolids Application

Day after Biosolids Application	Sulfamethoxazole in Runoff (ng/L)	
	Liquid Biosolids (mostly anaerobic digested)	Dewatered Biosolids (mostly anaerobic digested)
Soil Structure	sand 18%, silt 67%, clay 15%, organic carbon 3.4%; pH = 7.5	
Application Rate	93500 L/ha	8T dw/ha
t=1 day	115	3.2
t=3 days	30	2.5
t=7days	10	1.9
t=22 days	5	1.5[a]
t=36 days	<4.3	1.0
t-266 days	<4.3	Not reported
Reference	Topp *et al*. 2008	Sabourin *et al*. 2009

[a] t=21 days LOD = level of detection

Transport in Soil

The presence of fluoroquinolones on agricultural soils amended with one application [application and incorporation methods not specified] of anaerobically digested sludge at 50 T/ha once every third year was monitored by Golet *et al*. (2003). [This rate was ten times the allowable rate of 5 T/ha every third year in Switzerland; the mass basis was not specified as wet or dry solids]. In the top 60 cm investigated, the soil was predominantly sand (approx. 60%), with roughly equal amounts of silt and clay. The pH of the top 10 cm of soil ranged from 6.7 to 7.1, while for the layers from 10 to 20 cm deep, the pH ranged from 7.6 to 7.8. Reported concentrations of ciprofloxacin and norfloxacin in the soil strata 5 months and 21 months after the previous

biosolids application are provided in Table 10. Five months after the biosolids application the two antibiotics remained in the top 5 cm of the soil. When measured again 21 months after the biosolids application, the concentrations in the top 5 cm of soil were essentially unchanged from the sampling at 5 months. Some downward mobility of trace amounts of the fluoroquinolones to the upper 15 cm was noted. Golet *et al*. (2003) concluded that the fluoroquinolones are persistent when applied to soils in biosolids, but they are relatively immobile and unlikely to leach to groundwater.

Table 10. Concentrations of Ciprofloxacin and Norfloxacin in Soil Levels following Biosolids Application of 50 T/ha every third Year (Golet *et al*., 2003)

Soil depth, cm	concentration (ng/g DW) in different depths of sludge-amended soil following sludge application			
	after 5 months		after 21 months	
	Ciprofloxacin	Norfloxacin (NOR)	Ciprofloxacin	Norfloxacin (NOR)
0-2.5 cm	220 – 450	200 – 350	180 – 300	180 – 300
2.5-5 cm	<0.05 – 220	<0.05 – 200	<0.18	<0.18
5-7.5 cm	<0.05	<0.05	<0.18	<0.18
7.5-10 cm	<0.05	<0.05	<0.18	<0.18
10-15 cm	<0.05	<0.05	<0.18	<0.18
15-20 cm	<0.05	<0.05	<0.18	<0.18

Fate in Soil

Biodegradation is a major fate mechanism because many microbes in the soil have enzymes that can attack polar or ionic positions of the antibiotic molecule, (Thiele-Brun, 2003), although Chee-Sandford *et al*., (2009) observed in their literature review that antibiotic residues may have a toxic effect on indigenous soil microbes, and that the effects of antibiotic entry by livestock manure to natural environments on microbes resident in the environments is still unknown.

Concentrations of norfloxacin and ciprofloxacin in two Swiss agricultural soils amended with one application of anaerobically digested biosolids at a rate of 25 T/ha were summarized by Golet *et al*. (2002). The data in Table 11 appear to indicate that the fluoroquinolones declined slightly in the Wetzikon site, but not in the Reckenholz site, in the interim between the eighth and twenty-first month samplings. The authors also indicated that some partial biodegradation of the antibiotics might have occurred before the first sampling eight months after the biosolids application. Overall, however, Golet *et al*. (2002) concluded that the compounds were persistent in the soil following amendment with biosolids. Discussion of the relative concerns of these concentrations is found in Section 4 of this report.

In the literature review of livestock manure applied to soil, Chee-Sandford *et al.* (2009) found that some tetracyclines could accumulate in soil but none of the antibiotics studied were detected at soil depths greater than 30 cm, and only sulfamethazine was detected in ground water. The antibiotics oxytetracycline, sulfadiazine, sulfathiazole, sulfamerazine, sulfamethoxypyridazine, sulfamethoxazole, sulfadimethoxine and tylosin were never detected in soil or groundwater.

Chee-Sandford *et al.* (2009) concluded the antibiotics underwent limited transport, even in highly porous sandy soils.

Table 11. Concentrations of Fluoroquinolones in Soils of Two Biosolids Application Sites (Golet *et al.*, 2002)

Measurement	Concentration in Soil (ng/g DM)			
	Experimental site 1-Wetzikon		Experimental site 2-Reckenholz	
	8 months after application	21 months after application	8 months after application	21 months after application
Soil structure	7% organic carbon[2]; 38% clay, 23% sand, 27% silt; pH = 6.7		4% organic carbon, 18% clay, 54% sand, 21% silt, pH = 6.9	
Ciprofloxacin	350 ± 40	280 ± 10	270 ± 40	400 ± 30
Norfloxacin (NOR)	320 ± 10	270 ± 10	300 ± 10	290 ± 10

No of replicates = 2

Antibiotic Resistance in Soil Bacteria

The presence of antibiotics in biosolids applied to land had no significant effect on the antibiotic resistance (ABR) of soil bacteria as determined using heterotrophic plate count (HPC) as the indicator (Brooks *et al.* 2007b). The HPC concentrations in the biosolids-applied soil did not deviate from the pre-application concentrations due to the presence of ampicillin, cephalothin, ciprofloxacin and tetracycline. The fraction of soil bacteria resistant to the same four antibiotics did not vary statistically from pre-application levels throughout the duration of the 15 month study. Similarly, the fraction of antibiotic resistant bacteria (ABR) in both the control (non-applied) site and the continuously applied biosolids site were not statistically different ($P>0.05$), as shown in Table 12. Although Brooks *et al.* (2007b) concluded that the presence of the antibiotics in biosolids would not increase levels of ARB in soils following biosolids applications.

Table 12. Fraction of Antibiotic-Resistant Bacteria in Biosolids and Soils with and Without Biosolids Applications (from Brooks *et al.*, 2007b).

Matrix	Antibiotic Resistance (% of Total HPC Concentration)			
	Ampicillin	Cephalothin	Ciprofloxacin	Tetracycline
Biosolids (other U.S. sites)	4.4	21.2	1.8	1.9
Biosolids (applied to Field)	3.6	63.6	0.1	0.4
Field, no biosolids applied	8.1	10.1	3.1	2.4
Field, continuous biosolids applied	7.9	11.0	9.2	2.8

Antibiotic concentrations used in biosolids: ampicillin 32 mg/L; cephalothin 32 mg/L; ciprofloxacin 4 mg/L; tetracycline 16 mg/L.

[2] This 7% is high and not representative of most soils in Ontario

Thiele-Brun (2003) did not discuss specifically antibiotic resistance of soil microbes resulting from biosolids amendment. Some tetracycline-resistant *Clostridia* in soil were identified due to livestock manure spreading. The author also noted, however, that many soil microbes have a natural tolerance to antibiotics. Discussion of the introduction of antibiotic resistant bacteria to soils was limited only to livestock waste as the source. Gene transfer of antibiotic-resistant bacteria to indigenous bacteria was shown to be possible, but the effect disappeared within one month.

Based on data from a literature review, Chee-Sandford *et al.* (2009) concluded that the level of tetracycline-resistant bacteria initially increased following an application of livestock manure, but after five months, the proportion of tetracycline-resistant bacteria in all manure-treated soils returned to levels in the range of the non-treated control sites.

The Panel on Contaminants of the Norwegian Scientific Community on Food Safety (VKM, 2009) expressed potential concern regarding the development of antibiotic resistance to the fluoroquinolone ciprofloxacin due to its persistence and limited mobility into the subsoil. (Brooks, 2009) has also expressed concerns regarding antibiotic resistance in soil microbes, and has studies in progress investigating the influence of land applied manures and biosolids on antibiotic resistance in the soil population.

Effect on Soil Biota

Antibiotics can have an influence on soil microbes and change the composition of the indigenous microbes. Some antibiotics have an inhibitory effect on the soil microbes (streptomycin, tetracycline) while others stimulate the growth of the microbes (Thiele-Brun, 2003). At a higher trophic level, soil fauna are not affected by antibiotics, even at what Thiele-Brun (2003) referred to as "excessive" doses. Anti-helminth pharmaceuticals, however, more typically used with livestock, can exert a toxic effect. The extent of influence of antibiotics is governed by the bioavailability of the antibiotics, which in turn is dependent on soil properties, availability of nutrient and root exudates. Thiele-Brun (2003) concluded information on the ecotoxicity of antibiotics is scarce, thus leading to the conclusion that the effect of antibiotics in the terrestrial environment is a knowledge gap.

The Panel on Contaminants of the Norwegian Scientific Community on Food Safety (VKM, 2009) estimated probable no effect concentrations (PNECs) for pharmaceuticals in soil, with values established using aquatic PNEC values. Based on this assessment method, the Panel on Contaminants concluded that drug substances in sewage sludge (the Panel did not differentiate between sludge and biosolids) constitute a low risk for soil-living organisms.

Plant Uptake of Antibiotics

The potential uptake of antibiotics by plant species was assessed by Thiele-Brun (2003) to be variable between reports (i.e. inconsistent results), and also to be dependent on the plant species and antibiotics tested. Potential detrimental effects noted in plant growth due to manure amendment were considered due to excessive loadings of nitrogen or metals rather than antibiotics present. Many reported results were based on laboratory *in vitro* tests involving antibiotic concentrations in excess of concentrations due to normal soil amendment practices.

One study involving radio-labelled ^{14}C-sulfadimidine reported translocation from the root to shoots of maize was less than 0.04%, while other studies involving uptake of tetracyclines by pinto beans and coconut trees was non-detectable. Chee-Sandford *et al.* (2009) summarized their literature review by indicating that a number of studies have indicated that while antibiotics are taken up by plants, biotransformation of the antibiotics can occur through "well-known detoxification mechanisms."

General Observations and Summary

The overall assessment of the literature review by Thiele-Brun (2003) was that in most fields of investigation of the fate, transformation and effect of antibiotics in the terrestrial environment, the available data were limited. Most data reviewed by the author was related to antibiotics in livestock manures rather than municipal biosolids. The author recommended more responsible use and reduction in consumption of antibiotics.

3.2.3 Nervous System

Anti-Epileptics (Anti-Convulsants)

Occurrence Data

Anti-epileptic (also called anti-convulsive) drugs are used in the control of epilepsy. Occurrence data were primarily found for carbamazepine. The only reference to a second anti-epileptic drug, Primidone, stated the concentrations in sludge samples from three Ohio treatment plants were lower than the level of quantitation (Spongberg and Witter, 2008). Concentrations of carbamazepine in biosolids and sludge samples typically fell into a relatively narrow range of 5 to 400 ng/g TS dw (Table 13), with a reported range from non-detectable to a maximum of 850 ng/g TS dw (Jones-Lepp and Stevens (2007).

Fate and Transport in the Terrestrial Environment

Depending on the method of application of biosolids, contaminants in the biosolids may be leached through the soil column or washed from the soil surface in runoff. Maximum concentrations of carbamazepine in tile drainage following application of liquid or dewatered biosolids are summarized in Table 14.

The decline in concentrations of carbamazepine and other pharmaceuticals in surface runoff over time, following biosolids applications, has been monitored by Topp *et al*. (2008) and Sabourin *et al*. (2009). Both studies were conducted near London, ON in a silt loam soil of composition 18% sand, 67% silt and 15% clay with organic matter content of 3.4% and pH = 7.5. Sabourin *et al*. (2009) used micro-plots with the dewatered biosolids incorporated into the soil. Topp *et al*. (2008) used micro-plots with liquid biosolids followed by incorporation. The results for carbamazepine are provided in Table 15.

Table 13. Occurrence Data for Carbamazepine in Sludges and Biosolids

Biosolids Source	Concentration (ng/g TS dw)	Reference
Dewatered biosolids	9	Edwards *et al*. (2009)
Biosolids (unspecified)	390	Kinney *et al*. (2008)
Dewatered biosolids	6.7 ± 0.6	Sabourin *et al*. (2009)
Not specified (Sewage treatment plant 1)	nd - 78	Nieto *et al*. (2007b)
Not specified (Sewage treatment plant 2)	50 - 165	
Not specified (3 urban WWTPs)	4.8 - 12.9	Spongberg and Witter (2008)
Not specified (A rural WWTP)	21.1	
Not specified (sludge survey)	135 (55)[b]	U.S. EPA (2009a)
Biosolids class A + sludge	nd-850	Jones-Lepp and Stevens (2007)
Anaerobic digested sludge	258.1 ±4.7[a]	Miao *et al*.(2005)
Digested sludge	281	Heidler and Halden (2008)
Anaerobic digested sludge	80 ±10	Radjenović *et al*. (2009)
Dewatered sludge	64 ng/g OC	Kinney *et al*. (2006)
Compost	15-180 ng/g OC	
Heat dried biosolids	140 ng/g OC	
Air dried biosolids	51 ng/g OC	
Anaerobic digested sludge	1,200 ng/g OC	

nd = not detected [a] mean ± standard deviation [b] mean (median)

Table 14. Concentration of Carbamazepine in Tile Drainage Water Following Biosolids Application

Source		Maximum Concentration in tile drainage (ng/L)	Reference
Tile Drainage	2005 Post liquid biosolids (93,500 L/ha)	1140	Edwards *et al*. (2009)
	2006 post dewatered biosolids (8 T dw/ha)	50	

Table 15. Concentration of Carbamazepine in Surface Runoff Following Application of Liquid and Dewatered Biosolids

Time after application	Carbamazepine concentration in runoff (ng/L)	
t=1 day	300	38.5
t=3 days	250	49.3
t=7days	300	59.4
t=22 days	100	35.3[a]
t=36 days	150	30.2
t-266 days	10	
Application rate	93500 L/ha	8T dw/ha
Biosolids Type	Liquid biosolids (mostly anaerobic digested)	Dewatered biosolids (mostly anaerobic digested)
Reference	Topp *et al* (2008)	Sabourin *et al*. (2009)

[a] after 21 days

Sabourin *et al*. (2009) noted the difference in release of certain contaminants such as carbamazepine, to surface runoff when biosolids were applied in dewatered form compared to liquid form. In Table 15, the highest concentration of carbamazepine in surface runoff from a liquid biosolids-applied site was on the first day after application, whereas with the runoff from the dewatered biosolids site, the highest concentration was observed seven days after application. Slower release from dewatered biosolids was attributed to weathering, drying and physical deterioration of the biosolids aggregates. Sabourin *et al*. (2009) concluded that availability of contaminants such as carbamazepine for transport off-site in runoff is dependent in part on the form of biosolids applied as well as the depth of soil application and incorporation processes.

No data were found that identified the persistence of carbamazepine in soils amended with biosolids, the bioaccumulation of carbamazepine in soil flora and fauna, or environmental impact (lack of toxicity data).

Mood-altering Pharmaceuticals

Occurrence Data

Different categories of pharmaceuticals identified in this survey include anti-anxiety (Amitriptyline, Diazepam and Paroxetine), anti-depressants (Fluoxetine), psycho-stimulants (amphetamine, methamphetamine and caffeine), and anti-psychotics (Chlorpromazine and Thioridazine). Data concerning these drugs in biosolids are generally scarce. The concentration data for fluoxetine in sludges indicate it is found typically in a range between 100 and 1,000 ng/g TS dw (Table 16). Concentrations of fluoxetine and paroxetine in a sample of primary sludge were of approximately the same magnitude (Radjenović *et al*., 2009).

Fate and Transport in the Terrestrial Environment

No data on fate, persistence, transport or bioaccumulation by soil flora or fauna for the anti-anxiety and anti-depressant pharmaceuticals were found in this review.

Table 16. Concentrations of Representative Anti-Anxiety and Anti-Depressants in Sludges and Biosolids

Sludge Source	Concentration (ng/g TS dw)		Reference
	Fluoxetine	Paroxetine	
Dewatered Biosolids (mostly anaerobically digested)	<3		Sabourin *et al*. (2009)
Dewatered Biosolids (mostly anaerobically digested)	<3		Edwards *et al*. (2009)
Primary Sludge	100±50[a]	70±50	Radjenović *et al*. (2009)
Anaerobic digestion	150 ±60 [a]	50 ± 20	Radjenović *et al*. (2009)
Biosolids class A + sludge (literature review)	nd-59		Jones-Lepp and Stevens (2007)
Not specified (sludge survey)	245 (147)[b]		U.S. EPA (2009a)
Heat drying	480 ng/g OC		Kinney *et al*. (2006)
Composting	255-705 ng/g OC		
Air drying	2,800 ng/g OC		
Anaerobic digestion	4,700 ng/g OC		

[a] mean ± standard deviation [b] mean (median)
OC = organic carbon LOD = limit of detection

Psycho-stimulants

Only a few studies provided any data on concentrations of psycho-stimulants in sludges or biosolids. The occurrence data appear in Table 17. The data indicate that caffeine and its metabolite can be present in variable concentrations from 5 to 5,000 ng/g TS dw. Gielen (2007) demonstrated that different extraction procedures in the analysis of caffeine in sludges can have a significant effect on the concentration reported. The data for amphetamine and methamphetamine are limited, with amphetamine exhibiting a higher concentration range than methamphetamine.

Table 17. Concentrations of Psycho-Stimulants in Sludges

Constituent	Sludge Type	Concentration (ng/g TS dw)	Reference
Amphetamine	Biosolids class A + sludge (literature review)	5-300	Jones-Lepp and Stevens (2007)
Methamphetamine	Biosolids class A + sludge (literature review)	0-4	
Caffeine	Dewatered biosolids (mostly anaerobically digested	35.4 ± 12.8[a]	Sabourin *et al*. (2009)
	Dewatered anaerobically digested biosolids	<LOD	Kinney *et al*. (2008)
	Unknown sludge (WWTP 1)	57 - 69	Nieto *et al*. (2007b)
	Unknown sludge (WWTP 2)	<LOQ - 65	
	Unknown sludge (An urban WWTP)	<1.44 - 5.2	Spongberg and Witter (2008)
	Unknown sludge (A rural WWTP)	4.8	
	compost	7.4/43 [c]	Gielen (2007)
	primary sludge	4,530/1,585	
1,7-Dimethylxanthine	Not specified (sludge survey)	1,180 (987) [b]	U.S. EPA (2009a)

LOQ = limit of quantitation LOD = limit of detection [a] mean ± standard deviation
[b] mean (median) [c] Soxhlet extraction/Supercritical fluid extraction

Fate and Transport in the Terrestrial Environment
Published data on the fate and transport of psycho-stimulant drugs in the terrestrial environment are sparse. Caffeine was detected in samples of surface runoff from a site amended with dewatered biosolids, as indicated in Table 18 (Sabourin *et al*., 2009). The data indicated that the maximum concentration of caffeine was not reached until 7 days after the biosolids application. Even after 36 days, the concentration of caffeine in the runoff was not greatly reduced from the concentration observed in the initial runoff sample.

Table 18. Concentration of Caffeine in Surface Runoff Following Application of Liquid and Dewatered Biosolids

Time after application	Caffeine concentration in runoff (ng/L)
t=1 day	25.8
t=3 days	30.1
t=7days	35.2
t=21 days	32.0
t=36 days	20.8
Application rate	8T dw/ha
Biosolids Type	Dewatered biosolids (mostly anaerobic digested)
Reference	Sabourin *et al*. 2009

Other than the surface runoff data of Sabourin *et al*. (2009) for caffeine presented above, no data on fate, persistence, transport or bioaccumulation by soil flora or fauna for the psycho-stimulants were found in this review.

3.2.4 Analgesics and Anti-Inflammatory Drugs
Occurrence
Analgesics are drugs that relieve pain (i.e., "pain-killers"). Non-steroidal-anti-inflammatory drugs (NSAIDs) may be used both as analgesics and for their anti-inflammatory purposes, in which they inhibit an enzyme (cyclooxygenase) contributing to the inflammation process.

Occurrence data for these pharmaceuticals are found in Table 19. The only analgesic compound identified in this review is acetaminophen (also called paracetamol in other countries). Several NSAIDs were identified in sludge and biosolids samples, including diclofenac, ibuprofen, naproxen, ketoprofen, indometacin and mefenamic acid. The most commonly reported NSAIDs were ibuprofen, naproxen and diclofenac.

Fate and Transport in Terrestrial Environment
Concentrations of acetaminophen, ibuprofen and naproxen in surface runoff following applications of biosolids were monitored for liquid biosolids (Topp *et al*., 2008) and dewatered biosolids (Sabourin *et al*., 2009). The reported data are presented in Table 20. Naproxen concentrations declined steadily with time for the application of liquid biosolids, however both acetaminophen and ibuprofen were found to persist in the runoff samples after 36 days whether biosolids were applied in liquid or dewatered form.

Table 19. Occurrence of Analgesics and Non-Steroidal Anti-Inflammatory Drugs (NSAIDs) in Sludges and Biosolids

Biosolids Source	Concentration (ng/g TS dw)								Reference
	Acetamin-ophen	Codeine	Diclofenac	Ibuprofen	Indomet-acin	Ketoprofen	Naproxen	Mefen-amic acid	
Dewatered biosolids (mostly anaerobically digested)	17			750			470		Edwards *et al*. 2009
Dewatered biosolids (mostly anaerobically digested) (n=3)	28.6 ± 11.4			657 ± 334			394 ± 35.5		Sabourin *et al*. 2009
Not specified (Sewage treatment plant 1) (n=5)	nd - 34		nd - 65		70 - 99		nd - 242		Nieto *et al*. (2007b)
Not specified (Sewage treatment plant 2) (n=5)	nd - 42		nd - 183		nd - 75		nd - 87		
Not specified (literature survey)	0.0006–4535								Harrison *et al*. (2006)
Not specified (An urban WWTP) (n=3)			<1.37 - 23.1						Spongberg and Witter (2008)
Not specified (A rural WWTP) (n=1)			28.5						
Not specified (sludge survey)	462 (396)[a]	30.6 (19.9)		653 (143)			86.2 (31.6)		EPA (2009a)
Primary sludge			215±130[b]	535±193		220±110		10±5	Radjenović *et al*. (2009)
Anaerobic digested sludge			190±130	300 ±70		40±40		50±15	
Biosolids class A + sludge	nd-1400								Jones-Lepp and Stevens (2007)
Compost				<5					Gielen (2007)
Primary sludge				153 - 299					

LOQ = Limit of Quantitation nd = not detected

[a] mean (median) [b] mean ± standard deviation

Table 20. Concentrations of Acetaminophen and NSAIDs in Runoff from Soils Amended with Biosolids

Time after application	Concentration in runoff (ng/L)					
	Acetaminophen	Naproxen	Ibuprofen	Acetaminophen	Naproxen	Ibuprofen
t=1 day	120	515	1,200	20.3	0.5	35.5
t=3 days	171	350	630	17.5	18.1	45.2
t=7days	85	190	220	15.3	0	43.1
t=22 days	56	55	410	12.5	0	35.3
t=36 days	170	30	900	10.8	0.0	79.2
t-266 days	0	10	<6.4			
Application rate	93,500 L/ha			8T dw/ha		
Biosolids Type	Liquid biosolids (mostly anaerobic digested)			Dewatered biosolids (mostly anaerobic digested)		
Reference	Topp *et al* (2008)			Sabourin *et al*. (2009)		

LOQ = limit of quantitation

Edwards *et al*. (2009) reported concentrations of acetaminophen, ibuprofen and naproxen in tile drainage following application of biosolids, both in liquid and dewatered form (Table 21). Concentrations were substantially higher in the drainage from the liquid biosolids application, particularly for the ibuprofen and naproxen, compared to the dewatered biosolids application.

Table 21. Concentration of Analgesics and NSAIDs in Tile Drainage (Edwards *et al*. 2009)

Pharmaceutical	Maximum Concentration in tile drainage (ng/L)	
	2005 Post Liquid Biosolids application (93,500L/ha)	2006 Post Dewatered Biosolids application (8 T dw/ha)
Acetaminophen	440	230
Naproxen	1,050	30
Ibuprofen	4,120	70

Several studies have investigated the mobility of analgesics and NSAIDs applied in biosolids to soils (i.e., in surface runoff and tile drainage). Otherwise, data on the fate, persistence and bioaccumulation of these compounds by soil flora and fauna were not identified in this review.

3.2.5 Bacteriostat Antibiotics

Occurrence

Trimethoprim is a pharmaceutical with bacteriostatic properties, often used for fighting urinary tract infections. Concentrations of trimethoprim in sludges are generally low (less than 100 ng/g TS) as indicated in Table 22.

Table 22. Concentrations of Trimethoprim in Sludges and Biosolids

Sludge source	Concentration (ng/g TS dw)	Reference
Not Specified (Sludge survey)	30.4 (10.8)[a]	U.S. EPA (2009a)
Biosolids Class A &B and sludge	nd – 22	Jones-Lepp and Stevens (2007)
Primary sludge	40±15[b]	Radjenović *et al*. (2009)
Anaerobic digestion	20 ±5	
Digested sludge	<0.1	Heidler and Halden (2008)
Anaerobic digestion	<100	Göbel *et al*. (2005)
Not specified (2 plants)	<20	Nieto *et al*. (2007a)

nd = not detected LOQ = limit of quantitation
[a] mean (median) [b] mean ± standard deviation

Fate and Transport in the Terrestrial Environment
Few data on fate and transport data for the bacteriostatic antibiotics were found in this review. In one study, Kinney *et al*. (2008) examined concentrations of trimethoprim in the soils and earthworms at sites with and without biosolids amendment (Table 23). Trimethoprim was detected in only one soil sample, and that was from the site without biosolids amendment. Because the worms from that site had no detectable concentration of the compound, a bioaccumulation factor of 0 was applied. At the site with the biosolids amendment, earthworms from the May 19-05 sample had a trimethoprim concentration of 127 ng/g of dry matter (dm); the concentration in the soil was non-detectable, however, so no bioaccumulation factor could be determined.

Table 23. Concentrations of Trimethoprim in soil and Earthworm Samples (Kinney *et al*., 2008)

Site Description	Sample Matrix	Trimethoprim (ng/g dm)
Site 1 (without biosolids application)	Soil Jun 6-05	0.64
	Worm Jun 6-05	ND
	Soil Sep 29-05	ND
	Worm Sep 29-05	ND
Site 2 (with biosolids application on April 18, 2005)	Soil May 19-05	ND
	Worm May 19-05	127
	Soil Sep 21-05	ND
	Worm Sep 21-05	ND

Other than the limited data for trimethoprim in earthworms by Kinney et al. (2008) presented above, no data on fate, persistence, transport or bioaccumulation by soil flora or fauna for bacteriostats were found in this review.

3.2.6 Cardiovascular Pharmaceuticals

Occurrence
This class of pharmaceuticals are those which affect the cardiovascular system. Drugs in this class have generic actions including beta-blockers (atenolol, propanolol), calcium-channel

blockers (diliatazem), thiazides (hydrochlorothiazide) and digoxin. These pharmaceuticals are used to control heart arrhythmia and hypertension (high blood pressure). Hydrochlorothiazide is prescribed as an anti-diuretic, which ultimately helps to reduce hypertension. Dehydronifedipine is a metabolite of the calcium-channel blocker nifedipine.

The compounds in this class that were identified in the literature review are provided in Table 24. The range of concentrations for pharmaceuticals in this class appears to be on the order of 10 to 400 ng/g TS dw.

Fate and Transport in the Terrestrial Environment
Concentrations of atenolol in tile drainage following applications of biosolids (Edwards *et al*., 2009) are summarized in Table 25.

Table 24. Concentrations of Cardiovascular Pharmaceuticals in Sludges and Biosolids

Sludge Source	Concentration (ng/g TS dw)						Reference
	Atenolol	Digoxin	Diltiazem	Hydrochloro-thiazide	Propranolol	Dehydro-nifedipine	
Liquid biosolids (n=3)	9 ± 0.6 [b]						Lapen *et al*. (2008a)
Dewatered biosolids (mostly anaerobically digested)	22						Edwards *et al*. (2009)
Dewatered biosolids (mostly anaerobically digested) (n=3)	1.6 ± 0.6						Sabourin *et al*. (2009)
Not Specified (Sludge Survey)		208 (99.4)[a]	40.2 (14.8)			5.03 (4.04)	U.S. EPA (2009a)
Biosolids class A + sludge			nd-26			8-390	Jones-Lepp and Stevens (2007)
Primary Sludge	90±30			40±20	40±20		Radjenović *et al*. (2009)
Anaerobically Digested Sludge	10±2			15±10	30±15		
Not specified (2 plants)			<0.26 - 12.8				Spongberg and Witter (2008)

nd = not detected [a] mean (median) [b] mean ± standard deviation

Table 25. Concentration of Atenolol in Tile Drainage (Edwards *et al*. 2009)

Pharmaceutical	Maximum Concentration in tile drainage (ng/L)	
	2005 Post Liquid Biosolids application (93,500L/ha)	2006 Post Dewatered Biosolids application (8 T dw/ha)
Atenolol	270	100

Concentrations of atenolol in runoff from the surface of biosolids-amended soil are summarized in Table 26. Both the data from Topp *et al*. (2008) and Sabourin *et al*. (2009) indicate that atenolol concentrations in runoff decline rapidly after the biosolids application.

Table 26. Concentration of Atenolol in Surface Runoff Following Application of Liquid and Dewatered Biosolids

Time after application	Atenolol concentration in runoff ng/L	
t=1 day	70	39.6
t=3 days	25	<2
t=7days	10	30.5
t=22 days	5	<2 [a]
t=36 days	<4	<2
t-266 days	<4	
Application rate	93,500 L/ha	8 T dw/ha
Biosolids Type	Liquid biosolids (mostly anaerobic digested)	Dewatered biosolids (mostly anaerobic digested)
Reference	Topp *et al* 2008	Sabourin *et al*. 2009

[a] after 21 days

Several studies investigated the mobility of atenolol applied in biosolids to soils (i.e., in surface runoff and tile drainage). Atenolol was the only cardiovascular drug identified with these data; mobility data for other cardiovascular drugs were not identified. Data on the fate, persistence and bioaccumulation of the cardiovascular compounds by soil flora and fauna were not identified in this review.

3.2.7 Alimentary Tract Pharmaceuticals

Occurrence

This class of pharmaceuticals includes anti-diabetic drugs, and anti-dyspeptics or acid reflux inhibitors. The latter group have technical names including hydrogen receptor agonists or proton pump inhibitors. In Table 27, the anti-diabetic drug metformin is higher in concentration than its alternate glibenclamide. Cimetidine was identified at the highest concentration (1,330 ng/g TS) of gastric reflux inhibitors by a wide margin. Other studies involving analysis of sludges (not included in the Table) revealed non-detectable concentrations of cimetidine (Spongberg and Witter, 2008) and the proton pump inhibitor omeprazole (< 7 ng/g TS dw) (Nieto *et al*., 2007a).

Fate and Transport in the Terrestrial Environment
No data on fate, persistence, transport or bioaccumulation by soil flora or fauna for alimentary tract pharmaceuticals were found in this review.

Table 27. Concentrations of Alimentary Tract Pharmaceuticals in Sludges and Biosolids

Compound	Application	Sludge Source	Concentration (ng/g TS dw)	Reference
Glibenclamide	anti-diabetic	Primary sludge	90±100[a]	Radjenović *et al*. (2009)
		anaerobic digested sludge	160±30	
Metformin (hydrochloride)	anti-diabetic	Not Specified (sludge survey)	533 (546)[b]	U.S. EPA (2009a)
Cimetidine	H_2-receptor antagonist (Anti-dyspeptic)	Not Specified (sludge survey)	1,330 (171)	U.S. EPA (2009a)
		Biosolids class A + sludge	nd-71	Jones-Lepp and Stevens (2007)
Famotidine	H_2-receptor antagonists (Anti-dyspeptic)	Primary sludge	20±20	Radjenović *et al*. (2009)
		anaerobic digested sludge	60±30	
Ranitidine (hydrochloride)	H_2-receptor antagonists (Anti-dyspeptic)	Not Specified (sludge survey)	57.5 (12.5)	U.S. EPA (2009a)

nd = not detected [a] mean ± standard deviation [b] mean (median)

3.2.8 Blood-Modifying Pharmaceuticals

Occurrence
This class of drugs includes anti-lipid (cholesterol lowering) (e.g., gemfibrozil, bezafibrate and clofibric acid) and anti-coagulants (e.g. Warfarin). Gemfibrozil was the compound reported most frequently in the literature, with concentrations ranging as high as 1,500 ng/g TS dw in the review of sludges and biosolids by Jones-Lepp and Stevens (2007) (Table 28). Maximum concentrations of the other pharmaceuticals in this class were substantially lower. The study completed by Radjenović *et al*., (2009) indicated that gemfibrozil was not likely to be removed by the anaerobic digestion process.

Fate and Transport in the Terrestrial Environment
Gemfibrozil was detected at a concentration of 1040 ng/L in tile drainage following application of liquid biosolids (Table 29), but the compound was not detected in tile drainage following application of dewatered biosolids (Edwards *et al*., 2009).

Table 28. Concentrations of Blood-Modifying Pharmaceuticals in Sludges and Biosolids

Sludge Source	Concentration (ng/g TS dw)				Reference
	Bezafibrate	Clofibric Acid	Gemfibrozil	Warfarin	
Dewatered biosolids (mostly anaerobically digested) (n=3)			31 ± 2.2		Sabourin *et al*. (2009)
Dewatered biosolids (mostly anaerobically digested)			24		Edwards *et al*. (2009)
Not specified (sludge survey)			214 (101)[a]	10.5 (9.9)	U.S. EPA (2009a)
Literature review			nd - 1500	nd - 92	Jones-Lepp and Stevens (2007)
Literature review			nd - 1190		Harrison *et al*. (2006)
Unknown sludge (3 urban WWTPs)		<4.20 - 8.1	<1.57 - 3.4		Spongberg and Witter (2008)
Unknown sludge (A rural WWTP)			18.3		
Two treatment plant sludges	<LOQ - 88	<LOQ - 64			Nieto *et al*. (2007b)
Primary sludge			50±50[b]		Radjenović *et al*. (2009)
Anaerobic digested sludge			140 ±80		

nd = not detected
LOQ = limit of quantitation
[a] mean (median)
[b] mean ± standard deviation

Table 29. Concentration of Gemfibrozil in Tile Drainage (Edwards *et al*. 2009)

Pharmaceutical	Maximum Concentration in tile drainage (ng/L)	
	2005 Post Liquid Biosolids application (93,500L/ha)	2006 Post Dewatered Biosolids application (8 T dw/ha)
Gemfibrozil	1,040	<2

Concentrations of gemfibrozil in runoff from the surface of biosolids-amended soil are summarized in Table 30. The data from Topp *et al*. (2008) indicate that residues of gemfibrozil are detected in runoff samples collected 266 days after application of liquid biosolids. In another study, following application of dewatered biosolids, the concentrations in runoff were non-detectable (Sabourin *et al*., 2009). Taken together, the data from Tables 29 and 30 appear to indicate that gemfibrozil is more tightly bound in the dewatered biosolids and is less susceptible to transfer to either leaching or runoff than gemfibrozil in liquid biosolids.

Table 30. Concentration of Gemfibrozil in Surface Runoff Following Application of Liquid and Dewatered Biosolids

Time after application	Gemfibrozil concentration in runoff (ng/L)	
t=1 day	630	<5
t=3 days	410	<5
t=7days	228	<5
t=22 days	80	<5 (after 21 days)
t=36 days	50	<5
t-266 days	20	
Application rate	93,500 L/ha	8 T dw/ha
Biosolids Type	Liquid biosolids (mostly anaerobic digested)	Dewatered biosolids (mostly anaerobic digested)
Reference	Topp *et al* 2008	Sabourin *et al*. 2009

Several studies investigated the mobility of gemfibrozil applied in biosolids to soils (i.e., in surface runoff and tile drainage). Gemfibrozil was the only blood-modifying drug identified with these data; mobility data for other blood-modifying drugs were not identified. Data on the fate, persistence and bioaccumulation of these compounds by soil flora and fauna were not identified in this review.

3.2.9 Respiratory and Anti-Allergenic Pharmaceuticals

Occurrence

Antihistamine drugs are used to prevent the formation of histamine as a result of allergic reactions to triggers such as pollens and insect stings. Occurrence data in sludges and biosolids are limited (Table 31) and generally focus on the compound diphenylhydramine.

Table 31. Concentrations of Anti-Allergenic Pharmaceuticals in Sludges and Biosolids

Compound	Sludge Source	Concentration (ng/g TS dw)	Reference
Diphenylhydramine	Not specified (sludge survey)	871 (541)[a]	U.S. EPA (2009a)
	Dewatered anaerobically digested biosolids	7,000	Kinney *et al*. (2008)
	Biosolids class A + sludge	15-7,000	Jones-Lepp and Stevens (2007)
	Dewatered sludge	170 ng/g OC	Kinney *et al*. (2006)
Loratidine	Primary sludge	50 ± 40[b]	Radjenović *et al*. (2009)
	anaerobic digestion	160 ± 40	
Albuterol	Not specified (sludge survey)	5.23 (5.29)	U.S. EPA (2009a)
	Literature review	nd – 1,400	Jones-Lepp and Stevens (2007)

[a] mean (median)
[b] mean ± standard deviation
nd = not detected
OC = organic carbon

The data provided by Jones-Lepp and Stevens (2007) suggest the concentrations can be quite variable. The mean concentration of loratidine in primary sludge at 50 ng/g TS dw (Radjenović *et al*., 2009) was lower than those observed for diphenylhydramine. Although the anti-bronchospasm drug albuterol was found at relatively low concentrations of 5 ng/g TS dw in the EPA's TNSSS (Table 31), the literature review by Jones-Lepp and Stevens (2007) indicated much higher concentrations have been observed in sludges and biosolids.

Fate and Transport in the Terrestrial Environment

Few data on fate and transport of the anti-allergenic pharmaceuticals were found in this review. Kinney *et al*. (2008) examined concentrations of diphenylhydramine in the soils and earthworms at sites with and without biosolids amendment (Table 32). Diphenylhydramine was detected in only one soil sample, from the site receiving the biosolids amendment. Because the earthworms from that site had no detectable concentration of the compound, a bioaccumulation factor of 0 was applied.

Table 32. Concentrations of Diphenylhydramine in Soil and Earthworm Samples (Kinney *et al*., 2008)

Site Description	Sample Matrix	Diphenylhydramine (ng/g DM)
Site 1 (without biosolids application)	Soil Jun 6-05	ND
	Worm Jun 6-05	ND
	Soil Sep 29-05	ND
	Worm Sep 29-05	ND
Site 2 (with biosolids application on April 18, 2005)	Soil May 19-05	1.1
	Worm May 19-05	ND
	Soil Sep 21-05	ND
	Worm Sep 21-05	ND

Other than the limited data for diphenylhydramine in earthworms by Kinney et al. (2008) presented above, no data on fate, persistence, transport or bioaccumulation by soil flora or fauna for respiratory and anti-allergenic pharmaceuticals were found in this review.

3.2.10 Anti-Parasitics and Anti-Fungal Compounds

Occurrence

Occurrence data for these compounds were identified in two sources as indicated in Table 33. Of the three anti-parasitics identified in sludges in this review, carbadox was present at the highest concentration with a median value on 103 ng/g TS. The median concentration of miconazole was 207 ng/g TS. Considerable variability was associated with this substance in the survey as the mean value is approximately six times the median value.

Fate and Transport in the Terrestrial Environment

No data on fate, persistence, transport or bioaccumulation by soil flora or fauna for anti-parasitic and anti-fungal pharmaceuticals were found in this review.

Table 33. Concentrations of Anti-Parasitics and Anti-Fungals in Sludges and Biosolids

Pharmaceutical	Use	Sludge Source	Concentration (ng/g TS dw)	Reference
Carbadox	Anti-parasitic	Not Specified (Sludge Survey)	232 (103)[a]	U.S. EPA (2009a)
Ormetoprim	Anti-parasitic	Not Specified (Sludge Survey)	4.16 (3.96)	
Thiabendazole	Anti-parasitic	Not Specified (Sludge Survey)	36.6 (16.5)	
		Biosolids class A + sludge	nd - 420	Jones-Lepp and Stevens (2007)
Miconazole	Anti-fungal	Not Specified (Sludge Survey)	1,240 (207)	U.S. EPA (2009a)
		Biosolids class A + sludge	nd - 460	Jones-Lepp and Stevens (2007)

[a] mean (median) nd = not detected

3.2.11 Miscellaneous Pharmaceuticals

Occurrence

The drugs included here depart from the classification provided by Gielen (2007) due to the limited number of compounds for each use or presence in sludges. Concentrations of the compound salicylic acid were present at a wide range in the literature on sludges reviewed by Harrison *et al*. (2006) (Table 34). Cotinine is a metabolite of nicotine and is a marker of human presence in wastewaters and sludges. Digoxigenin is used to induce an immune system response in humans. The median concentration of this marker compound, at 39.8 ng/g TS dw, was relatively low in the EPA TNSSS, as was the median concentration of 19.9 ng/g TS dw for the ovulation inhibitor norgestimate.

Fate and Transport in the Terrestrial Environment

Cotinine was detected at a concentration of 300 ng/L in tile drainage following application of liquid biosolids (Table 35), and at a much lower concentration of 10 ng/L in tile drainage following application of dewatered biosolids (Edwards *et al*., 2009).

Concentrations of cotinine in runoff from the surface of biosolids-amended soil are summarized in Table 36. The data from Topp *et al*. (2008) indicate that cotinine levels declined steadily through the first 36 days after application of liquid biosolids, with a low concentration of 10 ng/L of cotinine detected in runoff samples collected after 36 days. While runoff samples from the dewatered biosolids site were lower in concentration than in the runoff from the liquid biosolids application, the concentrations did not decline as rapidly (Sabourin *et al*., 2009).

Table 34. Concentrations of Miscellaneous Pharmaceuticals in Sludges and Biosolids

Compound	Use/Presence	Sludge source	Concentration (ng/g TS dw)	Reference
Digoxigenin	steroid immunohisto-chemical marker	Not specified (sludge survey)	57.2 (39.8)[a]	U.S. EPA (2009a)
Norgestimate	ovulation inhibitor	Not specified (sludge survey)	27.5 (19.9)	
Salicylic Acid	skin-care	Literature review	0.002–13,740	Harrison *et al*., (2006)
		Unknown sludge (An urban WWTP)	<25.4 - 253	Spongberg and Witter (2008)
		Unknown sludge (A rural WWTP)	253	
Cotinine	nicotine metabolite	Not specified (sludge survey)	58.0 (13.2)	U.S. EPA (2009a)
		Liquid anaerobically digested biosolids	90 ± 16[b]	Lapen *et al*. (2008a)
		Dewatered biosolids (mostly anaerobically digested) (n=3)	1.8 ± 0.0	Sabourin *et al*. (2009)
		Dewatered biosolids (mostly anaerobically digested)	<LOD	Edwards *et al*. (2009)

LOQ = limit of quantitation LOD = limit of detection
[a] mean (median) [b] mean ± standard deviation

Table 35. Maximum Concentration of Cotinine in Tile Drainage (Edwards *et al*. 2009)

Pharmaceutical	Maximum Concentration in tile drainage (ng/L)	
	2005 Post Liquid Biosolids application	2006 Post Dewatered Biosolids application
Cotinine	300	10
Application rate	93,500 L/ha	8 T dw/ha

Table 36. Concentration of Cotinine in Surface Runoff Following Application of Liquid and Dewatered Biosolids

Time after application	Cotinine concentration in runoff ng/L	
t=1 day	120	6.9
t=3 days	50	14.7
t=7days	30	13.2
t=22 days	20	5.6[a]
t=36 days	10	2.7
t-266 days	<0.8	
Application rate	93,500 L/ha	8 T dw/ha
Biosolids Type	Liquid biosolids (mostly anaerobic digested)	Dewatered biosolids (mostly anaerobic digested)
Reference	Topp *et al*. 2008	Sabourin *et al*. 2009

[a] after 21 days

Several studies investigated the mobility of the nicotine metabolite cotinine applied in biosolids to soils (i.e., in surface runoff and tile drainage). Although other miscellaneous pharmaceuticals were identified as being present in biosolids, only data for cotinine were identified. Data on the fate, persistence, mobility and bioaccumulation of these other compounds by soil flora and fauna were not identified in this review.

3.2.12 Section Summary

The pertinent points from this review of pharmaceuticals in sludges and biosolids follow.

1. There is a wide range of data available for the different pharmaceuticals that may be present in sludges and biosolids. Some compounds like carbamazepine have been widely characterized, while others have only one or two references (e.g. beta-blockers, alimentary tract pharmaceuticals) in the literature.
2. With the exception of data on the presence of a limited number of pharmaceuticals in tile drainage or surface runoff, there are few studies documenting the fate and transport of pharmaceutical compounds in the terrestrial environment, or plant uptake, after applying biosolids to soil.
3. Golet *et al*. (2003) noted that the fluoroquinolone antibiotics were persistent in soil, but were tightly bound to the soil, and thus would not tend to leach through the soil.
4. Only one study (Kinney *et al*., 2008) attempted to compare and document the difference in accumulation of some limited pharmaceutical (and other) compounds in soils and earthworms between biosolids treated and control soils.
5. Only one review was identified which assessed the potential uptake of pharmaceutical compounds in plants grown on soils amended with biosolids.

Virtually all of the considerable quantity of pharmaceutical information for sewage biosolids reported here has been generated since the WEAO (2001) report was published. Much of the information is very recent because as late 2005 there was some pharmaceutical information for municipal wastewaters but very little for sewage biosolids (Webber and Sidhwa 2005). The several Ontario studies reported here are a direct result of the WEAO (2001) report recommendations suggesting that they are in Group II And require more research. As can be determined from the summary points above, however, the data describing the fate, persistence, mobility, and bioaccumulation of all classes of pharmaceuticals by soil flora and fauna is sparse, and thus can be considered as research gaps. Consequently, it is recommended that pharmaceuticals in sewage biosolids be classified as Group II compounds requiring additional research.

3.3 Alkylphenol and Their Ethoxylates

Alkylphenol ethoxylates (APEs) are among the most commonly used surfactants (surface active agents) around the world. Nonylphenol ethoxylates (NPEs) account for approximately 80% of the total use, while octylphenol ethoxylates (OPEs) represent most of the remaining 20% (Melcer *et al*., 2007). The predominant uses of APEs are in pulp and paper production, textile manufacturing and in the production of crop protection chemicals (Melcer *et al*., 2007).

Under the appropriate conditions, APEs are biologically transformed to the alkylphenol (AP) intermediate, such as nonylphenol (NP) and octylphenol (OP) which has been implicated in aquatic toxicity responses in fish, mammals, invertebrates and algae, although it was not found to be bioaccumulative (Environment Canada, 2009a). The APs have also been implicated as weakly estrogenic compounds, in particular capable of inducing feminization of male fish. Smith (2009a) indicates that the use of nonylphenol and its ethoxylates in commercial products is significantly reduced to concentrations less than 0.1% by mass based on European Union (EU) Directive 2003/52/EC, and that under the Water Framework Directive of the EU, nonylphenol has been classified as a priority hazardous substance and thus will be subject to further source controls with the goal of phasing out emissions to the environment.

APEs enter municipal wastewater treatment facilities in industrial wastewater discharges to municipal sewers, as well as being present in domestic sewage. During biological (secondary or tertiary) wastewater treatment, alkylphenols (APs) with longer polyethoxylate chains are biotransformed to mostly mono- or di-ethoxylated APs, or to the parent AP itself (Melcer *et al*. 2007). Biological treatment also results in formation of carboxylated forms of the APEs, which are more soluble than the mono- or di-ethoxylated APs. As the polyethoxylate chain decreases, the compound becomes more hydrophobic (less water soluble), causing the compound to adsorb onto wastewater and sludge particles (Melcer *et al*. 2007). As a result, wastewater sludge streams tend to concentrate the metabolites AP and mono- or di-ethoxylated APs.

3.3.1 Occurrence Data

Concentration data for these compounds are generally reported in the part per million (mg/kg or (μg/g) units range because they are substantially higher in biosolids samples than are other micro-constituents such as pharmaceuticals.

Concentrations of alkylphenols (AP) and their ethoxylates in anaerobically digested sludges from Canadian municipalities were surveyed by Lee and Peart (2002) (Table 37). The median value of 4-nnylphenol (4-NP) in digested sludge samples was 413 μg/g TS dw. Concentrations of the di-ethoxylated NP (NP2EO) and higher congeners were lower in digested sludges than the base compound 4-NP and the mono-ethoxylated NP (NP1EO). The median concentration of 4-tert-octyl phenol reported in the study was 10.4 μg/g TS dw in the digested sludge sample.

Concentrations of NP for many types of sludges in different countries fall in the range of 500 to 2,500 μg/g TS dw, with the highest maximum value of 7,214 μg/g TS dw reported from Sweden although minimum levels may be as low as approximately 25 μg/g TS dw (Table 38). One very low value of 0.0195 μg/g TS dw for Norwegian final sludge was reported by Soares *et al*. (2008). The data indicate there may be differences in concentrations of 4-NP in biosolids samples between countries, with some countries such as Italy (Soares *et al*., 2008), Denmark (Jaganyi 2007) and France (Ghanem *et al*., 2007) having lower concentration ranges than other countries. Changes in formulation of household laundry detergents may be responsible; Ahel *et al*. (2000) reported that effluent concentrations of NPEs declined after Switzerland imposed a ban on use of NPEs in laundry detergents.

Table 37. Concentrations of Alkylphenol (AP) and Ethoxylates (EO) in Anaerobically Digested Canadian Municipal Sludges (Lee and Peart, 2002)

Municipal Treatment Plant and Sludge Type	Concentration (μg/g TS dw)					
	4-nonyl phenol (NP)	NP mono-EO (NP1EO)	NP di-EO (NP2EO)	NP tri-EO (NP3EO)	Higher NP-EOs NP(4-17)EO	4-tert-octyl phenol
Vancouver	457	124	26.6	17.7	47.6	10.7
Vancouver	468	74.1	31.6	7.7	4.5	10.4
Calgary (Bonnybrook)	413	154	33.1	<2	8.1	6.2
Calgary (Fish Creek)	393	154	20.5	16.5	5.1	6
Edmonton (Goldbar)	848	160	36.8	6	11.1	11.3
Regina	568	228	1.8	1.9	11.5	10.8
Saskatoon	26.5	39.3	39.3	6.8	2.1	1.9
Saskatoon	139	97.2	24.8	4.5	<2	3.8
Burlington	435	66	3.2	<2	17.7	13.1
Galt	1210	126	24.1	12.4	23	20.5
Guelph	1230	130	36.4	8.4	120	43.9
Hamilton	403	114	26.4	6.9	5.5	15.6
Ingersoll	232	32	6.7	3.9	67	8.5
Kitchener	617	19.8	3	<2	<2	11.6
Ottawa	298	83.7	11	2	<2	7.2
Waterloo	518	146	38	4.1	5.9	8.2
Windsor Digested	203	307	127	34.7	139	13
Toronto (Ashbridges Bay)	450	36.8	4.7	1.5	<2	12.8
Toronto (Humber)	495	53.2	16.8	4.6	25.1	12.3
Toronto (North)	233	28	2.2	<2	<2	6.5
Granby	18.3	46.8	64.8	8.1	7.7	1.3
Moncton	4.6	29.8	17.8	10.9	55.7	0.8
Truro	18.3	30.4	68	15.8	9.9	2.1
Median	413	83.7	24.8	6.9	11.3	10.4

The literature survey of Harrison *et al*. (2006) indicated concentrations of total alkylphenol ethoxylates could be observed at up to 7,214 μg/g TS dw. Ruel *et al*. (2008) reported concentrations of total polyethoxylated nonylphenols in French biosolids as 44 μg/g TS dw, but noted analytical problems with the sludge matrix. These difficulties were reflected in the high standard deviation value of 970 μg/g TS dw (Table 39). In the same sampling survey, the mean value of total octylphenols was only 2.6 μg/g TS dw. Low concentrations of the mono- and di-ethoxylated forms of nonylphenol (maximum values of 41 and 25 μg/g TS dw, respectively) were found by Stasinakis *et al*. (2008), with similar values reported by Kinney *et al*. (2008) and Gejlsbjerg *et al*. (2001). Kinney *et al*. (2008) reported a concentration of 5.03 μg/g TS dw of octylphenol monoethoxylate in anaerobically digested biosolids.

Table 38. Concentrations of Nonylphenol in Sludges and Biosolids from Other Countries

Country	Sludge Treatment	4-nonylphenol (μg/g TS dw)	Reference
Switzerland	Anaerobic Digestion	450-2530	Soares *et al*. (2008)
	Aerobic Digestion	120-650	
	Final sludge	540-1000	
Germany	Aerobic Digestion	80-500	
	Unidentified	128.2	
Italy	Sludge after anaerobic digestion	308	
Norway	Final sludge	0.0195	
Norway	Biosolids	25-2298	Jaganyi (2007)
Sweden	Biosolids	23-7214	
Denmark	Biosolids	0.3-537	
Africa	Biosolids	0.15-2790	
Denmark	Dewatered air-dried waste activated sludge	1,154	Gejlsbjerg *et al* (2001)
Denmark	Anaerobically digested biosolids	60	Jacobsen *et al*. (2004)
France	Mixed sludge sources (anaerobically digested, composted, limed or dried) in different conventional secondary or tertiary plants	132 ± 730	Ruel *et al*. (2008)
U.S.A.	Aerobically digested biosolids	nd-180	Xia *et al*. (2005)
	Anaerobically digested biosolids	300-1300	
U.S.A.	Dewatered anaerobically digested biosolids	483	Kinney *et al*. (2008)
U.S.A.	Anaerobically digested biosolids	900	Brown *et al*. (2009)
Greece	Dewatered anaerobically digested or dewatered secondary sludge	<0.04 -0.45	Stasinakis *et al*. (2008)
France	Unknown/not specified prior to pelletization	16.5 – 125	Ghanem *et al*. (2007)
	Unknown/not specified prior to composting	75.6-173	
	Unknown/not specified prior to lime treatment (Plant 2)	49.6-136	
	Unknown/not specified prior to lime treatment (Plant 3)	89.8-217	
U.S.A.	Digested sludge (aerobic and anaerobic)	13-898	Heidler and Halden (2008)
UK	Dewatered anaerobically digested biosolids	238	Gibson *et al*. (2005)
Mexico and UK	Anaerobically digested sludge before composting	114	Gibson *et al*. (2007)

nd=not detected. [a] mean ± standard deviation

Table 39. Concentrations of Nonylphenol Ethoxylates and Other Alkylphenol in Sludges and Biosolids

Biosolids Type	Concentration (μg/g TS dw)						Reference
	Nonylphenol monoethoxylate (NP1EO)	Nonylphenol diethoxylate (NP2EO)	Nonylphenol (1-17) ethoxylates NP(1-17)EO	Alkylphenol carboxylates	4-tert-octylphenol	octylphenol, monoethoxylate	
dewatered anaerobically digested or dewatered secondary sludge	1.01 - 41.3	<0.96 - 24.7					Stasinakis *et al*. (2008)
Mixed sludge sources (anaerobically digested, composted, limed or dried) in different conventional secondary or tertiary treatment plants			44 ± 970 [a]		2.6 ± 4 (as Octyl phenols)		Ruel *et al*. (2008)
Unknown/not specified (literature review)			nd–7214	10–14			Harrison *et al*. (2006)
Dewatered anaerobically digested biosolids	25.3	0.76				5.03	Kinney *et al*. (2008)
Dewatered air-dried waste activated sludge		2.00					Gejlsbjerg *et al*. (2001)

nd = not detected; [a] mean ± standard deviation

3.3.2 Fate and Transport in the Terrestrial Environment

Many studies have examined nonylphenol fate and transport in soils, however less attention has been focused on the ethoxylated forms or on other alkylphenol and their ethoxylates.

The half-lives of nonylphenol and the diethoxylate form were investigated by Gejlsbjerg *et al*. (2001) in several Danish soils (Table 40). The observed half-lives for nonylphenol fell within a narrow range of 7.3 to 10.6 days, even though soils with different structural properties were tested. Similar results were obtained with the diethoxylated nonylphenol, with the exception of a coarse sandy soil with a higher biosolids:soil ratio of 1:20. Topp and Starratt (2000) observed a range of half-lives in a sandy soil of 4.5 to 16.7 days. Jacobsen *et al*. (2004) observed a similar half-life for nonylphenol in a sandy soil, but also noted that the initial half-life in the first 10 days following application was faster than the longer term half-life of 37 days when the study was extended to 100 days. Brown *et al*. (2009) determined that the half-life of NP in a silt loam was 23 days on un-planted plots, but declined to 16 days on plots planted with wheat, demonstrating a beneficial effect of crops on the degradation of NP in soils amended with biosolids.

Table 40. Half-lives of Nonylphenol and NP Diethoxylate in Soils

Test Conditions	Half-life $t_{½}$ (Days)		Reference
	4-nonylphenol (4-NP)	Nonylphenol diethoxylate (NP2EO)	
1:100, Coarse sandy soil (in Jyndevad)	9.8 (0.94)[a]	8.4 (0.19)	Gejlsbjerg *et al*. (2001)
1:100, Sandy soil (in Lundgaard)	9.1 (0.18)	7.8 (0.20)	
1:100, clayey soil (in Askov)	8.8 (0.17)	8.8 (1.40)	
Soil only (coarse sandy soil)	10.6 (0.26)	10.0 (0.11)	
1:20, 40% moisture, coarse sandy soil (in Jyndevad)	7.3 (0.07)	17.1 (0.84)	
1:100, 40% moisture, coarse sandy soil (in Jyndevad)	8.6 (0.16)	8.5 (0.26)	
biosolids alone, silt loam soil	23		Brown *et al*. (2009)
biosolids + plant treatment, silt loam soil	16		
Sandy soil	10 (initial); 37 (long-term)		Jacobsen *et al*. (2004)
Sandy soil	4.5 – 16.7		Topp and Starratt (2000)

[a] mean (standard deviation) of 4 replicates

The importance of soil water saturation and initial sludge:soil ratio on mineralization of nonylphenol and nonylphenol diethoxylate to carbon dioxide were tabulated by Gejlsbjeg *et al*. (2001) (Table 41). The largest effect on extent of mineralization appeared to result from the degree of soil water saturation. Mineralization was more complete at the lower soil water saturation (40%) than at the higher saturation of 80%. A higher degree of soil water saturation and biosolids loading were considered to result in reduced oxygen available in the soil to promote biological activity. The sludge loading to the soil was not as critical to mineralization of NP, as it was for NP2EO. Some mineralization of NP and NP2EO did occur in the biosolids alone over the test period of 60 days, suggesting biodegradation of the compounds by the biosolids microbes.

Table 41. Effect of Biosolids Loading and Soil Water Saturation on Mineralization of Nonylphenol and NP Diethoxylate (Gjeilsbjerg *et al*., 2001)

Sludge:soil ratio	Soil Water Saturation	4-nonylphenol (NP)		Nonylphenol diethoxylate (NP2EO)	
		Initial conc. In test sludge-soil mixture mg/kg DM	Mineralization after two months (% of added ^{14}C)	Initial conc. in test sludge-soil mixture mg/kg DM	Mineralization after two months (% of added ^{14}C)
Sludge alone	not appl.	1,154	28.5 (6.3)	2,002	14.8 (6.7)
1:20	40%	55	63.2 (2.3)	95	61.4 (2.1)
	80%	55	56.0 (3.5)	95	12.4 (3.9)
1:100	40%	11.4	58.4 (16.6)	19.8	70.2 (2.6)
	80%	11.4	44.2 (7.0)	19.8	43.4 (9.3)

Brown *et al*. (2009) investigated the reduction of total nonylphenol isomers over a 45 day trial in soil plots with and without growing plants (Table 42). In the top 4 cm of soil, the NP isomers declined with time, but were still detectable after 45 days. The concentration in the samples declined more rapidly in the plots with plants than without. At the 4 – 8 cm depth, NP isomer concentrations were also lower in the plots with plants than without. Although in the 4 – 8 cm depth, the concentration of NP isomers was non-detectable at the start of the test, concentrations did increase by the 15th day, but they were far lower than in the top 4 cm stratum. Concentrations of the NP isomers remained unchanged from very low initial concentrations over the 45 day duration of the test. Movement of the NP through the soil column was slight.

Jacobsen *et al*. (2004) tracked the reduction of NP in a biosolids-amended soil (Table 43). From an initial concentration of 560 ng/g DM in the loamy sand soil (pH = 5.6), the concentration declined to non-detectable levels by the 50th day of the study.

Table 42. Reduction of Nonylphenol Isomer Concentrations over Time (Brown *et al*., 2009)

Time after biosolids application	Concentration of total NP isomers (mg/kg DM) at soil depth					
	0-4 cm		4-8 cm		8-14 cm	
	biosolids alone treatment	biosolids + plant treatment	biosolids alone treatment	biosolids + plant treatment	biosolids alone treatment	biosolids + plant treatment
t=0 day	7.31	7.2	0	0	0	0
t=15 days	5.06	3.33	0.16	0.09	0.09	0.08
t=30 days	2.31	1.68	0.04	0	0	0
t=45 days	2.04	1.06	0.08	0.02	0.02	0.02

Table 43. Reduction of Nonylphenol in Soil Lysimeter Study (Jacobsen *et al*., 2004)

Time after Study Start	Conc. Of NP In biosolids-soil mixture (ng/g DM)
(t=0 day)	560
t=10 days	256 ± 50[a]
t=20 days	190 ± 10
t=30 days	190 ± 10
t=50 days	<LOD (50)
t=110 days	<LOD (50)

[a] mean ± std deviation (n=4) LOD = limit of detection

The effects of increased NP supplemental loadings in biosolids and of two different soil types were reported by Hseu *et al*. (2006) (Table 44). One soil was a calcareous sandy soil while the other was an acidic mostly clay soil. At lower loading supplements of 80 mg/kg DM of NP, detectable percentages of the initial loading were evident after 25 days, but not by the 50th day of the test. The calcareous sandy soil had a lower percentage remaining than did the acidic clay soil. Similar results were obtained at the intermediate supplement loading of 160 mg NP/kg DM. In both soils, the added NP had disappeared by the 85th day of the study. The added NP disappeared from the calcareous soil by the 85th day at both the intermediate and high supplement levels. Conversely, the acidic soil required up to 120 days for complete elimination of the NP supplement. The acidic environment is more inhospitable to the soil bacteria responsible for elimination of the NP.

The transport of nonylphenol in a long-term biosolids application site near Chicago, IL was investigated by Hundal *et al* (2009). The site received a maximum cumulative loading of 2,218 tonne dry biosolids/ha from 1973-2002. Samples of soil from different depths were analyzed for NP, with results appearing in Table 45.

Table 44. Reduction of Nonylphenol by Two Soil Types (Hseu *et al*., 2006)

Days after application	Remaining Percentage (%) of 4-Nonylphenol in biosolids treated soils following 4-NP supplement					
	Soil A (calcareous sandy soil, pH=8.3)			Soil B (acidic clayey soil, pH=4.1)		
	4-NP= 80 mg/kg	4-NP = 160 mg/kg	4-NP = 240 mg/kg	4-NP = 80 mg/kg	4-NP = 160 mg/kg	4-NP = 240 mg/kg
t=20 days	5 ± 0	20 ± 1	40 ± 3	25 ± 2	38 ± 2	48 ± 2
t=50 days	0	1 ± 0	3 ± 0	0	10 ± 1	20 ± 1
t=85 days	0	0	0	0	0	3 ± 0
t=120 days	0	0	0	0	0	0

Table 45. Concentrations of Nonylphenol at Soil Depths from a Long-Term Biosolids Application Site (Hundal *et al*. 2009)

Soil Depth	Nonylphenol Concentration (mg/kg DM)
0-15 cm	8.83
15-30 cm	1.84
60-120 cm	0.068

At the 60 – 120 cm depth, the NP concentration was very low, at 0.068 mg/kg DM, indicative of little transport of the NP after 30 years of biosolids application. The 0 – 15 cm surface layer has an elevated concentration of NP of 8.83 mg/kg, declining to 1.84 mg/kg DM in the 15 – 30 cm layer. Because of the long-term application of biosolids, the top 30 cm of soil was considered by the authors to be comprised mostly of biosolids. The data indicated that, even after long-term biosolids application, nonylphenol was relatively immobile in the soil. The authors reported that microbial populations in the biosolids-amended plots were more diverse and more biologically active than in control plots with no biosolids applications (Hundal *et al*., 2009).

The effect of weathering (break-down of biosolids by varying climate cycles of freeze-thaw, drying-wetting, etc.) on concentrations of nonylphenol and low molecular weight ethoxylates in two types of surface applied biosolids was reported by LaGuardia *et al*. (2009). The aerobic/lime biosolids had a significantly lower level of nonylphenol, and a much higher concentration of NP1EO, than the anaerobically digested sludge. Concentrations of the compounds declined in the weathered biosolids over time, especially between the samples collected on days 50 and 175 following the original application. The data are provided in Table 46.

At the biosolids amended sites, artificial rainfall was applied to generate surface runoff (LaGuardia *et al*., 2009). Elevated concentrations of nonylphenol were found in the runoff from the site receiving anaerobically digested biosolids 50 days following the biosolids application

Table 46. Concentrations of Nonylphenol and Ethoxylates in Fresh and Weathered Biosolids Aggregates. (LaGuardia *et al*., 2009).

Collection Time	Biosolids Type	Concentration in Biosolids (mg/kg TS dw)			
		NP	NP1EO	NP2EO	Total
At application	anaerobic	843	119	10	972
	aerobic/lime	59	413	22	494
After 50 days	anaerobic	664	38	3	705
	aerobic/lime	117	438	11	556
After 175 days	anaerobic	70	3	n.d.	73
	aerobic/lime	2	6	n.d	8

(Table 47). The mean concentration of 5.35 µg/L was statistically different from the control site and aerobic/lime biosolids applied site. Nonylphenol concentrations 150 days after the biosolids application were lower than from the 50 day sampling time, and were not statistically different between the treatments. NP1EO was only detected in runoff from the aerobic/lime biosolids applied site 50 days after the application, but not in any other samples. NP2EO was not detected in runoff from either time or from any of the treatments. The continued presence of nonylphenol in the aerobic/lime amended plot after 175 days was hypothesized as being derived from the biotransformation of NP1EO to NP (LaGuardia *et al*., 2009). A significant correlation between particulate matter (as particulate organic carbon) in the runoff and the concentration of nonylphenol was established ($r^2 = 0.562$).

Table 47. Concentrations of Nonylphenol and Ethoxylates in Artificial Runoff following Biosolids Application (LaGuardia *et al*., 2009)

Days after Application	Site	Mean Concentration in Runoff (µg/L)		
		NP	NP1EO	NP2EO
50	Control	2.54	nd	nd
	Anaerobic	5.35	nd	nd
	Aerobic/lime	3.82	1.57	nd
175	Control	1.37	nd	nd
	Anaerobic	1.69	nd	nd
	Aerobic/lime	2.36	nd	nd

nd = not detected

Dettenmeier and Doucette (2007) reported one of the more detailed studies of the fate and transport of nonylphenol and related ethoxylates in plants grown on biosolids-amended soils. The fate in soils and uptake by crested wheatgrass grown on soils with three concentrations of the target ^{14}C-labelled analytes spiked into biosolids was compared to the fate in lysimeters receiving the same spiked biosolids with no plants, and lysimeters receiving the spiked biosolids but treated with mercuric chloride as a soil bacteria poison (Table 48).

In the lysimeters with plants, very little of either the nonylphenol or the two ethoxylates were taken up in the plant roots or foliage, with a maximum of 0.2% of the applied nonylphenol detected in the plant roots. For all three analytes, the majority of the applied compounds resided

in the soils. More of the two ethoxylates were mineralized than was the nonylphenol in the lysimeters with and without plants, but involving the biosolids non-poisoned by mercuric chloride. In the lysimeter set involving poisoned biosolids, the fraction of all three compounds mineralized was approximately the same, on the order of 4 – 7% (Dettenmeier and Doucette, 2007).

Kinney *et al*. (2008) compared the accumulation of alkylphenols and ethoxylates in soils and earthworms in a biosolids-amended site compared to a non-amended control site (Table 49). The biosolids amendment consisted of a one-time application at a rate of 18 T/ha, with no details of soil incorporation. The soil and earthworms from the site without biosolids amendment had mostly all non-detectable concentrations of the target compounds, with the exception of two soil samples, one with a low but detectable concentration of octylphenol diethoxylate, and a different soil sample with a low concentration of 4-cumylphenol. Of interest with the biosolids-amended site was the relative lack of detectable concentrations of the alkylphenols and ethoxylates in the soils (except for octylphenol diethoxylate and 4-nonylphenol). More of the target compounds were detected in the earthworm samples. Kinney *et al*. (2008) were not able to attribute any significant bioconcentration factors to the earthworms as a result of the target compounds observed in the biosolids-amended soils.

The Panel on Contaminants of the Norwegian Scientific Community on Food Safety (VKM, 2009) recognized that the predicted soil concentrations of nonylphenols and octylphenols from land-applied sewage sludge would exceed the predicted no effect concentrations (PNECs) of these compounds. The Panel further noted, however, that the compounds degrade rapidly in soil, and thus considered them to be of low concern.

Smith (2009a) cited a Danish study by Peterson *et al*., (2003), which examined a number of trace organic contaminants (including nonylphenol (NP) and its ethoxylates (NPEs)) when sludge (not differentiated from biosolids by Smith, 2009) was applied to soil. No accumulation of the of the NP/NPEs and other contaminants was observed in the soil, no uptake by plants grown on the amended soil, and no adverse effects of the sludge application on soil biota or crop growth were found (Peterson *et al*., 2003 in Smith, 2009).

Table 48. Fate of Spiked Nonylphenol and Ethoxylates in Soils and Plants (Dettenmeier and Doucette. 2007)

Contaminant	initial spiked conc'n, mg/kg	Planted Plots				Unplanted Plots		Poisoned Plots (with $HgCl_2$ addition)	
		% Mineralized	% in foliage	% in roots	% in soil	% Mineralized	% in soil	% Mineralized	% in soil
4-nonylphenol (NP)	6	6.0 (1.5)[a]	0.11 (0.01)	0.21 (0.06)	95 (1.5)	10 (0.4)	80 (21)	4.8 (1.3)	100 (17)
	24	7.8 (0.75)	0.16 (0.04)	0.11 (0.04)	77 (3.8)	11 (0.68)	81(6.5)	6.3 (0.9)	94 (17)
	47	8.0 (1.4)	0.11 (0.01)	0.16 (0.06)	82 (11)	12 (1.1)	87 (6.6)	7.1 (1.9)	110 (13)
Nonylphenol tetraethoxylate (NPE4)	6	19 (4.3)	no data	0.17 (0.02)	72 (9.2)	29 (3.5)	63 (15)	6.0 (1.0)	120 (3.5)
	24	12 (4.6)	no data	0.17 (0.04)	66 (18)	29 (3.1)	61 (15)	4.6 (0.44)	80 (2.5)
	47	19 (4.4)	no data	0.15 (0.06)	74 (8.7)	21 (5.0)	62 (7.3)	5.4 (0.3)	80 (15)
Nonylphenol nonylethoxylate (NPE9)	6	24 (3.9)	0.14 (0.04)	0.12 (0.03)	63 (8.4)	27 (1.5)	63 (8.7)	5.5 (0.6)	91 (4.2)
	24	23 (3.8)	0.14 (0.01)	0.19 (0.04)	69 (9.2)	27 (1.2)	63 (2.7)	4.2 (0.5)	110 (2.8)
	47	17 (3.2)	0.13 (0.03)	0.17 (0.00)	50 (3.3)	28 (7.1)	51 (1.1)	6.5 (1.2)	73 (5.1)

[a] mean (95% confidence interval), n = 3 replicates

Table 49. Concentrations of Alkylphenol and Ethoxylates in Soil and Earthworm Samples (Kinney *et al*., 2008)

Site Description	Sample Matrix	Concentration (ng/g DW)						
		4-tert-octylphenol	4-nonylphenol total	Nonylphenol, monoethoxy total	Nonylphenol, diethoxy total	octylphenol, monoethoxy	octylphenol, diethoxy	4-Cumyl-phenol
Site 1 (without biosolids application)	Soil Jun 6-05	ND	ND	ND	ND	ND	ND	37
	Worm Jun 6-05	ND	ND	ND	ND	ND	ND	ND
	Soil Sep 29-05	ND	ND	ND	ND	ND	42	ND
	Worm Sep 29-05	ND	ND	ND	ND	ND	ND	ND
Site 2 (with biosolids application on April 18, 2005)	Soil May 19-05	ND	ND	ND	ND	ND	74	ND
	Worm May 19-05	570	5,200	ND	ND	ND	ND	140
	Soil Sep 21-05	ND	3,570	ND	ND	ND	46	ND
	Worm Sep 21-05	186	7,690	1,520	ND	ND	ND	ND

ND = not detected

3.3.3 Section Summary

The important points from this section of the current review follow.

1. Nonylphenol has been well characterized in biosolids and in soils. The ethoxylates of nonylphenol or other alkylphenol and their ethoxylates are less well characterized.
2. There appear to be differences in APE and AP concentrations between biosolids samples collected from different countries, possibly due to different regulations for detergent product formulation.
3. Of the biosolids treatment processes examined, anaerobic digestion consistently results in the highest concentrations of 4-NP because anaerobic biotransformation processes convert mono- and di-ethoxylate species to the non-substituted AP.
4. With a half-life in the range of 10 to 25 days, nonylphenol is not persistent in soil, and thus does not tend to bioaccumulate in soil biota such as earthworms.
5. Nonylphenol is not readily mobile in the soil column.
6. Most of the nonylphenol subject to biotransformation in the soil remains in the soil in some form, as opposed to being mineralized to carbon dioxide, leaching through the soil column or being taken up by plants.

Considerable research on the fate and significance of alkylphenols and their ethoxylates in biosolids and soils has been done since publication of the WEAO (2001) report, however the findings and conclusions are consistent with those stated in the 2001 report which were:

- …. alkylphenols and alkylphenol ethoxylates do not persist in soils for extended periods and, in fact, are readily broken down by the microbial populations in the soil.
- …. initial concentrations of alkylphenols and alkylphenol ethoxylates immediately after sewage biosolids application should not impact crop growth, or present any leaching potential because as shown ……., the uptake of alkylphenols by plants is minimal. Additionally, no leaching occurs into the groundwater and there is no transfer via the food-chain to animals.
- ….alkylphenols and alkylphenol ethoxylates would be considered as Group I contaminants for which no further study is recommended at this time.

As a result of the considerable body of work provided in the WEAO (2001) report, and identified in this review, it is recommended that the alkylphenols and their ethoxylates continue to be classified as Group I contaminants.

3.4 Linear Alkylbenzene Sulphonates

Linear alkylbenzene sulphonates are a class of surfactants widely used in commercial products, but especially in detergent formulations. In wastewater treatment, because of relatively high solid:liquid partition coefficients, these surfactants tend to sorb onto wastewater solids and thus concentrate in the residual sludges. There are two potential concerns related to these compounds in biosolids destined for land application. The first issue involves possible ecotoxic effects, such as the potential to dissolve biomembranes, on soil microbes and invertebrates. Elevated concentrations of LAS in soil, ranging from 1,143 to 1437 µg/g DM, were observed to cause an

adverse effect to 50% of the population of several microbial species (Jacobsen *et al*., 2004), however these concentrations are high, and LAS soil concentrations resulting from normal biosolids amendment rates do not represent a significant risk to soil fauna or flora. A second concern is that the surfactants can potentially increase the mobilization of other hydrophobic contaminants in the soil, resulting in higher concentrations of the contaminants in leachate and drainage water (Jacobsen *et al*., 2004).

3.4.1 Occurrence Data

Concentration data for this class of surfactants is presented in Table 50. Relative to the other micro-constituents discussed in this review, LAS are present at very high concentrations. As a result, concentration units are expressed as µg/g TS dw (equivalent to parts per million), rather than the more usual concentration units of ng/g TS (equivalent to parts per billion) for micro-constituents. In the review by Jaganyi (2007), aerobically digested sludge from Germany and untreated sludges from Spain had lower concentrations of LAS than did anaerobically digested sludges from the same and other countries. Similarly, in the review by Angelidaki *et al*. (2004), the concentrations range of LAS in aerobically digested sludges was much lower than the range in anerobically digested sludges. A dewatered waste activated sludge in Denmark (Gejlsbjerg *et al*., 2001), had substantially lower concentration than a Danish anaerobically digested sludge (Jacobsen *et al*., 2004).

Table 50. Concentrations of Linear Alkylbenzene Sulfonates in Sludges and Biosolids

Sludge Source	Concentration (µg/g TS dw)	Reference
Denmark – dewatered activated sludge	759	Gejlsbjerg *et al*. (2001)
Denmark – anaerobically digested	4,500	Jacobsen *et al*. (2004)
sludges (not specified)	1,000 - 10,000	Fent (1996)
Norway – sludges (not specified)	1 - 424	Jaganyi (2007)
Denmark – sludges(not specified)	11 – 16,100	
Germany – anaerobically digested sludges	1,600 – 11,800	
Germany – aerobically digested sludges	182 – 432	
Italy - anaerobically digested sludges	11,500 – 14,000	
Spain - anaerobically digested sludges	12,100 – 17,800	
Spain – untreated sludges	40 – 700	
Switzerland - anaerobically digested sludges	2,900 - 11,900	
UK - anaerobically digested sludges	9,300 – 18,800	
primary sludge	5,340 - 6,310	Angelidaki *et al*. (2004)
Anaerobically digested (literature)	2,000 - 30,200	
Aerobically digested (literature)	100 – 2,900	
Air-dried digested (literature)	150 - 160	

Other data presented by Cavalli (2004) indicated that LAS was much less likely to be biodegraded in an anaerobic sludge environment than in aerobic sludge. Use of the OECD (Organization for Economic Cooperation and Development) biodegradability screening test indicated that LAS was not biodegraded in anaerobic tests after 28 days. Further inhibition concentrations of LAS in anaerobic sludge digestion were identified in Cavalli (2004) as 25 mg/L, corresponding to 17 µg/g TS dw. The data of Table 50 appear to indicate that aerobic digestion can result in lower concentrations of LAS in the treated sludge than anaerobic digestion.

The composition of LAS homolog (compounds of similar chemical structure but with varying lengths of carbon chain) in a Danish biosolids sample was documented by Jacobsen *et al*. (2004). Carbon chain lengths reported were from C_{10} to C_{13}, as indicated in Table 51.

Table 51. Composition of LAS Homologs in a Danish Biosolids Sample (Jacobsen *et al*., 2004)

LAS Homolog	Conc. In biosolids before land application, µg/g DW	% of Total LAS
C_{10} LAS	135	3
C_{11} LAS	1035	23
C_{12} LAS	1755	39
C_{13} LAS	1575	35
Total LAS	4500	100

3.4.2 Fate and Transport in the Terrestrial Environment

The mineralization of labelled ^{14}C-LAS in coarse sandy soil was monitored by Gejlsbjerg *et al.* (2001). Experimental factors in the tests included the sludge:soil ratio (expressed as a dry matter ratio) and the degree of water saturation of the soil during the test (used to assess the effect of different soil oxygen levels). Results of the experiments are summarized in Table 52. The degree of water saturation of the soil had the most significant effect on mineralization of the added LAS. Only 19 – 29% of the LAS was mineralized after two months of study when the soil water saturation was maintained at 80%, compared to 77 – 78% when it was maintained at 40%.

The influence of soil type on mineralization of LAS was also examined by Gejlsbjerg *et al*. (2001). Three soil types, including a coarse sandy soil, a sandy soil and a predominantly clay soil, were tested by spiking the LAS in the soil, both with biosolids incorporated at a biosolids:soil mixture of 1:100, and without any biosolids (Table 53).

Without biosolids addition the quantity of LAS mineralized after two months of study was similar in all three soil types (61 – 67%), with half-lives ranging from 7.5 to 8.2 days. When biosolids were applied to the three soil types, the greatest mineralization rate was observed in the coarse sandy soil, while mineralization rates in the other two soils were lower but similar in magnitude. Half-lives for the LAS in the biosolids-amended soils ranged form 7.2 – 7.9 days, slightly shorter than in the soils without added biosolids. Two additional tests comparing

biosolids:soil mixtures in the coarse sandy soil resulted in a shorter half-life (7.0 d) at the higher mixture level (1:20) relative to the half-life at the lower mixture of 1:100 (8.5 d). In all the tests by Gejlsbjerg *et al*. (2001), the half-lives were less than 10 d.

Table 52. Effect of Biosolids Loading and the Degree of Soil Water Saturation on Mineralization of LAS (Gejlsbjerg *et al*., 2001)

Sludge:soil ratio	Water saturation	Initial conc. in test sludge-soil mixture (mg/kg DM)	Mineralization after two months (% of added ^{14}C)
Sludge alone	not appl.	759	14.8 (6.7)[a]
1:20	40%	36	76.7 (4.2)
	80%	36	18.9 (4.1)
1:100	40%	7.5	78.4 (2.9)
	80%	7.5	29.3 (13.4)

[a] Mean (std. deviation), n = 4

Table 53. Effect of Soil Type on Mineralization of LAS (Gejlsbjerg *et al*., 2001)

Test Conditions	Initial Conc. In test mixture (mg/kg DM)	Mineralization after two months (% of added ^{14}C)	Half-life $t_{½}$ (Days)
1:100[b], Coarse sandy soil (in Jyndevad)	7.5	81.1 (5.49)[a]	7.9 (0.19)
1:100, Sandy soil (in Lundgaard)	7.5	72.9 (5.14)	7.9 (0.41)
1:100, clayey soil (in Askov)	7.5	68.8 (7.54)	7.2 (0.14)
Soil only (coarse sandy soil)	1.3	61.8 (0.83)	8.2 (0.15)
Soil only, sandy soil (in Lundgaard)	1.3	67.1 (3.41)	7.9 (0.14)
Soil only, sandy soil (in Askov)	1.3	64.4 (1.08)	7.5 (0.20)
1:20, 40% water holding capacity; coarse sandy soil (in Jyndevad)			7.0 (0.55)
1:100, 40% water holding capacity; coarse sandy soil (in Jyndevad)			8.5 (0.20)

[a] Mean (std. deviation), n = 4 [b] Biosolids:sludge mixture

The disappearance of total LAS in a loamy sand soil was monitored in a lysimeter study by Jacobsen *et al*. (2004). The half-life for total LAS reported by the authors was 20 d, longer than the results of the Gejlsbjerg *et al* (2001) study. Concentrations in the soil were at very low levels after 50 days of the trial (Table 54), suggesting that long term accumulation would not be likely.

Table 54. Reduction of LAS in Soil Lysimeter Study (Jacobsen *et al*., 2004)

Time after Study Start	Conc. of Total LAS in biosolids-soil mixture, (ng/g DM)
(t=0 day)	38
t=10 days	9 ± 1[a]
t=20 days	5 ± 0.5
t=30 days	4.5 ± 0.5
t=50 days	0.350 ± 0
t=110 days	0.224 ± 0

[a] mean ± std deviation (n=4) LOD = limit of detection

Several homologs of the LAS were monitored in the study by Jacobsen *et al*. (2004). There was a clear shift in the distribution of homologs in the top 15 cm of the soil that occurred over the duration of the study, relative to the composition in the applied biosolids. The C_{10} homolog disappeared by the 20th day of the test and the C_{11} homolog was significantly reduced. By the 50th day of the test, the C_{12} homolog was also significantly reduced from initial levels, leaving the C_{13} homolog as the predominant species. The persistence of the higher chain length homologs was deemed to result from their higher hydrophobicity relative to the shorter chain homologs. The higher homologs were thought to bind more tightly to the organic fraction of the soils, making them less available for biodegradation.

Because the leachate from the lysimeters contained no detectable concentrations of the LAS homologs, transport through the soil column by percolation was considered negligible (Jacobsen *et al*., 2004).

De Wolf and Feijtel (1998) conducted an environmental assessment with particular reference to LAS in sewage biosolids and concluded on the basis of a worst case scenario that there is no human health risk from indirect exposure to LAS from either food or drinking water. Also they concluded that current LAS use does not pose a risk to terrestrial organisms such as plants and invertebrates.

The Panel on Contaminants of the Norwegian Scientific Community on Food Safety (VKM, 2009) recognized that the predicted soil concentrations of LAS from land-applied sewage sludge would exceed the predicted no effect concentrations (PNECs) of these compounds. The Panel further noted, however, that the compounds degrade rapidly in soil, and thus considered them to be of low concern.

A Danish study by Peterson *et al*., (2003), cited by Smith (2009a), examined a number of trace organic contaminants, including LAS when sludge (not differentiated from biosolids by Smith, 2009) was applied to soil. No accumulation of the of the LAS and other contaminants was observed in the soil, no uptake by plants grown on the amended soil, and no adverse effects of the sludge application on soil biota or crop growth were found (Peterson *et al*., 2003 in Smith, 2009).

3.4.3 Section Summary

1. Linear alkylbenzene sulphonates are present at higher concentrations (e.g. mg/kg TS dw level) in biosolids than are many of the other microconstituents.
2. The compounds do not appear to be persistent in soil, with reported half-lives of 7 to 9 d.
3. Mineralization of LAS was reduced in a coarse sandy soil as the degree of water saturation of the soil was increased – presumably due to reduced soil oxygen.
4. Only the limited data of Jacobsen *et al*. (2004) indicated that transport of LAS through a soil column was negligible. No studies of mobility through soils to groundwater or in runoff to surface waters were identified in this review.
5. No studies of bioaccumulation of LAS were observed, although with a short half-life of less than 10 days, little bioaccumulation would be expected.

The above findings for LAS are similar to those contained in the WEAO (2001) report, which were that:

- the literature review indicates that high concentrations (e.g., thousands of mg/kg dry wt.) of linear alkylbenzene sulphonates or their degradation products can occur particularly in anaerobically digested biosolids.
- linear alkylbenzene sulphonates degrade rapidly (within a few days or weeks) under aerobic soil conditions and therefore do not present a significant health or environmental hazard.
- based on the literature review, it is concluded that linear alkylbenzene sulphonate surfactants fall into the Group I category, not requiring further study at this time.
- the authors are not aware of linear alkylbenzene sulphonate data for Ontario soils and recommend that some should be obtained.

Evidence in this and the WEAO (2001) report is convincing that LAS degrades rapidly in aerobic soils. Since agricultural crop production requires aerobic soils, it can be assumed that LAS does not persist in biosolids treated Ontario soils. No data were identified in the current literature review that supported the potential concerns about biomembrane dissolution or enhanced mobility of other hydrophobic contaminants.

Based on the evidence in this review and the WEAO (2001) report, it is recommended that linear alkylbenzene sulfonates (LAS) continue to be classified as Group I contaminants. The need to obtain the above-mentioned soil data, as recommended in the WEAO (2001) report, is considered to be of secondary importance relative to characterization of other contaminants in soils.

3.5 Brominated Flame Retardants

Studies of brominated flame retardants are almost exclusively focused on a family of compounds called polybrominated diphenyl ethers (PBDEs). A Swiss study by Gerecke et al. (2006) examined the biodegradation of PBDEs and two other flame retardants, tetrabromobisphenol A (TBBPA) and hexabromocyclododecane (HBCD). Other than the study by Gerecke et al. (2006), however, PBDEs are the main focus of published data on brominated flame retardants.

PBDEs are compounds used as flame retardants in a wide variety of applications. They have been historically sold as commercial mixtures having a predominant homolog class (compounds with the same number of bromine substituents located at different locations on the diphenyl ether structure). The main commercial classes of the PBDEs sometimes referred to generically as brominated flame retardants (BFRs) are the pentabromo-, octabromo- and decabromo diphenyl ethers (US DHHS, 2004). PBDEs cannot be manufactured in Canada, and use of the pentabromo- and octabromo- diphenyl ethers is prohibited in Canada (Canada Gazette, 2008). Only the decabromo diphenyl ether (DPE) product is allowed for use in Canada.

PBDEs are added to plastics to reduce flammability and fire damage; products incorporating these retardants are used in domestic, commercial and industrial settings, and include polyurethane furniture foam, carpets, high impact cases, circuit boards, appliances and electrical equipment (USGS, 2004). As the products age, the PBDEs can dissociate from the host plastic to become part of indoor dust. Cleaning by wet mopping of floors and washing of dusting cloths or floor-mats is therefore a probable source of entry to wastewater treatment facilities. Municipal landfill leachate piped to wastewater treatment plants are another potential source of the PBDEs (Environment Canada, 2009c). At wastewater treatment facilities, the PBDEs, because of high octanol:water partition coefficients, are expected to sorb strongly to wastewater solids, and thus end up mainly in the residual wastewater solids.

The environmental and health concerns with PBDEs centre on their persistence, potential toxicity and ability to bioaccumulate. Elevated concentrations of the compounds have been found in human breast milk, particularly in North America (USGS, 2004), and in Arctic mammals near the top of the food chain (ringed seals and beluga whales) (Environment Canada, 2006). In humans, these compounds can disrupt thyroid hormone activity due to the similarity of PBDE metabolites to the hormone thyroxin, and may impair neurodevelopment (USGS, 2004).

3.5.1 Occurrence Data

Concentrations of specific PBDE congeners in wastewater sludges and biosolids from two Canadian treatment plants are provided in Table 55.

The study by Rayne and Ikonomou (2005) at the Kelowna BC treatment plant examined many of the 209 congeners. The study by Song *et al*. (2006) focused on the predominant congeners, excluding decabromo-DPE 209, at the Windsor Little River treatment plant. In the Kelowna data, the isomer decabromo DPE (BDE 209) was observed in all the samples at the highest concentration of any of the isomers, followed by the penta BDE99 and tetra BDE47 isomers. The two isomers detected at the highest concentrations in the Little River primary sludge were the penta BDE99 and the tetra BDE47.

Biosolids at the Kelowna plant include not only the primary sludge, but other sludges including thickened waste activated sludge. A comparison of the concentration data of Rayne and Ikonomou (2005) for the primary sludge and treated biosolids demonstrates how the secondary biological sludge concentrates the PBDEs and increases the overall concentration in the biosolids. The concentrations of the PBDEs in the Windsor Little River primary sludge are substantially higher than corresponding congener concentrations in the Kelowna primary sludge.

Clarke *et al*., (2008), compared concentrations of PBDE congeners in eight urban and eight rural biosolids samples. Table 56 presents the concentration data for the different PBDE isomers included in the analytical method for the urban wastewater treatment plants sampled. Decabromo DPE (BDE209) was present at the highest concentration (mean 881 ng/g TS dw).

Table 55. Concentrations of PBDE Congeners in Two Canadian Sludges and Biosolids

Polybrominated diethyl ethers Isomer	Concentration (ng/g TS dw)		
	Primary sludge	Biosolids	Primary sludge
2,4-Dibromodiphenyl Ether (di BDE7)	0.007	0.0806	
2,4' + 3,3'- Dibromodiphenyl Ether (di BDE8/11)	0.007	0.0764	
3,4'- Dibromodiphenyl Ether (di BDE13)	0.007	0.0753	
4,4'- Dibromodiphenyl Ether (di BDE15)	0.0651	0.348	
2,2',4- Tribromodiphenyl Ether (tri BDE-17)	0.379	4.88	
2,3',4- Tribromodiphenyl Ether (tri BDE25	0.0279	0.279	
2,4,4'-Tribromodiphenyl Ether (tri BDE 28)	1.15	7.67	8.0 ± 3.1[a]
2,2',4,4'-Tetrabromodiphenyl Ether (tetra BDE47)	58.46	401.95	586 ± 207
2,2',4,5'-Tetrabromodiphenyl Ether (tetra BDE49)	1.67	11.82	
2,3',4,4'-Tetrabromodiphenyl Ether (tetra BDE66)	1.33	9.17	
2,3',4',6-Tetrabromodiphenyl Ether (tetra BDE-71)	0.16	1.47	
3,3',4,4'-Tetrabromodiphenyl Ether (tetra BDE77)	0.007	0.106	
2,2',4,4',5-Pentabromodiphenyl Ether (penta BDE85)	3.19	22.16	
2,2',4,4',5-Pentabromodiphenyl Ether (penta BDE99)	71.81	523.98	757 ± 272
2,2',4,4',6-Pentabromodiphenyl Ether (penta BDE100)	10.65	79.64	122 ± 42
2,3,3',4,4'-Pentabromodiphenyl Ether (penta BDE105)	0.0139	0.118	
2,3',4,4',6-Pentabromodiphenyl Ether(penta BDE119)	0.0488	0.437	
3,3',4,4',5-Pentabromodiphenyl Ether (penta BDE126)	0.0581	0.192	
2,2',3,4,4',5'-Hexabromodiphenyl Ether (hexa BDE 138)	0.99	6.73	9.1 ± 4.3
2,2',3,4,4',6'-Hexabromodiphenyl Ether (hexa BDE140)	0.204	1.67	
2,2',4,4',5,5'-Hexabromodiphenyl Ether (hexa BDE 153)	10.89	78.06	84 ± 27
2,2',4,4',5,6'-Hexabromodiphenyl Ether (hexa BDE 154)	5.61	43.89	49 ± 19
2,2',4,4',6,6'-Hexabromodiphenyl Ether (hexa BDE155)	0.265	1.82	
2,2',3,4,4',5,6-Heptabromodiphenyl Ether (hepta BDE181)	0.0163	0.1214	
2,2',3,4,4',5',6-Heptabromodiphenyl Ether (hepta BDE 183)	2.41	8.16	12 ± 6
2,3,3',4,4',5,6-heptabromodiphenyl ether (BDE-190)	0.1	0.48	
2,2',3,3',4,4',5,5',6-Nonabromodiphenyl Ether (nona BDE206)	2.04	11.06	
2,2',3,3',4,4',5,6,6'-Nonabromodiphenyl Ether (nona BDE207)	2.17	14.44	
2,2',3,3',4,5,5',6,6'-Nonabromodiphenyl Ether (nona BDE208)	0.251	1.93	
2,2',3,3',4,4',5,5',6,6'-Decabromodephenyl Ether (deca BDE209)	122.44	558.66	
TOTAL PBDEs	300.1	1809.15	
Reference	Rayne and Ikonomou (2005)		Song *et al*. (2006)

[a] Mean ± std deviation, n = 3

Results for the eight rural samples in the Australian survey are provided in Table 57. Only one of

Table 56. PBDE Concentrations in Sludges and Biosolids from Australian Urban Municipalities (Clarke *et al*., 2008)

	Concentration of PBDE congeners (ng/g TS dw) by designated plant and sludge treatment								
	U1	U5	U6	U8	U2	U3	U4	U7	
BDPE Isomer	An Dig + Dewater	An Dig + Dewater	An Dig + Dewater	An Dig + Dewater	Dewater	DAF filtration	IFAS	Dewater + Lime	Mean ± Std Dev.
2,2',4-Tribromo DPE (BDE17)	0.96	0.16	7.75	1.85	2.7	2.7	0.27	0.46	2.1 ± 2.5
2,4,4'-Tribromo DPE (BDE28) + (BDE33)	2	<0.2	4.55	5.2	3.1	25	1.1	0.85	6±8.6
2,2',4,4'-Tetrabromo DPE (tetra BDE47)	120	17	205	285	180	36	72	45	120±95
2,2',4,5'-Tetrabromo DPE (BDE49)	3.8	1.9	7.95	8.45	5.6	2.3	2.3	1.5	4.2±2.8
2,3',4,4'-Tetrabromo DPE (BDE66)	3.3	0.59	7.15	7.7	6.1	1.4	2.9	1.5	3.8±2.8
3,3',4,4'-Tetrabromo DPE (BDE77)	0.049	<0.004	0.58	0.092	0.055	0.0099	<0.01	<0.03	0.2±0.2
2,2',4,4',5-Pentabromo DPE (BDE85)	4.8	1	8.8	11.5	6.7	1.1	3.1	1.8	4.9±3.9
2,2',4,4',5-Pentabromo DPE (BDE99)	130	22	230	315	190	31	84	48	131±106
2,2',4,4',6-Pentabromo DPE (BDE100)	26	4.4	47.5	63.5	39	8.6	16	9.6	27±21.0
2,3',4,4',6-Pentabromo DPE (BDE119)	<0.9	0.04	0.695	0.465	<1	<0.1	<0.4	0.11	0.33±0.31
2,2',3,4,4',5'-Hexabromo DPE (BDE138)			3.3	2.7				1.9	2.6±0.7
2,2',3,4,4',6-Hexabromo DPE (BDE139)	1.5	0.31	2.8	3.15	2	0.49	0.82	0.42	1.4±1.1
2,2',3,4,4',6'-Hexabromo DPE (BDE140)	0.45	0.16	1.27	0.84	0.71	0.18	0.29	0.13	0.5±0.41
2,2',4,4',5,5'-Hexabromo DPE (BDE153)	13	4.9	23	28	20	4.8	8.2	4.4	13.3±9.3
2,2',4,4',5,6'-Hexabromo DPE (BDE154)	10	3.2	19.5	24.5	16	4.3	6.1	3.9	10.9±8.1
2,2',3,3',4,4',6-Heptabromo DPE (BDE171)	<0.09	0.41	3.87	0.375	<0.2	0.097	<0.4	0.099	0.97±1.63
2,2',3,4,4',5,5'-Heptabromo DPE (BDE180)	0.37	0.81	3.95	0.615	1.7	0.14	0.29	0.11	1±1.3
2,2',3,4,4',5',6-Heptabromo DPE (BDE183)	9.6	15	13	10	19	3.9	5.1	1.9	9.7±5.9
2,2',3,4,4',6,6'-Heptabromo DPE (BDE184)	0.16	0.2	2.23	0.41	0.39	0.094	0.11	0.064	0.46±0.73
2,2',3,3',4,4',5',6-Octabromo DPE (BDE196)	4.7	<2	7.4	4.2	7.7	<0.2	<1	1.6	5.1±2.5
2,2',3,3',4,4',6,6'-Octabromo DPE (BDE197)	2.9	8.4	8.75	4.3	3.6	0.89	1.1	0.85	3.8±3.2
2,2',3,3',4,4',5,5'-Octabromo DPE (BDE201)	1.1	14	4.85	1.3	<4	<1	<0.7	0.38	4.3±5.7
2,2',3,4,4',5,5',6-Octabromo DPE (BDE203)	<3	40	8.35	5.1	<3	<1	<2	1.3	13.7±17.8
2,2',3,3',4,4',5,5',6-Nonabromo DPE (BDE206)	32	98	30	27.5	9.7	3.1	4.5	6	26±31
2,2',3,3',4,4',5,6,6'-Nonabromo DPE (BDE207)	13	110	19.5	12.5	12	5.7	6	6.3	23±35
2,2',3,3',4,5,5',6,6'-Nonabromo DPE (BDE208)	7.9	97	15.7	7.95	6.5	2.7	2.8	3.7	18±32
2,2',3,3',4,4',5,5',6,6'-Decabromo DPE (BDE209)	1170	3780	530	910	360	93	81	130	880±1200

An Dig = Anaerobic Digestion DAF=dissolved air flotation IFAS= integrated fixed-film activated sludge

Table 57. PBDE Concentrations in Sludges and Biosolids from Australian Rural Municipalities (Clarke *et al*., 2008)

BDPE Isomer	Concentration of PBDE congeners (ng/g TS dw) by designated plant and sludge treatment								
	R1	R2	R3	R4	R5	R6	R7	R8	
	Dewater	Dewater	Dewater	An Dig + Dewater	Lime	Dewater + Lime	Land Dried	Solar Dried	Mean ± Std Dev.
2,2',4-Tribromo DPE (BDE17)	4.3	0.25	12	2.6	0.69	0.4	0.0065	3.6	3.2 ± 4.5
2,4,4'-Tribromo DPE (BDE28) + (BDE33)	8.1	0.92	2.6	2.4	1.2	1.4	<0.06	11	3.7± 4.1
2,2',4,4'-Tetrabromo DPE (tetra BDE47)	170	74	120	140	56	89	<0.4	410	160 ± 140
2,2',4,5'-Tetrabromo DPE (BDE49)	16	1.9	6.4	5.6	2	3.1	0.035	23	6.7 ±8.3
2,3',4,4'-Tetrabromo DPE (BDE66)	8.4	1.9	4.2	4.8	1.7	2.8	0.017	14	4.6 ±4.9
2,3',4',6-Tetrabromo DPE (BDE71)	1.6	0.17	8	1.9	<4	0.18	<0.009	1.4	2.9 ±3.5
3,3',4,4'-Tetrabromo DPE (BDE77)	0.1	0.027	0.06	0.069	<0.03	0.06	<0.004	0.16	0.09 ±0.05
2,2',4,4',5-Pentabromo DPE (BDE85)	5.1	5.8	3.9	5.8	1.8	4.2	0.013	14	5 ±4.9
2,2',4,4',5-Pentabromo DPE (BDE99)	210	120	130	170	51	130	0.37	400	150 ±140
2,2',4,4',6-Pentabromo DPE (BDE100)	41	21	24	32	11	21	<0.08	94	36 ± 33
2,3',4,4',6-Pentabromo DPE (BDE119)	0.28	0.14	0.28	0.29	<0.6	0.21	<0.002	0.68	0.37 ±0.21
2,2',3,4,4',5'-Hexabromo DPE (BDE138)	4.2	4.7	3.9	6.1	nd	4.2		11	6.3 ±3.3
2,2',3,4,4',6-Hexabromo DPE (BDE139)	1.6	1.9	1.1	1.5	0.4	1.3	<0.002	3.9	1.6 ±1.3
2,2',3,4,4',6'-Hexabromo DPE (BDE140)	0.61	0.54	0.47	0.59	0.16	0.36	<0.01	1.1	0.54±0.35
2,2',4,4',5,5'-Hexabromo DPE (BDE153)	23	14	13	17	4.6	13	0.064	35	13.8±12.1
2,2',4,4',5,6'-Hexabromo DPE (BDE154)	19	9.8	12	15	3.8	8.4	0.04	33	12±11.6
2,2',3,3',4,4',6-Heptabromo DPE (BDE171)	0.38	0.11	0.17	0.27	0.13	0.2	<0.009	0.47	0.25±0.13
2,2',3,4,4',5,5'-Heptabromo DPE (BDE180)	0.57	0.17	0.26	0.41	0.16	0.33	<0.003	0.67	0.37±0.19
2,2',3,4,4',5',6-Heptabromo DPE (BDE183)	13	3.3	3.7	11	3.3	7.3	0.083	11	6.1±4.5
2,2',3,4,4',6,6'-Heptabromo DPE (BDE184)	0.67	0.098	0.2	0.47	0.075	0.19	<0.002	0.38	0.26±0.16
2,3,3',4,4',5',6-heptabromo DPE (BDE191)	0.2	0.047	0.14	0.092	0.053	0.082	<0.005	0.22	0.12±0.07
2,2',3,3',4,4',5',6-Octabromo DPE (BDE196)	6.4	2.2	4.7	4.2	3	4.3	<0.3	6.5	4.5±1.3
2,2',3,3',4,4',6,6'-Octabromo DPE (BDE197)	6.6	1.4	2.2	5.4	1.5	3	0.022	4.3	2.7±1.9
2,2',3,3',4,4',5,5'-Octabromo DPE (BDE201)	2.8	0.44	1.8	1.2	0.59	1	0.015	2.7	1.2±0.9
2,2',3,4,4',5,5',6-Octabromo DPE (BDE203)	7.8	2.4	5.7	4.5	2.3	3.7	<0.03	8.7	5±2.4
2,2',3,3',4,4',5,5',6-Nonabromo DPE (BDE206)	28	7.6	31	8.5	8.2	7.9	0.093	31	14±13
2,2',3,3',4,4',5,6,6'-Nonabromo DPE (BDE207)	21	5.9	20	8.7	7.4	9.9	0.094	19	11±7.5
2,2',3,3',4,5,5',6,6'-Nonabromo DPE (BDE208)	14	3.4	10	4.4	3.9	5.7	0.064	14	6.3±4.9
2,2',3,3',4,4',5,5',6,6'-Decabromo DPE (BDE209)	990	280	1210	260	250	180	3.4	1050	490±510

the rural plants utilized anaerobic digestion as a biosolids treatment process, while most relied instead on dewatering and drying of the biosolids. Decabromo DPE was present in all the rural biosolids samples at the highest concentration of any isomer, as was the case with the urban biosolids samples. The sample derived for solar drying had the highest concentrations of almost all isomers in the rural biosolids samples. Based on statistical analysis, Clarke *et al*. (2008) concluded that the sum of the PBDE isomers were not statistically different between the urban and rural biosolids.

Kleywegt (2006) reported concentrations of total PBDE congeners in raw sludges and biosolids derived from aerobic and anaerobic digestion. Overall results for the study of 25 treatment facilities in Ontario are presented in Table 58. Aerobic digestion was practised only at the smaller treatment plants of capacity less than 22,700 m^3/d. There was no substantial difference in concentrations of the total PBDEs in the non-stabilized, aerobic and anaerobic digested solids, falling in a range of approximately 2,000 to 2,700 ng/g TS dw, with the aerobic stabilized biosolids having the lowest mean concentrations and the anaerobically digested sludges the highest mean concentrations. Concentration data for the medium (22,700 m^3/d – 45,400 m^3/d) and large (>45,400 m^3/d) capacities indicated that levels were higher in the anaerobically digested biosolids than in the non-stabilized sludges, suggesting the biological recalcitrance of this class of compounds to anaerobic degradation. Kleywegt (2006) concluded that neither the plant capacity (community size) nor the type of biosolids treatment had a significant effect on concentrations of the PBDEs. Further, at current biosolids application frequency and rates, the concentrations of the total PBDEs in biosolids-amended soils was estimated to increase by 3 ng/g DM each year.

Table 58. Concentrations of Total PBDEs in Ontario Sludges and Biosolids (Kleywegt, 2006)

Sludge/Biosolids Type	Plant Capacity	PBDEs-total (ng/g TS dw)
Biosolids (aerobic)	Small	2,000
	Medium	not appl
	Large	not appl
Biosolids (anaerobic)	Small	2,650
	Medium	2,900
	Large	2,600
Wastewater Sludge (no stabilization)	Small	2,500
	Medium	2,450
	Large	1,500

The recently published US EPA's Targeted National Sewage Sludge Survey documented concentrations of many target analytes including PBDEs. Biosolids from a total of 74 municipal treatment plants in 35 states were included in this comprehensive national survey. The data were statistically analyzed to determine median, mean and standard deviations for the target contaminants. The results for the PBDEs are presented in Table 59. The sludges represent a wide range of process types, geographic locations and treatment plant capacities, although all

facilities tested had a treatment capacity greater than 3,780 m^3/d (1 MGD) with a minimum of secondary treatment (US EPA 2009a).

Table 59. PBDE Concentrations in Sludges and Biosolids Based on U.S. EPA's Targeted National Sewage Sludge Survey (US EPA, 2009a)

PBDE Isomer	Concentration (ng/g TS dw)		
	median	mean	std dev
2,4,4'-Tribromodiphenyl Ether (tri BDE28) + tri BDE33	8.90	15.35	24.07
2,2',4,4'-Tetrabromodiphenyl Ether (tetra BDE47)	570.4	709.2	523.8
2,3',4,4'-Tetrabromodiphenyl Ether (tetra BDE66)	12.00	17.40	18.55
2,2',4,4',5-Pentabromodiphenyl Ether (penta BDE85)	23.00	27.94	22.00
2,2',4,4',5-Pentabromodiphenyl Ether (penta BDE99)	574.6	716.4	533.4
2,2',4,4',6-Pentabromodiphenyl Ether (penta BDE100)	120.0	150.4	143.8
2,2',3,4,4',5'-Hexabromodiphenyl Ether (hexa BDE138)	7.00	10.75	12.63
2,2',4,4',5,5'-Hexabromodiphenyl Ether (hexa BDE153)	54.12	68.33	52.69
2,2',4,4',5,6'-Hexabromodiphenyl Ether (hexa BDE154)	46.50	59.90	57.92
2,2',3,4,4',5',6-Heptabromodiphenyl Ether (hepta BDE183)	10.00	16.66	20.47
2,2',3,3',4,4',5,5',6,6'-Decabromodephenyl Ether (deca BDE209)	1,163	2,181	3,463

The data show that decabromo BDE209 is present at the highest concentration in the sludges tested, almost twice the concentration of the isomers with next highest concentrations, the penta BDE99 and tetra BDE47.

Occurrence data retrieved from the literature for other countries are summarized in Table 60. The data indicate that the isomer concentrations are much higher in biosolids samples from the U.S. than from samples from European facilities or from the sites in Kuwait. The lower European concentrations are likely a result of major restrictions on the use and sale of products containing one or both of the pentaBDE and octaBDE mixtures in Europe effective August 15, 2004 (smith, 2009). The mean concentration data from the US EPA's sludge survey in Table 59 are similar to the U.S. concentration values in Table 60. Canadian concentration data presented in Table 55 are more similar to the U.S. values, while the Australian data found in Tables 56 and 57 lie between the North American and European/Kuwaiti data.

The sum of PBDE congeners in biosolids from a Mid-Atlantic wastewater treatment plant ranged in concentration from 950 to 2,000 ng/g DW (Andrade *et al.*, 2009). Background concentrations of the total PBDEs in the soils (n=10) ranged from 0.6 to 15 ng/g, rising to a range of 17 to 71 ng/g following one application of biosolids (n=10 sites, application rates were not indicated). For sites receiving multiple biosolids applications (n=10 sites, application rates were not indicated), the range on concentrations of total PBDEs was 9.5 to 210 ng/g DW. The predominant congeners in the soils receiving biosolids amendment were BDE47, BPE99 and PBDE209, the same as found in the biosolids. The authors concluded that PBDEs are relatively persistent in agricultural soils amended with biosolids (Andrade *et al.*, 2009).

Table 60. Occurrence data for PBDEs (ng/g TS dw) in Biosolids Samples from Other Countries

Biosolids Source	2,2',4,4'-Tetrabromo diphenyl Ether (BDE47)	2,2',4,4',5-Pentabromo diphenyl Ether (BDE99)	2,2',4,4',6-Pentabromo diphenyl Ether (BDE100)	2,2',4,4',5,5'-Hexabromo diphenyl Ether (BDE 153)	2,2',4,4',5,6'-Hexabromo diphenyl Ether (BDE 154)	2,2',3,4,4',5',6-Heptabromo diphenyl Ether (BDE 183)	2,2',3,3',4,4',5,5',6,6'-Decabromo diphenyl Ether (deca BDE209)	Reference
Palo Alto STP CA, U.S.	722-778	894-973	158-172	83-91	61-72		not anal.	from Song *et al*. (2006)
11 U.S. sites	359-754	931-1157	89-255	56-199	58-172	85-4890		from Gevao *et al*. (2008)
European STPs	15-91	19-120	3.5-28	1.0-15.5	0.7-14.8		not anal.	from Song *et al*. (2006)
Spain 5 sites	17.0-40.9 (22.9)[a]	25.0-50.9 (26.9)	5.60-11.0 (6.29)	3.31-5.70 (3.68)	2.47-4.08 (3.42)	3.66-29.6 (3.90)	80.6-1082 (393)	Eljarrat (2006)
Spain 6 sites	1.8-83.6	23.4-64.2	0.2-14	1.2-7	1.1-5.8	8.5-275		from Gevao *et al*. (2008)
Kuwait Treatment plant 1	0.24-2.72 (0.97)	0.61-5.96 (1.95)	0.06-0.85 (0.29)	0.04-0.62 (0.19)	0.06-1.05 (0.31)	0.04-0.78 (0.21)	4.8-157.5 (48.5)	Gevao *et al*. 2008
Kuwait Treatment plant 2	0.95-7.81 (4.16)	2.04-14.74 (8.4)	0.82-2.3 (1.34)	0.24-1.37 (0.82)	0.35-1.98 (1.18)	0.15-0.86 (0.44)	16.4-1595.6 (360.4)	Gevao *et al*. 2008
Kuwait Treatment plant 3	0.97-2.35 (1.86)	1.53-4.84 (3.8)	0.28-0.75 (0.4)	0.16-0.54 (0.40)	0.18-0.81 (0.58)	0.11-0.50 (0.33)	28.4-286.8 (136.5)	Gevao *et al*. 2008
Sweden 14 sites	<2-80	<2-104	<2-25	<dl-16.4	<dl-10.4	785-18032		from Gevao *et al*. (2008)
Stockholm, Sweden	39-91	48-120	11-28	not anal.	not anal.	not anal.		from Gevao *et al*. (2008)
Klippen, Sweden	22	18	5.4	not anal.	not anal.	not anal.		from Gevao *et al*. (2008)
Rimbo, Sweden	53	53	13	not anal.	not anal.	not anal.		from Gevao *et al*. (2008)
Bjergmarken, DN	96.8	86.2	19.1	7.8	6.1	248		from Gevao *et al*. (2008)

[a] median value in parentheses; dl = detection limit

LaGuardia *et al*. (2004) compared PBDE concentrations in four biosolids treatment processes at four different sites, including composting, lime treatment, heat drying, and anaerobic digestion. The concentration data from these treatments are provided in Table 61. Concentrations of the PBDEs in the biosolids prior to treatments or in the composting supplement were not reported.

Table 61. Comparison of PBDE Concentrations in Four Biosolids Treatment Processes (LaGuardia *et al*., 2004).

Treatment Process	2,2',4,4'-Tetrabromodiphenyl Ether (BDE47)	2,2',4,4',5-Pentabromodiphenyl Ether (BDE99)	2,2',4,4',6-Pentabromodiphenyl Ether (BDE100)	2,2',4,4',5,5'-Hexabromodiphenyl Ether (BDE153)	2,2',4,4',5,6'-Hexabromodiphenyl Ether (BDE154)	2,2',3,3',4,4',5,5',6,6'-Decabromodiphenyl Ether (BDE209)
Compost-A	498	743	106	55.6	98.8	308
Compost-B	754	1157	167	87.9	121	1460
Compost-C	536	516	112	71.8	58.2	368
Average Compost	596	805	128	72	93	712
Lime-A	359	513	88.5	64.3	82.6	553
Lime-B	525	584	200	179	172	84.8
Average Lime	442	549	144	122	127	319
Heat-A	518	714	115	58.8	95.2	1940
Heat-B	673	815	255	119	169	4890
Average Heat	596	765	185	89	132	3415
An Dig-A	605	572	125	68.9	57.2	347
An Dig-B	421	391	113	116	61	340
An Dig-C	686	648	129	67.7	61.9	40
An Dig-D	674	613	176	80.6	74.5	389
Average An Dig	597	556	136	83	64	279

The data suggest that for the hexabromo and lower brominated congeners, the different treatment processes had relatively little effect on the observed concentrations. The data are less clear with respect to the decabromo isomer. The sites using anaerobic digestion appeared to have substantially lower concentrations than the other treatment processes. The two sites using heat drying had biosolids with the highest decabromo DPE concentrations observed in the survey. Two of three composted samples exhibited relatively low concentrations of the isomer, as did the two limed samples.

3.5.2 Fate and Transport in the Terrestrial Environment

The movement of PBDEs in a long-term biosolids application sites was investigated by Hundal *et al* (2009). The site received a maximum cumulative loading of 2,218 tonne dry biosolids/ha from 1973-2002. Cumulative loading of the PBDE congeners in biosolids to the soil for this period

was not reported. Samples of soil from different depths were analyzed for total PBDEs with results appearing in Table 62.

Concentrations in the top 30 cm of soil at the long-term application site were greatly elevated compared to the concentration of 4.2 ng/g determined in the soil at the 60 – 120 cm depth. The concentration of 658 ng/g in the top 15 cm of soil, reported to be predominantly biosolids by the authors, declined substantially to 10 5 ng/g in the 15 – 30 cm soil depth (Hundal *et al*., 2009). The data indicated that the PBDEs would not migrate downward through the soil column to any extent.

Table 62. Concentrations of Total PBDEs at Soil Depths from a Long-Term Biosolids Application Site (Hundal *et al*. 2009)

Soil Depth	Total PBDEs Concentration ng/g DW
0-15 cm	658
15-30 cm	105
60-120 cm	4.2

Matscheko *et al*. (2002) investigated the concentrations of PBDEs in four Swedish locations receiving different biosolids applications. Concentrations in the biosolids-amended soils at the four locations were compared to corresponding values in control plots (Table 63). The congeners BDE47 and BDE99 were detected at the highest concentrations in all plots. With the exception of the Björketorp site, concentrations of the various congeners in the biosolids-amended soils were in the range of 0.01 to 0.35 ng/g DM. The PBDE concentrations in biosolids-amended soils were approximately 3 to 10 times higher than in the control plots at the Igelösa, Lamna and Petersborg sites. At the Björketorp site, the soil concentrations were closer in magnitude to those reported by Hundal *et al*. (2009).

In addition to the soil accumulation data, Matscheko *et al*. (2002) also measured concentrations of the PBDE congeners in earthworms inhabiting the sites. Bioaccumulation factors were calculated by dividing the concentrations of the PBDEs in the worm lipid matter by the concentrations in the soil organic matter. The bioaccumulation factors (BAFs) reported for the earthworms in this study are summarized in Table 64. Although the BAFs were mostly less than 8, there were some notable differences. The autumn test of the Lamna site exhibited BAFs of different congeners ranging from 11 to 34. At the Petersborg site, the BDE66 congener had identical BAF values of 17 in the two sampling plots and loading rates examined.

Concentrations of the flame retardant tributylphosphate in soils with and without amendment with anaerobically digested biosolids (single application of 18 T dw/ha), and in the earthworms inhabiting the soils, were measured by Kinney *et al*. (2008). The concentration data and calculated bioaccumulation factors are provided in Table 65. On one sampling occasion, the biosolids-amended soil had substantially higher concentrations of total tributylphosphate than did the control site but not in the other sampling event. In contrast however, there was no effective difference between the tributylphosphate concentrations in earthworms inhabiting either the

Table 63. PBDEs in Biosolids-amended and Control Soil Plots (Matscheko *et al*., 2002)

Study Sites	Treatment		Conc. In soil after sludge application to soil (ng/g DM)				
		2,2',4,4'-Tetra BDE47	2,3',4,4'-Tetra BDE66	2,2',4,4',5-Penta BDE99	2,2',4,4',6-Penta BDE100	2,2',4,4',5,5'-Hexa BDE 153	2,2',4,4',5,6'-Hexa BDE 154
Igelösa [I] (Medium Clays soil) - Sludge application date: 1991-1997, applied every 4th year - Date of sampling: April 2000	Control	0.033	ND	0.033	0.009	0.005	0.003
	I1 1 tonne dry matter/ha/yr	0.14	0.002	0.17	0.052	0.02	0.017
	I2 3tonne dry matter/ha/yr	0.3	0.004	0.35	0.1	0.048	0.035
Petersborg [P] (Light clay soil) - Sludge application date: 1991-1997, applied every 4th year. - Date of sampling: April 2000	Control	0.027	ND	0.02	0.007	0.002	0.001
	P1 1 tonne dry matter/ha/yr)	0.09	0.001	0.096	0.026	0.013	0.009
	P2 3 tonnes dry matter/ha/yr)	0.08	0.001	0.098	0.027	0.012	0.01
Lamna [L] (Slightly clayey soils) - Sludge application date: 1998 -Date of sampling: Spring: April 3 2000; Autumn: September 2000	Control - Spring	0.022	ND	0.01	0.002	ND	ND
	LS_{spring} -2.3 tonnes/ha in 1998	0.034	ND	0.035	0.009	ND	ND
	Control - autumn	0.008	ND	0.008	0.002	ND	ND
	LS_{autumn} 2,3 tonnes/ha in 1998	0.026	ND	0.031	0.008	ND	ND
Björketorp [B] (Not classified soil) - 1978-1982. - 25 tonnes dry matter applied/ha in total - Sampling date: September 2000.	Control	0.039	0.0007	0.05	0.011	0.006	0.004
	BS (applied sludge)	230	1.5	410	120	28	49

ND = not detected

Table 64. PBDE Bioaccumulation Factors for Earthworms Inhabiting Biosolids-amended and Control Soil Plots (Matscheko *et al*., 2002)

Study Sites	Treatment	Bioaccumulation factors (BAFs) of contaminants in earthworms in soils from different sampling sites			
		2,2',4,4'-Tetra BDE47	2,3',4,4'-Tetra BDE66	2,2',4,4',5-Penta BDE99	2,2',4,4',6-Penta BDE100
Igelösa [I] (Medium Clays soil) - Sludge application date: 1991-1997, applied every 4th year - Date of sampling: April 2000	Control	5	ND	4	6
	I1 1 tonne dry matter/ha/yr	8	ND	7	ND
	I2 3tonne dry matter/ha/yr	10	ND	ND	ND
Petersborg [P] (Light clay soil) - Sludge application date: 1991-1997, applied every 4th year. - Date of sampling: April 2000	Control	4	ND	7	7
	P1 1 tonne dry matter/ha/yr)	3	17	4	4
	P2 3 tonnes dry matter/ha/yr)	5	17	5	6
Lamna [L] (Slightly clayey soils) - Sludge application date: 1998 -Date of sampling: Spring: April 3 2000; Autumn: September 2000	Control - Spring	2	ND	3	6
	LS_{spring} -2.3 tonnes/ha in 1998	2	ND	1	ND
	Control - autumn	3	ND	ND	ND
	LS_{autumn} 2,3 tonnes/ha in 1998	18	ND	11	34
Björketorp [B] (Not classified soil) - 1978-1982. - 25 tonnes dry matter applied/ha in total - Sampling date: September 2000.	Control	5	6	5	8
	BS (sludge applied)	3	4	2	3

Table 65. Concentrations of Tributlyphosphate in Soil and Earthworm Samples (Kinney *et al*., 2008)

Site Description	Sample Matrix	Tributylphosphate (ng/g DW)
Site 1 (without biosolids application)	Soil Jun 6-05	2,130
	Worm Jun 6-05	200
	Bioaccum Factor Jun 6-05	0.09
	Soil Sep 29-05	1,100
	Worm Sep 29-05	169
	Bioaccum Factor Sep 29-05	0.15
Site 2 (with biosolids application on April 18, 2005)	Soil May 19-05	523
	Worm May 19-05	250
	Bioaccum Factor May 19-05	0.50
	Soil Sep 21-05	3,570
	Worm Sep 21-05	196
	Bioaccum Factor Sep 21-05	0.06

control or biosolids-treated soils. The resulting BAF values in these tests were less than 1, indicating no accumulation of the tributylphosphate flame retardant.

No published data were found for transport of PBDEs in surface runoff or leachate, studies of persistence or mineralization in soils, or any studies of either plant uptake or toxicity. These are knowledge gaps that future research may address.

3.5.3 Section Summary

The main points of interest for this section follow.

1. There are apparent differences in concentrations of PBDE isomers in North America and other countries (e.g., Europe, Kuwait, and Australia) in which the concentrations in biosolids are lower, with restrictions on use and/or sale being the most probable cause for the differences.
2. The isomer decabromo DPE (BDE 209) was observed in virtually all the biosolids samples reviewed at the highest concentration of any of the isomers, followed by the penta BDE99 and tetra BDE47.
3. No occurrence data were identified for other types of flame retardants, such as tributyl phosphate, HBCD and TBBPA in biosolids.
4. Because of their high hydrophobicity, when applied to land in biosolids, PBDEs are not likely to migrate downward through the soil column.
5. Concentrations of PBDEs in soils exhibited a wide variability from 0.01 ng/g to 658 ng/g DW, possibly due to differences in the biosolids application rates and concentrations in the biosolids in different countries.
6. Bioaccumulation factors for earthworms growing on biosolids amended sites ranged up to 34, compared to a range of 4 to 8 in control fields.
7. No published data were found for transport of PBDEs in surface runoff or leachate, studies of mineralization in soils, or any studies of either plant uptake

or toxicity. These are knowledge gaps that future research may address.

The WEAO (2001) report contained no information about polybrominated diphenyl ethers (PBDEs) because they were not identified as compounds of concern in sewage biosolids when that report was prepared. However, they are structurally akin to the PCB's and other polyhalogenated compounds, consisting of two halogenated aromatic rings, and scientists have questioned their safety (as animal carcinogenic agents) since the 1990s and so are likely to be subject to similar concerns as were the PCBs.

PBDEs have been used in a wide array of products, including building materials, electronics, furnishings, motor vehicles, airplanes, plastics, polyurethane foams, and textiles. People are exposed to them domestically because of their prevalence in common household items. Studies in Canada have found significant concentrations in common foods such as salmon, ground beef, butter, cheese and high concentrations in indoor dust. Increasing PBDE levels have been detected in the blood of marine mammals such as harbor seals.

Given the high levels of exposure to PBDEs in the domestic environment it is unlikely that the very low concentrations of these compounds in soils observed as a result of soil amendment with biosolids represent a significant human health hazard. However, their fate, transport and effects in the environment are unknown and warrant further study. For this reason, they are recommended for classification as Group II compounds requiring additional research.

3.6 Plasticizers and Metabolites

Plasticizers are added to polymeric materials to increase flexibility and suppleness. Phthalate and adipate esters are two common classes of plasticizers. A main health concern appears to be the potential for harm to developing male reproductive organs (e.g., Our Stolen Future, 2009). Health Canada in June 2009 proposed a ban on six common phthalate esters used in manufacture of children's plastic toys (Health Canada, 2009c).

3.6.1 Occurrence Data

Concentrations of phthalate esters found recently in the literature are provided in Table 66. Data for an array of phthalate esters provided by Gibson *et al*. (2005) and Bright and Healey (2003) show that bis(2-ethylhexyl) phthalate (BEHP, also referred to as di-2-ethylhexyl phthalate or DEHP) is the predominant compound in this class, at concentrations several orders of magnitude higher than the other phthalate esters. Concentration data from several nations provided in Table 66 focus almost exclusively on BEHP, without analysis or reporting of other phthalates.

Table 66. Concentrations of Phthalate Esters in Municipal Wastewater Solids

Sludge Source	Concentration (ng/g TS dw)[c]						Reference
	Dimethyl phthalate	Diethyl phthalate	Di-n-butyl phthalate	Butylbenzyl phthalate	Bis (2-ethylhexyl) phthalate	Di-n-octyl phthalate	
Vancouver BC biosolids	130 ± 340[a]	150 ± 140		380 ± 400	2,700 ± 2,700		Bright and Healey (2003)
U.S. Anaerobic digested sludge					3,300		Kinney *et al*. (2008)
U.S.A. Biosolids (n=9)					3,460 – 31,700 (10,500)[b,h]		Kinney *et al*. (2006)
UK mesophilic anaerobic digested sludge	26	18	393	201	62,482	570	Gibson *et al*. (2005)
Denmark Dewatered waste act. sludge					64,000		Gejlsbjerg *et al*. (2001)
Norway sewage sludges[d]					27,000 - 115,000 (83,000)[b,g]		Jaganyi (2007)
Sweden sewage sludges[d]					25,000 - 661,000 (170,000) [b,g]		
Denmark sewage sludges[d]					3,900 - 170,000 (24,500) [b,g]		
Canadian sludge (1995-1998)e					1,600 - 245,000 (160,000) n=6?		XCG (2007)
Homogenized sludge[f]					80,000 ± 10,000[g]		Barnabé *et al*. (2008)
Dewatered sludge[f]					90,000 ± 12,000 [g]		

[a] mean ± standard deviation [b] range (median) [c] equivalent to parts per billion
[d] based on definition of sewage sludge used in Jaganyi (2007), this material is believed to be an untreated or "raw" sludge
[f] from chemically assisted primary treatment only [g] number of samples not specified in citation [h] ng/g OC

In addition to phthalate esters, other similar types of compounds are used as plasticizers excluding Bisphenol A, which is discussed separately. Concentrations of the compounds bis(2-ethylhexyl) terephthalate and bis(2-ethylhexyl) adipate are shown in Table 67 for two sludge samples from a chemically enhanced primary treatment facility in Montreal (Barnabé *et al.*, 2008). Comparing concentrations of these two compounds with those of BEHP in the same sludges in Table 66 indicates that the terephthalate and adipate esters are present in similar concentrations to the BEHP. The chemicals 2-ethylhexanol and 2-ethylhexanal are metabolites of the bis(2-ethylhexyl) organic acid esters (phthalates, adipates, terephthalates, etc.). The aldehyde (2-ethylhexanal) was observed at a higher mean concentration than was the alcohol (2-ethylhexanol) in the data of Barnabé *et al*. (2008), particularly in the dewatered sludge sample.

Table 67. Concentrations of Other Plasticizers and Metabolites in Primary-Assisted Clarifier Sludge (Barnabé *et al*., 2008)

Sludge Source	Concentration (ng/g TS dw)				
	Bis (2-ethylhexyl) terephthalate	Bis (2-ethylhexyl) adipate	2-ethyl-hexanol	2-ethyl-hexanal	2-ethyl-hexanoic acid
Homogenized sludge	45,000 ± 2,300[a]	34,000 ± 1,000	12,500 ± 900	34,000 ± 1,400	20,700 ± 400
Dewatered sludge	104,000 ± 5,00	340,000 ± 10,000	4,500 ± 300	85,000 ± 3,400	14,600 ± 300

[a] mean ± standard deviation; number of samples not specified

Concentrations of plasticizer and chemical intermediate compounds in treated biosolids samples are presented in Table 68. The highest concentration of BEHP was observed in the group of biosolids treatment data developed by Ruel *et al*. (2008), consisting of anaerobically digested, limed and dried biosolids. BEHP concentrations in the other reported literature were in the range of 15,000 to 53,000 ng/g TS. Barnabé *et al*. (2008) reported on concentrations of three plasticizers in dried sludge from the Montreal QC, chemically-assisted primary treatment plant. Gibson *et al*. (2007) provided concentrations of BEHP at the inlet and outlets of composting and heat drying processes. Composting appeared to result in lower concentrations than heat drying, but the data are limited. Concentrations of the biosolids alone prior, or in the composting supplement prior to mixing, were not reported.

3.6.2 Fate and Transport in the Terrestrial Environment

Gejlsbjerg *et al*. (2001) observed no significant effect of either the sludge:soil ratio or degree of water saturation of a coarse sandy soil on the rate of mineralization of ^{14}C-labled BEHP to carbon dioxide (Table 69). In all tests the range of mineralization two months after the start of the test was from 17% to 22%.

Table 68. Concentrations of Plasticizers and Chemical Intermediates following Biosolids Treatment Processes

Biosolids Treatment	Concentration (ng/g TS dw)					Reference
	Bis (2-ethyl-hexyl) phthalate	Bis (2-ethylhexyl) terephthalate	Bis (2-ethylhexyl) adipate	2-ethyl-hexanol	2-ethyl-hexanal	
Dried sludge	15,000 ± 2000[a]	12,200 ± 600	19,300 ± 1,000	nd	nd	Barnabé *et al*., (2008)
Heat dried	31,700 [c]					Kinney *et al*., (2006)
Composted	3,460 – 12,700[c]					
Air dried	3840 [c]					
Anaerobic digestion	10,500 [c]					
Anaerobic digestion, limed, drying	2,197,000 ± 11,000,000[b]					Ruel *et al*., (2008)
Composting	In = 53,000 out = 15,000					Gibson *et al*., (2007)
Heat drying	In = 44,000 out = 34,000					
Compost	27,900 - 154,000					Williams (2007)

nd = not detected
[a] mean ± standard deviation; number not specified
[b] mean ± standard deviation from literature database; number not specified
[c] ng/g OC

Table 69. Effect of Biosolids Loading and Degree of Soil Water Saturation on Mineralization of Bis(2-ethylhexyl) Phthalate (Gejlsbjerg *et al*., 2001)

Sludge:soil ratio	Water Saturation	Initial conc. in test sludge-soil mixture ng/g DM	Mineralization after two months (% of added ^{14}C)
Sludge alone	not appl.	64,000	17.3 (1.7)[a]
1:20	40%	3,000	19.7 (2.0)
	80%	3,000	21.8 (1.7)
1:100	40%	630	20.3 (4.8)
	80%	630	17.8 (0.62)

[a] Mean (std. deviation), n = 4

The effect of soil types, including a coarse sandy soil, a sandy soil and a predominantly clay soil, on the mineralization of BEHP was also examined by Gejlsbjerg *et al*. (2001). The tests involved spiking the BEHP in the soil, both with biosolids incorporated at a biosolids:soil mixture of 1:100 (on a dry weight ratio), and without any biosolids (Table 70).

Table 70. Effect of Soil Type on Mineralization of BEHP (Gejlsbjerg *et al*., 2001)

Test Conditions	Initial Conc. In test mixture (mg/kg DM)	Mineralization after two months (% of added ^{14}C)
1:100[b], Coarse sandy soil (in Jyndevad)	0.63	18.0 (2.16)
1:100, Sandy soil (in Lundgaard)	0.63	6.8 (2.30)
1:100, clayey soil (in Askov)	0.63	5.8 (0.46)
Soil only (coarse sandy soil)	0.24	21.8 (1.25)
Soil only, sandy soil (in Lundgaard)	0.24	9.43 (1.95)
Soil only, sandy soil (in Askov)	0.24	8.46 (1.64)

[a] Mean (std. deviation), n = 4 [b] Biosolids:sludge mixture

Mineralization was more complete in the coarse sandy soil than in the other two soil types, whether or not the plots were amended with biosolids. The organic carbon content of all three soils was reported by the authors to be similar. Differences in sorptive properties of the soils were ruled out for causing the observed differences. The authors speculated that different zones of biological activity may have been responsible for the differences in mineralization observed (Gejlsbjerg *et al*., 2001).

In tests with three types of soils, De Jonge *et al*. (2002) determined that BEHP in biosolids was firmly adsorbed to the biosolids, based on lysimeter-based soil leaching tests (Table 71). For the three soils tested, the percent of total applied BEHP that was leached through the columns, following water applications to achieve 200 mm of outflow, was typically less than 0.3%, only rising to 2.4% in one sandy loam sample. Of the total leached BEHP, the percentage of BEHP in the leachate associated with mineral content from the undisturbed columns ranged from 14% to 40%. The contribution to the leached BEHP by dissolved organic matter (DOM) ranged from 17 to 77%. The DOM was believed to be derived from the biosolids rather than from naturally occurring soil-derived DOM (De Jonge *et al*., 2002). The homogeneous applications resulted in higher leachate concentrations because the biosolids source was more finely divided and provided greater surface area for leaching than did the heterogeneous sludge aggregates. The authors noted that the recovered leachate and BEHP were directly associated with the clay content of the soil, which affected the macropore flow.

Concentrations of phthalates in two soils following amendment with anaerobically digested biosolids are provided in Table 72 (Gibson *et al*., 2005). Both the Brickearth and Gault clay soils had substantial background levels of di-n-butyl phthalate, BEHP and di-n-octyl phthalate. Amendment of the soils with the biosolids resulted in increases in the soil concentrations of all the phthalates with the exception of the di-n-octyl phthalate, which surprisingly declined in both

soils following the biosolids application. The BEHP and butylbenzyl phthalate exhibited the greatest increases in concentrations due to the biosolids addition.

Kinney *et al*. (2008) found no detectable concentrations of BEHP in soils either with amendment of anaerobically digested biosolids (18 T dw/ha), or without biosolids amendment, nor in the earthworms inhabiting the soils of either site.

Table 71. Leaching Properties of BEHP in Different Soils (De Jonge *et al*. 2002)

Soil Type	Sludge Application Type	Soil Condition	Total leached BEHP (% of amount applied)	Leached BEHP sorbed to particles (>0.24 um) (% of total leached BEHP)	Leached BEHP sorbed to DOM (% of total leached BEHP)
Lundgaard soil (Sand, undisturbed, pH=6.34	Heterogeneous	Undisturbed	0.09	19.8	76
	Homogeneous	Undisturbed	0.23	18.8	73.3
Askov soil (Loamy sand, undisturbed, pH=6.78),	Heterogeneous	Undisturbed	0.16	23.6	69.1
	Homogeneous	Undisturbed	0.31	14	77
	Heterogeneous	Re-packed	0.03	12.1	30.3
Rogen soil (Sandy loam, undisturbed, pH=6.64),	Heterogeneous	Undisturbed	0.32	36.9	16.5
	Homogeneous	Undisturbed	2.38	40.6	37.4
	Heterogeneous	Re-packed	0.4	2.42	81.3

DOM = dissolved organic matter

Table 72. Concentrations of Phthalates in Soils With and Without Biosolids (Gibson *et al*., 2005)

Phthalate	Concentration ng/g DM			
	Brickearth	Sludge-amended Brickearth	Gault clay	Sludge-amended Gault clay
Dimethyl phthalate	0.1	0.2	0.1	0.3
Diethyl phthalate	0.2	0.5	0.9	0.5
Di-n-butyl phthalate	8	11.8	7.9	11.3
Butylbenzyl phthalate	0.2	2.4	0.8	3.9
Bis(2-ethylhexyl) phthalate	22.2	316.2	75.8	549.9
Di-n-octyl phthalate	11.5	6.8	13.7	5.6

In a recent major review of the environmental significance of contaminants in biosolids, prepared in the United Kingdom, Smith (2009a) reviewed literature sources and concluded the following about BEHP:

- The risk of human exposure to BEHP from soils amended with biosolids is very minor based on the degradability and biotransformation in aerobic soils and the absence or minimal transfer of BEHP to crops and the food chain.
- Research into the potential effects of BEHP and other phthalates on soil micro-organisms and macrofauna has shown that they are unlikely to have ecotoxic effects at the concentrations found in contemporary operationally produced sewage sludges.

The Norwegian Scientific Community for Food Safety (VKM, 2009) performed a risk assessment of select contaminants, including BEHP, in sewage sludge applied to Norwegian soils (no differentiation was made between the terms sludge and biosolids). The Panel concluded that sewage sludge is not expected to constitute a significant risk to the aquatic environment nor to food producing animals.

3.6.3 Section Summary

1. Concentrations of bis(2-ethylhexyl) phthalate (BEHP) are the highest among the phthalate esters in biosolids, at concentrations typically in the range of 2,000 – 200,000 ng/g TS dw.
2. Mineralization of BEHP in soil is slow.
3. BEHP appears to be tightly bound to the soil, with little opportunity for leaching.
4. Limited data indicate that BEHP does not bioaccumulate in earthworms in biosolids-amended soils.
5. No studies were identified that investigated plant uptake of phthalate esters or related compounds from biosolids-amended soils; thus this lack of studies constitutes a knowledge gap.

Concentration data for phthalates in biosolids are similar in this and the WEAO (2001) report. Both data sets show much greater concentrations of bis (2-ethylhexyl) phthalate (sometimes >200,000 ng/g TS dw) than of the other phthalates (generally <10,000 ng/g TS dw).

However, phthalates were considered to be organics of secondary importance in the WEAO (2001) report for the following reasons:

- They were not included among the organics of concern identified by the screening methodology used by the US EPA during development of Reg. 503 (US EPA 1993).
- In a synopsis of the properties, occurrence, fate and transfer of the principal organic contaminant groups found in sewage sludge and sludge amended soils. Smith (1996) reported that phthalates were lipophilic, hydrophobic and non-volatile, with short half-lives in soil <50 days, no leaching potential, possible retention on plant roots but no translocation, and very limited transfer to animals.
- They were not included among the organics of concern identified by a Stakeholder Advisory Group consulted during report preparation.

Except for data showing that BEHP may be more persistent in soils than was previously thought, evidence in this and the WEAO (2001) report are in agreement. The data in this review, that of Smith (2009), the Norwegian Scientific Committee for Food Safety - Panel on Contaminants (VKM, 2009), and the WEAO (2001) all indicate that phthalates, including BEHP, in land-

applied sewage biosolids do not present significant human or environmental health risks. Based on the above, phthalates including BEHP are recommended as Group I compounds.

3.7 Bisphenol A

Bisphenol A (BPA) is mostly used to manufacture polycarbonate plastics and epoxy resins. Uses of the compound are for food and beverage storage, and in sealants in canned food products. Entry to the wastewater system is possible through food preparation and clean-up, through human excretion after oral intake, and via landfill leachate pumped to municipal wastewater treatment. The primary concerns with BPA related to food and drink packaging relate to possible harmful effects on the brain, behaviour and prostate gland of foetuses, infants and children (U.S. National Institutes of Health, 2009).

3.7.1 Occurrence

Bisphenol A has received considerable attention in wastewater sludges and biosolids. Lee and Peart (2002) included BPA as a target analyte in a survey of Canadian digested sludges (Table 73).

Table 73. Bisphenol A Concentrations in Canadian Digested Sludges (Lee and Peart, 2002)

Municipal Treatment Plant	Bisphenol A (BPA) concentration (ng/g TS dw)
Vancouver	300
Vancouver	440
Calgary (Bonnybrook)	800
Calgary (Fish Creek)	790
Edmonton (Goldbar)	3,180
Regina	490
Saskatoon	260
Saskatoon	1,170
Burlington	1,860
Galt	9,560
Guelph	460
Hamilton	4,440
Ingersoll	470
Kitchener	230
Ottawa	640
Waterloo	2,540
Windsor	11,100
Toronto (Ashbridges Bay)	620
Toronto (Humber)	280
Toronto (North)	100
Granby	240
Moncton	130
Truro	300
Median	555

The highest concentration of BPA in that survey (11,100 ng/g TS dw) was observed in digested biosolids from the Windsor (ON) wastewater treatment plant, whereas the minimum concentration was noted in a sample from the North Toronto sewage treatment facility. Other high concentrations of BPA were observed on the digested biosolids of highly urbanized centres such as Galt (ON), Hamilton (ON) and Edmonton (AB). The median concentration of BPA in the digested sludge samples was 555 ng/g TS dw. Based on accompanying raw sludge concentration data, it appears that BPA is not removed during sludge anaerobic digestion. Concentrations of BPA in other biosolids or sludges are summarized in Table 74.

Table 74. Concentrations of Bisphenol A in Other Sludges and Biosolids

Sludge Source	Sludge Type	Concentration (ng/g TS dw)	Reference
U.S.	anaerobic digested sludge	4,600	Kinney *et al*. (2008)
Toronto sewage sludge	digested sludge	120 – 13,000 (1090)	Webber and Sidwha (2005)
(Literature review)	not specified	0.10 – 32,100,000	Harrison *et al*. (2006)
Greek sludge	dewatered secondary or anaerobic digested sludge	560 – 1,750 (530)	Stasinakis *et al*. (2008)
Various	Not specified	4 – 1,363	Williams (2007)
U.S. Plant H	Dewatered	1,090[c]	Kinney *et al*. (2006)

[a] range (median) [b] mean ± standard deviation [c] ng/g organic carbon

Only limited data were identified which characterised the concentrations of BPA resulting from biosolids treatment processes. BPA concentrations in several treatment processes at different locations as documented by Kinney *et al*. (2006) are summarised in Table 75. Of the various treatment processes, the concentration of BPA was lowest in the heat dried biosolids and highest in the anaerobically digested sludge. Additional data are needed to determine if these trends can be extrapolated on a more universal basis.

Table 75. Concentrations of Bisphenol A following Biosolids Treatment Processes (Kinney *et al*., 2006)

Biosolids Treatment	Concentration (ng/g OC)
heat drying	1,680
composting	4,690 – 9,030
other drying	3,550
anaerobic digestion	14,400

3.7.2 Fate and Transport in the Terrestrial Environment

The data on the fate and transport of BPA in soils and biota are sparse. Environment Canada (Health Canada, 2008) has indicated that transfer of BPA from biosolids to soils or biota in the soil is possible, however based on this review, the data supporting this hypothesis are few.

Smith (2009a) indicated that biphenols (which would include bisphenol A) have short half-lives of a few days in soil, and thus cannot persist long enough to transfer to the human food chain.

Kinney *et al*. (2008) measured concentrations of BPA in the soil of two sites, one of which received a single biosolids application of 18 T dw/ha, and one which did not. Concentrations of BPA in the earthworms inhabiting the two sites were also determined. Detectable concentrations of BPA were only found in one of two soil samples from the biosolids-amended site (81 ng/g DM), and one of two samples of soil from the non-amended site (147 ng/g DM) (Table 76). There were no detectable concentrations of BPA in any of the earthworm samples from either site.

Table 76. Concentrations of Bisphenol A in Soil and Earthworm Samples (Kinney *et al*., 2008)

Site Description	Sample Matrix	Bisphenol A (ng/g DM)
Site 1 (without biosolids application)	Soil Jun 6-05	147
	Worm Jun 6-05	ND
	Soil Sep 29-05	ND
	Worm Sep 29-05	ND
Site 2 (with biosolids application on April 18, 2005)	Soil May 19-05	ND
	Worm May 19-05	ND
	Soil Sep 21-05	81
	Worm Sep 21-05	ND

No data were found on the potential bioaccumulation of BPA by plants growing on soils amended with biosolids.

3.7.3 Section Summary

1. Concentrations of BPA in biosolids and sludges have been well documented in the literature, at concentrations typically in the range of 100 to 10,000 ng/g TS dw.
2. There are few data available regarding the fate of BPA in the terrestrial environment following land application of biosolids.
3. One review indicated that bisphenols (which includes BPA) have short half-lives of a few days in soil.
4. One study indicated that BPA did not bioaccumulate in earthworms.
5. No studies were identified investigating mobility of BPA in percolation water, surface runoff, dissipation, mineralization or accumulation in soils or plants grown on biosolids-amended soils; thus this lack of information constitutes a knowledge gap.

BPA was not identified as an organic compound of concern in sewage biosolids applied on agricultural land and was not assessed in the WEAO (2001) report.

Because of its wide use in polycarbonate plastics for food and beverage storage, and in sealants in canned food products it seems reasonable to conclude that human health risks associated with these domestic uses substantially outweigh those associated with health risks from BPA in

agricultural land amended with biosolids. There are, however, only sparse data on the fate, mobility and potential bioaccumulation in the terrestrial environment as a result of land application of biosolids. Consequently, it is recommended that BPA be considered a Group II contaminant.

3.8 Perfluorinated Organic Compounds

Perfluorinated organic compounds (PFOCs) and derivative products have been used as constituents in stain repellents for fabrics, non-stick cookware and food wrappers, personal care products and fire-fighting foams. The major producer of the compounds in North America, the 3M Company, voluntarily phased out production in the year 2000. These compounds are highly persistent (Sinclair and Kannan, 2006) and bioaccumulative (Swackhamer *et al*., 2004). Environment Canada has determined that human exposure to perfluorinated substances is below levels that would cause adverse health effects. Environment Canada has determined however, that accumulation of compounds such as perfluorooctane sulphonate (PFOS) and perfluorooctanoic acid (PFOA), may have adverse effects in species at risk, such as polar bears and birds. (Health Canada, 2009a,b). In addition PFOA has been implicated as a carcinogen to rats, to adversely affect the immune system in mice and to cause adverse reproductive and developmental toxicity in rodents (Health Canada, 2009b). The probable source of the compounds in domestic wastewater is through routine household activities such as bathing, cooking, dishwashing and laundry. According to the U.S. EPA (2009b), PFOS and PFOA can cause systemic and developmental toxicity in laboratory animals; and require years to be eliminated from the human body.

Another class of related compounds are the fluorotelomer alcohols, which are present in the manufacturing process for the perfluorinated chemicals. These alcohols can be biotransformed microbially to the corresponding carboxylic acid (e.g. PFOA), which are mobile in the environment. Ellington *et al*. (2009) indicate that they are present in both humans and biota, and can cause toxicity in mammalian systems.

3.8.1 Occurrence

Concentrations of the perfluorinated compounds in various sludges and biosolids are provided in Table 77. There are many compounds in this class as is evident from the Table. In many other sludges, the predominant compounds are the perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS). The maximum concentration of PFOA found in this review was 241 ng/g TS found in a sample of a sludge from New York state (Sinclair and Kannan, 2006) and the maximum for PFOS was 160 ng/g TS dw in a sample of Oregon sludge (Schultz *et al*., 2006). Concentrations of perfluorodecanoic acid (PFDA) and perfluoroundecanoic acid (PFUnDA) were found at higher mean concentrations of 52 and 60 ng/g TS dw, respectively in sludge from Plant A in NYS in the testing by Sinclair and Kannan (2006), although in most other studies these compounds had much lower concentrations.

In the only study in this review with perfluorodecane sulfonate (PFDS) as a target compound, Schultz *et al*. (2006) observed concentrations of a similar magnitude as those for PFOS.

Table 77. Concentrations of More Common Perfluorinated Organic Acids and Derivatives in Sludges and Biosolids

Compound	Concentration (ng/g TS dw)									Reference
	Perfluoro-octanoic acid (PFOA)	Perfluoro-octane sulfonate (PFOS)	Perfluoro-octane sulfonamide (PFOSA)	Perfluoro-hexane sulfonate (PFHxS)	Perfluoro-nonanoic acid (PFNA)	Perfluoro-decanoic acid (PFDA)	Perfluoro-decane sulfonate (PFDS)	Perfluoro-undeca-noic acid (PFUnDA)	Perfluoro-dodecanoic acid (PFDoDA)	
Sewage sludge – Denmark	0.7-19.7 (4)[a]	4.8-74.1 (18.4)	0.5-3.6 (0.8)	0.4-10.7 (3.6)	0.4-8.0 (1.5)	1.2-32.0 (7.2)		0.5-4.4 (1.2)		Bossi *et al*., (2008)
Bossi literature review	0.3-0.7 (0.5)	0.3-1.0 (0.6)		0.09-0.01 (0.01)	<0.6-0.2 (0.1)					
Plant A: dewatered cake	39	154	24	<2.5	<13	47		6.9	12	Loga-nathan *et al*., (2007)
Plant A: solar dried sludge	8.3-219	8.2-110	<2.5-21	<2.5	<2.5-4.4	2.5-34		<2.5-7.7	<2.5-28	
Plant B: dewatered cake	15	20	<2.5	<2.5	<2.5-11	19-41		<2.5	<2.5-10	
Plant B: Ash	7.0 - 35	<2.5 - 50	<2.5 - 7.0	<2.5	<2.5	7.0 - 35		<2.5	<2.5	
NYS Plant A	69 - 241 (144)	26 - 65 (37)		<10 - 18 (<10)		25 - 91 (52)		35 - 115 (60)		Sinclair and Kannan (2006)
NYS Plant B	18 - 89 (80)	<1-0 - 34 (25)		<10		<25 - 39 (27)		<25		
Primary Sludge	<6 - 12 (7.1)	18 - 3.8 (53)		nd - 12 (3.4)	nd - 10 (4.2)	1.6 - 3.9 (2.8)	14 - 2.9 (19.4)	2.0 - 4.2 (2.6)	1.3 - 1.6 (1.5)	Schultz *et al*., (2006)
Thickened Sludge	<6	20 - 18 (42)		nd	nd	3.4 - 5.3 (3.9)	57 - 71 (62)	3.9 - 5.0 (4.4)	4.1 - 5.1 (4.3)	
Anaerobic Digested Sludge	<3	81 - 160 (100)		nd	9.2 - 0.3 (9.9)	5.4 - 6.4 (5.9)	90 - 93 (91)	5.9 - 8.4 (6.8)	3.6 - 4.2 (3.8)	

nd = not detected [a] range (mean)

Perfluorohexane sulfonate (PFHxS) and perfluorododecanoic acid (PFDoDA) were found in relatively low concentrations compared to the predominant compounds identified above.

The concentration of a total of six perfluorinated carboxylic acids (perfluorooctanoic acid, perfluorononanoic acid, perfluorodecanoic acid, perfluoroundecanoic acid, perfluorododecanoic acid, perfluorotetradecanoic acid) in domestic sewage sludge from the U.S. ranged from 5 to 152 ng/g TS dw, while a total of six perfluoroalkyl sulfonyl-based chemicals (Perfluoro hexane sulfonate, perfluorooctane sulfonate, perfluorodecane sulfonate, perfluorooctane sulfonamidoacetate, 2-(N-methylperfluorosulfonamido) acetate, 2-(N-ethylperfluorosulfonamido) acetate) ranged from 55 to 3,370 ng/g TS dw (Higgins *et al*., 2005). Polyfluoroalkyl phosphoric acid diesters are used with paper food wrappers, The concentration of these compounds in municipal sludges, at congener concentrations up to 200 ng/g TS dw, can be over 100 times higher the concentrations of corresponding perfluorocarboxylic acids, (D'Eon *et al*., 2009; Renner, 2009b).

Several other perfluorinated organic compounds were identified by Schultz *et al*. (2006) in the study of sludges from an Oregon treatment plant. Data for most of these compounds are provided in Table 78. The magnitude of these compounds, with the exception of the perfluotetradecanoic acid (PFTA), is at least as great as for the more commonly analyzed PFOA and PFOS compounds. The presence of the compounds 2-(N-methylperfluorooctanesulfonamido)acetate (N-MeFOSAA) and 2-(N-ethylperfluorooctanesulfonamido)acetate (N-EtFOSAA) are thought to occur as metabolites of parent sulfonamido alcohols during aerobic secondary treatment with adsorption on the settled mixed liquor (Schultz *et al*., 2006). The data presented by Schultz *et al*. (2006) indicate that biotransformation of these compounds and precursor compounds can occur in both aerobic and anaerobic environments.

Table 78. Concentrations of Additional Perfluorinated Organic Acids and Derivatives in Sludges and Biosolids (Schultz *et al*., 2006)

Sludge Type	Concentration (ng/g TS dw)			
	PFOSAA	N-MePFOSAA	N-EtPFOSAA	PFTA
Primary Sludge	<3 - 3.4 (<3)[a]	5.2 - 8.9 (6.3)	15 - 5.8 (20)	nd
Thickened Sludge	6.2 - 7.6 (6.9)	35 - 52 (41)	43 - 52 (48)	0.9 - 1.3 (1.2)
Anaerobic Digested Sludge	9.4 - 12.4 (11)	130 - 140 (130)	91 - 100 (98)	<3

PFOSSA = perfluorooctanesulfonamidoacetate
N-MePFOSAA = 2-(N-methylperfluorooctanesulfonamido)acetate
N-EtPFOSAA = 2-(N-ethylperfluorooctanesulfonamido)acetate
PFTA = perfluotetradecanoic acid
[a] range (mean)

The perfluorinated compounds were not included in the U.S. EPA's TNSSS (U.S. EPA, 2009a) because analytical methods were not available at the time, and the samples were stored in Teflon (polyfluorinated) containers, thereby contaminating the samples (Rudzinski of the U.S. EPA, as cited by Renner, 2009a).

3.8.2 Fate and Transport in the Terrestrial Environment

Dr. Christopher Higgins of the Colorado School of Mines, as cited in Renner (2009a), states that "published data on the concentrations of perfluorinated chemicals in sludge are minimal and almost nothing is known about concentrations in soils".

The limited data concerning perfluorochemicals in soils following applications of biosolids are not representative of normal situations. Farm plots received biosolids from the Decatur, GA wastewater treatment plant, which had been contaminated by an industrial wastewater discharge. The reported concentration data for the perfluorochemicals in the Decatur sludge were identified as being in the low parts per million range (Renner 2009a), which are several orders of magnitude higher than those listed in Table 77. EPA has not established action levels for either PFOS or PFOA in biosolids or soils (U.S. EPA, 2009b).

3.8.3 Section Summary

1. Concentrations of PFOS and PFOA are typically the highest identified for this category of contaminants, ranging from approximately 1 to 100 ng/g TS dw.
2. Perfluoroalkyl phosphoric acid diesters have been identified as additional perfluorinated compounds that can accumulate in biosolids, but the data are limited to one recent study (D'Eon *et al*., 2009).
3. The fate and transport of perfluoroalkyl compounds in the terrestrial environment is virtually unknown, with only one highly contaminated site providing any data. The lack of information on the fate, transport and bioaccumulation of these compounds in the terrestrial environment represents a knowledge gap.

Perfluorinated organic acid and derivative compounds were not identified as organics of concern in sewage biosolids applied on agricultural land prior to 2001 and hence were not assessed in the WEAO (2001) report. The almost complete lack of data on the fate, transport and bioaccumulation potential of these compounds in the terrestrial environment represents a knowledge gap, and it is recommended that they be considered as Group II contaminants.

3.9 Fragrance Compounds

Two main classes of fragrance compounds are used in consumer and commercial products, namely the nitro musks and the polycyclic musks. Nitro musks were first used as synthetic replacements for the natural musk obtained from glands of the male musk deer (Lee *et al*., 2003). Peck and Hornbuckle (2004) identified a number of health concerns related to nitro musks, including estrogenic activity and accumulation in human adipose tissue and breast milk. Polycyclic musks have now become the most commonly used synthetic musk due to health concerns and concerns over persistence of the nitro musks in the environment. Both classes of musks are used not only for their own unique smell that influences the odour characteristic, but also for enhancing the quality of a fragrance (OSPAR, 2000). The musk compounds are used in fragrances for detergents, fabric softeners, fabric conditioners, cleaning agents, air fresheners,

and cosmetics such as soaps, shampoos and perfumes (OSPAR, 2000). Common fragrance compounds in use are found in Table 79.

Table 79. Identification and Formulations of Common Synthetic Fragrance Compounds

Class of Fragrance	Compound (Trade) Name	Chemical name
Polycyclic Musk	HHCB (Galaxolide)	(1,3,4,6,7,8-hexahydro-4,6,6,7,8-hexamethylcyclopenta-ç-2-benzopyran)
	AHTN (Tonalide)	7-acetyl-1,1,3,4,4,6-hexamethyl-1,2,3,4-tetrahydronaphthalene
	ATII (Traseolide)	5-acetyl-1,1,2,6-tetramethyl-3-isopropylindan
	ADBI (Celestolide)	4-acetyl-1,1-dimethyl-6-*tert*-butylindan
	AHMI (Phantolide)	6-acetyl-1,1,2,3,3,5-hexamethylindan
	DPMI (Cashmeran)	6,7-dihydro-1,1,2,3,3-pentamethyl-4(5*H*)-indanone
	OTNE (Iso E super)	Ethanone, 1-(1,2,3,4,5,6,7,8-octahydro-2,3,8,8-tetramethyl-2-naphthalenyl
Nitro Musk	Musk xylene	1-*tert*-butyl-3,5-dimethyl-2,4,6-trinitrobenzene
	Musk ketone	4-*tert*-butyl-3,5-dinitro-2,6-dimethylacetophenone

Many products formulated with fragrance compounds (shampoos, soaps, cleaning products, fabric softeners) are contacted with water through bathing and laundry, with subsequent release to municipal sewers. Synthetic musks are generally refractive (non-biodegradable) and highly lipophilic (high octanol:water partition coefficient) (Daughton and Ternes, 1999). At a municipal wastewater treatment plant, these properties cause the compounds either to be discharged in treated wastewater effluents, or to accumulate in wastewater residual solids. Biodegradation would play only a minor role, if at all, in elimination of the compounds in wastewater treatment.

3.9.1 Occurrence

Concentrations of polycyclic and nitro musk fragrances from a survey of Canadian biosolids samples are presented in Table 80 (Lee *et al*., 2003a). Galaxolide (HHCB) and Tonalide (AHTN) were the two predominant polycyclic musks. The highest concentration of HHCB was in a digested sludge sample from the Toronto Humber Wastewater Treatment Plant, at 26,700 ng/g TS dw, while the highest for AHTN was 20,600 from the Calgary Bonnybrook facility. Traesolide (ATII) was observed with a median value of 1,345 ng/g TS dw, approximately an order of magnitude lower than the HHCB or AHTN. The remaining two polycyclic musks investigated, Celestolide (ADBI) and Phantoloide (AHDI or AHMI) were substantially lower at 175 and 110 ng/g TS dw, respectively. With respect to the nitro musks analyzed, musk ketone was usually found at higher concentrations than musk xylene. Musk ketone was observed at the highest concentration of 36.7 ng/g TS dw in Windsor digested biosolids, while musk xylene was found at the highest concentration, 13 ng/g TS dw, in a sample of digested biosolids from Toronto's Ashbridge's Bay facility. Additional concentration data are provided in Table 81 for polycyclic musks and Table 82 for nitro musk compounds.

Table 80. Fragrance Concentrations in Canadian Municipal Digested Sludges (Lee *et al*., 2003a)

Biosolids Source	Fragrance Concentration (ng/g TS dw)						
	Galaxolide (HHCB)	Tonalide (AHTN)	Celestolide (ADBI)	Phantolide (AHDI or AHMI)	Traesolide (ATII)	Musk Xylene (MX)	Musk Ketone (MK)
Anaerobic digested Burlington	12,000	8,010	190	80	1,360	3.3	3.7
Anaerobic digested Calgary (Bonnybrook)	20,800	20,600	570	130	4,150	5.1	7.3
Anaerobic digested Calgary (Fish Creek)	18,100	18,500	480	180	3,250	3.9	4.1
Anaerobic digested Edmonton (Goldbar)	17,800	18,600	350	150	3,680	2.9	6.4
Anaerobic digested Guelph	14,500	14,900	350	130	2,180	1.8	2.4
Anaerobic digested Ingersoll	4,460	6,270	160	60	1,200	2.3	2.8
Anaerobic digested Ottawa	18,800	16,700	370	130	3,080	2.7	4.9
Anaerobic digested Regina	12,600	12,000	320	120	1,870	2	4.1
Anaerobic digested Saskatoon	8,890	9,440	180	110	1,650	3.3	4.8
Anaerobic digested Toronto (Ashbridges Bay)	24,300	12,400	300	120	2,290	13	8.3
Anaerobic digested Toronto (Humber)	26,700	12,300	310	110	1,610	6.9	4.5
Digested sludge Toronto (North)	24,500	12,100	220	90	2,330	3.8	7.2
Anaerobic digested Vancouver	9,580	9,050	260	60	1,240	1.4	1.4
Anaerobic digested Waterloo	7,340	12,700	490	90	1,810	2.9	2.2
Anaerobic digested Windsor	7,810	9,510	370	150	1,380	3.4	36.7
Median concentration anaerobic digested	14,500	12,300	320	120	1,870	3.3	4.5

Table 81. Polycyclic Musk Compounds in Canadian Biosolids Samples

Sludge Source	Fragrance Concentration (ng/g TS dw)						Reference
	Galaxolide (HHCB)	Tonalide (AHTN)	Celestolide (ADBI)	Phantolide (AHDI or AHMI)	Traesolide (ATII)	Cashmeran (DPMI)	
Aerobic Digested sludge #1	9,430	2,110	67.3	57.4	465	nd	Smyth *et al*. (2007)
Aerobic Digested sludge #2	40,300	8,490	255	162	1,890	nd	
Anaerobic Digested sludge #3	42,000	10,400	280	201	1,910	nd	
Anaerobic Digested sludge #4	55,500	13,800	424	432	2,880	nd	
Anaerobic Digested sludge #5	46,300	10,500	510	441	1,720	nd	
Digested sludge (Canadian survey)	4,500 – 25,000 (15,000) [a]	6,300 – 21,000 (12,000)	160 – 570 (320)	60 - 180 (120)	1,200 – 4,200 (1,900)	na	Webber and Sidwha (2005)
Digested sludge	6,788	1,349	51.2	33.8	413	57.3	Yang and Metcalfe (2005)
median aerobic sludge (n=2)	24,870	5,300	161	110	1,178		
median anaerobic sludge (n=4)	44,150	10,450	352	317	1,815		

na = not analysed; nd = not detected

[a] median value in parentheses

Table 82. Nitro Musk Compounds in Canadian Biosolids Samples

Sludge Source	Fragrance Concentration (ng/g TS dw)					Reference
	Musk Xylene (MX)	Musk Ketone (MK)	Musk Ambrette (MA)	Musk Moskene (MM)	Musk Tibetene (MT)	
Aerobic Digested sludge #1	18.9	45.3	31.3	nd	nd	Smyth *et al*. (2007)
Aerobic Digested sludge #2	25.1	242	nd	6	67.2	
Anaerobic Digested sludge #3	61	8.16	nd	nd	nd	
Anaerobic Digested sludge #4	81.5	11.2	7.6	nd	nd	
Anaerobic Digested sludge #5	3.4	27.6	nd	nd	nd	
Digested sludge (Canadian survey)	1 – 7 (3) [a]	1 – 37 (5)				Webber and Sidwha (2005)
Digested sludge	95.1	53	nd	nd	nd	Yang and Metcalfe (2005)
median aerobic sludge (n=2)	22	143.7				
median anaerobic sludge (n=4)	71.25	19.4				

nd = not detected
[a] median value in parentheses

The data provided by Smyth *et al*. (2007) are a survey of five wastewater treatment plants in the Grand River watershed of Ontario, while data provided by Yang and Metcalfe (2005) is from the Peterborough, ON facility. Data compiled by Webber andSidwha (2005) are a summary of the data of Lee *et al*. (2003) presented above in Table 80. The concentration profiles in Tables 81 and 82 follow those in Table 80. Of the polycyclic musks, HHCB and AHTN were present at the highest concentrations, followed by ATII. Concentrations of ADBI and AHMI were of similar magnitude but much lower than the other polycyclic musks identified. The musk DPMI was not detected in the five Ontario plants tested by Smyth *et al*. (2007). Concentrations of the polycyclic musks from the Peterborough facility (Yang and Metcalfe, 2005) were substantially lower than those identified by Smyth *et al*. (2007) and Lee *et al*. (2003a). It is not clear whether the differences in magnitude were due to differences in site-specific inputs, differences in analytical procedures, or other unidentifiable factors.

With respect to nitro musks, the data in Table 82 indicate that musk ketone and musk xylene were the dominant compounds. Musk ambrette, musk moskene and musk tibetene were detected sporadically in the survey by Smyth *et al*. (2007), and were not detected in the Peterborough sludge samples by Yang and Metcalf (2005).

The median concentrations of the polycyclic musks following aerobic sludge digestion in Table 81 were all lower in magnitude than concentrations of the compounds in anaerobically digested sludges. In Table 82, the median concentration of musk xylene was also higher in anaerobically digested sludges than in aerobic digested sludges, although the opposite was true for musk ketone.

Additional polycyclic musk concentration data from other biosolids samples are provided in Table 83. HHCB an AHTN are the most commonly characterized polycyclic musks in these samples. When other polycyclic musk data are presented, the concentrations are much lower than those reported for HHCB and AHTN.

In addition to the polycyclic and nitro musks identified above, a number of other fragrance compounds have been identified. These are summarized in Table 84. Most of the additional compounds were identified in the literature survey of biosolids completed by Harrison *et al*. (2006).

Kinney *et al*. (2006) reported high levels of indole (7,000 ng/g OC) and d-limonene (630 ng/g OC) in a sample of dewatered sludge cake. Otherwise, with the exception of musk ketone, and its derivative, amino musk ketone, the maximum concentrations of the alternate fragrance compounds were less than 100 ng/g TS dw.

Table 83. Concentrations of Polycyclic Musk Compounds in Biosolids from Other Studies

Biosolids Source	Concentration (ng/g TS dw)						Reference
	Galaxolide (HHCB)	Tonalide (AHTN)	Celestolide (ADBI)	Phantolide (AHDI or AHMI)	Traesolide (ATII)	Cashmeran (DPMI)	
Digested	26,000	4,000					Jones-Lepp and Stevens (2007)
Biosolids Class A	5,000-18,000	2,000-4,000					
Biosolids Class B	10,000	3,000					
Biosolids Class A	13-177,000	78-427,000					
Dewatered sludge	3,150 ng/g OC	16,700 ng/g OC					Kinney *et al*. (2006)
Anaerobic Digested biosolids	427,000	177,000					Kinney *et al*. (2008)
Digested sludge	3,068 - 6,788	1,525-1,349					Heidler and Halden (2008)
Not specified	ND – 8,100	ND – 5,100	10–1,100	32–1,800	44–1,100	ND – 332	Harrison *et al*. (2006)
Unknown sludge (Germany)	4,300 – 13,000 (8,900)	4,000 – 13,000 (8300)	120 – 290 (200)				Webber and Sidwha (2005)

Table 84. Concentrations of Other Fragrance Compounds in Biosolids

Fragrance Compound	Concentration (ng/g TS dw)			Concentration (ng/g OC)
	Not specified	Unknown sludge (Germany)	Anaerobic Digested	Dewatered
Musk Xylene (MX)	ND – 32.5	<5		
Musk Ketone (MK)	ND – 1300	<10 – 60		
Acetyl Cedrene	9.0 – 31.1			
Amino Musk Ketone	ND – 362			
Amino Musk Xylene (AMX)	ND –31.5			
Diphenyl Ether	ND – 99.6			
Galaxolide lactone	0.6 – 3.5			
Hexyl salicylate	Trace – 1.5			
Hexylcinnamic Aldehyde (Alpha)	4.1			
Methyl ionone (gamma)	1.1 – 3.8			
OTNE	7.3 – 30.7			
D-Limonene			1,600	630
Indole			6,800	7,000
Acetophenone			3,450	
Isoborneol			n.d.	
Camphor			n.d	
Isoquinoline			n.d	
Menthol			n.d.	
Reference	Harrison *et al*. (2006)	Webber and Sidwha (2005)	Kinney *et al*. (2008)	Kinney *et al*. (2006)

n.d. = not detected

Concentration data for fragrance compounds in four biosolids treatment processes, including composting, lime treatment, heat drying, and anaerobic digestion are provided in Table 85 (LaGuardia *et al*., 2004; Kinney *et al*., 2006).

Exceptionally high concentrations of HHCB and AHTN were observed in the anaerobically digested sample reported by Kinney *et al*. (2006). A heat-dried sludge sample reported by LaGuardia *et al*. (2004) had low concentrations of both HHCB and AHTN. In the study by Kinney *et al*. (2006), the composted and heat dried samples exhibited lower concentrations of d-limonene than did sludges produced by other drying procedures or by anaerobic digestion. Indole concentrations suggested that there was no significant effect between processes on compound reductions.

3.9.2 Fate and Transport in the Terrestrial Environment

Concentrations of the polycyclic musks HHCB and AHTN in a soil amended with anaerobically digested biosolids were monitored over a six month time period post-application by Yang and Metcalfe (2005). The results are provided in Table 86.

Table 85. Comparison of Fragrance Compound Concentrations in Biosolids Treatment Processes

Treated Biosolids	Concentration (ng/g TS)				Reference
	Galaxolide (HHCB)	Tonalide (AHTN)	D-limonene	Indole	
Compost	47-12,300 (ng/g OC)	281-11,600 (ng/g OC)	255-705 (ng/g OC)	4,210-38,200 (ng/g OC)	Kinney *et al*. (2006)
Compost-B	7,000	5,600			LaGuardia *et al*. (2004)
Lime-A	12,400	7,400			
Heat dry	3,900 (ng/g OC)	11,000 (ng/g OC)	520 (ng/g OC)	20,700 (ng/g OC)	Kinney *et al*. (2006)
Heat-A	1,100	400			LaGuardia *et al*. (2004)
Air dry	21,900 (ng/g OC)	43,900 (ng/g OC)	2,120 (ng/g OC)	19,400 (ng/g OC)	Kinney *et al*. (2006)
Anaerobic digestion	554,000 (ng/g OC)	1,340,000 (ng/g OC)	3,340 (ng/g OC)	21,300 (ng/g OC)	
Anaerobic digestion -A	17,900	9,000			LaGuardia *et al*. (2004)
Anaerobic digestion –B	11,400	5,400			
Anaerobic digestion –E	10,200	6,600			

Table 86. Post-Application Concentrations of Polycyclic Musks HHCB and AHTN in a Biosolids Amended Soil (Yang and Metcalfe, 2005)

t (days) after biosolids application to soil	Conc. in soil post-application ng/g wet wt	
	Galaxolide (HHCB)	Tonalide (AHTN)
t = 0 (pre-application)	not detected	not detected
t=1day	2.0 ± 0.1	2.6 ± 0.1
t=2 weeks	2.8 ± 0.4	2.0 ± 0.1
t=4 weeks	detected	detected
t=6 weeks	detected[a]	detected[a]
t= 6 months	detected[a]	not detected[a]

[a] Limit of quantification 2.0 – 11.9 ng/g wet weight

Prior to the biosolids application the concentrations of the two musks were non-detectable. For the first two weeks following the biosolids application, concentrations of the musks were detected at the 2 – 3 ng/g DM range. In the following weeks and up to six months, low but detectable concentrations of the musk HHCB were observed. Low but detectable concentrations of AHTN were noted up to six weeks after the biosolids application, but not after six months.

Concentrations of several fragrance compounds in soils and earthworms are reported by Kinney *et al*. (2008), from both biosolids-amended soil and without biosolids amendment (Table 87).

Table 87. Concentrations of Fragrance Compounds in Soil and Earthworm Samples (Kinney *et al*., 2008)

Site Description	Sample Matrix	Fragrance Concentration (ng/g DM)							
		Galaxolide (HHCB)	Tonalide (AHTN)	D-limonene	Indole	acetophenone	isoborneol	camphor	menthol
Site 1 (without biosolids application)	Soil Jun 6-05	633	113	393	ND	627	267	ND	177
	Worm Jun 6-05	61	19	ND	2,320	150	ND	NA	31
	Soil Sep 29-05	ND	ND	ND	673	ND	ND	ND	26
	Worm Sep 29-05	ND	ND	41	1,480	137	NA	20	ND
Site 2 (with biosolids application on April 18, 2005)	Soil May 19-05	1,050	287	ND	285	ND	ND	ND	ND
	Worm May 19-05	3,340	279	ND	1,950	110	ND	NA	ND
	Soil Sep 21-05	2,770	773	40	540	ND	ND	ND	ND
	Worm Sep 21-05	131	75	48	1,300	101	ND	26	ND

ND = not detected

The concentrations of the synthetic musks HHCB and AHTN increased substantially in the biosolids-amended site compared to the non-applied site. Two synthetic musks were detected even in the soil and earthworms in the non-amended site in the first sampling round of June 6, 2005. There is also a great difference in the concentrations of these musks in the earthworms from the biosolids-amended site. In the first sampling effort of May-June, 2005, the concentrations in the earthworms were of similar or even greater magnitude than the soil concentrations, but in the second sampling of September 2005, the concentrations in the earthworms were an order of magnitude lower than the soil concentrations.

Other than indole, most of the other fragrance compounds tested were detected sporadically. There was no evidence of these other fragrance compounds accumulating in soil due to biosolids amendment. Concentrations of indole in the soils and earthworms of both the biosolids-amended and non-amended sites were of similar magnitude, indicating that detectable concentrations of indole in earthworms could not be attributed to biosolids amendment. The occurrence in both sites was possibly due to natural background levels of the compound, or possibly from sample contamination during collection.

As part of their study, Kinney *et al*. (2008) calculated bioaccumulation factors (BAFs) for the earthworms residing in the soils from the two sites (Table 88). Because many of the reported concentrations of the fragrance compounds were below the analytical detection limit in either or both of the soil and earthworm matrices, it was not possible to calculate BAFs in a number of cases. In the cases were BAFs could be calculated, only indole appeared to be accumulated by the earthworms on a consistent basis, with factors ranging from 2.2 to 6.8. Musk fragrances did not appear to be accumulated by the earthworms, with most calculated BAF values being less than 0.2. Only in one case was the BAF factor for HHCB greater than unity, at 3.1, in the biosolids-amended site soon after the application took place. The calculated BAF values for HHCB, AHTN and indole were all higher in samples collected one month following the biosolids application compared to values from five months following the application. Possible reasons for the decline in the BAF values are that the concentrations of these fragrance compounds declined in the soil, or that they became less available for accumulation by the worms. In a subsequent publication, Furlong *et al*. (2009) have suggested the bioaccumulation factor for HHCB in a biosolids-amended soil is 0.05.

3.9.3 Section Summary

1. Polycyclic musks are present at higher concentrations in sludges and biosolids (e.g., 5,000 – 50,000 ng/g TS dw) than nitro musks (e.g., 25 – 150 ng/g TS dw).
2. HHCB and AHTN are the predominant polycyclic musks, followed by ATII.
3. The two main nitro musks identified in sludge samples were musk ketone and musk xylene.
4. Full-scale anaerobic digestion does not appear to reduce concentrations of polycyclic musks in sludges, as concentrations in the digested sludges have been found to be higher than in the raw sludge.
5. Concentrations of individual fragrance compounds in biosolids-amended soils can range up to 3,000 ng/g TS dw, with polycyclic musks occurring at higher concentrations than nitro musks.

6. Bioaccumulation factors of a few fragrance compounds (e.g. HHCB and indole) in earthworms inhabiting biosolids-amended soils were low (bioaccumulation factor 6 or less), while others were not detected.
7. Low but detectable concentrations of the compound AHTN were observed 6 months after amendment of a soil with biosolids.
8. Because of their high hydrophobicity, fragrance compounds are not expected to be mobile in soil.
9. No studies on percolation or surface run-off, dissipation, mineralization or plant uptake of fragrance compounds were noted in this review; thus this lack of knowledge constitutes a knowledge gap.

Table 88. Bioaccumulation Factors for Fragrance Compounds in Earthworms (Kinney *et al*., 2008)

	Biosolids Accumulation Factors			
Fragrance Compound	BAF in Site 1 (without biosolids application)		BAF in Site 2 (with biosolids application on April 18, 2005)	
	Jun 6-05	Sep 29-05	May 19-05	Sep 21-05
Galaxolide (HHCB)	0.1	not present in soil or earthworm	3.1	0.05
Tonalide (AHTN)	0.17	not present in soil or earthworm	1	0.1
D-limonene	0	not detected in soil	not present	1.2
Indole	not detected in soil	2.19	6.8	2.4
Acetophenone	0.24	not detected in soil	not detected in soil	not detected in soil
Isoborneol	0	not present in soil or earthworm	not present in soil or earthworm	not present in soil or earthworm
Camphor	not present in soil or earthworm	not detected in soil	not present	not detected in soil
Menthol	0.17	0	not present	not present

Synthetic musk compounds were not identified as organics of concern in sewage biosolids applied on agricultural land prior to 2001, and were not assessed in the WEAO (2001) report. Because the almost complete lack of data on the fate, transport and bioaccumulation potential of these compounds in the terrestrial environment represents a knowledge gap, it is recommended that this class of compounds be considered Group II contaminants.

3.10 Antimicrobials

Triclosan and triclocarban are compounds displaying antimicrobial activity against both gram-positive and gram-negative organisms, resulting in their use in an array of consumer products such as soaps, detergents and cosmetics (Heidler and Halden, 2007). Hexachlorophene is used as a topical anti-bacterial agent in soaps and some toothpastes.

As of October 2008, the U.S. EPA determined that triclosan did not pose a human health hazard when used in personal care products as intended. Although it is anticipated to be immobile in soils, in the aquatic environment, however, EPA expressed concern that triclosan could bioaccumulate in organisms to levels posing a concern (U.S. EPA, 2008). Corresponding information for triclocarban is not available. According to IPCS (2009), hexachlorophene is acutely toxic to aquatic organisms, and bioaccumulation in the food chain can be expected. In humans, long term exposure to hexachlorophene may cause dermatitis, skin sensitization, while prolonged inhalation may cause asthma, and affect the nervous system. Tests with animals indicate it may cause deformation in babies (IPCS, 2009).

Due to their use in personal care products, the antimicrobials are transferred to grey water as a result of bathing, laundry and other domestic activities. At a wastewater treatment plant, the compounds are likely to be either sorbed onto solids, biodegraded to some extent or discharged in the treated effluent. As reported in the CCME Review of State of Knowledge of Municipal Effluent Science and Research (Hydromantis *et al*., 2005), removal efficiency of triclosan by treatment plants can be variable.

3.10.1 Occurrence

Lee and Peart (2002) assessed the concentrations of triclosan and hexachlorophene as two of a suite of micro-constituents in Canadian digested sludges (Table 89).

The median value of triclosan in digested sludge samples was 16,200 ng/g TS dw, while for hexachlorophene, the median values in digested sludge samples was substantially lower at 421 ng/g TS dw. The highest concentration of triclosan in digested sludges was observed in a sample from Guelph (ON) treatment plants, at 28,200 ng/g TS dw. A sample of digested sludge from the Granby, QC, facility had the lowest concentration of triclosan at 900 ng/g TS dw. The highest concentration of hexachlorophene in digested sludge in this survey was observed in a sample from Ingersoll, ON at 1,190 ng/g TS dw. The lowest concentration of hexachlorophene at 22.6 ng/g TS dw was recorded in a digested sludge sample from the Granby plant.

Table 89. Occurrence of Triclosan and Hexachlorophene in Canadian Municipal Digested Sludges (Lee and Peart, 2002)

Municipal Treatment Plant	Triclosan (ng/g TS dw)	Hexachlorophene (ng/g TS dw)
Vancouver Digested (1994)	8,410	477
Vancouver Digested (1999)	24,700	420
Calgary (Bonnybrook) Digested	12,800	371
Calgary (Fish Creek) Digested	19,500	218
Edmonton (Goldbar) Digested	22,000	285
Regina Digested	18,900	420
Saskatoon Digested	9,900	352
Burlington Digested	19,400	597
Galt Digested	7,480	451
Guelph Digested	28,200	421
Hamilton Digested	16,200	727
Ingersoll Digested	11,500	1,190
Kitchener Digested	16,100	640
Ottawa Digested	18,600	254
Waterloo Digested	11,700	693
Windsor Digested	8,840	311
Toronto (Ashbridges Bay) Digested	20,300	548
Toronto (Humber) Digested	16,600	328
Toronto (North) Digested	5,400	572
Granby Digested	900	22.6
Moncton Digested	1,920	68.7
Truro Digested	7,530	701
median digested	16,200	421

Concentrations of triclosan in other sludge samples are provided in Table 90. A number of studies on triclosan have been published in the technical literature in 2009 (e.g. U.S. EPA, 2009a; Edwards *et al*., 2009; Brown and Clarke, 2009; Chalew and Halden, 2009), with concentrations typically in the 10,000 – 40,000 ng/g TS dw range. A recent survey of Canadian sludges by XCG Consultants (2007) reported concentrations of triclosan in a range of 900 – 28,000 ng/g TS dw, with a median value of 13,000 ng/g TS dw. In four Ontario treatment plants, concentrations of triclosan ranged between 680 and 11,550 ng/g TS dw. Concentrations reported in other publications were of a similar magnitude, between 3,200 and 42,000 ng/g TS dw.

Only a few studies have examined the concentrations of triclosan following biosolids treatment processes. Based on the data presented in Table 91, it appears that biosolids treatment processes had no real discernible effect on reducing concentrations of triclosan. Concentrations of triclosan in all the treatment processes are similar in magnitude.

Table 90. Concentration of Triclosan in Other Sludge and Biosolids Samples

Sludge Source	Concentration (ng/g TS dw)		Reference
	Range	mean (median)	
Canadian sludge (1995-1998)	900 - 28,000	13,000	XCG (2007)
Treated Biosolids (4 Ontario plants)	680 – 11,550		Chu and Metcalfe (2007)
Mid-Atlantic U.S. plant	20,000 - 55,000	30,000 ± 11,000[a]	Heidler and Halden (2007)
Not specified (literature review)	nd – 15,600		Harrison *et al*. (2006)
dewatered anaerobically digested or dewatered secondary sludge (Greece)	190 – 9,850	3,210 (2,710)[b]	Stasinakis *et al*. (2008)
Not specified (France)		41,900 ± 37,000	Ruel *et al*. (2008)
Dewatered anaerobically digested biosolids		14,000	Edwards *et al*. (2009)
Not specified (U.S. survey)		16,100 (3,860)	U.S. EPA (2009a)
Anaerobically digested biosolids		10,500	Kinney *et al*. (2008)
Biosolids – U.S.		34,973 ± 1,240	Brown and Clarke (2009)
Three Michigan, U.S.A. biosolids	90 – 7,060		Cha and Cupples (2009)
Literature survey	90 - 32,900		Chalew and Halden (2009)

nd = not detected [a] mean ± standard deviation [b] mean (median)

Table 91. Concentration of Triclosan following Biosolids Treatment Processes

Sludge Source	Concentration (ng/g TS dw)	Reference
Compost-B	7,400	LaGuardia *et al*. (2004)
Lime-A	4,700	
Heat treated-A	6,900	
Anaerobic digestion -A	5,200	
Anaerobic digestion -B	5,500	
Anaerobic digestion -E	3,600	
Anaerobic Digested sludge	1,200 - 30,000	Heidler and Halden (2008)
Anaerobic Digested Sludge	20,000 ± 18,000 [a]	Halden (2007)

[a] mean ± standard deviation

The other main anti-microbial compound, triclocarban, although generally less well characterized than triclosan, has been investigate in depth by Snyder (2009). The concentration data in Table 92 indicate that triclocarban is likely present in biosolids at concentrations similar to those of triclosan. In examining the data developed in her thesis, Snyder (2009) speculated that, based on relatively low concentrations of TCC in the aerobic and composted samples, the biosolids processing method was an important factor in the final TCC concentration.

Other concentrations of TCC in biosolids reported in the literature are summarized in Table 93.

Table 92. Concentrations of Triclocarban in Biosolids from U.S Southeast (Snyder, 2009)

Treatment Plant Identifier	Treatment Process	TCC concentration ng/g TS
DYMK	Mixed compost	8,000 (2,000)[a]
DYSK	Compost	6,000 (1,000)
GRBC	Aerobic digestion	7,000 (1,000)
ORBC-BL	Untreated	25,000 (1,000)
ORBC-AL	Lime stabilization	18,000 (1,000)
CFBC	Anaerobic digestion	40,000 (2,000)
GEPZ	Anaerobic digestion	29,000 (3,000)
RCKF	Anaerobic digestion	21,000 (3,000)
OSBC	Anaerobic digestion	14,000 (2,000)
UNKD	Anaerobic digestion	43,000 (3,000)
UNKG	Anaerobic digestion	35,000 (1,000)
UNKH	Anaerobic digestion	31,000 (700)
UNKB	Anaerobic digestion	25,000 (1,000)
UNKC	Anaerobic digestion	24,000 (1,000)
UNKF	Anaerobic digestion	23,000 (300)
CHST-AD	Anaerobic digestion	14,000 (800)
CHST-CC	Anaerobic digestion	13,000 (900)
UNKE	Anaerobic digestion	10,000 (300)
UNKI	Anaerobic digestion	8,000 (400)
CHCM-AD	Anaerobic digestion	8,000 (800)
CHCM-CC	Anaerobic digestion	7,000 (900)
UNKJ	Unknown	31,000 (400)
UNKK	Unknown	31,000 (1,000)
UNKL	Unknown	12,000 (500)

[a] Mean $\pm$ standard deviation (n=3)

Table 93. Concentrations of Triclocarban in Biosolids

Biosolids Material	Triclocarban concentration (ng/g TS dw)	Reference
Concentration in dewatered municipal biosolids – Ontario	8,000	Edwards *et al*. (2009)
Literature survey	3,050-51,000	Chalew and Halden (2009)
Not specified (U.S. survey)	39,000 $\pm$ 60,000[a]	U. S. EPA (2009a)
4 Biosolids - U.S.	4,890 – 9,280	Cha and Cupples (2009)

[a] Mean $\pm$ standard deviation

Snyder (2009) also noted that the effect of the acid dissociation constant (Ka) for triclocarban is significant in lime-stabilized Class B biosolids. At a pH of 12 following addition of lime to the sludge, much of TCC is ionized, making it more soluble and releasing it from the solids. At lower pH values, more representative of soils, much of TCC remains bound to solids.

3.10.2 Fate and Transport in the Terrestrial Environment

Concentrations of triclosan and triclocarban in soils following biosolids applications were monitored by Cha and Cupples (2009), using a biosolids with characterized concentrations of triclosan at 7,060 ng/g TS and triclocarban at 9,280 ng/g TS in the biosolids. The biosolids were applied at an application rate of 3.25 dry tons/acre (7.22 Mt/ha) to soils characterized as either sandy loams or loamy sands. The data of Table 94 indicate that in the year between sampling, concentrations of triclosan in the soil decreased substantially, while those of triclocarban did not.

Table 94. Concentrations of Triclosan and Triclocarban in Soils Following Biosolids Application (Cha and Cupples, 2009)

Soil Application Site	Concentration in Soil (ng/g DM)			
	Triclosan		Triclocarban	
	2007	2008	2007	2008
Soil 1 (sandy loam, pH=6.6, last application: April, 2004)	0.45	<0.05	1.24	1.2
Soil 2 (Loamy sand, pH=5.9, last application: May 2007)	0.056	0.28	8.05	9.5
Soil 3 (Sandy loam, pH=4.9, last application: June 2004)	0.50	<0.05	7.01	2.2
Soil 4 (Sandy loam, pH=6.1, last application: Aug. 2004)	0.21	0.12	6.05	9.5
Soil 5 (Loamy sand, pH=5.5, last application: May 2007)	0.30	<0.05	2.10	4.2
Soil 6 (Sandy loam, pH=5.7, last application, June 2004)	0.38	0.15	3.08	3.5
Soil 7 (Sandy loam, pH=5.9, Last application: April 2007)	0.16	<0.05	4.50	10
Soil 8 (Loamy sand, pH=6.4. Last application: May 2003)	0.20	<0.05	1.52	10
Soil 9 (Loamy sand, pH=5.7, last application: April 2007)	1.02	<0.05	4.15	3.2
Soil 10 (Sandy loam, pH=7.7. Last application, Aug. 2004).	0.19	0.08	3.10	65.1
Avg. conc. ± Std deviation.	0.39 ± 0.26	0.16 ± 0.08	3.2 ± 2.1	11.6 ± 19.2
Conc. Range	0.056 - 1.02	<0.05 - 0.28	1.24 - 7.01	1.2 - 65.1

Concentrations of triclosan in experimental soil plots grown with turf grass were reported by Brown and Clarke (2009). Although the biosolids applied had a triclosan concentration of almost 35,000 ng/g TS, the concentration in the soil at the conclusion of the experiment was 39 $\pm$ 13 ng/g DM, close to the detection limit of triclosan in soil. The compound was not detected in water leaching through the soil column. The turf grass itself was not analyzed for the compound.

Studies conducted in fields amended with biosolids in Maryland indicated that triclosan concentrations declined to levels similar to control sites without biosolids addition within two years following the application (Lozano *et al*., 2009). Triclocarban was more persistent than

triclosan, and was found at higher concentrations than triclosan at the biosolids-amended sites. Some dissipation of the triclocarban was observed. The presence of the metabolite methyl-triclosan, at concentrations similar to the parent triclosan in sites receiving one or more biosolids applications, was considered to be a result of biotransformation in the soil, due to very low concentrations of the methylated species present originally in the biosolids.

The concentrations of triclosan and triclocarban at different soil depths in a long-term biosolids amendment site were monitored and reported by Hundal *et al*. (2009). The data are summarized in Table 95. Although triclocarban concentrations declined significantly with soil depth at the site, concentrations of triclosan were more consistent at the different depths. The concentration of triclosan in the top 15 cm of soil was much lower than the triclocarban concentration, perhaps indicating the triclosan is more readily degraded in the soil than is triclocarban. Below the 60 cm depth, the concentrations of the two anti-microbials were similar. Half-lives of the two compounds in soil, of 18 and 108 days for triclosan and triclocarban, respectively, were estimated by Ying *et al*. (2007), and support the hypothesis of faster degradation of triclosan. Topp *et al*. (2008) estimated that 50 % of applied triclosan would be dissipated from the soil after 23 d.

Table 95. Concentrations of Triclosan and Triclocarban in Soil from a Long-Term Biosolids Application Site (Hundal *et al*., 2009).

Soil Depth (cm)	Conc'n (ng/g DM)	
	Triclosan	Triclocarban
0-15	52	1,251
15-30	25	371
60-120	19	23

Because of the tendency of TCC to be held by the land-applied biosolids, Snyder (2009) observed that a greater fraction of TCC in biosolids-amended soils will be initially available for leaching in a sandy soil compared to a finer-textured loam soil with more sorption sites. Sorption of TCC is less complete in a sandy soil than finer-textured soils. Moreover, TCC desorption is faster and more complete in a sandy soil compared to loamy soil (Snyder, 2009).

Concentrations of triclosan and triclocarban were monitored in tile drainage in Ontario following applications of either liquid anaerobically digested biosolids, or dewatered anaerobically digested biosolids (Edwards *et al*., 2009). The data are summarized in Table 96. The concentration of triclosan in the drainage was higher following a liquid biosolids application than when the biosolids were applied in a dewatered form. The data for triclocarban were inconclusive.

Concentrations of triclosan and triclocarban in surface runoff from fields amended with either liquid or dewatered anaerobically digested biosolids have been examined by Sabourin *et al*. (2009) and Topp *et al*. (2008) (Table 97). With triclosan, the maximum concentration in the surface runoff appeared immediately after the biosolids application, whether the biosolids was applied as either a liquid or dewatered form. The maximum concentration of triclocarban in runoff appeared 7 days following the biosolids application, suggesting it is initially bound more tightly to the applied site (Sabourin *et al*, 2009). Hydrophobicity of the compounds may partly

explain the difference in these observations, as Sabourin *et al.* (2009) note that compounds which have octanol:water partition coefficients above log 3.18 are less prone to transport in runoff.

Table 96. Concentrations of Triclosan and Triclocarban in Tile Drainage following Biosolids Applications (Edwards *et al*., 2009)

Application Type and Time	Application rate	Concentration in Tile Drainage (µg/L)	
		Triclosan	Triclocarban
2005 Post Liquid Biosolids application	93,500 L/ha	3.68	NA
2006 Post Dewatered Biosolids application	8 T dw/ha	0.24	<LOQ

NA = not analyzed LOQ = Limit of Quantitation

Table 97. Concentration of Triclosan and Triclocarban in Surface Runoff Following Application of Liquid and Dewatered Biosolids

Time after application	Triclocarban concentration in runoff (ng/L)	Triclosan concentration in runoff (ng/L)	
t=1 day	0.5	109.7	400
t=3 days	1.2	60.5	300
t=7days	3.4	80.2	200
t=22 days	1.5 [a]	50.2	150
t=36 days	1.0	41.2	100
t-266 days	n.a.	n.a.	20
Application rate	8T/ha	8T/ha	93500 L/ha
Biosolids Type	Dewatered biosolids (mostly anaerobic digested)	Dewatered biosolids (mostly anaerobic digested)	Liquid biosolids (mostly anaerobic digested)
Reference	Sabourin *et al*. 2009	Sabourin *et al*. 2009	Topp *et al* 2008

[a] after 21 days n.a. = not analyzed

Snyder (2009) examined the leachability of triclocarban through a sandy soil when amended with biosolids at rates equivalent to 18-52 T/ha. A series of leaching events (bi-weekly for 14 weeks, approximately 60 mL of leachate per event) were then applied to the 11 test columns filled with the sandy soil and biosolids from the different locations. The leachate concentration data revealed that the mass of TCC leached from the biosolids-amended soils was in the range of <0.02% to 0.18% of the mass in the applied biosolids.

Most quantified TCC concentrations from the first three leaching events (with one exception) were above the chronic no-observable-effect-concentrations (NOEC) and concentrations that exerted adverse effects in 50% of test populations (EC_{50}) for aquatic invertebrates. The tests using a sandy soil were considered as worst case by Snyder (2009) who suggested the potentially toxic effects would be less for finer-textured soils. All leachate concentrations were below documented acute and chronic toxicity endpoints for fish and aquatic plants. In summary, Snyder

(2009) concluded that acutely toxic levels of TCC in biosolids-amended soil leachate to *Ceriodaphnia dubia*, *Daphnia magna* and *Mysidopsis bahia* would likely be rare, and that both acutely and chronically toxic levels would likely be short-lived following a single application of biosolids.

The persistence of TCC in sandy and silty clay loam soils was estimated by Snyder (2009) using both linear and non-linear models. The half-life for TCC in a sandy soil ranged from 20 to 26 years (depending on the model used), while in the silty clay loam, the estimated half-life ranged from 6.6 to 8 years.

Kinney *et al*. (2008) measured concentrations of triclosan in the soil of two sites, one of which received a biosolids application and one which did not. Concentrations of triclosan in the earthworms inhabiting the two sites were also determined. With one exception, the site receiving no biosolids application exhibited non-detectable concentrations (Table 98). At the site receiving the biosolids application, detectable concentrations of triclosan were observed in both the soil and earthworm samples, with the earthworms having significantly higher concentrations than the soils. The bioaccumulation factors (BAFs) for triclosan based on the biosolids-amended soils were 11 and 27 for the May and September samples, respectively. Furlong *et al*. (2009) reported the value of 27 as the BAF for triclosan in soil.

Table 98. Concentrations of Triclosan in Soil and Earthworm Samples (Kinney *et al*., 2008)

Site Description	Sample Matrix	Triclosan (ng/g DM)
Site 1 (without biosolids application)	Soil Jun 6-05	833
	Worm Jun 6-05	ND
	Soil Sep 29-05	ND
	Worm Sep 29-05	ND
Site 2 (with biosolids application on April 18, 2005)	Soil May 19-05	160
	Worm May 19-05	1,740
	Soil Sep 21-05	96
	Worm Sep 21-05	2,610

ND = not detected

Bioaccumulation of TCC in earthworms growing in biosolids-amended soils was also investigated by Snyder (2009). The measured concentrations of TCC in earthworm tissue prepared from the fine sand, silty clay loam, and artificial soils amended with 707 μg TCC/ kg biosolids at a 22 T/ha rate were 127 $\pm$ 14, 142 $\pm$ 8.4, and 36.5 $\pm$ 0.89 mg TCC kg worm^{-1} (d.w.), corresponding to whole soil BAF values of 18 + 3.5, 20 + 2.1, and 2.2 + 0.22, respectively. The BAF values for triclocarban determined by Snyder (2009) are thus similar in magnitude for those determined by Kinney *et al*. (2008) and Furlong *et al*. (2009).

Plant uptake of triclocarban was found to be very slight by Snyder (2009), as only 0.041-0.82% of the TCC concentration in the biosolids-amended soils was present in above-ground Bahia grass biomass grown on four different biosolids. Snyder (2009) concluded that potential uptake of TCC by humans and wildlife by ingestion of plant material grown on biosolids-amended soils was not a significant exposure pathway.

Snyder (2009) determined that respiration by soil microbes (measured as evolved $^{14}CO_2$) was not affected by TCC concentrations up to 717 µg TCC/g biosolids (or ~30 y of land-applying biosolids containing 24 µg TCC/kg biosolids at a 22 T/ha rate), assuming no loss of TCC or decrease in bioavailability. Only biosolids addition affected CO_2 evolution, and the increase was attributed to the addition of carbon and other nutrient sources as a component of the biosolids.

With respect to environmental risk assessment, Snyder (2009) determined using the hazard index (HI) values for the American woodcock and the short-tailed shrew (animals used in EPA risk assessments) that current, typical (i.e. 5-10 Mg/ha) one-time land-application practices do not pose an ecological health risk. Conversely, under the one-time worst-case (50 T/ha one-time) and 100-year (5 T/ha for 100 years) application scenarios, Snyder (2009) determined that biosolids-borne TCC concentration limits are needed to guide sustainable long-term land-application of biosolids. With respect to surface water, Snyder (2009) determined that the hazard index from a typical runoff concentration of 3.4 ng/L was very small, and that aquatic organisms would face far more risk from TCC present in treated municipal effluents and combined sewage overflows.

A cautionary note was put forward by Smith (2009a) in his review of the environmental effects of organic compounds in biosolids applied to land, suggesting that further research is necessary to evaluate the impacts of antimicrobials on soil health.

No published data on the fate of hexachlorophene in the terrestrial environment were identified in this review.

3.10.3 Section Summary

1. Concentrations of triclosan in biosolids are well characterized, with a typical range of 1,000 to 40,000 ng/g TS dw in biosolids. Triclocarban is not as well characterized in biosolids, but available data indicate a similar concentration range.
2. Data from one publication indicate hexachlorophene concentrations in biosolids are lower than those of triclosan by up to an order of magnitude.
3. Triclosan appears to be less persistent in soils than triclocarban, with half-lives on the order of 18 and 108 days for triclosan and triclocarban, respectively.
4. Triclosan may be biotransformed in soils to methyl-triclosan.
5. Triclosan may be more mobile in soil columns than triclocarban.
6. Triclosan is released to surface runoff faster than triclocarban.
7. Triclocarban is more mobile in sandy soils than fine-textured soils.
8. The bioaccumulation factor for triclosan ranged from 11 to 27 in earthworms from biosolids-amended soils; a similar value was determined for triclocarban.
9. The accumulation of triclocarban by Bahia grass grown on biosolids-amended soil was very small.
10. The persistence, fate, mobility and bioaccumulation of hexachlorophene in the terrestrial environment are poorly documented.

Triclosan and triclocarban were not identified as organics compounds of concern in sewage biosolids applied on agricultural land and were not assessed in the WEAO (2001) report. Much

new data on the fate, transport and effects of triclocarban in the terrestrial environment were documented by Snyder (2009). Data for triclosan is somewhat more scattered through the literature, but in general results are similar to those provided for triclocarban. Although both triclosan and triclocarban are bioaccumulative in earthworms (data on accumulation in other species was not identified); the effects of this bioaccumulation are unknown. Based on the lack of information about bioaccumulative effects, concern regarding soil microbial health recently expressed by Smith (2009), and the lack of any data for hexachlorophene, it is recommended that antimicrobial compounds be considered as Group II contaminants.

3.11 Other Personal Care Products in Biosolids

3.11.1 Fluorescent Whitening Agents

Fluorescent whitening agents (FWAs) are chemicals used with textiles and papers to increase the appearance of whiteness by absorbing invisible ultraviolet light and re-emitting it in the blue region of the visible spectrum. Concentrations of FWAs in sludge samples were reported in the survey of Harrison *et al*. (2006). The compound DAS 1 was observed to have the highest levels in this class of compounds, with a maximum value of 112,000 ng/g TS dw (Table 99). The agent DSBP was present at approximately half the concentration of DAS 1, while the compound BLS was an approximate order of magnitude lower than the DSBP levels.

Table 99. Concentration of Fluorescent Whitening Agents in Biosolids (Harrison *et al*., 2006)

Fluorescent Whitening Agent	Formulation	Concentration (ng/g TS dw)
BLS	(4,4'-bis(4-chloro-3-sulfostyryl)-biphenyl)	5,400 – 5,500
DSBP	(4,4'-bis(2-sulfostyryl)biphenyl)	31,000 – 50,000
DAS 1	(4,4'-bis[(4-anilino-6-morpholino-1,3,5-triazin-2-yl)-amino]stilbene-2,2'-disulfonate)	86,000 – 112,000

No removal efficiency data for biosolids treatment processes were found for fluorescent whitening agents.

No data were found describing the fate and transport of fluorescent whitening agents in the terrestrial environment.

3.11.2 Quaternary Ammonium Compounds

Quaternary ammonium compounds represent an important class of cationic surface-active agents which are used in a variety of commercial products. They are associated with an anion, which may include either a halide salt (chloride, bromide, etc.), sulfate, carbonate, acetate, or nitrate. Quaternary ammonium compounds are generally classified as monoalkyltrimethyl ammonium salts, monoalkyldimethylbenzyl ammonium salts, and dialkyldimethyl ammonium salts.

Quaternary ammonium compounds (QAC) have an extremely strong affinity for negatively charged substrates. Their highly adsorptive properties make them suitable for a wide variety of commercial applications. They are used as agents in personal care products such as fabric softeners, laundry detergents, anti-static sprays. In heavy industrial applications, they are used to enhance flotation properties in the mining industry, in asphalt and petroleum additives, and in the manufacturing of drilling muds. Other major uses include corrosion inhibitors, germicides/deodorizers, and biocides. Because of their germicidal and biocidal properties, quaternary ammonium compounds may be acutely toxic to specific aquatic organisms at concentrations as low as 10 µg/L (Free Patents Online, 2009). In Europe, the detergent industry began a voluntary phase-out of the QAC ditallowdimethylammonium chloride in the 1990s.

Concentrations of the QAC ditallowdimethylammonium cation (DTDMAC) in the anaerobically digested biosolids of six Swiss wastewater treatment plants were documented by Fernández *et al* (1996). Concentrations were high compared to other micro-constituents, in the mg/g dry weight range corresponding to concentrations in the parts per thousand range. The intent of the study was to monitor the decline of the QAC following its substitution in laundry products in 1991. In the base year of 1991, prior to the phase-out of the compound, the mean concentrations in digested sludges from the six treatment plants ranged from 2.57 to 5.87 mg/g TS dw (Table 100). Over the span of three years, the mean concentration of the DTDMAC declined by approximately 90% from 1991 levels. Because no concentration data were reported for the digester feed sludge, it is not possible to determine the removal of this compound by anaerobic digestion.

Table 100. Concentrations of the QAC Ditallowdimethylammonium Cation (DTDMAC) in Anaerobically Digested Biosolids from 6 Swiss Wastewater Treatment Plants (Fernández *et al*., 1996).

Date	Conc'ns of Ditallowdimethylammonium Cation (mg/kg TS dw) in Digested Biosolids						
	Adliswil	Niederglatt	Winterthur	Zu¨rich-Glatt	Zu¨rich-Werdho¨lzli	Mean	Range
Feb, 1991	5.87 ± 0.39[a]	3.05 ± 0.05	3.59 ± 0.05	3.29 ± 0.07	2.57 ± 0.03	3.67 ± 1.28	2.57-5.87
Nov, 1992	1.51 ± 0.09	0.73 ± 0.07	0.87 ± 0.03	0.94 ± 0.07	0.73 ± 0.06	0.96 ± 0.32	0.73-1.51
Sept, 1993	0.57 ± 0.04	0.54 ± 0.03	0.48 ± 0.03	0.46 ± 0.04	0.30 ± 0.03	0.47 ± 0.10	0.30-0.57
Sept, 1994	0.30 ± 0.02	0.15 ± 0.02	0.15 ± 0.03	0.28 ± 0.01	0.15 ± 0.01	0.21 ± 0.08	0.15-0.30

[a] Mean + s.d. (n = 3 samples)

More recently, Martinez-Carballo *et al*. (2007) reported concentrations of several QACs in sludges (type not revealed) from three Austrian wastewater treatment plants, collected during two sampling campaigns in 2004. The compound C18-chain DTDMAC (ditallowdimethylammonium cation), which was replaced in fabric softeners by the European detergent industry in the early 1990s, continued to be the predominant species present, with a median concentration (n=6) of approximately 10 mg/kg TS dw. Other QACs at lower, but elevated concentrations included C12-chain benzalkonium chloride (BAC-C12), C14-chain benzalkonium chloride (BAC-C14), and C10-chain DDDMAC (didecyldimethylammonium

cation). The C16-chain trialkylammonium chloride was also detected at elevated concentrations, ranging from 0.16-8.4 mg/kg TS dw (Martinez-Carballo *et al*., 2007). Total concentrations of all QACs ranged from 22 to 103 mg/kg TS dw (ppm).

No other publications for removal efficiency of QAC concentrations through treatment processes were identified for biosolids and sludges. No data were found describing the fate and transport of quaternary ammonium compounds in the terrestrial environment.

3.11.3 Siloxanes

Siloxanes are organic silicon polymers manufactured as additives that improve the properties of personal care products such as cosmetics, shampoos and deodorants. Industrial applications include paper coatings and textile manufacturing. Their use is widespread due to beneficial properties of low surface tension and water-repelling activity.

There are no human health-related issues identified with siloxanes. The compounds are described as non-toxic (Appels *et al*., 2008). With respect to environmental concerns, siloxanes are noted for their persistence in the aquatic environment and potential for harm to fish and other aquatic organisms (Environment Canada, 2009b). To limit the amount of D4 and D5 that is released to the environment, the Government of Canada proposed on January 30, 2009 to set a concentration limit for D4 and D5 in products and in the wastewater produced by the manufacturing process.

Siloxanes enter the wastewater system as a result of personal bathing and domestic household work. In wastewater treatment, physical-chemical properties of interest include volatilization and hydrophobicity. The compounds are reportedly not biodegraded aerobically in the activated sludge process (Appels *et al*., 2008). Consequently, at a treatment plant they tend to mostly sorb to solids (ending up in residual sludges) and then to volatilize.

The main concern with these compounds results from the anaerobic digestion process, when the biogas produced in the process is used for energy recovery in combined heat and power applications. In the digestion process, as the sludge biomass is broken down, the bound siloxanes are released, with transfer to the biogas. Octamethylcyclotetrasiloxane (D4) and decamethylcyclopentasiloxane (D5) are the most common cyclical siloxanes found (Tower, 2003). When the digester gas is combusted to produce useful energy, the organic part of the siloxanes is oxidized, leaving behind silicates and micro-crystalline quartz, which strongly bond to the heated metal surfaces of the energy recovery equipment. The deposits are highly abrasive and cause excessive wear to the moving parts of the combustion chambers. Operating and maintenance costs can become very high for removal of the silica deposits.

Modeling of octamethylcyclotetrasiloxane (D4) in wastewater treatment plants was employed by Mueller *et al*. (1995) to estimate the potential adverse effect of D4 in treated sewage effluents on aquatic organisms. Based on an estimated influent wastewater concentration of 150 μg/L, the predicted concentration in the treated effluent ranged from 0.39 to 0.44 μg/L, which was substantially lower than the reported lowest chronic no effect concentration of 4.4 μg/L for aquatic organisms.

Concentrations of siloxanes in sludges and biosolids are poorly documented, due to the primary concern over their presence in biogas. A publication by Mueller *et al*. (1995) reported octamethylcyclotetrasiloxane (D4) concentrations in dewatered "sludge" cakes ranging from 0.21 to 0.48 mg/kg TS dw, while the concentration of D4 in a sample of secondary sludge was less than 0.21 mg/kg TS dw. Dewil *et al*. (2007) reported concentrations of siloxanes in waste activated sludges in the U.K. up to 0.03 g/g DS (i.e. 3% by weight), reinforcing the importance of sorption as a transfer mechanism from the liquid to the solid phase.

Watts *et al*. (1995) investigated the effect of linear polydimethylsiloxanes (PMDS) on biosolids treatment processes. Aerobic digesters loaded with sludge at concentrations up to 10,000 mg PDMS/kg TS dw (i.e., 10,000 ppm) exhibited pH values, oxygen uptake rates and mixed liquor solids concentrations identical to control reactors. In anaerobic digesters loaded with sludge at concentrations up to 10,000 mg PDMS/kg DS, pH, suspended solids concentrations and biogas production rates were virtually identical to values in control digesters. The compounds were thus concluded to be inert to wastewater treatment.

No removal efficiency data for biosolids treatment processes were found for organic siloxanes.

No data were found describing the fate and transport of organic siloxanes in the terrestrial environment.

3.11.4 UV Filters

Increasing concern over skin cancers and aging from exposure to the sun's ultraviolet (UV) rays has led to wider use of sunscreens. In these products are compounds used as so-called "UV filters". In addition to sunscreens, the compounds are found in other products such as beauty creams, hairspray, shampoos and shower gels, while non-personal applications of UV filters include plastics, clothing and varnish (Plagellat *et al*., 2006). The main concerns with UV filters are potential endocrine disrupting effects, with detection in human milk, plasma and urine, and in fish (Plagellat *et al*., 2006).

Concentrations of four UV filters, commonly used in Switzerland, were documented in biosolids by Plagellat *et al*. (2006) in a survey of 14 wastewater treatment plants, ranging in connected capacity from 210 to 369,900 inhabitants. Each treatment plant was tested twice, once under winter conditions and once under summer conditions. Summary statistics of the concentration data are provided in Table 101.

Table 101. Concentrations of UV Filters in Swiss Biosolids (Plagellat *et al*., 2006)

UV filter compound	Concentration (ng/g TS dw)			
	Mean	Median	Minimum	Maximum
3-(4-methylbenzylidene) camphor (4-MBC)	1,780	1,580	150	4,980
octyl-methoxycinnamate (OMC)	110	100	10	390
octocrylene (OC)	4,840	3,270	320	18,740
octyl-triazone (OT)	5,510	3,450	700	27,700

With the exception of the octyl-methoxycinnamate (OMC), median concentrations of the UV filters ranged from 1,500 to 3,500 ng/g TS dw. Both the octocrylene and octyl-triazone exhibited wide variations in concentration, as indicated by the minimum and maximum values.

No removal efficiency data for biosolids treatment processes were found for UV filter compounds. No data were found describing the fate, transport and bioaccumulation of UV filters in the terrestrial environment.

3.11.5 Section Summary

1. A number of personal care products were identified as being present in biosolids, such as fluorescent whitening agents, quaternary ammonium compounds, organic siloxanes and UV filters, but their concentrations are poorly characterized in general.
2. Concentrations of quaternary ammonium compounds in biosolids are in the range of 20,000 to 100,000 ng/g TS dw.
3. Concentrations of UV filters in biosolids are in the range of 100 to 30,000 ng/g TS dw.
4. A knowledge gap for these types of compounds exists because there is virtually no information present on the fate, transport and bioaccumulation in the terrestrial environment.

Fluorescent whitening agents, quaternary ammonium compounds, siloxanes and UV filters were not yet identified by the industry as organic compounds of concern in sewage biosolids applied on agricultural land, and therefore were not assessed in the WEAO (2001) report. The sparse data show that these various types of organic compounds are poorly characterized in biosolids, particularly siloxanes and fluorescent whitening agents. Further, there are virtually no published data encountered concerning the fate, transport, bioaccumulation or environmental effect of these compounds in the terrestrial environment. Consequently, it is recommended that the classes of compounds included in this Section be categorized as Group II compounds.

3.12 Steroidal Hormones and Sterols[3]

Compounds in this category include both natural and synthetic estrogens, and androgens, all of which can affect the human endocrine system. The synthetic estrogens, used for birth control and hormone replacement therapies, and the natural estrogens and androgens are excreted on a daily basis to sewage. Phytosterols are naturally occurring alcohols of steroids, and are present in vegetable oils used in cooking and salads. These can be ingested and excreted, or end up in household grey water during dish washing. Animal sterols are present in animal tissues (meat and dairy products) and in animal feces. The presence of the animal sterols such as coprostanol in receiving waters is typically viewed as a marker for sewage contamination. Environmental concerns arising from this group of compounds is mostly focused on the synthetic estrogens, which have potency orders of magnitude higher than the natural estrogens. Animal and plant sterols also exert weak estrogenicity.

[3] Discussion has focused on estrogenic hormones, but this does not imply that there may not be concerns with other classes such as androgenic or thyroid compounds.

3.12.1 Occurrence

Natural and synthetic estrogens found most regularly in wastewater sludges are summarized in Table 102. Concentrations of these compounds in sludges are typically less than 100 ng/g TS dw, although in the biosolids analyzed by Brown and Clarke (2009) the concentration of the natural hormone estrone (E1) had a mean concentration of 152 ng/g TS dw. The data suggest that estrone (E1) is higher than most of the other common estrogenic compounds. In an analysis of New Zealand sludge, Gielen (2007) reported a mean value of 185 ng/g TS dw for the synthetic hormone 17α-ethinylestradiol (EE2), however the standard deviation of the mean was also very high indicating a wide spread of experimental values.

Table 102. Concentrations of Common Estrogenic Compounds in Sludges and Biosolids

Sludge Source	Concentration (ng/g TS dw)				Reference
	17α-ethinylestradiol (EE2)	17β-estradiol (E2)	Estriol (E3)	Estrone (E1)	
Sludge Survey	24.9 (25)[a]	34.3 (21.5)	38.7 (24.8)	106 (51.2)	U.S. EPA (2009a)
Literature review	<1.5 – 17	4.9 – 49		16 – 27.8	Harrison *et al*. (2006)
Compost	<5				Gielen (2007)
Primary sludge	185 ± 185[b]				
Biosolids	4.8 ± 0.3	10.6 ± 0.3	152 ± 2		Brown and Clarke (2009)
Primary sludge	<1.5	30		30	Andersen *et al*. (2003)

nd = not detected

[a] mean (median) [b] mean ± standard deviation

Other natural and synthetic estrogenic compounds are present in biosolids in addition to those listed in Table 102. Additional estrogens detected in sludges and biosolids in the EPA's TNSSS (U. S. EPA, 2009a) are provided in Table 103. The concentration of the natural hormone progesterone was the highest of the others observed, with a median concentration of 139 ng/g TS dw. The median concentrations of the other estrogens were less than 50 ng/g TS dw.

Table 103. Concentrations of Other Estrogenic Compounds in Sludges and Biosolids (U.S. EPA, 2009a)

Estrogenic Compound	Concentration (ng/g TS dw)
17α-Dihydroequilin	20.6 (19.4)[a]
β-Estradiol 3-Benzoate	146.9 (23.2)
Equilenin	16 (10.9)
Equilin	34.8 (23)
Mestranol (MEE2)	22.5 (21.4)
Norethindrone	101 (22.3)
Norgestrel	66.5 (42)
Progesterone	323 (139)

[a] mean (median)

Concentrations of androgens in sludges were reported less frequently than estrogens (Table 104). Results from the EPA TNSSS (U.S. EPA, 2009a) reported three androgens with mean values ranging from a low of 85 ng/g TS dw for androsterone to a high of 158 for androstenedione.

Table 104. Concentrations of Androgenic Compounds in Sludges and Biosolids (U.S. EPA, 2009a)

Androgens	Concentration (ng/g TS dw)
Androstenedione	327 (158)[a]
Androsterone	120 (84.9)
Testosterone	163 (95.2)

nd = not detected [a] mean (median)

Concentrations of plant sterols in sludges and biosolids (Table 105) were among the highest observed in this literature review, with concentrations in the tens of thousands of ng/g TS dw, and the median concentration of 207,000 ng/g TS dw reported for β-sitosterol in the EPA's TNSSS (U.S. EPA, 2009a). The concentrations for the plant sterols reported in the literature review by Harrison *et al*. (2006) were much lower than those found in the EPA's TNSSS (U.S. EPA, 2009a) and in the study by Kinney *et al*. (2008).

Table 105. Concentrations of Plant Sterols in Sludges and Biosolids

Compound	Concentration (ng/g TS dw)			Concentration (ng/g OC)
	Literature review	not specified Sludge Survey	Dewatered anaerobically digested biosolids	Dewatered
Campestanol (5α+5β)	3,000 – 14,000			
Campesterol	6,300	100,900 (46,500)[a]		
Desmosterol		15,650 (10,800)		
Ergosterol		19,830 (12,600)		
Sitostanol (5α-β+5β-β)	14,100 – 93,900			
Sitosterol (β-)	29,600 – 31,100	291,400 (207,000)	177,000	112,000
Stigmastanol; β-Stigmastanol; Stigmastanol (5α+5β)	1,900 – 12,900	168,100 (62,500)	77,000	40,500
Stigmasterol	6,700	321,200 (41,500)		
Reference	Harrison *et al*. (2006)	EPA (2009a)	Kinney *et al*. (2008)	Kinney *et al*. (2006)

[a] mean (median) OC = organic carbon

The concentrations of plant sterols in treated biosolids were documented in Kinney *et al*. (2006). Composting and heat drying resulted in lower concentrations of the phytosterols in the biosolids than did alternate drying methods or anaerobic digestion (Table 106). For both the β-sitosterol

and β-stigmastanol, anaerobic digestion treatment had the highest concentrations of the four treatment methods examined.

Table 106. Concentrations of Plant Sterols following Biosolids Treatment Processes (Kinney *et al*., 2006)

Biosolids treatment	Concentration (ng/g OC)	
	Sitosterol (β-)	Stigmastanol; Stigmastanol (5α+5β)
Heat drying	110,000	9,310
Compost	50,800-200,000	2,760-17,400
Air drying	257,000	113,000
Anaerobic digestion	554,000	243,000

OC = organic carbon

Concentrations of the animal sterols reported in sludges varied substantially from one reference source to the next, but were in any case among the highest concentrations observed in this review, as shown in Table 107. The literature review of Harrison *et al*. (2006) reported the lowest concentrations of the compounds, while the highest values were documented in the EPA's TNSSS (U.S. EPA, 2009a), with the fecal indicator 3β-coprostanol having a median concentration of 827,000 ng/g TS. The reported concentration of 3β-coprostanol by Kinney *et al*. (2008) was intermediate between the EPA (2009a) value and the value from the review data by Harrison *et al*. (2006).

Table 107. Concentrations of Animal Sterols in Sludges and Biosolids

Compound	Concentration (ng/g TS dw)			Concentration (ng/g OC)
	Literature review	Not specified (Sludge Survey)	Dewatered anaer. digested biosolids	Dewatered
Cholestanol (5α-); Cholestanol	22,700	680,000 (187,200) [a]		
Cholesterol	57,400		66,700	333,000
Coprostanol; 3β-Coprostanol	216,900	4,367,000 (827,100)	467,000	325,000
Epicoprostanol		1,703,000 (108,000)		
Reference	Harrison *et al*. (2006)	U.S. EPA (2009a)	Kinney *et al*. (2008)	Kinney *et al*. (2006)

[a] mean (median) OC = organic carbon

Concentrations of animal sterols in biosolids treated by different processes are limited to two compounds in the work by Kinney *et al*. (2006) (Table 108). The results are not consistent for the two compounds. The highest concentration of cholesterol was found in biosolids treated by heat drying, whereas the highest concentration of 3β-coprostanol was observed following

anaerobic digestion. For both compounds, however, composting resulted in the lowest concentrations. There are too few additional published data to determine whether composting would produce the lowest concentrations of these compounds.

Table 108. Concentrations of Animal Sterols following Biosolids Treatment Processes (Kinney *et al*., 2006)

Biosolids treatment	Concentration (ng/g OC)	
	Cholesterol	Coprostanol; 3β-Coprostanol
Heat Drying	402,000	221,000
Compost	19,100-157,000	8,100-72,800
Air Drying	236,000	126,000
Anaerobic Digestion	209,000	1,460,000

Biosolids treatment processes in the three NC plants examined in a study by Linden *et al.* (2008) included anaerobic digestion with dewatering, aerobic digestion followed by either lime stabilization or composting, and aerobic digestion followed by thermal drying. They concluded that the best final treatment for biosolids for reducing estrogenic activity involved thermal drying, which appeared to remove or degrade estrogenic activity and EDCs to below 2 µg/kg TS dw from 50 µg/kg TS dw in the aerobic digestion stage. Lorensen *et al* (2004) undertook a survey of hormonal activities in 25 Ontario biosolids clearly showing aerobic digestion to be effective at removing hormonal activity, A paper by Lorenzen *et al* (2006) summarizes information on hormonal content in some Ontario biosolids, and the fate of various types in Ontario soils.

3.12.2 Fate and Transport in the Terrestrial Environment

The disappearance of two hormones 17β-estradiol (an estrogen) and testosterone (an androgen) from soil microcosms was monitored by Jacobsen *et al*. (2005). The hormones were mixed directly with soils that were either non-amended or amended with biosolids. Initial concentrations of the two compounds, expressed as hormone equivalents, were higher in the soil without the biosolids amendment than were the initial concentrations in the soil receiving the biosolids amendment (Table 109). Concentrations of the two hormones declined rapidly and were virtually eliminated from both soil microcosms either 96 hours (for the estradiol) or 48 hours (for the testosterone) after the biosolids application, whether having received a biosolids amendment or not. Because the initial concentrations of the hormone equivalents spiked into the soil with biosolids present were lower than the spiked concentrations without biosolids present, and also because the time required to reach non-detectable concentrations of the hormone equivalents with and without biosolids amendment was the same, it appeared that the presence of biosolids might cause a slightly slower rate of biodegradation of the hormones, perhaps by binding them to the organic matter present in the biosolids.

Investigation as to whether the hormones were mineralized in the soils was monitored by spiking ^{14}C-labelled hormones in the soils, and then tracking the recovery of labelled $^{14}CO_2$. The testosterone was mineralized more readily than was the E2, with up to 45% of the original labelled mass of testosterone recovered as CO_2 after 120 hours. By comparison only 10% of the

labelled E2 mass was mineralized over 96 hours in the biosolids-amended soil. Although mineralization of the E2 proceeded more quickly in the microcosm with the biosolids amendment than in the microcosm without the biosolids addition, the reverse was true for the testosterone. Potential reasons for the slower rate of testosterone mineralization due to the increasing presence of biosolids were lower oxygen levels in the soil due to the biochemical oxygen demand of the biosolids, or inhibition of microbial activity due to toxicity of the biosolids (Jacobsen *et al*. 2005).

Table 109. Reduction and Mineralization of Two Human Hormones in Soils following Biosolids Application (Jacobsen *et al*., 2005)

Hormone	Hours after application	Hormone equivalents. (ng/g DM) after biosolids application to soil		Mineralization (% ^{14}C recovered as $^{14}CO_2$) in soil amended with biosolids in concentrations of 10% (v/w).	
		Non-amended soil	Biosolids amended soil	Non-amended soil	Biosolids amended soil
17β-Estradiol (E2)	t=0	1300 ±200 [a]	600 ±100		
	t=6	400 ±50	250 ± 50	No data	No data
	t=24	10 ± 0	300 ± 100	1 ± 0	5 ± 0
	t=48	5 ± 0	220± 10	2 ± 0	7.5 ± 0
	t=96	0	0	2.5 ± 0	10 ± 0
Testosterone	t=0	900 ± 150	400 ± 0		
	t=6	600 ±100	250 ± 50	No data	No data
	t=24	50 ±30	50 ± 30	28 ± 1	18 ± 1.5
	t=48	10 ± 0	10 ± 0	40 ± 1.5	25 ± 0
	t=120	0	0	45 ± 1	30 ± 0

[a] mean ± standard deviation (n=3)

The proportion of biosolids in a soil mixture was demonstrated by Jacobsen *et al*. (2005) to have an effect on the rate of mineralization of ^{14}C-labelled testosterone. As indicated in Table 110, as the proportion of biosolids in the mixture with the loam soil increased, the fraction of labelled compound that was mineralized declined. While there was not an appreciable difference in mineralization rates at biosolids:soil mixtures up to 10% v/w, the mineralization rates declined significantly at 20% v/w, and were almost non-existent at 50% v/w. The authors presented data indicating the testosterone was much less extractable (i.e. more highly bound) as the proportion of biosolids in the soil increased.

Table 110. Mineralization of ^{14}C-labelled Testosterone over Time in Different Biosolids:Soil Mixtures (Jacobsen *et al*., 2005)

Time after Biosolids Application	Mineralization (%) in loam soil amended with biosolids in concentrations from 0-50% (v/w)				
	Unamended soil (biosolids:soil = 0% (v/w)	Biosolids:soil = 5% v/w	Biosolids:soil = 10% v/w	Biosolids:soil = 20% v/w	Biosolids:soil = 50% v/w
t=24 hours	25 ± 2 [a]	20 ±1	18± 2	8± 2	1± 0

t=48 hours	35 ± 3	28 ± 2	25± 0	15± 0	2± 0
t=120 hours	40 ± 3	33 ± 2	32± 0	22± 0	5± 0

[a] mean ± standard deviation (n=3)

The persistence of testosterone in different soil types was investigated by Lorenzen *et al* (2005), using radio-labelled ^{14}C-testosterone in soil microcosms. This study investigated the hormone fate in soil without being applied in biosolids. Both the disappearance of the androgen over time and the recovery of labelled ^{14}C-CO_2 were reported, as shown in Table 111.

Table 111. Persistence and Fate of ^{14}C-Testosterone in Different Soils (Lorenzen *et al*., 2005)

Measurement	Time after application, h	Sandy loam	Loam	Silt loam
Extractable ^{14}C-Testosterone (% of total)	3	80 ± 5 [a]	78± 5	80 ± 5
	6.5	75 ± 5	60± 0.5	75 ± 5
	24	40± 3	10± 0	38± 3
	30	28± 1	5± 0	28± 1
Testosterone equivalents (ng/g soil DM)	3	580± 100	400 ± 200	700 ± 250
	6.5	560± 250	230 ± 50	380 ± 120
	24	205 ± 100	15 ± 0	230 ± 80
	30	120 ±25	5 ± 0	200 ± 50
^{14}C-Testosterone Recovered as $^{14}CO_2$ (% of total)	0	0%	0%	0%
	22	22 ± 1	37 ± 2	29± 1.5
	100	45 ± 2	53 ± 1	53 ± 1
	265	51 ±1	57 ± 1	57 ± 1

[a] mean ± standard deviation (n=3)

The disappearance of the labelled testosterone was much faster in the loam soil compared to the sandy loam or silt loam soils, which were similar in the removal rate. Thirty hours following the application of the labelled compound to the loam soil, only 5% of the extractable compound was present, while for the other two soils, 28% of the extractable compound was still present. A similar result was observed when the concentrations were expressed as testosterone equivalents. In terms of mineralization, the loam and silty loam soils exhibited similar rates of recovery of $^{14}CO_2$ over the 265 hour monitoring period, while the rate of recovery of the $^{14}CO_2$ in the sandy loam soil was somewhat slower.

Soil temperature was demonstrated to have an effect on the dissipation of initial ^{14}C-testosterone in a loam soil (Lorenzen *et al*., 2005) As indicated in Table 112, there is a significant change in the level of extractable testosterone over a 72 hour monitoring period between 12 and 23 ^{o}C. The rate of disappearance of the extractable labelled testosterone is similar at 4 and 12 ^{o}C. The rate of disappearance of the extractable testosterone is similar at 23 and 30 ^{o}C. The authors concluded that testosterone would be rapidly dissipated under conditions of temperature and moisture content typical of a temperate growing season, primarily due to biodegradation by soil microbes (Lorenzen *et al*., 2005).

The estimated dissipation half-lives of several hormones in different soils were documented by Lee *et al*. (2003). The ranges of half-lives were 0.8 to 1.1 days for E2, from 3.1 to 6.5 days for the synthetic estrogen EE2, and from 0.3 to 6.5 days for testosterone (Table 113). The data indicate that these hormones dissipate quickly in soils.

Table 112. Dissipation of Applied ^{14}C-Testosterone in a Loam Soil at Different Temperatures (Lorenzen *et al*., 2005)

Time after application, hours	% of Initial Extractable Radioactivity at Soil Temperature			
	4 °C	12 °C	23°C	30°C
0	85 ± 5	85 ± 5	85 ± 5	85 ± 5
6	68 ±1	60± 2	28 ± 2	20.5 ± 2
24	23 ±0.5	12± 0.5	0 ± 0	0 ± 0
72	10 ±5	15± 1	0 ± 0	0 ± 0

Table 113. Dissipation Half-Lives for Hormones in Soils (Lee *et al*., 2003)

Soil/Location	Estimated Dissipation Half-life (days)		
	17β-Estradiol (E2)	17α-ethinylestradiol (EE2)	Testosterone
EPA14 (soil from an eroded hillside in SE Ohio)			1.8-5.3
Soil in Bloomfield		3.7-6.5	3.0-6.5
Soil in Drummer sampled in 1994	0.8-1.1	3.1-3.9	
Soil in Drummer sampled in 1998			0.4-0.8
Soil in Toronto			0.3-4.1

Concentrations of plant and animal sterols in soils and earthworms residing in plots with and without biosolids amendments were monitored by Kinney *et al*. (2008). The results are summarized in Table 114.

Table 114. Concentrations of Hormones in Soil and Earthworm Samples (Kinney *et al*., 2008)

Site Description	Sample Matrix	Concentration (ng/g DM)			
		Cholesterol	β-Sitosterol	3β-Coprostanol	Stigmastanol
Site 1 (without biosolids application)	Soil Jun 6-05	18,900	24,000	ND	4,900
	Worm Jun 6-05	253,000	11,600	ND	ND
	Soil Sep 29-05	887	3,730	ND	1,090
	Worm Sep 29-05	17,600	4,770	ND	483

Site 2 (with biosolids application on April 18, 2005)	Soil May 19-05	7,700	4,570	1,910	1,300
	Worm May 19-05	166,000	7,030	ND	ND
	Soil Sep 21-05	2,270	3,530	1,360	927
	Worm Sep 21-05	19,100	4,360	ND	501

ND = not detected

Coprostanol was not detected in either soils or earthworms in the non-applied site. It was detected in the two soil samples collected from the site with biosolids amendment, but not in the earthworms. The phytosterols β-sitosterol and stigmastanol and the animal sterol cholesterol were generally as high in concentration, or even higher, in the non-applied site compared to the site receiving the biosolids. Animal and plant sterols, although among the highest concentrations in biosolids, are naturally-occurring products that can be found at concentrations of similar magnitude in both non-amended and biosolids-amended soils. Cholesterol bioaccumulation factors (BAFs) in worms varied from 8 to 21 in both biosolids-amended and non-amended sites (Kinney *et al*., 2008). The BAF values for β-sitosterol were much lower with a range of 0.5 to 1.5 in both the biosolids-amended and non-amended sites. The other two hormone compounds were mostly zero or less than one, indicating non-accumulation.

Brown and Clark (2009) investigated the fate of target hormones in the turf of a golf course following biosolids amendment. The hormone concentrations in the applied biosolids were presented earlier in Table 102. Concentrations in the grass leaf tissues, in leachate and in the soil after the test ended were all non-detectable.

In a review of the significance of organic contaminants in biosolids applied to agricultural lands, Smith (2009a) summarized available data as indicating estrogenic substances in farm livestock waste applied to land would contribute a much greater loading than sewage sludge (the review did not differentiate between recycled sewage sludge and biosolids).

3.12.3 Section Summary

1. 17α-ethinylestradiol (EE2), estrone (E1) and 17β-estradiol (E2) are among the most frequently characterized hormones in sludges and biosolids, and of these, estrone (E1) exhibits the highest concentrations.
2. Of the natural hormones, progesterone exhibited the highest concentrations, with a median value of 139 ng/g TS dw.
3. Concentrations of androgens in biosolids were reported less frequently than estrogens, with median values for three androgens from the EPA sludge survey ranging from 85 to 158 ng/g TS dw.
4. Concentrations of plant sterols in sludges and biosolids were among the highest observed in this literature review, with values in the tens of thousands of ng/g TS dw. They are naturally-occurring products that can be found at concentrations of similar magnitude in both non-amended and biosolids-amended soils
5. Concentrations of the animal sterols reported in sludges varied substantially from one reference or source to the next, but as with plant sterols they were among the highest observed in this review.

6. Removal efficiencies up to 85% were recorded for both 17α-ethinylestradiol (EE2) and a mixture of estrone (E1) and 17β-estradiol (E2) resulting from both thermophilic and mesophilic anaerobic sludge digestion. Removal efficiency data for hormones and sterols resulting from other biosolids treatment processes are scarce.
7. Human hormones in biosolids disappear rapidly (less than 96 hours) when incorporated into soils, with estimated half-lives of 1 to 7 days.
8. Testosterone is mineralized in soil to a greater extent (30-45%) than 17β-estradiol (E2) (2-10%).
9. Approximately 50-60% of ^{14}C-labelled testosterone added to three soils was mineralized to CO_2 within 265 days.
10. Human hormones were not taken up by turf grass grown on biosolids-amended soils.

Hormones and sterols were not identified as organic compounds of concern in sewage biosolids applied on agricultural land and were not assessed in the WEAO (2001) report. The weight of data examined in this review indicates the human hormones (estrogens and androgens) have short half-lives in soil. One review indicates there is no accumulation by plant matter from biosolids-amended soils. Animal and plant sterols, although among the highest concentrations in biosolids, are naturally-occurring compounds that can be found at concentrations of similar magnitude in both non-amended and biosolids-amended soils. Because farm livestock waste appears to provide a much greater loading of these contaminants to soils, it is recommended that these compounds be considered as Group I contaminants.

3.13 Metals and Radionuclides

Concentrations of metals in sludges and biosolids have been of concern for decades because of the use of biosolids as a soil amendment in agriculture and silviculture (not in Ontario). Concentrations of metals have been reported and have been well documented in other surveys dating back to the early 1970s (e.g., Leeper, 1972; Page 1974) and later in the 1980s and 1990s (e.g., Monteith, 1987; Canviro Consultants Ltd. 1988; Webber and Nichols, 1995; WEAO 2001) and more recently (XCG, 2007). Reported concentrations of the most common metals and elements are typically in the mg/kg (ppm) range. Radionuclides in sludges and biosolids are also of concern and very limited information for them was included in the (WEAO 2001) report. The intent of this review is not to duplicate the earlier information given the project schedule, but to retrieve and expand the body of literature in a review of more recent data with a particular focus on non-regulated metals.

Metals and radionuclides accumulate in sludges at wastewater treatment when they are discharged by domestic and industrial sources. Work undertaken in Québec has shown that source control has been working to reduce metals getting into the sewer systems to the wastewater treatment plant and into the final effluents and biosolids (Marc Hébert, personal communication, 2010).

For example, aluminum and selenium are present in personal care products, copper, lead and zinc can enter wastewater from plumbing, mercury was previously used in dental amalgams, and silver is used in hospital X-ray films. Radionuclides are used in numerous medical diagnostic

techniques and frequently enter the sewer system in patient excreta. Concerns with the metals in biosolids are related to their potential toxicity to or uptake by agricultural crops or foraging animals.

3.13.1 Metals

Occurrence
A comprehensive survey of concentrations of metals in the U.S. was recently released by the EPA (2009a) in the Targeted National Sewage Sludge Survey (TNSSS) report. Concentrations from this survey are presented in Table 115. The EPA survey provides a list of both commonly reported metals and those that are less well documented, which are those which are presented in the Table. Some limited concentration data for metals in biosolids from five treatment facilities in Vancouver, BC are also provided. For those metals with data in both surveys, the mean concentrations are very similar in magnitude.

Table 115. Concentrations of Metals in Sewage Sludges and Biosolids.

Metal	Concentration (mg/kg)	
	sewage sludge survey	Vancouver Biosolids (5 plants)
Aluminum (Al)	13,480 (11,200)[a]	
Antimony (Sb)	2.26 (1.42)	
Barium (Ba)	572 (452)	460 (180-660) [b]
Beryllium (Be)	0.38 (0.27)	
Iron (Fe)	24,740 (13,250)	
Silver (Ag)	31 (22)	44 (9.6-120)
Thallium (Th)	0.17 (0.13)	
Tin (Sn)	43.5 (36.2)	43 (10-84)
Titanium (Ti)	221 (80.9)	
Vanadium (V)	33.9 (11.6)	
Yttrium (Y)	4.55 (3.54)	
Reference	U.S. EPA (2009a)	Bright and Healey (2003)

[a] mean (median) [b] mean (range)

Table 116 provides a comparison of concentrations of regulated metals in Canada and the U.S., as previously documented in the 2001 WEAO report (WEAO, 2001), with newer data from 2009. New Canadian data are unpublished data provided to WEAO by Hale (2009), which are still subject to ongoing statistical assessment. The U.S. data are extracted from the recently published EPA Targeted National Sewage Sludge Survey (EPA, 2009a). Metal concentrations in both Canadian and U.S. biosolids have generally declined over the past decade as a result of more stringent controls on their entry to municipal sewer systems. In some cases, the decline of some metals in Canadian biosolids appears to be dramatic (e.g., nickel and molybdenum), with apparent reductions of approximately an order of magnitude compared to the data from 1995.

Reductions in metal concentrations in U.S. biosolids between 1996 and 2009 are not as dramatic, possibly due to earlier implementation of sewer use control programs in Canada.

Concentrations of unregulated metals in biosolids from the WEAO (2001) report are compared in Table 117 to more recent concentrations from Canada (Hale, 2009), and the U.S. (EPA, 2009a).

Table 116. Comparison of Regulated Metal Concentrations in Canada and the U.S. over Time

Metal	Concentration in Biosolids (mg/kg TS dw)[a]						
	Canadian Surveys			US Surveys			
	1981	1995	2009 (Hale, 2009)	1979	1988	1996	2009 (US EPA, 2009a)
Arsenic		2.3	4.3 (1.2-64.3)	6.7	9.9	11.5	6.8
Cadmium	35	6.3	1.4 (0.19-14.1)	69	6.9	6.4	2.5
Chromium	1040	319	75.4 (12.4-398)	429	119	103	78.2
Copper	870	638	551 (142-2,920)	602	741	506	559
Lead	545	124	46.4 (0.93-324)	369	134	111	74.0
Mercury		3.5	1.3 (0.21-4.7)	2.8	5.2	2.1	1.3
Molybdenum		22	2.8 (0.33-28.8)	17.7	9.2	15	15
Nickel	160	38	1.2 (0.61-161)	135	43	57	47.4
Selenium		3.3	2.8 (0.37-45.5)	7.3	5.2	5.7	7.1
Zinc	1390	823	486 (156-1,720)	1594	1202	830	970

[a]Data from WEAO (2001) unless otherwise specified

Table 117. Comparison of Unregulated Metal Concentrations in Biosolids over Time

Metal	Concentration in Biosolids (mg/kg TS dw)								
	Canada				USA			United Kingdom	
	2001		2009 (Hale, 2009)		2001	2009 (US EPA, 2009a)		2001	
	Range	Median	Range	Median	Typical	Range	Median	Range	Median
Aluminum (Al)			2390-116700	13,160		1,400-57,300	11,200		
Barium (Ba)	300-688	417	236-700	403	9-1004	77-2,117	572	23-3104	363
Cyanide (CN)					~800				
Fluorine (F)					~100	7.6-234	54.1	60-40000	250[(1)]
Beryllium (Be)				<0.56	<1.5	0.04-2.34	0.38	1-30	
Boron (B)	20-134	68			16-680	5.7-131	33.0	15-1000	30[(1)]
Titanium (Ti)	61-244	147	3.4-372	53.9		18.5-7,020	80.9	355-1677	1795
Vanadium (V)	8-54	15	1.5-178	12.9	20-400	2.04-617	11.6	7-660	26
Manganese (Mn)			2.4-7,750	4,670	60-3900	35-14,900	1,165	55-13902	318
Iron (Fe)			2,050-28,0000	52,500		1,580-131,000	13,250	2480-106812	12479
Cobalt (Co)						0.87-290	4.44	<2-617	8
Gallium (Ga)								<2-15	3
Germanium (Ge)								<2-9	<2
Bromine (Br)								4-1049	29
Rubidium (Rb)								<2-232	16
Strontium (Sr)	91-584	199	8.2-1,810	250				45-1335	174
Yttrium (Y)						0.70-26.3	11.6	<2-34	7

Table 117 cont'd

Metal	Concentration in Biosolids (mg/kg TS dw)								
	Canada				USA			United Kingdom	
	2001		2009 (Hale, 2009)		2001	2009 (US EPA, 2009a)		2001	
	Range	Median	Range	Median	Typical	Range	Median	Range	Median
Zirconium (Zr)	3-38	10						14-2500	70
Niobium (Nb)								<2-41	5
Silver (Ag)	5-81	43	0.16-74.3	16.3	<930	2-856	23	<2-1252	5
Tin (Sn)	7-394	33	1.0-3,640	25.1	40-700	7.5-522	36.2	19-683	101
Antimony (Sb)	24-117	64	0.29-23.6	2.23	44 - 308	0.45-20.5	1.42	<2-572	7
Tellurium (Te)								<2	<2
Tungsten (W)								<2-1418	4
Thallium (Tl)	nd-131	16	0.02-25.0	0.26				<2-5	<2
Bismuth (Bi)	nd-14	9						<2-10	8
Uranium (U)								<2-2	2

(1) Listed as “common value” in WEAO (2001) report Table 7.9

Fate and Transport of Metals in the Terrestrial Environment
Recent published data (since 2001) on the non-regulated (Ontario) metals in the terrestrial environment are scarce. There were no recent studies identified that discussed mobility of the metals once applied to soil in biosolids amendments, or the potential uptake by crops or animals including earthworms and foraging livestock, growing on biosolids-amended sites.

3.13.2 Radionuclides

Occurrence
Municipal wastewater may contain both man-made and naturally occurring radionuclides which can accumulate in the sludges and biosolids. A survey of 311 publicly owned treatment works (POTWs) conducted from 1998 to 2000 by EPA and other federal agencies who are members of the Interagency Steering Committee on Radiation Standards (ISCORS) has provided detailed information on radioactivity in sludge and ash from wastewater treatment plants http://www.epa.gov/rpdweb00/docs/tenorm/832-r-03-002.pdf .

The objectives of the survey were to:
(1) obtain national estimates of high-probability occurrences of elevated levels of radioactive materials in sludge and ash at POTWs,
(2) estimate how much radioactive contamination comes from U.S. National Regulatory Commission (NRC) and Agreement State licensees and how much from naturally occurring radioactivity, and
(3) support rulemaking decisions by NRC and EPA.

Concentrations of radionuclides in the municipal sludges and/or biosolids are provided in Table 118. A few specific radionuclides (as opposed to total alpha or beta emitters) were detected in most of the sludge samples; these included potassium-40, lead-212 and radium-226. More radionuclides were detected very infrequently or not at all, including cerium-141, cesium-134, europium-154, iron-59, lanthanum-138, radium-223, radon-219, samarium-153 and zinc-65.

Table 118. Concentrations of Radionuclides in U.S. Sludges (ISCORS, 2003)

Radionuclide	Min	Median	95th Pctle	Max	No. Detects/No. Analyses
Alpha	ND	7	34	137	309/311
Beta	1.7	13	34	93	311/311
Am-241	ND	ND	ND	2.5	10/311
Be-7	ND	1.2	9	22	263/311
Bi-212	ND	ND	1.3	13	101/311
Bi-212	ND	ND	1.3	13	101/311
Bi-214	ND	0.3	2.3	16	238/311
C-14*	ND	ND	1	3	63/158
Ce-141	ND	ND	ND	0.016	1/311
Co-57	ND	ND	ND	0.26	6/311
Co-60	ND	ND	ND	5.1	13/311
Cr-51	ND	ND	ND	3.5	6/311

Continued

Table 118 (cont'd)

Radionuclide	Min	Median	95th Pctle	Max	No. Detects/No. Analyses
Cs-134	ND	ND	ND	0.04	1/311
Cs-137	ND	ND	0.11	3.6	133/311
Eu-154	ND	ND	ND	21	1/311
Fe-59	ND	ND	ND	0.4	1/311
H-3*	ND	0.3	5	8	111/158
I-125	ND	ND	ND	40	11/311
I-131	ND	1.8	51	840	246/311
In-111	ND	ND	0.04	3.6	19/311
K-40	ND	4	12	26	308/311
La-138	ND	ND	ND	0.07	1/311
Pa-234m	ND	ND	7	27	80/311
Pb-210	ND	ND	4	13	135/311
Pb-212	ND	0.44	1.9	15	303/311
Pb-214	ND	0.31	2.6	17	253/311
Pu-238	ND	0.01	0.07	0.19	75/92
Pu-239	ND	0.003	0.04	0.12	68/92
Ra-223	ND	ND	ND	0.09	2/311
Ra-224	ND	ND	0.9	12	47/311
Ra-226	ND	2	13	47	289/311
Ra-228	ND	0.82	5.1	38	271/311
Rn-219	ND	ND	ND	ND	0/311
Sm-153	ND	ND	ND	27	1/311
Sr-89	ND	0.35	20	70	68/98
Sr-90	ND	0.1	1	9.4	64/98
Th-227	ND	ND	0.1	0.5	49/207
Th-228	0.07	0.605	4.1	9	92/92
Th-230	0.09	0.34	1	1.7	92/92
Th-232	0.02	0.2	0.6	1.6	92/92
Th-234	ND	0.6	6.7	23	191/311
Tl-201	ND	ND	46	241	151/311
Tl-202	ND	ND	0.53	1.16	73/311
Tl-208	ND	0.07	0.96	4.8	180/311
U-234	0.18	1.95	17	44	92/92
U-235	ND	ND	0.45	3.1	112/311
U-238	0.18	1.4	12	26	92/92
Zn-65	ND	ND	ND	0.06	1/311

nd = not detected (detection limit not reported);
All concentrations are expressed in picocuries (pCi)/g dry unless noted;
(1 pCi = 10^{-12} Ci = 37 radioactive disintegrations per second, or 37 becquerels)

Based on the results of the analyses, the report concluded that samples primarily contained naturally occurring radioactive material (NORM) such as radium. With the exception of NORM,

most other samples were at or near the limit of detection. Based on the results obtained, the report concluded that the radionuclide levels in sludge (or by extension in biosolids) are generally comparable to what is found in other media (e.g. soil and fertilizer), as indicated in Table 119. No widespread or nationwide public health concern was identified by the survey because no significant adverse condition or excessive concentrations of radioactivity were observed in sludge or ash.

Table 119. Comparison of Radiation Levels in U.S. Sludges and Soils (ISCORS, 2003)

Matrix	Radiation Level		
	Low	Medium	High
U.S. Sludges	0.0 pCi/L	2 pCi/L	4.7 pCi/L
U.S. Sludge Ash	0.0 pCi/L	2 pCi/L	22 pCi/L
U.S. Soils	0.2 pCi/g	na	4.2 pCi/g

na= not available

Recommendations were provided in the report for POTW operators on issues such as determining sources of radioactivity at POTWs, description of sampling and analysis procedures, and suggestions for alternative courses of action if circumstances (e.g. location in a high NORM area) or actual measurements indicate that a problem may exist. The reports and laboratory data used in the sewage sludge analyses of radionuclides can be publicly accessed at http://www.iscors.org/.

Fate and Transport of Metals in the Terrestrial Environment
No studies were identified examining the fate, transport and bioaccumulation issues with respect to radionuclides in soils following amendment with biosolids.

3.13.3 Section Summary

1. The recent database for concentrations of metals and metalloids is limited because this review was focused on data from the year 2000 on, and much of the documented research on metals occurred previously.
2. After iron and aluminum, the non-regulated metals of highest concentration were barium and titanium.
3. There are few data characterizing concentrations of elements such as silver, thallium, antimony, vanadium, yttrium and others in biosolids.
4. There is virtually no information present on the fate, transport and bioaccumulation of these non-regulated metals in the terrestrial environment, thus constituting a knowledge gap.
5. Based on a major survey of U.S. sludges, radionuclide levels in municipal sludge (or by extension in biosolids) are generally comparable to what is found in other media (e.g. soil and fertilizer), and do not represent a widespread or nationwide public health concern.
6. No studies were identified which investigated fate, transport of bioaccumulation of radionuclides in the terrestrial environment resulting from amendment of soils with biosolids.

The WEAO (2001) report contained the following findings and conclusions concerning metals in sewage biosolids applied to agricultural land:

- Sewage biosolids are products of wastewater treatment and depending upon sewer use controls, they can contain variable amounts of whatever metals are used, domestically and industrially, in the sewerage district. However, biosolids quality has improved dramatically over the years due to industrial pretreatment programs, household hazardous waste education and changes in water supply management.

- Large amounts of research have focused on a few metals considered to be the most hazardous and guidelines/regulations for land application of sewage biosolids have been developed to limit loadings of these constituents to agricultural land. Sewage biosolids application rates are generally agronomically based so as not to exceed crop nutrient requirements.

- There is much less Canadian than US and international research on the effects of metals in land applied sewage biosolids. However, Canadian and in particular, Ontario recommended practices are among the most conservative in the world. Considering the absence of detrimental effects in studies with high metal concentrations and application rates, it is concluded that the recommended land application practices in Ontario present no significant risk to humans and the environment.

- The regulated metals can be considered Group I contaminants for which current Ontario guidelines are adequate to protect the well being of soils, crops, animals, humans and ground and surface water qualities.

- The following unregulated metals and compounds in biosolids were considered: aluminum, antimony, asbestos, barium, beryllium, boron, cyanide, fluoride, manganese, silver, thallium and tin. Based on very limited information, it was concluded that loadings of unregulated metals in land applied sewage biosolids are unlikely to exceed Ontario MOEE "Effects Based Limits" (MOEE 1997) developed for contaminated site clean-up of soil for agricultural use, however, a few of them (e.g., silver, antimony) may exceed the Ontario MOEE "Background Limits" (MOEE 1993). Thus, the unregulated metals are Group II contaminants requiring further research.

Recent concentration data for non-regulated metal concentrations in Ontario sewage biosolids were obtained in response to the WEAO (2001) recommendation (above) for further research concerning these metals. The recent evidence indicates no increase in regulated metal concentrations in Ontario sewage biosolids. There is good agreement among these and the previous 2001 data, with current levels at or near the concentrations reported in the 2001 report. It may be assumed, therefore, as was concluded previously, that loadings of unregulated metals in land applied sewage biosolids are unlikely to exceed Ontario MOEE "Effects Based Limits" developed for contaminated site cleanup of soil for agricultural use. This current review found that little new research has been conducted on the fate, transport and bioaccumulation of the unregulated metals in the terrestrial environment resulting from biosolids applications to soil, and this remains a knowledge gap. The WEAO (2001) conclusion (above) concerning these metals

remains valid and unchanged, and thus it is recommended that the unregulated metals be categorized as Group II contaminants.

The conclusions based on the U.S. study (ISCORS, 2003) and contained in the WEAO (2001) report regarding radionuclides are essentially the same, although their derivations are different. The U.S. conclusion was based on extensive sampling, analysis and risk assessment, whereas the WEAO (2001) conclusion that radionuclides are "Group I contaminants for which no further study is necessary at this time" was based on the facts that medically used radionuclides are short-lived and that Ontario sewer use by-laws prohibit discharge of long-lived radionuclides into municipal sewer systems. In the absence of any recent data that characterize radionuclide concentrations in Ontario or other Canadian biosolids, it is probable that the concentrations of radionuclides reported in the broad U.S. sludge survey, using mostly similar approaches, would be representative of the Canadian situation.

The results of the U.S. study would thus support the WEAO (2001) assumption of low radionuclide levels that are not a detriment for biosolids land application. It is recommended that radionuclides be categorized as Group I contaminants, as they were in the WEAO (2001) report.

3.14 Polyaromatic Hydrocarbons (PAHs)

PAHs are a product of carbon combustion, and enter the environment from volcanoes, forest fires, residential wood burning, and exhaust from automobiles and trucks (NRCC, 1983). Atmospheric deposition, and road oils and exhaust particulates are thus major routes to wastewater treatment via combined sewers. Food cooked at high temperatures (e.g., grilling or barbecuing) may also produce PAHs, which may then be discharged with dishwater. Health concerns related to the PAH and polychlorinated polyaromatic classes of compounds are their potential human carcinogenic properties.

As with certain other groups of contaminants reviewed herein, the PAHs and polychlorinated aromatic compounds have received considerable attention in past reviews (e.g. Canviro Consultants, 1988) and thus this section is intended to provide a more recent update on these compounds.

3.14.1 Occurrence

Concentrations of the PAHs in sludges are provided in Table 120. Based on the survey of Canadian sludges (XCG, 2007), these compounds have median concentrations typically lying in the range of 100 to 1500 ng/g TS. The simplest PAHs, naphthalene and phenanthrene, consisting of two and three fused benzene rings, respectively, have the highest median concentrations of the PAHs in the Canadian survey (XCG, 2007) at 2,700 (phenanthrene) and 1,500 (naphthalene) ng/g TS. While limited, the mean concentration data provided by Bright and Healey (2003) are similar to median values reported in the XCG (2007) study. The literature review of Harrison *et al*. (2006) demonstrated that the maximum concentrations of the PAHs could be higher than those

Table 120. Concentrations of Polyaromatic Hydrocarbons in Sludges

Compound	Concentration (ng/g TS dw)					
	19 Canadian sludges	Anaerobic digested biosolids	Sludge survey	Literature review	Anaerobic digested biosolids	Dewatered sludge[d]
Acenaphthene	nd - 3,000 (400)[a]			nd - 6,600		
Acenapthylene	nd – 3,400 (100)			3.6 - 300		
Anthracene	3 – 3,300 (200)			nd - 44,000	320	74
Phenanthrene	900 - 14,000 (2,700)			<10 - 44,000	1,730	166
Benzo(a)anthracene				nd - 99,000		
Chrysene				nd - 32,400		
Benzo(a)anthracene + Chrysene	170 – 36,000 (1,100)					
Benzo(b)fluoranthene + Benzo(k)fluoranthene	130 – 39,000 (700)			6 - 34,200		
Benzofluorene congeners				nd - 8,100		
Benzo(g,h.i)perylene	30 - 15,000 (300)			nd - 12,900		
Benzo(a)pyrene	50 - 25,000 (300)	310 $\pm$ 220[c]	661 (320)[b]		nd	
Benzopyrene congeners				nd - 24,700		
Dibenzo(ah)anthracene	nd - 5,100 (20)					
Dibenzoanthracene congeners				nd - 13,000		
Fluoranthene	250 - 27,000 (1,000)			nd - 60,000	950	166
Fluorene	nd - 3,300 (800)			<10 - 8,100		
Indeno(1,2,3-cd)pyrene	nd - 15,000 (200)			nd - 9,500		
Naphthalene	80 - 13,000 (1,500)			nd - 6,610,000	610	
Perylene				nd - 69,300		
Pyrene	260 - 24,000 (1,300)	1700 $\pm$ 840		10 - 37,100	740	169
2-methylnaphthylene			449 (200)		nd	
2,6-dimethylnaphthylene					915	
Methylnaphthalene isomers				nd - 136,000		
Methylphenanthrene isomers				nd - 37,400		

Continued

Table 120 (cont'd)

	Concentration (ng/g TS)					
19 Canadian sludges	Anaerobic digested sludge, 5 Vancouver WWTPs	Sludge survey	Literature review	Dewatered anaerobic digested biosolids	Dewatered sludge[d]	
Reference	XCG (2007)	Bright and Healey (2003)	EPA (2009a)	Harrison *et al*. (2006)	Kinney *et al*. (2008)	Kinney *et al*. (2006)

nd = not detected
[a] range (median)
[b] mean (median)
[c] mean ± standard deviation
[d] ng/g organic carbon (OC)

summarized by XCG (2007), with the upper range of naphthalene, methylnaphthalene isomers and benzo(a)anthracene at or above 100,000 ng/g TS. The U.S. EPA's TNSSS (EPA, 2009a) included only two PAHs on its list of target analytes. Median concentrations of benzo(a)pyrene and 2-methylnaphthlene were 302 and 200 ng/g TS, respectively. Concentrations of four PAHs reported by Kinney *et al*. (2006) in waste activated sludge and dewatered sludge were less than 200 ng/g organic carbon.

Concentrations of PAHs following biosolids treatment processes were provided by Kinney *et al*. (2006) and appear in Table 121. For the lower molecular weight PAHs anthracene and phenanthrene, composted and air dried biosolids have apparent lower concentrations than biosolids produced by heat drying or after anaerobic digestion. This trend did not follow through in the two higher molecular weight PAHs fluoranthene and pyrene, for which there was no discernible difference between composting, air drying and heat drying. The anaerobic digested sludge had the highest concentrations of the four PAHs examined. There are too few data in the publication of Kinney *et al.* (2006) to determine whether anaerobic digestion is the least effective biosolids treatment for reduction of PAHs.

Table 121. Concentrations of Polyaromatic Hydrocarbons following Biosolids Treatment Processes (Kinney *et al*., 2006)

Biosolids Process	Concentration (ng/g OC)			
	phenanthrene	anthracene	fluoranthene	pyrene
Heat drying	1,090	324	1,090	1,310
Compost	176 - 376	56 - 253	744 – 2,470	43 – 1,420
Air drying	535	359	1,150	1,110
Anaerobic digestion	5,430	1,000	2,980	2,320

OC = organic carbon

3.14.2 Fate and Transport in the Terrestrial Environment

The degree of water saturation which is a surrogate for dissolved oxygen availability, was determined to have more of an effect on the mineralization rate of ^{14}C-labled pyrene in a coarse sandy soil than did the sludge:soil ratio (Gejlsbjerg *et al*., 2001) (Table 122). The mineralization rate was similar to that observed for the biosolids alone at the high saturation level (80% of water holding capacity). At the low saturation level, (40% of water holding capacity), the mineralization rate was higher by almost an order of magnitude

The effect of soil types, including a coarse sandy soil, a sandy soil and a predominantly clay soil, on the mineralization of pyrene was also examined by Gejlsbjerg *et al*. (2001). The tests involved spiking the labelled pyrene in the soil, both with biosolids incorporated at a biosolids:soil mixture of 1:100, and without any biosolids (Table 123). There was no substantial difference in rates of mineralization of the pyrene between the different soils amended at a ratio of 1:100 biosolids:soil, or also between the soil sample without biosolids relative to those receiving the biosolids amendment.

Table 122. Effect of Biosolids Loading and Degree of Soil Water Saturation on Mineralization of Pyrene (Gejlsbjerg *et al*., 2001)

Sludge:soil ratio	Water Saturation	Initial conc. in test sludge-soil mixture ng/g DM	Mineralization after two months (% of added ^{14}C)
biosolids alone	not appl.	2,900	1.30 (0.94)[a]
1:20	40%	130	15.0 (1.10)
	80%	130	2.23 (0.24)
1:100	40%	28	12.5 (0.81)
	80%	28	1.52 (0.81)

[a] Mean (std. deviation), n = 4

Table 123. Effect of Soil Type on Mineralization of Pyrene (Gejlsbjerg *et al*., 2001)

Test Conditions	Initial Conc. In test mixture ng/g DM	Mineralization after two months (% of added ^{14} C)
1:100[b], Coarse sandy soil (in Jyndevad)	70	4.0 (0.21) [a]
1:100, Sandy soil (in Lundgaard)	70	2.2 (0.49)
1:100, clayey soil (in Askov)	70	4.8 (1.77)
Soil only (coarse sandy soil)	10	4.7 (0.11)

[a] Mean (std. deviation), n = 4 [b] Biosolids:sludge mixture

Concentrations of several PAHs in soils and earthworms are reported by Kinney *et al*. (2008), from both biosolids-amended soil and without biosolids amendment (Table 124). The biosolids-amended site received a single application on April 5, 2005 at a rate of 18 T/ha. In the site without the biosolids application, only fluoranthene was detected in one of the two soil samples collected. A number of PAHs were detected in the earthworms from the non-amended site in the two samples analyzed. No PAHs were detected in either soil or earthworm samples in the first sampling (May 19-05) that took place in the biosolids-amended site. In the second round of samples (Sep 21-05), several PAHs were detected in both soil and earthworm samples, but the PAHs identified in the earthworm samples differed from those detected in the soil samples. No clear trends emerge from the earthworm PAH data. Detectable concentrations of PAHs in worms were identified in both biosolids-amended and non-amended sites. PAH presence in both sites may result from sources other than biosolids, such as brush fires or vehicle exhausts.

Kinney *et al*. (2008) were unable to calculate any bioaccumulation factors for the PAHs due to the frequency of non-detectable concentrations or concentrations in soils that had no corresponding concentrations in earthworms, or vice versa.

Table 124. Concentrations of PAHs in Soil and Earthworm Samples (Kinney et al., 2008)

PAH	Concentration (ng/g DM)							
	Site 1 (without biosolids applic'n)				Site 2 (with biosolids applic'n on			
	June 6-05		Sep 29-05		May 19-05		Sep 21-05	
	Soil	Worm	Soil	Worm	Soil	Worm	Soil	Worm
naphthalene	ND[a]	ND	ND	15	ND	ND	ND	22
phenanthrene	ND	ND	ND	ND	ND	ND	6	ND
anthracene	ND	ND	ND	ND	ND	ND	ND	ND
1-methyl-naphthalene	ND	19	ND	7	ND	ND	ND	8
2,6-dimethyl-naphthalene	ND	ND	ND	3	ND	ND	ND	6
2-methyl-naphthalene	ND	19	ND	11	ND	ND	ND	11
benzo(a)-pyrene	ND	ND	ND	ND	ND	ND	10	ND
fluoranthene	ND	ND	23	ND	ND	ND	22	ND
pyrene	ND	ND	ND	ND	ND	ND	ND	ND

[a] analytical detection limits not specified

3.14.3 Section Summary

1. The upper range of naphthalene, methylnaphthalene isomers and benzo(a)anthracene in sludges and biosolids were at or above 100,000 ng/g TS dw in the literature review of Harrison *et al*. (2006), although a survey of Canadian sludges resulted in median concentrations typically lying in the range of 100 to 2,700 ng/g TS dw.
2. The simplest PAHs, naphthalene and phenanthrene, consisting of two and three fused benzene rings, respectively, have the highest median concentrations (e.g., 1,500 to 2,700 ng/g TS dw), but not the highest maximum levels, of all of the PAHs in the Canadian survey.
3. The fate of PAHs in the terrestrial environment is not well documented, often with only one representative compound (e.g., pyrene) tested.
4. A high degree of soil water saturation exhibited a detrimental effect on the mineralization of the one PAH (pyrene) tested.
5. Pyrene was mineralized in different soil types at a slow rate, with only 2-5% mineralization after two months.
6. There were no studies identified in this review that examined percolation of the compounds through soil, or mobilization in surface runoff, or uptake by plants.

Concentration data for PAHs in sludges are similar in this and the WEAO (2001) report. PAHs were considered to be organics of secondary importance in the WEAO (2001) report for the following reasons:

- In a synopsis of the properties, occurrence, fate and transfer of the principal organic contaminant groups found in sewage sludge and sludge amended soils Smith (1996) reported that PAHs occurred at 1,000 – 10,000 ng/g concentrations, were water soluble/volatile to lipophilic, with half-lives in soil ranging from weeks for the low

molecular weight/volatile compounds such as naphthalene and phenanthrene to 10 years for the high molecular weight lipophilic compounds such as benzo(a)pyrene. In addition, they sorb strongly to organic matter in soil, exhibit no leaching potential, little if any foliar absorption and are rapidly metabolized and not accumulated following ingestion by animals.

- PAHs were not included among the organics of concern identified by a Stakeholder Advisory Group consulted during [the 2001] report preparation.

Benzo(a)pyrene, however, was identified as a compound of concern by the screening methodology used by the US EPA during development of Reg. 503 (US EPA, 1993). Despite this concern there has not been a strong research focus on benzo(a)pyrene and although sparse, recent information provides no evidence for heightened concern.

There were no studies identified in this current review that examined percolation of the compounds through soil, or mobilization in surface runoff, or uptake by plants; however most of these concerns were addressed in the 2001 report, and thus the lack of recent information does not constitute a knowledge gap.

Thus, evidence in this current review and the WEAO (2001) report are in agreement, and indicate that PAHs, and particularly benzo(a)pyrene in land applied sewage sludges do not present significant human or environmental health risks. As a result, it is recommended that the contaminants remain as Group I contaminants.

3.15 Polychlorinated Polyaromatic Compounds

Polychlorinated biphenyls (PCBs) were widely used in a variety of products such as electrical transformer fluids, but their import, manufacture and sale in Canada was banned in 1977 (Health Canada, 2009d). Polychlorinated dibenzodioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) are not manufactured or used, but result from combustion of products consisting of chlorinated organics (e.g. polyvinyl chloride plastics) and as a by-product of pentachlorophenol production. Atmospheric deposition of these chlorinated substances is likely a major contributor in wastewater treatment.

In late December 1999, the U.S. EPA proposed a rule governing use of sewage sludge that contained a numeric limit of 300 parts per trillion (equivalent to 300 ng/g TS dw) of toxic equivalents of PCDDs, PCDFs and co-planar PCBs. Observed concentrations of the polychlorinated compounds in the 2001 U.S. National Sewage Sludge Survey were lower than in the previous survey in 1988. (U.S. EPA, 2003). Based on data from the 2001 National Sewage Sludge Survey, however, in 2003 the EPA Administrator decided not to regulate dioxins with a numeric limit. EPA determined that the dioxins in municipal sludge did not pose a significant health risk to human health or the environment (U.S. EPA, 2003).

As with certain other groups of contaminants reviewed herein, the polychlorinated polyaromatic compounds have received considerable attention in past reviews (e.g. Canviro Consultants, 1988) and thus this section is intended to provide a more recent update on these compounds.

3.15.1 Occurrence

Concentrations of PCBs, PCDDs and PCDFs in sludges are summarized in Table 125 in two different units of expression. Some reports list the PCDDs and PCDFs in terms of toxic equivalents (TEQ) of the 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD), the most toxic congener of this class of compounds. The isomer 2,3,7,8-tetrachlorodibenzofuran (2,3,7,8-TCDF) is considered the most toxic congener of that class of compounds. For the literature surveyed, the range and means of dioxins and furans expressed as TEQ reported from different countries appear to be very similar, with mean values in the range of 0.020 ng TEQ/g TS. Concentrations of the PCDDs and PCDFs as total congener concentrations were documented by XCG (2007), with mean values of the total congeners at least an order of magnitude higher than the TEQ-based concentrations, indicating that other congeners were present at higher concentrations than the 2,3,7,8-TCDD and 2,3,7,8-TCDF.

For the PCB data summarized by XCG (2007), the upper end of the concentration range, at 2,027 ng/g TS, is substantially higher than the maximum values reported in sludges from European countries. The mean concentration likewise is higher in the XCG (2007) report than for the sludges from Norway, Sweden and Germany as documented by Jaganyi (2007).

Concentrations of dioxins, furans and dioxin-like PCBs were categorized by the type of biosolids process and plant capacity, in a presentation to the Water Environment Association of Ontario (Kleywegt, 2006), as shown in Table 126. It was not clear from the data that the size of the treatment plant (i.e. population served) had any significant effect on the levels of the dioxins or furans, or dioxin-like PCBs in the treated biosolids or untreated sludge. The concentrations of these compounds were higher in the anaerobically digested sludge categories than in the aerobic or untreated sludge categories.

Table 125. Concentrations of Polychlorinated Polyaromatics in Biosolids and Sludges

Sludge Source	Concentration (ng TEQ/g TS)			Concentration (ng/g TS)			
	Polychlorinated Dibenzo-p-Dioxins and Furans (PCDD/Fs)			Total Polychlorinated Dibenzo-p-Dioxins (PCDD)	Total Polychlorinated Dibenzofurans (PCDFs)	Total Polychlorinated Biphenyls (PCBs)	
Denmark sludge (not specified)	0.0007 - 0.055 (0.021)[a]	0.010 - 0.034 (no mean)[a]					
Germany sludge (anaerobic digested)	0.0007 - 1.21 (0.020 - 0.040)	no range (0.019)					
Germany sludge (not specified)							154 - 340
Spain sludge (anaerobic digested)	no range (0.064)						
UK sludge (not specified)	0.009 - 0.192 (no mean)						
Austria (not specified)	0.008 - 0.038 (0.015)						
Sweden sludge (not specified)	0.00002 - 0.115 (0.020)	0.0057 - 0.115 (no mean)					0.6 - 232 (113)
Norway sludge (not specified)							17 - 100 (42)[a]
Canadian sludge (1995-1998)			0.004 – 0.12 (0.022)[a]	1.1 - 22 (4.1)[a]	0.07 – 4.2 (0.7)[a]	nd – 2,027 (345)[a]	
Reference	Jaganyi (2007)	Langenkamp *et al*. (2001)	XCG (2007)	XCG (2007)			Jaganyi (2007)

[a] range (mean) nd = not detected

Table 126. Concentrations of Dioxins, Furans and Dioxin-Like PCBs in Biosolids and Municipal Sludge (Kleywegt, 2006).

Biosolids Treatment	STP Size	ng/g DW (TEQ)	
		Dioxin and Furan	Dioxin, Furan and Dioxin-like polychlorinated biphenyls (DL-PCBs)
Aerobic	Small	6,000	7,800
	Medium	not applicable	not applicable
	Large	not applicable	not applicable
Anaerobic	Small	7,000	10,500
	Medium	7,000	10,700
	Large	8,300	13,900
Wastewater Sludge (no stabilization)	Small	4,200	7,600
	Medium	1,000	14,300
	Large	5,300	6,000

Concentrations of individual PCB congeners in biosolids were reported by Gibson *et al*. (2005). The data are summarized in Table 127. Individual congener concentrations ranged from non-detectable to 11.1 ng/g TS dw. The total sum of the individual congeners was 85.5 ng/g TS dw. This total concentration is similar to values reported in Table 125 by Jaganyi (2007).

Table 127. Concentrations of Speciated PCB Congeners in Biosolids (Gibson *et al*., 2005).

PCB congener	Mesophilic Anaerobic Digested Biosolids (ng/g DW)	PCB congener	Mesophilic Anaerobic Digested Biosolids (ng/g DW)
PCB52	6.14	PCB138	10.9
PCB44	3.81	PCB183	1.59
PCB61	1.66	PCB180	6.11
PCB66	9.52	PCB188	nd
PCB101	6.15	PCB170	3.42
PCB99	2.47	PCB201	1.81
PCB110	5.49	PCB194	1.85
PCB82	nd	PCB208	0.288
PCB118	5.53	PCB205	nd
PCB151	1.70	PCB206	nd
PCB149	5.72	PCB209	0.287
PCB153	11.1	Total	85.5

Concentration data for dioxins/furans and PCBs in sludges are similar in this review and the WEAO (2001) report.

3.15.2 Fate and Transport in the Terrestrial Environment

Concentrations of total dioxin equivalents in Ontario soils receiving biosolids and without biosolids amendment have been documented by the Ontario Ministry of Agriculture, Food and Rural Affairs (OMAFRA, 2009), with the results appearing in Table 128. Concentrations were all very similar, at 1.5-1.6 ng/kg of soil, with the exception of the two samples from Oakville, where concentrations ranged from 2.6-3.8 ng/kg.

Table 128. Concentrations of Total Dioxin Equivalents in Ontario Soils with and without Biosolids Treatment (OMAFRA, 2009)

Location	Total Dioxin Equivalent Concentration (ng/kg soil)	
	Biosolids-treated	Non-treated
Smithville	1.6	1.5
Whitby	1.5	1.6
Port Perry	1.6	1.5
Ayr	1.5	1.5
Oakville #1	2.6	2.9
Oakville #2	3.5	3.8
Owen Sound	1.6	1.5
Southampton	1.6	1.5
Hanover #1	1.5	1.5
Hanover #2	1.6	1.5

Concentrations of individual PCB congeners in different types of Swedish soils, resulting from biosolids amendments, were monitored by Matscheko *et al*. (2002). The results are summarized in Table 129. Concentrations of the individual PCB congeners increased in the biosolids-amended plots by a factor of 1 to 10 times relative to the control plots, although the more typical factor was in the range of 2 to 3 times the control plot value.

Bioaccumulation factors (BAFs) for the PCB congeners by earthworms in the study by Matscheko *et al*. (2002) are provided in Table 130. The data indicated that the lighter PCB congeners were concentrated by the earthworms to a greater extent than was the more highly chlorinated congener PCB169. For the lighter congeners, higher BAFs were noted in the biosolids-amended soils compared to the control plots. The highest BAF values of 17 and 18 were observed for the congener PCB149 in the medium clay soil. PCBs 101 and 110 were also observed to bioaccumulate in the earthworms in the Lamna (slightly clay soil) and Björketorp non-classified soil.

Table 129. PCBs, Dioxins and Furans in Biosolids-amended and Control Soil Plots (Matscheko *et al*., 2002)

Study Sites	Conc. In soil after sludge application to soil, ng/g DW										
	Application Test	PCB 101	PCB 110	PCB 118	PCB 149	PCB 153	PCB 138	PCB 126	PCB 169	Poly-chlorinated Dibenzo-p-Dioxins (PCDDs)	Poly-chlorinated Dibenzo-Furans (PCDFs)
Igelösa [I] (Medium Clay soil) - Sludge application date: 1991-1997, applied every 4th year - Date of sampling: April 2000	Control	0.13	0.13	0.081	0.18	0.39	0.43	0.002	0.0008	0.059	0.05
	I1 1	0.19	0.18	0.12	0.22	0.45	0.47	0.0022	0.001	0.29	0.062
	I2 3	0.34	0.31	0.2	0.43	0.82	0.85	0.0032	0.0011	0.13	0.071
Petersborg [P] (Light clay soil) - Sludge application date: 1991-1997, applied every 4th year. - Date of sampling: April 2000	Control	0.098	0.092	0.057	0.14	0.29	0.33	0.0016	0.0005	0.028	0.038
	P1 1	0.19	0.18	0.1	0.32	0.65	0.76	0.0022	0.0006	0.048	0.046
	P2 3	0.24	0.22	0.11	0.41	0.77	0.91	0.0022	0.0006	0.047	0.044
Lamna [L] (Slightly clayey soils) - Sludge application date: 1998 -Date of sampling: Spring: April 3 2000; Autumn: September 2000	Control - Spring	0.067	0.056	0.025	0.07	0.13	0.12	0.0008	0.0005	0.016	0.014
	LS_{spring} -2 3	0.07	0.058	0.03	0.081	0.15	0.14	0.0008	0.0006	0.02	0.018
	Control - autumn	0.058	0.049	0.021	0.064	0.13	0.12	0.0008	0.0006	0.017	0.018
	LS_{autumn} 2 3	0.075	0.062	0.03	0.08	0.15	0.15	0.0009	0.0006	0.018	0.019
Björketorp [B] (Not classified soil) - 1978-1982. - 25 tonnes dry matter applied/ha in total - Sampling date: September 2000.	Control	0.084	0.078	0.042	0.11	0.2	0.21	0.0012	0.0006	0.04	0.042
	BS (applied sludge)	0.41	0.44	0.23	0.52	1	1.2	0.0025	0.0008	7.9	0.34

Table 130. PCB Bioaccumulation Factors for Earthworms in Biosolids-amended and Control Soil Plots (Matscheko *et al.*, 2002)

Study Sites	Bioaccumulation Factor in Earthworms								
	Application Test	PCB 101	PCB 110	PCB 118	PCB 126	PCB 138	PCB 149	PCB 153	PCB 169
Igelösa [I] (Medium Clay soil) - Sludge application date: 1991-1997, applied every 4th year - Date of sampling: April 2000	Control	7	8	3	2	5	10	3	1.5
	I1 1	9	12	3	3	9	18	5	1
	I2 3	7	8	3	3	9	17	5	1
Petersborg [P] (Light clay soil) - Sludge application date: 1991-1997, applied every 4th year. - Date of sampling: April 2000	Control	4	5	3	3	5	7	5	1
	P1 1	4	4	3	2	4	6	4	1
	P2 3	4	3	3	3	4	6	4	1
Lamna [L] (Slightly clayey soils) - Sludge application date: 1998 -Date of sampling: Spring: April 3 2000; Autumn: September 2000	Control - Spring	4	4	3	2	3	5	3	0.9
	LS_{spring} -2 3	11	10	6	2	4	10	6	1
	Control - autumn	6	7	6	2	3	5	3	1
	LS_{autumn} 2 3	7	8	7	3	4	10	6	0.8
Björketorp [B] (Not classified soil) - 1978-1982. - 25 tonnes dry matter applied/ha in total - Sampling date: September 2000.	Control	10	11	8	2	5	7	5	1
	BS (applied sludge)	2	1	0.9	0.9	1	3	1	0.6

3.15.3 Section Summary

1. For the literature surveyed, the range and means of the PCDDs and PCDFs reported from different countries appear to be very similar, with mean values in the range of 0.020 ng TEQ/g TS dw.
2. Concentrations of total PCBs listed in Canadian sludge samples appeared to be higher than corresponding sludge samples from Europe.
3. Concentrations of PCBs in soils may be elevated by 2 to 10 times the background concentrations as a result of biosolids amendment.
4. Bioaccumulation factors for one PCB congener (PCB149) in earthworms on control and biosolids-amended soils generally ranged from 3 to 7, but for PCB149 in one biosolids amended clay soil, they ranged up to 18.
5. Fate, transport and bioaccumulation of these compounds through the terrestrial environment are not well documented.

Evidence to date indicates that PCBs in land-applied sewage sludge have not been associated with significant human or environmental health hazards. Moreover, given the consistently low (<3000 ng/g TS dw) concentrations of total PCBs in Canadian sludges and the fact that use of these compounds has been banned in Canada since the mid-1970s, there is no reason to believe that they will become significant hazards in the future.

Dioxins and furans were identified as organics of concern in land-applied sludge, and they received special attention in the WEAO (2001) report. Although there were no Ontario dioxin/furan guidelines related to sludge use on agricultural land, it was calculated that, at the maximum (sludge) application rate of 8 dry tonnes/hectare/5 years, and assuming no degradation of dioxins and furans in soil, biosolids containing median concentrations of dioxins and furans could be applied repeatedly to the same field 66 times or (for) 330 years before the “Effects Based” soil concentration would be reached (see Table 9.6, WEAO, 2001). The WEAO (2001) report concluded “Thus they are Group I contaminants for which no further study is necessary, at this time.”

This conclusion was supported by the EPA (2003) final decision not to regulate dioxins in land-applied sewage sludge. After five years of study, including outside peer review, the Agency determined that dioxins from sludge did not pose a significant risk to human health or the environment. EPA (2003) considered that the most highly exposed people, theoretically, were those people who applied sewage sludge as a fertilizer to their crops and animal feed, and then consumed their own crops and meat products over their entire lifetimes. EPA's analysis showed that even for this theoretical population, only 0.003 new cases of cancer could be expected each year or only 0.22 new cases of cancer over a span of 70 years. The risk to people in the general population of new cancer cases resulting from sewage sludge containing dioxin was even smaller due to lower exposures to dioxin in land-applied sewage sludge than the highly exposed farm family which EPA modeled for their assessment.

Based on the above discussion, and on the absence of new evidence of adverse effects to the terrestrial environment from these compounds as a result of application of biosolids to land, it is

recommended that the polychlorinated dioxins, furans and PCBs remain as Group I contaminants, as was recommended in the WEAO (2001) report.

3.16 PATHOGENIC MICROORGANISMS

In response to citizen concerns regarding the safety of applying biosolids to land, the U.S. National Academy of Sciences issued a report in 2002 addressing the human health aspects of the practice (U.S. NAS, 2002). In their study, the NAS committee identified pathogens of concern in biosolids. The list of pathogens is replicated in Table 131.

Table 131. Microbial Contaminants of Concern to Human Health in Biosolids (U.S. NAS, 2002)

Bacterial Pathogens	Virus Diseases	Helminth Worms and Diseases
Classic		
Salmonella	Poliovirus	*Ascaris lumbricoides*
Shigella	Coxsackievirus	*Ascaris suum*
Enteropathogenic *E. coli*	Echovirus	*Trichuris trichiura A*
Yersinia enterocolitica	Hepatitis A virus	*Toxocara canis*
Campylobacter jejuni	Rotavirus	*Taenia saginata*
Vibrio cholera	Norwalk agents	*Taenia solium*
Leptospira	Reovirus	*Necator americanus*
		Hymenolepis nana
Emerging		
E. coli 0157:H7	H5N1 Avian influenza*	
Listeria	H5N2 Avian influenza*	
Helicobacter	H1N1 Swine influenza*	
Mycobacteria		
Aeromonas		
Legionella		
Burkholderia		
Endotoxins		
Antibiotic resistance		

* not included in U.S. NAS (2002) study

3.16.1 Occurrence

Concentrations of bacteria in liquid municipal biosolids were determined by Akhand et al. (2008) for experiments investigating impacts of tile drainage. Concentrations in biosolids from three application periods are provided in Table 132. *C. perfringens* was present at slightly higher

concentrations than the total coliforms. Total coliforms were lower in the aerobically digested sludge than in the anaerobically digested sludges.

Table 132. Concentrations of Indicator Bacteria in Liquid Municipal Biosolids, Southwestern Ontario (Akhand *et al*., 2008)

Application Period	Biosolids Process	Total Solids (g TS/L)	Bacterial Concentration (CFU/ 100 mL)		
			E. coli	Total coliforms	*C. perfringens*
Spring, 2003	Aerobic digestion	30 (2) [a]	0.122×10^6 (0.0102×10^6)	0.730×10^6 (0.0636×10^6)	7.275×10^6 (1.374×10^6)
Fall, 2003	Anaerobic digestion	50 (3)	0.250×10^6	3.200×10^6 (1.808×10^6)	13.20×10^6
Spring, 2003	Anaerobic digestion	20 (3)	0.0465×10^6 (0.0255×10^6)	3.700×10^6 (2.186×10^6)	7.000×10^6

[a] Mean (standard deviation, n=3)

Inactivation of target pathogens by mesophilic anaerobic digestion of municipal sludge was investigated at laboratory scale in spiked organism tests by Horan *et al.* (2004). A properly operated digester was found to be able to reduce densities of *E. coli, Salmonella seftenberg*, and *Listeria monocytogenes* by greater than 99% in combined primary and secondary digestion. Results are provided in Table 133. *Campylobacter jejuni* was apparently unaffected by the mesophilic anaerobic primary digestion process, although some minor additional reduction was observed as a result of a 14 day storage time in the unheated secondary digester.

Table 133. Reduction of Pathogenic Bacteria by Mesophilic Digestion (Horan *et al.*, 2004)

Organism	Initial Densities (in unspiked sludge) No. cells/g TS dw	Reduction (log) of spiked sludge (spiked at 10^6 to 10^7 cells per g TS dw)		
		Primary Digester	Secondary Digester	Combined
E. coli	5.0×10^5-1.3×10^6	1.7	1.7	3.36
S. seftenberg	20-40	2.2	not reported	min 2.23
L. monocytogenes	60-80	2.2	2.1	4.33
C. jejuni	Nd	no die-off observed	0.36	min 0.36

Nd non detected

Frequency of detection of pathogens in primary sludge and liquid biosolids, dewatered biosolids and the dewatered biosolids stored for two to three days at 30°C was documented by Flemming *et al.* (2009a) based on culturing techniques. The frequency of detection of pathogenic bacteria in the different stages of the biosolids treatment process is summarized in Table 134, for pooled data from six wastewater treatment plants that employed mesophilic anaerobic digestion.

Table 134. Frequency of Detection of Pathogenic Bacteria in Stages of Biosolids Treatment (Flemming *et al.*, 2009a)

Organism	Percent of Positive Samples (%)				
	Raw sludge	Liquid Biosolids	Dewatered Biosolids	Stored Biosolids	All Samples
Listeria monocytogenes	72.2	85.7	47.6	16.7	56.4
Salmonella spp.	94.4	100	57.1	83.3	83.3
Yersinia enterocolitica	33.3	28.6	23.8	22.2	26.9
Campylobacter spp.	0	0	0	0	0
Clostridium perfringens	100	100	100	100	100
No. of samples	18	21	21	18	78

In all samples tested, *Campylobacter* species were below detection (i.e., <2 MPN/g TS dw), while *C. perfingens* was detected in all samples. Both *Listeria* spp. and *Salmonella* spp. were present in a majority of the samples of raw, primary sludge and the liquid anerobically digested biosolids (70 – 100%). The two microorganisms were detected less frequently following dewatering of the liquid biosolids. Higher frequencies of the *Salmonella* only (not *L. monocytogenes*) were then observed following two to three days of storage at 30°C, with the *Salmonella* detected in more samples (83%) while the *L. monocytogenes* declined during storage (17%). *Yersinia enterocolitica* was detected in all stages of the biosolids treatment at a low frequency (approximately 20 to 30% of samples) (Flemming *et al.*, 2009a).

Relative changes in these microorganisms' densities between the different stages are quantified in Table 135. Non-detected values were substituted with the limit of detection, making these conservative estimates.

Table 135. Reductions and Increases of Microbes at Stages of the Biosolids Treatment Process showing averaged results from six discrete WWTPs (Flemming *et al.*, 2009a)

Organism	Average $\log_{10}$ change ± std. dev[c] (n=6)		
	Reduction after digestion	Increase after dewatering	Increase after storage
E. coli	1.7 ± 0.9	-0.03 ± 0.7[b]	1.1 ± 0.9
Fecal coliforms	1.8 ± 0.7	-0.02 ± 0.7	0.9 ± 0.8
Clostridium perfringens	-0.02 ± 0.2[a]	-0.4 ± 0.2	-0.2 ± 0.6[b]
Enterococci	1.3 ± 0.8	0.4 ± 0.4	0.3 ± 0.7
Listeria monocytogenes	1.6 ± 1.2	0.9 ± 0.4	0.3 ± 0.4
Salmonella spp.	0.6 ± 1.9	0.1 ± 0.5	1.5 ± 1.5
Yersinia enterocolitica	0.1 ± 1.0	0.9 ± 0.6	0.2 ± 0.5

[a] a negative reduction represents an increase across this process
[b] a negative increase represents a reduction across this process
[c] conservative estimates: non-detected values were substituted with limit of detection for statistical purposes

The data in Table 135 reveal greater than one log reductions in *E. coli*, fecal coliforms, *Enterococcus* species and *L. monocytogenes* due to the mesophilic digestion process. Only *C.*

perfringens exhibited a minor increase through the digestion process. When the liquid biosolids were dewatered, *Salmonella* spp., *Enterococcus* spp., *L. monocytogenes* and *Y. enterocolitica* increased in density by less than one log, which was considered to be a minor increase given the variability in the data. Storage at 30°C for two to three days resulted in an increase the density of most pathogens, with *E. coli*, fecal coliforms and *Salmonella* spp. increasing by one or more logs. Only *C. perfringens* displayed a slight decline in density as a result of the storage process.

Concentrations of *Listeria* spp. in biosolids and sludges in France were investigated by Paillard *et al.* (2005). The predominant species was *L. monocytogenes*. The concentrations of all *Listeria* spp. in the raw sludges prior to composting or lime stabilization were in the range of 100 – 1000 MPN/g TS dw. Lime treatment or composting was able to reduce significantly the density of all *Listeria* spp. In a final compost product, the density of all *Listeria* spp. was less than 5 MPN/g TS dw. Paillard *et al*. (2005) could not conclude definitely one way or another whether *Listeria* spp. could be used as an indicator of other fecal bacteria activity. They also concluded that digesters operating at retention times of 12 days or greater at 35 °C would achieve the required microbial reductions for land application of biosolids.

The reductions in a series of indicator microbes by composting dewatered secondary sludge from a rural wastewater treatment plant in France was reported by Pourcher *et al*. (2005). The ratio of sludge cake (15 % TS dw) to straw (85 % dry matter) was 1:0.17 on a wet weight basis. Initial concentrations of microbes in the sludge cake and wheat straw are found in Table 136.

Table 136. Concentration Ranges of Microbes in Sludge Cake and Wheat Straw used for Composting (Pourcher *et al.*, 2005).

Bacteria	Concentration in Compost Feed Materials (MPN or cells/g TS dw sludge; MPN or cells/g DM straw)		Results
	Sludge Cake	Wheat straw	
E. coli	4.4E05-1.1E06	<5	4 $\log_{10}$ reduction after 7 months
Enterococci	7.2E05-2.6E06	<5	4 $\log_{10}$ reduction after 7 months
C. perfringens	4.5E06-1.9E07	<23	3 $\log_{10}$ reduction after 4 months; no further reduction
L. monocytogenes	3.8-380	<0.2	not detected after 7 months
Salmonella spp.	1.2-3.2	<0.2	not detected after 2 months
Enteroviruses	15-80 MPNCU*	<0.7 MPNCU	not detected after 1 month

*MPNCU = most probable number of colony units

After one month of composting, when the pile was turned, infectious enteroviruses were not detected. *Salmonella* spp. were not detected after two months of composting. After seven months

of composting (maturation of the pile), the *E. coli* and enterococci were reduced by approximately 4 $\log_{10}$. *L. monocytogenes* was not detected at the end of the composting cycle (7 months), while *C. perfringens* declined by approximately 3 log after 4 months and then remained at a constant level. Pourcher *et al*. (2005) concluded that the composting technique resulted in a significant but not complete inactivation of enteric microbes.

Application of molecular techniques for following pathogenic microorganisms during biosolids treatment processes was described by Novinscak *et al.* (2008). Denaturing gradient gel electrophoresis (DGGE) was used to follow the change in the dominance of different bacterial species in composting biosolids at different stage of the composting process. The researchers suggested that knowledge of bacterial groups together with their presence and function in compost, could be used to more completely understand the composting process. Novinscak *et al.* (2008) also examined quantitative polymerase chain reaction (qPCR) to determine that the number of *Salmonella* species in biosolids declined substantially over a composting time of 24 months.

Concentrations of heterotrophic plate count (HPC) and total coliform bacteria and coliphage virus in U.S Class B biosolids samples (stabilization process information not provided) were enumerated by Tanner *et al.* (2008). HPC counts were generally two to three orders of magnitude higher than the total coliform counts (Table 137). With the exception of the biosolids sample from Houston, TX, concentrations of the microbes within each classification were similar. The lower solids concentration in the Houston biosolids resulted in lower concentrations of all the microbes.

Table 137. Concentrations of Pathogen Indicators in U.S. Biosolids (Tanner *et al.* 2008)

General location	Total Solids (%)	Conc'n (cfu/g TS dw)		Conc'n (pfu/g TS dw)
		HPC bacteria	Total coliforms	Coliphage
Laughlin, NV	21	6.1E+08	9.7E+05	assay not completed
Sacramento, CA	20	5.4E+09	4.3E+08	assay not completed
Seattle, WA	16	2.6E+07	1.4E+05	8.7E+03
Yakima, WA	20	1.7E+10	4.6E+05	2.8E+03
Chicago, IL	20	1.4E+08	1.5E+06	1.0E+03
Tucson, AZ	8	4.0E+08	2.8E+05	1.7E+03
Houston, TX	2	5.2E+06	4.1E+01	7.0E+00

cfu = colony-forming units pfu – plaque-forming units

Dr. Pepper's research group in Arizona (Rusin *et al.* 2003) reported results of testing of biosolids and bioaerosols from 15 sites across the U.S. for the pathogen *Staphylococcus aureus*. Although the pathogen was detected in some raw sludge samples, it was not detected in any treated biosolids or biosolids aerosols, leading the authors to conclude that biosolids or biosolids aerosols are not a likely exposure route of *S. aureus* to humans.

While no published data on *Helicobacter* occurrence in biosolids was identified in this review, Flemming (2009b) identified that work is currently being done by Agriculture Canada in Ottawa on *Helicobacter* in manure and biosolids.

The presence and reduction in parasites in biosolids have also been studied. The ability of four biosolids treatment processes to inactivate eggs of the helminth *Ascaris suum* was investigated by Paulsrud *et al.* (2004). The four processes (thermophilic aerobic pretreatment, pre-pasteurization, thermal vacuum drying and lime treatment) are allowed for use in Norway to sanitize the biosolids prior to land application. A requirement is that the processes result in no viable helminth ova. Following 45 minutes of detention at 61 to 62.5°C in a full-scale thermophilic aerobic pretreatment stage prior to mesophilic anaerobic digestion, no viable eggs of *A. suum* were detected. Pre-pasteurization involves increasing the sludge temperature to 65-66.5°C for a period of time. Paulsrud *et al.* (2004) determined that *A. suum* ova could be inactivated in as little as 15 minutes with pre-pasteurization, although a detention time of 30 minutes is more common recommended. A process involving heat and lime treatment of sludge in a membrane filter press, termed thermal vacuum drying, involves raising the temperature of the sludge/lime mixture to 80 to 85°C, followed by application of vacuum and pressing to remove moisture. No viable *A. suum* ova were observed after a thermal vacuum drying cycle time of 50-90 minutes. Lastly, the full-scale test involving lime treatment at 50-51.5°C was not successful in inactivating the helminths ova, which the researchers attributed to the inserted test bag containing the eggs failing to rise above a neutral pH range of 7.6-7.7. Based on follow-up laboratory studies, Paulsrud *et al.* (2004) recommended that addition of lime to achieve a pH of 12.4-12.5 for two hours at 55°C for complete inactivation of the *A. suum* ova.

Chauret *et al*. (1999) researched the effect of a full-scale mesophilic anaerobic digester in Ottawa, ON, Canada on pathogen reduction. The estimated retention time at 36 °C was 20 days. Pertinent results from this investigation are summarized in Table 138.

Table 138. Arithmetic Mean Concentrations of Pathogens in Feed Sludge and Anaerobically Digested Biosolids Cake (Chauret et al., 1999).

Pathogen description	Mean concentration (n=10) organisms /100 g TS wet weight		Log_{10} reduction	Statistical significance
	Mixed sludge feed	Digested biosolids cake[a]		
Cryptosporidium oocysts	5.29×10^2	2.65×10^2	0.30	NSSD[b] (P=0.623)
Giardia cysts	4.41×10^2	1.28×10^3	NR[d]	NSSD (P>0.05)
Total coliforms	1.31×10^{10}	5.85×10^9	0.35	SSD[c] (P=0.021)
Fecal coliforms	1.59×10^9	4.41×10^7	1.56	SSD (P<0.001)
Enterococcus spp.	3.88×10^7	9.81×10^7	NR	NSSD (P0.076)
Clostridium perfringens	1.68×10^7	1.37×10^8	NR	NSSD (P>0.05)
Total heterotrophic bacteria	5.04×10^{11}	6.97×10^9	1.86	SSD (P<0.001)
Somatic coliphages	1.74×10^6	1.41×10^6	0.09	NSSD (P=0.645)

[a] Average total solids content of cake biosolids was 32% TS dw.
[b] No statistically significant difference (probability of no difference, P).
[c] Statistically significant difference (probability of no difference, P).
[d] No reduction.

Statistically significant reductions of total and fecal coliforms, and total heterotrophic bacteria were observed. There were no significant reductions of the total microscopic counts of parasitic cysts or oocysts by the mesophilic digestion process. The method used for enumerating the cysts and oocysts at the time of publication (1999), however, did not differentiate between viable and non-viable cysts/oocysts. As well, there were no significant reductions of the somatic coliphages, or the bacteria *Enterococcus* spp. or *Clostridium perfringens*. The relative persistence of the protozoa through the digestion process was noted by Chauret *et al*. (1999).

The fate of a number of types of pathogens in simulated lime treatment of biosolids was investigated at bench-scale by Bean *et al*., (2007) by raising the pH of an inoculated aqueous lime suspension to pH 12 for 2 hours, followed by a reduction to pH 11.5 for the duration of the test (72 hours), representative of Class B biosolids stabilization procedures. The equivalent lime dosage was 80 g/kg (wet or dry basis was not specified). After two hours at pH 12, fecal coliform and *Salmonella* were reduced by 7 $\log_{10}$ to non-detectable levels. The test viruses, adenovirus type 5, bacteriophage MS-2 and rotavirus, after the two hour period at pH 12 were reduced to non-detectable levels, representing a 4 $\log_{10}$ reduction. Both the ova of *Ascaris lumbricoides* and oocysts of *Cryptosporidium parvum* were viable after 72 hours of the simulated liming process, while the oocysts of *Giardia lamblia* did not appear to be viable. Finally Bean *et al* (2007) conducted infectivity assays for *Cryptosporidium* oocysts and *Giardia* cysts in neonatal mice and gerbils, respectively. In the case of *Cryptosporidium* a 24 h lime treatment of oocysts in solution (not in sludge) did not inactivate the oocysts but rather increased infectivity four fold. *Giardia* cysts in lime solution were infective at 24 h, but were inactivated after 48 hr, while cysts in sludge were completely inactivated, i.e., resulted in no infectivity, after 24 hr after lime treatment.

Bean *et al*. (2007) concluded that, due to greater prevalence and potential for infectivity, *C. parvum* was a better indicator of the effectiveness of the biosolids liming process than *A. lumbricoides*, and that MS-2 phage might provide a cost-effective indicator for human viruses in biosolids. They also suggested that additional research on the survival of enteric viruses in sludges and biosolids due to association with the particles following lime treatment was warranted. Molloy *et al*. (2006) also emphasized that *A. lumbricoides* was rarely detected in biosolids, and so was a poor choice as the indicator helminths, whereas protozoa such as *C. parvum* are not addressed in biosolids regulations. However, recovery of oocysts from sewage biosolids is typically very poor, ranging from 5 to 40% (McCuin and Clancy, 2005; Molloy *et al*., 2006). Development of an efficient and successful method for assaying *C. parvum* in biosolids appears to be a research gap.

Graczyk *et al*. (2007) examined enteric pathogens in various “dewatered and biologically stabilized” wastewater sludges from four wastewater treatment plants in Ireland. It was not clear whether the stabilization procedure was considered to be the dewatered waste activated sludge, or whether an additional stabilization process such as aerobic digestion was applied. Concentrations of the pathogens examined are provided in Table 139. Of interest was the reporting of two human-virulent microsporidia (*Encephalitozoon intestinalis* and *Enterocytozoon bieneusi*), which were not identified in other publications in this review. Concentrations of the *Encephalitozoon intestinalis* were only documented in two of the plants, and the concentrations of the two microsporidia were an order of magnitude lower than the *Cryptosporidium* or *Giardia* cysts.

Graczyk *et al*. (2007) noted that the pathogens were overwhelmingly viable, with only about 1% at most being non-viable organisms.

Table 139. Concentrations of Pathogens in Dewatered Biologically Stabilized Sludges from Ireland (adapted from Graczyk et al., 2007)

Pathogen	Median Concentration (cells/kg of sludge)[a]	Mean[b] Concentration (cells/kg of sludge)[a]	Concentration Range (cells/kg of sludge)[a]
Cryptosporidium parvum/ C. hominis	35	45	0 – 110 (n = 4)
Giardia lamblia	24	41	3 – 114 (n = 4)
Enterocytozoon bieneusi	9	13	0 – 33 (n = 4)
Encephalitozoon intestinalis	4	4	3 – 5 (n = 2)

[a] Weight basis wet or dry not specified
[b] non-detects were reported as zero and were used in as zero in calculation of means.

No published data on either the occurrence of the H1N1 (Swine Influenza) virus in biosolids or in soils amended with biosolids were identified in this literature review. The Alexandria, VA Sanitation Authority in March of 2009 (Alexandria Sanitation Authority, 2009) issued a news release stating that it was most unlikely the virus would survive the 30-day detention in the Authority's anaerobic digester. The news release suggests that 3 days of digestion time are sufficient to reduce virus levels to below detectable levels, although no specifics were offered. The digested biosolids at the Alexandria facility are then subjected to pasteurization, which would further reduce any surviving viruses. In addition two studies investigated the pathogenic avian (bird) influenza viruses, H5N1 and H5N2 (Lucio-Forster *et al*., 2006; Rice *et al*., 2007) in wastewater, including biosolids. The conclusions from these studies were that the viruses would be unlikely to survive wastewater and further biosolids treatment.

Gerba (2009) suggests that research into the occurrence of adenoviruses in biosolids is required as these viruses may occur in greater concentrations in biosolids than other enteric viruses. He also indicates that in general better analytical methods are needed for the recovery of viruses from biosolids.

Hinckley *et al.*, (2008) used laboratory-scale reactors to evaluate the fate of a prion (designated PrP^{TSE}) during both activated sludge and mesophilic anaerobic digestion. Anaerobic digestion was simulated by incubating the prion-dosed anaerobic sludge and waste activated sludge mix for 10 and 20 days at 37^{o}C to mimic the full-scale plant in Madison, WI. Those authors noted that although a substantial decline in detectable prion was observed, a "significant fraction" of the dosed PrP^{TSE} survived both the 10 and 20 day anaerobic sludge digestion trials, based on infectivity assays using Syrian hamsters. Hinckley *et al.* (2008) suggested the observed reduction in detectable prion could be attributed to either stronger sorption to the digester solids during the incubation period, or to microbial degradation. Supplemental studies involving inactivation of the anaerobic microbes prior to incubation with the prion resulted in higher levels of detectable prion than in non-inactivated samples, indicating that microbial degradation was an observable removal mechanism. Hinckley *et al.* (2008) observed that the risk of entry of human prions to

wastewater treatment facilities was “exceedingly small”, as was the risk from ingesting them with biosolids-amended soil. Lastly, those authors noted that there is no published information on the detection or fate of human prions in wastewater treatment, and that appropriate analytical detection methods for prions in environmental matrices need to be developed. Both areas can be considered knowledge gaps.

The fate of prions in soil (not from a biosolids source) was discussed by Cooke *et al.* (2007). Soil properties such as pH and cation exchange capacity appeared to affect the binding ability of the prion in the soils. Electrostatic and polar forces were proposed as the mechanisms binding prions to the soil components. The prion was more readily extracted from the soil when the pH was more acidic (e.g., 4.73 in one soil tested, 6.98 in another). A soil higher in sand and clay had greater binding capacity for the prion than did a soil higher in sand and silt. Cooke *et al*. (2007) hypothesized that the presence of cations may exert a stronger binding capacity for the prions. Iron oxides and dissolved organic matter were also proposed as possible binding media for prions. Although there is a lack of evidence to date that prions are present in biosolids, Gerba (2009) has indicated that the removal of infectious prions by wastewater treatment and their survival after being applied to land in biosolids is a research gap that needs to be addressed.

The ability of montmorillonite, a clay mineral found in many soils, was shown to strongly, selectively and irreversibly bind a recombinant prion by Rigou *et al.* (2006), thus preventing washing through the soil column or contaminating groundwater, according to those authors. Based on observation of declining prion concentrations in the soil tests, Rigou *et al*. (2006) suggested that soil microbes may be involved in degradation of the prion.

3.16.2 Microbial Regrowth in Biosolids

The potential for regrowth of fecal coliforms in dewatered biosolids was the focus of a recent Technical Practice Update (TPU) prepared by the Water Environment Federation (WEF, 2008). It comprised a significant review of the published information on the fecal coliform “sudden increase” or regrowth in dewatered biosolids. The review noted that the phenomenon was most frequently observed with combined factors of anaerobic digestion followed by high solids centrifugation to produce biosolids cake concentrations of 25 to 35% solids.

The TPU authors postulated that during the anaerobic digestion process, the fecal coliform bacteria entered a state in which they were viable but non-culturable, thus seemingly at low acceptable concentrations based on culturing analyses (WEF, 2008). Tests with filtered centrate from a sterilized centrifuge revealed that, upon centrifugation, a biochemical signal or agent was released that caused the non-culturable fecal coliforms to once again become culturable. Use of quantitative polymerase-chain reaction testing demonstrated that a large pool of non-culturable *E. coli* could exist after anaerobic digestion, with higher populations following thermophilic digestion. After centrifugation these non-culturable *E. coli* were “re-activated” by the biochemical signal, fostering their immediate culturability. Conditions in the anaerobic biosolids cake are also favourable for continued “regrowth” of the bacteria after several hours and days.

The potential for human infection due to regrowth of *Salmonella* in biosolids was discussed by Pepper *et al.* (2008). Regrowth occurs when biosolids (Class A and B[4]) are maintained under saturated anaerobic conditions. Those authors advised that regrowth can be prevented by covering biosolids to prevent water logging from precipitation or other circumstances, and thereby precluding saturated anaerobic conditions. Risks of infection from land-applied Class B biosolids were low regardless of whether the exposure route was ingestion of *Salmonella* following direct exposure or ingestion following inhalation of bioaerosols. In contrast, risks from contact with Class A biosolids following regrowth were significant. Pepper *et al.* (2008) thus noted that care must be taken to prevent regrowth of *Salmonella* in Class A biosolids for land application. Brooks (2009) also expressed concern about bacterial regrowth in biosolids.

After land application there was no regrowth of *E. coli* found in Ontario soil receiving biosolids slurry (in contrast to swine manure) (Scott et al. 2006).

3.16.3 Microbial Risk Assessment of Pathogens in Biosolids

Brooks *et al.* (2005) investigated microbial risk to communities from bioaerosols resulting from land application of biosolids based on testing at 10 sites across the U.S. Indicators and pathogens analyzed included total coliforms, *Escherichia coli, Clostridium perfringens,* coliphage, enteroviruses, hepatitis A virus and norovirus. The greatest risk of infection was determined for the coxsackievirus A21 (an enterovirus) resulting from biosolids loading operations, with 4×10^{-4} chance of infection from inhaling the virus (i.e., 4 persons infected per 10,000 persons per year). The risk from land application operations was less than 2×10^{-4}. Brooks *et al.* (2005) concluded that bioaerosol exposure due to land application of biosolids posed little community risk.

Tanner *et al.* (2008) compared risks of biosolids workers exposed to bioaerosols during land application of biosolids by different methods at seven sites across the U.S. The risk of infection, based on bioaerosols concentrations of indicator bacteria, total heterotrophic plate count (HPC) and total coliforms, were no worse than for wastewater treatment plant operators or agricultural workers applying manure to fields. Tanner *et al.* (2008) compared site specific factors which may influence the risk of infection for the seven land application sites across the U.S. Temperature and humidity, which are factors that cause inactivation of airborne microorganisms, generally appeared to have less of an impact on concentrations of coliforms observed immediately downwind of biosolids than did windspeed. The authors concluded that bioaerosols from land application of biosolids pose a detectable, but manageable risk to biosolids workers. They suggested that risk reduction is possible through implementation and maintenance of tractor cab air-filters or application of biosolids such that the tractor operator remains upwind of the bioaerosol source.

In the U.K., regulations called the Safe Sludge Matrix have standards for a safe "harvest" period between when biosolids are applied to soils used for human crop production and the time of harvesting. The safe harvest period can last anywhere from 12 to 30 months depending on the crop. Gale (2005) used quantitative microbial risk assessment (QMRA) to evaluate the potential of human infection~~vity~~ by pathogens associated with root crops grown on biosolids-amended sites. Microbes investigated included salmonellas, *Listeria monocytogenes*, campylobacters,

[4] Class A and B biosolids makes referernce to the United States Environmental Protection Agency Part 503 rule.

Escherichia coli O157, *Cryptosporidium parvum*, *Giardia*, and enteroviruses. Based on assumptions of a 99% reduction of the microbes by mesophilic anaerobic digestion (Class B quality), a consumption of 35 g/d per capita of root crops in the UK, and neglecting any safe harvest period, Gale (2005) predicted less than one infection per year for all of the target pathogens except *Giardia*, for which 50 infections per year were predicted. When a 12-month safe harvest period was applied to the assessment, and assuming linear decay of microbes in the soil, the risks from all seven pathogens were eliminated, with the highest prediction being one infection of *C. parvum* in the UK every 45 years.

Using a QMRA approach, Brooks et al. (2009) assessed the annual risk of infection to a child with soil picaphagia from ingestion of Class B anaerobically digested biosolids contaminated with *L. monocytogenes*, *Salmonella*, adenovirus, coxsackievirus and *Cryptosporidium*. The assessment was based on either direct ingestion of soil (10 g/d) or from ingestion of vegetable crops grown on the biosolids-amended site with consumption of 292 g of vegetables per day. The estimated risk of infection from adenovirus and *Cryptosporidium* was higher than 1 in 10,000 annually if ingested only 1 month after the biosolids application, but after six months, the risk fell to below a 1 in 10,000 annual risk. Brooks et al. (2009) concluded that if the recommendations and restrictions set out by the U.S. Department of Agriculture and the U.S. EPA were followed, land application of biosolids and consumption of soil and vegetable crops associated with the application sites would present a minimal risk.

A screening level QMRA assessment by Flemming *et al.* (2009a) determined that in the most conservative scenario (health protective), the infection risk per exposure event (per day) for *Salmonella* and *C. perfringens* from direct soil ingestion by a child shortly after surface application of biosolids was low, even when accounting for any regrowth, in the case of *Salmonella*. Risk of infection (per hour) from indirect ingestion of aerosolized particles was exceedingly low, (Table 140). When less conservative and more realistic scenarios were assessed, in which part or all of the biosolids were incorporated into the soil, the risks per event were further reduced. The scenarios were developed from Ontario's regulated limit of biosolids application of 8 dry t/ha. In all scenarios, Flemming *et al.* (2009) concluded the risk of infection of *Salmonella* or *C. perfringens* to children was small.

Table 140. [131]Comparison of QMRA screening level human health risk estimates for Biosolids ingested as Aerosols or from Soils (Flemming *et al.*, 2009)

Risk Assessed	Scenario	Computed Theoretical Risk of infection or illness[a]			
		Statistic	*C. perfringens*	*Salmonella* spp. Dewatered biosolids	*Salmonella* spp. Stored dewatered biosolids
Risk to humans from biosolids aerosols Probability per event (hr^{-1})	Aerosol model	Median	10E-08	<10E-16	<10E-16
		95th percentile	10E-06	<10E-16	10E-10
Risk from children's soil ingestion Probability per event (day^{-1})	1 – Worst case direct ingestion	Median	10E-06	<10E-16	<10E-16
		95th percentile	10E-04	10E-13	10E-5
	2 – 20% surface biosolids	Median	10E-07	<10E-16	<10E-16
		95th percentile	10E-05	10E-11	10E-8

	3 - 100% soil incorporation of biosolids	Median	10E-9	<10E-16	<10E-16
		95th percentile	n.r.	n.r.	n.r.

n.r. = not reported

[a] risk of illness; in the case of *Salmonella*, all dose responses were from human feeding studies

3.16.4 Fate and Transport in the Terrestrial Environment

Unc *et al.* (2006) demonstrated in laboratory tests that when biosolids were applied to soils concentrations of *E.coli* increased, which they speculated as possibly resulting from nutrient addition in the biosolids, concentrations of the *E. coli* were higher when the biosolids were added to fresh soil compared to sterilized soil. Unc *et al*. (2006) concluded that the numbers of *E. coli* bacteria added with the biosolids were augmented in natural soils by unknown mechanisms that involve existing biota.

Lang *et al.* (2007) also investigated *E.coli* survival in soil following biosolids amendment. With dewatered mesophilic anaerobically digested biosolids, concentrations of *E.coli* in the soil, initially increased, in agreement with the findings of Unc *et al.* (2006); after three months however, concentrations of the bacteria had reverted to pre-application levels. Cooler-moist soil conditions were found to favour increases in *E.coli* concentrations, while warmer and drier soil conditions caused a decline in *E.coli* concentrations. Thermally dried dewatered sludge or composted sludge did not cause an increase in soil *E. coli* levels. Lang *et al.* (2007) concluded that *E. coli* numbers in soils amended with biosolids would be at background levels by the time of crop harvesting if the U.K. regulations regarding biosolids land application were followed. On a contrasting note, Brooks (2009) expressed the concerns related to low-level pathogen survival in soil and crops, and the inability of the scientific community to assess the risk from these low levels.

Abu-Ashour and Lee (2000) demonstrated with field soil plots that a pathogen applied to the soil surface can be transferred via overland flow for significant distances. A nalidixic acid-resistant strain of *E. coli* in water was sprayed on the clay loam soil plots as the biotracer. Following a significant rainfall event two days after the application of the biotracer, detectable concentrations of the tracer were found 20 m downslope from the centre of the plot on the site with the milder slope of 2%, while on the plot with a steeper slope of 6%, concentrations of the biotracer were found 30-35 m downslope. A second rainfall event that occurred 15 days after the biotracer application resulted in only low concentrations found in runoff samples from the centre of the plots and 5 m downslope at both plots. Survival of the *E.coli* strain over 13 days without rain was demonstrated. Abu-Ashour and Lee (2000) concluded that surface transport of pathogens on soil surfaces can be a significant transport mechanism.

Using a computer model to evaluate pathogen contamination of surface water, Dorner *et al.* (2006) determined that most pathogenic organisms enter a surface water as a result of tile drainage rather than overland flow (surface runoff). Organisms including in the modelling effort included *E. coli, E. coli O157H7*, *Cryptosporidium* spp., *Giardia* spp. and *Campylobacter* spp. The exception to this observation occurred during storm events and heavy precipitation, when overland flow resulted in the highest bacterial concentrations observed and modelled.

Unc and Goss (2003) examined the importance of soil macropores in the transport of pathogenic bacteria through soil columns to tile drainage. The studies involved surface applications of livestock manure, rather than biosolids, followed by onset of drip irrigation. Bacteria in the manure migrated downward through the soil faster than soil pore water did, consistent with the experimental hypothesis of soil macropore involvement. Factors contributing to occurrence of larger pores and faster bacterial velocities through the soil were a larger soil clay content, lower total soil porosity, and lower saturated hydraulic conductivity. Macropore transport of bacteria was more likely to occur in wet soils, but it was not necessarily restricted to soils with high initial soil water content. Unc and Goss (2003) concluded that macropores, but not total soil porosity, can play a significant role in the transport of bacteria in manure applied to soils, and thus provide a source of water contamination.

Akhand *et al*. (2008) examined different methods of incorporating liquid biosolids (20 to 50 g TS/L) to a silt loam soil, and the transport of bacterial contaminants to tile drainage. Methods of application included immediate post-application of biosolids to aerator-tilled soil, and a biosolids slurry injection system and broadcast over untilled soil. In all tests, the liquid biosolids were applied at a rate of 93,500 L/ha. Drainage tile were placed approximately 0.85 m below the soil surface. The system of applying the biosolids to the aerator-tilled soil did not result in any changes in tile drainage flow, and the applied biosolids were retained above a 0.25 m depth. Conversely, drainage flow was impacted within 0.5 h by the surface broadcast plus incorporation by shallow cultivation. The transport of water in the biosolids was attributed to desiccation fissures that were networked to worm burrows, which in turn were inter-connected with the drainage tiles. The subsurface injection method resulted in some increased flow to the drainage tiles in wet weather, but not in dry weather. Bacterial die-off rate coefficients (*E. coli*) for all types of application were on the order of 0.3 d^{-1}. Higher values (0.2 to 0.7 d^{-1}) for the die-off rate coefficient of *E. coli* in a predominantly sand soil were observed by Rahman *et al*. (2006).

Differences in the movement of nutrients and bacteria in liquid biosolids resulting from different application methods to a silty clay loam soil were reported by Lapen *et al*. (2008b). Application methods included the Aerway SSD method of immediate post-application following aerated tillage, and broadcast application followed by cultivation within 24 h. Biosolids application rates were 93,500 L/ha. Concentrations of *E. coli* and *C. perfringens* in the liquid biosolids (total solids = 11.93 g/L) were 17.5×10^6 and 19.7×10^6 cfu/L, respectively. In the silty clay loam, contamination of tile drainage from biosolids application can result in minutes, irrespective of the method of application, due to connections between macropores and the drainage tiles. Transport flow rates of 0.03 to 0.44 cm/s were observed for both application systems.

Contamination of ground water by *E. coli* resulting from biosolids application occurred to at least 2.0-m depth in ground water, but was more notable in ground water immediately beneath tile depth (1.2 m). The concentrations of total Kjeldahl nitrogen (TKN, i.e., ammonia-N + organic-N) and total phosphorus in ground water at a 1.2-m depth were significantly higher for the broadcast plus cultivation method of application, relative to the Aerway SSD treatment; there were, however, no significant treatment differences for the bacterial indicators. For the macroporous field conditions observed, Lapen *et al*. (2008b) concluded that the Aerway SSD application method involving pre-tillage resulted in significantly reduced application-induced

transport of contaminants in liquid biosolids to tile drains and shallow ground water, compared to surface broadcast spreading of the liquid biosolids followed by incorporation of the material into surface soils within 24 h. They suggested that by pre-tilling the soil, the Aerway SSD method provided a surface to better hold the applied liquid biosolids and to potentially disrupt transfer to macropores.

Application of dewatered biosolids (total solids approximately 300 g/L) to a silty clay loam by direct subsurface injection and by surface spreading followed by cultivation within a few hours were compared by Gottschall *et al*. (2009) in terms of nutrients and bacterial quality in drainage tile water. Comparisons were performed on data within 100 days following the biosolids application (equivalent rate of 8 T/ha), and post-100 days from the application.

The highest observed concentrations of *E. coli* in tile drainage occurred soon after the biosolids application, and then rapidly declined, while concentrations of *C. perfringens* remained more consistent throughout the study period. Both surface spreading and direct injection methods caused bacterial contamination of groundwater to at least 1.2 m depth. Both application treatments also caused significantly higher nitrate-nitrogen contamination to at least 2.0 m depth, on a seasonal basis, compared to control plot values. Direct injection did cause, however, significantly greater nitrogen, phosphorus and bacterial contamination of tile water than the surface spreading procedure over the long term (>100 d post-application), although peak mass loads during this "late" study period were relatively small compared to those observed during the early (<100 d) post-application study period flow events. Gottschall *et al*. (2009) suggested that based on their study results (in terms of water contamination and *E. coli* persistence due to land-applied biosolids), and the public health and aesthetic benefits of reduced vector attraction and odour afforded by the direct injection application method, direct injection of dewatered biosolids should be considered as a land application option, especially at biosolids application sited near populated areas and/or where surface runoff potential is a significant concern.

Transport of viruses to groundwater involves many factors, and can be much different than larger bacteria. Factors can include temperature, moisture content, pH, hydraulic conditions, organic matter, adsorption and desorption, salt content, type of virus, virus decay, soil properties, rainfall, source of the virus and water table depth (Chee-Sandford *et al*., 2009). In relative particle size, viruses are in the colloidal range and may move faster through the soil than dissolved solutes (salts) because the colloids can move through large soil apertures such as fractures and root holes. Viruses are capable of substantial movement in groundwater, at depths of 67 m and distances of up to 408 m in glacial till and 1600 m in fractured limestone (Chee-Sandford *et al*., 2009),

In pilot lysimeter and field studies Yates *et al.* (2006) determined that neither spiked *C. perfringens* spores nor *Listeria innocua* bacteria were found to move through the soil column, regardless of soil type or hydraulic flow rate. The inability to detect the pathogens in the lysimeter leachate was due to sorption in the soil, as determined by sacrificial analysis of the lysimeters following the conclusion of the tests. Although *E. coli* were found to be more mobile and move downward, movement in part was attributed to their growth in the columns. More transport was observed in columns filled with a sandy soil than with a loam soil. Yates *et al.* (2006) reported that field trials closely mirrored the pilot studies. Using the *C. perfringens* results as a surrogate for *Cryptosporidium* oocysts, Yates *et al.* (2006) indicated that *Cryptosporidium* oocysts may not be a problem to groundwater that underlies biosolids-amended

soils. Based on the strong sorption of the *L. innocua* to the soil and the lack of transport in the soil column, Yates *et al.* (2006) concluded that the risk of contaminating groundwater with *L. monocytogenes* from biosolids applied to land would be minimal, although they did suggest that further field studies and modeling of transport should be undertaken.

In the study of Yates *et al.* (2006) a bacteriophage ΦX174 exhibited the greatest potential for downward movement through the pilot soil columns. Based on results of the pilot study with the bacteriophage coupled with computer modeling, those authors concluded that viruses may pose a risk to groundwater contamination and human health.

The occurrence of endotoxins in soil following application of biosolids was reported by Brooks *et al.* (2007b). Endotoxin concentrations increased by approximately one-half log unit after one month following biosolids application compared to pre-application levels. The higher concentration following biosolids application was determined to be non-statistically different ($P>0.05$) from the pre-application level (Brooks *et al.*, 2007b). Because reaction to endotoxins is derived primarily from airborne agents such as aerosols, response to endotoxins from aerosols is no more likely at biosolids-applied sites than from non-applied sites. A number of caveats in the study were offered regarding conclusions from the study scope, including the number of antibiotics tested (4), the number of biosolids tested (1) and the number of soil types tested (1). Suggested recommendations for further research involved additional soil and climate types, biosolids from other locations, and additional antibiotics.

In the aforementioned microbial risk studies conducted by Brooks *et al.* (2005) total coliforms, *E. coli, C. perfringens* and coliphage were rarely detected in bioaerosols during land-spreading activities, and were not detected beyond 15 m from the biosolids loading site. Heterotrophic plate count (HPC) bacteria were not detected in bioaerosols when soil was not incorporated with biosolids during the loading operation, leading the authors to conclude that most HPC (and other airborne microorganisms resulting from biosolids applications procedures) are derived from soil rather than the biosolids. Although norovirus ribonucleic acid (RNA) was never detected more than 5 m downwind of the biosolids application site, Brooks *et al.* (2005) suggested that infectious norovirus could be aerosolized. They also noted however, that norovirus needs to be ingested rather than inhaled to be infectious.

A subsequent study by Brooks *et al.* (2007a) at a biosolids application site in Arizona supported the contention that most of the aerosolized bacteria downwind from a biosolids land application site appeared to be soil-related. Polymerase chain reaction (PCR) involving RNA sequencing was used in the study to develop bacterial community profiles for sites upwind and downwind of control and biosolids-amended soil sites. The results were considered representative of an arid environment in which aerosolization of soil and dust occurs more readily than in a humid environment.

The effect of high wind velocity during and after biosolids application was investigated by Baertsch *et al.* (2007) using microbial source tracking with molecular-based signatures from microorganisms unique to anaerobically digested biosolids. Two sets of experiments were conducted. The first set of tests involved analyzing air samples upwind and downwind of a site receiving dewatered anaerobically digested biosolids within 36 hours of application (the

application procedure was not indicated). The second set of tests was similar, except they were conducted while the biosolids were being disced into the soil following the actual surface application. Concentrations of particulate matter less than 10 μm in diameter (PM_{10}) were elevated in the tests with discing in operation as compared to the non-discing tests. According to Baertsch *et al.* (2007), when average wind speeds during biosolids application were greater than 5 m/s, source tracking confirmed the presence of biosolids microorganism biomarkers in 56% of the downwind samples versus 3% of the upwind samples. They concluded that soil discing of biosolids during high wind velocities can contribute to bioaerosolization. Off-site transport of biomarkers was demonstrated in bioaerosols originating from biosolids during disking at distances of up to 170 m from the source. Viability of organisms in these bioaerosols was not ascertained.

Gerba and Smith (2005) provided a review of the commonly accepted estimates of maximum survival times of different classes of pathogens in biosolids when applied to soil and plant surfaces (Table 141) from a U.S.EPA report that was used in setting the Part 503 regulations by the U.S.EPA. In soils, helminths are far more likely to survive as viable organisms than are the other pathogen classes. Protozoa are least likely to survive when applied in biosolids to either soil or plants. Pathogens survive longer in soils than on plants, with the possible exception of the protozoan pathogens. Brooks (2009) has bench-scale and field studies in progress investigating the survival of bacterial and viral pathogens in biosolids and manures in land-applied biosolids.

Table 141. Pathogen Survival Times on Soils and Plants (Gerba and Smith, 2005)

Pathogen	Soil		Plants	
	Absolute maximum	Common maximum	Absolute maximum	Common maximum
Bacteria	1 year	2 months	6 months	1 month
Viruses	6 months	3 months	2 months	1 month
Protozoa	10 days	2 days	5 days	2 days
Helminths	7 years	2 years	5 months	1 month

Results from an Australian study of survival of biosolids-derived bacteria in soil were similar but of a more cautionary note. Eamens *et al.* (2006) reported that bacteria such as *E. coli* and *Salmonella* were present in biosolids clumps at concentrations above background levels for six months, to as much as 11-12 months following application of biosolids. Survival of bacteria when the biosolids were surface-applied or sub-surface injected were similar. Eamens *et al.* (2006) suggested that regrowth of *E.coli* and *Salmonella* occurred within the biosolids present in the soil. A recommendation from the study was for reducing the opportunity for soil ingestion by grazing livestock following biosolids amendment, with an appropriate interval between the application of biosolids and when grazing was permitted.

Pepper *et al.* (2008) provided a review of research work conducted on land application of Class B biosolids in the U.S. Southwest, and concluded that Class B biosolids application to land as a soil amendment is a sustainable activity, with the cautionary note that the results were from studies in a warm arid climate, and might not necessarily be applicable to all climatic conditions. Moreover, the depth to the water table in the U.S. Southwest is very deep, and this also would not apply to other geographic areas.

3.16.5 Ecotoxicity Assessments of Land Application of Biosolids

The ecotoxicity of biosolids application was investigated in detail by Banks *et al.* (2006). A series of different tests (e.g. microbial respiration, seedling germination, root and shoot elongation, earthworm biomass and reproduction and nematode survival) initially involved 19 sites, which were then screened down to five sites for more intensive testing. Many of the toxic effects observed in the intensive test were attributable to soil transient effects such as high salinity or low pH. Of the 11 toxic events out of 110 samples attributed directly to applied biosolids, five were due to excessive metal loadings from sites that were non-compliant with the U.S. Part 503 regulations. Banks *et al*. (2006) noted that no clear trends in toxicity were observed at application site compliant with the 503 regulations. Thus they concluded that compliance with the Part 503 biosolids regulations would adequately protect agricultural resources.

McCarthy (2009a) presented results of ecotoxicity testing for biosolids at controlled application rates with a battery of terrestrial bioassays that included:

- Earthworm (*Lumbricus terrestris*) survivorship after 7 day acute and 28 day exposures;
- Springtail (*Folsomia candida*) avoidance and reproduction tests;
- Common bean (*Phaseolus vulgaris*) plant height, leaf length, days-to flowering and number of bean pods, total number of seeds and seed weight; root length, stem width and shoot length, total plant biomass and germination of F1 generation.

By applying a statistical analysis of variance to the bioassay end-points determined for biosolids-treated and reference soils, McCarthy (2009a) determined that in all the bioassays the endpoints determined for biosolids-amended soil were not statistically different from the reference un-amended soil. McCarthy (2009b) is continuing with the ecotoxicity approach for identification of potential adverse from biosolids applications by investigating reproduction and life-cycle tests with the suite of animal and plant species noted above, as well as potential sequestration of contaminants such as pharmaceuticals by plants in both laboratory and field assays.

3.16.6 Section Summary

1. Regrowth of *E. coli* and *Salmonella* spp. was observed in some cases when dewatered anaerobically digested biosolids were centrifuged, stored or rewetted.
2. Pathogens such as *Listeria*, and *Salmonella* were detected relatively frequently in biosolids.
3. The published data on occurrence of other bacterial pathogens in biosolids, such as *E. coli* O157:H7, *Campylobacter, Yersinia, and Helicobacter* are scarce although work is being done by Agriculture Canada in Ottawa and Lethbridge on *Campylobacter* and *Helicobacter* in manure and biosolids (Flemming, 2009b).
4. Data on concentrations of the parasites *Cryptosporidium* and *Giardia* in biosolids or biosolids-amended soils were limited, possibly due to inadequate analytical procedures.
5. Geometric mean densities of select indicator and pathogenic bacteria in biosolids can range from 10^6-10^7 (e.g., fecal coliforms, *Enterococci* spp and *C. perfringens*) to lower than 1 MPN/g TS dw (e.g., *L. monocytogenes* and *Salmonella* spp.).

6. Microbial risk assessment indicates that when biosolids are incorporated into soil at regulated rates in Europe or North America, there appears to be only a very small risk of infection from ingesting soil amended with the biosolids.
7. The risk of infection to communities from bioaerosols resulting from land application appears to be very slight, although occupational exposure appears to offer a slightly higher risk, particularly for coxsackievirus A21.
8. The work of Pepper and others indicates there is negligible risk of infection from *Staphylococcus aureus* resulting from biosolids applied to land or in biosolids aerosols.
9. Pathogens can enter surface water either as a result of surface runoff or tile drainage. Although tile drainage appears to contribute to pathogen loadings more regularly than surface runoff, heavy precipitation events can cause pathogen concentrations to rise to the levels higher than found in tile drainage.
10. Different types of pathogens survive in soils and plants for different durations; protozoa from biosolids can survive in soils for a period measured in days while helminth ova can survive for several years. Survival times of pathogens associated with plants following application of biosolids are shorter than the survival times of the same pathogens in soil.
11. One soil column study indicated that bacterial pathogens are tightly bound to soils following biosolids application.
12. Viruses are able to travel more widely in groundwater than other larger pathogens, and thus they may pose a risk to human health.
13. Transport of all pathogens through soil is aided by the presence of macropores, such as cracks in soils with high clay content, worm holes and roots.
14. There is no evidence of the presence of prions in municipal biosolids or in soils amended with biosolids; however improved analytical techniques for these substances are needed.
15. Published data on recent influenza-like viruses (e.g., H1N1, H5N1, H5N2) in biosolids and soils amended with biosolids are lacking.
16. Improved analytical methods are needed for identifying the number and viability of pathogens such as *Cryptosporidium* in biosolids and soils.

The Stakeholder Advisory Group consulted during preparation of the WEAO (2001) report expressed a high level of concern about the potential for disease transmission resulting from land application of sewage biosolids. Based on that concern and limited available study information, it was concluded that pathogens in land applied sewage biosolids are Group II contaminants requiring additional research. It was recommended that:

- A survey be conducted to develop a representative database of pathogen information for land applied sewage biosolids in Ontario; and
- Small field plot studies be conducted to determine pathogen persistence in biosolids-amended soils, runoff and tile waters, and the incidence and extent of surface and groundwater contamination with pathogens following sewage biosolids application to Ontario agricultural land.

Little specific published literature was identified in this new review with respect to addressing the recommendation that a sampling survey of biosolids across Ontario be conducted to develop a more comprehensive database of pathogen occurrence and concentration data. In addition, there are still large data gaps in available analytical microbiological methods for achieving effective recovery and enumeration of pathogens in environmental samples, particularly in biosolids and

soils, and even bigger gaps in acquiring relevant data on the viability and human infectivity of organisms such as *Giardia, Cryptosporidium, Campylobacter*, and others (Flemming, 2009b).

New literature regarding the fate and transport of pathogens (particularly bacteria) in the terrestrial environment has been published since the 2001 WEAO report that appears to address many of the issues of the second recommendation for field plot studies. A substantial body of this research has occurred in Ontario, conducted and/or funded by federal and provincial ministries. Agencies involved in the research include Agriculture and Agri-Food Canada, the Ontario Ministry of the Environment and Ontario Ministry of Agriculture, Food and Rural Affairs. Diverse studies have been published on the fate and transport of pathogens in surface runoff and tile drainage resulting from applications of liquid and dewatered biosolids to field plots.

The growing body of data from Canadian and international researchers appears to indicate that concerns regarding the transfer of pathogens in biosolids to soils have been or are being addressed. A number of research gaps or concerns remain, however, including development of adequate analytical procedures for pathogens in biosolids, viability of identified pathogens; occurrence and fate of identified pathogens such as *Helicobacter, Campylobacter* and *Yersinia*, occurrence and fate of newer pathogens (e.g. influenza viruses such as H1N1, H5N1 and H5 N2); and the potential human health risks from transport of viruses through ground water and into surface water via runoff. Consequently, it is recommended that pathogens as a class be categorized as Group II contaminants requiring additional research, as they were in the WEAO (2001) report.

4. SUMMARY OF REVIEW FINDINGS

4.1 Review of Data

Compared to the classes of contaminants reviewed in the WEAO (2001) report, the number of classes of contaminants that have been reviewed herein has grown substantially. Due to the relatively short timeframe of this interim, the ability of the scientific community to define and document publically all aspects of the different contaminant classes with respect to biosolids application to soils would clearly represent an enormous task. This review has identified that the attention awarded to and the understanding of the contaminants identified herein is very uneven. Some classes of compounds have been studied in detail for many years, such as nonylphenol and its ethoxylates and linear alkylbenzene sulfonates (LAS). Knowledge of the effect of other contaminants in soils, such as pharmaceuticals, polybrominated diphenyl ethers (PBDEs), perfluorinated organic compounds and Bisphenol A is very limited. For example, in the cases of fluoroquinolone antibiotics and PBDEs, the literature may show that they are persistent and even accumulate in the soil, but it is uncertain whether these observations represent an environmental health concern. Similarly, in this review, bioaccumulation factors (principally in earthworms) were often identified as greater than 1, (e.g., triclosan BAF value was 27, and for PBDEs was up to 20), indicating biomagnification by the organism; the environmental significance of BAF values greater than 1 has not been documented, and constitutes a knowledge gap.

The main results of the literature review are summarized in Table 142. In this table, it is clear that while many of the contaminants and pathogens have been characterized to some degree in biosolids, the knowledge base in soils, surface runoff or drainage, and biota is much less well documented. A few compounds, such as triclosan and nonylphenol, have the most data. Those areas indicated as “no data” in the table represent the knowledge gaps to which research should be addressed.

In the main body of the report, at the conclusion of each section on contaminants, the main points of knowledge were summarized and then put in context with the conclusions of the WEAO (2001) report. Lastly, in each section on contaminants, a recommendation was provided for categorizing the compounds in a manner similar to the 2001, namely as Group I compounds for which research and data were deemed sufficient, and Group II contaminants for which additional research was recommended.

In Table 143, the contaminants or classes of contaminants are summarized according to their recommended Group I or Group II designations with the specific knowledge gaps summarized for each and a priority ranking for research provided. There are insufficient research funds available to address all knowledge gaps identified, so the effort should be focused on addressing the data lacking for the Group II contaminants. Within the Group II contaminants, it is impossible to assign a ranking of priority, as this must be based on risk assessments which have not been conducted.

Table 142. Summary of Literature Review Findings

Contaminant	Typical Concentrations			Biota (Bioaccumulation factor)	Half Life in Soil (d)
	Biosolids	Soils	Drainage or Runoff		
Pharmaceuticals	varies widely	varies widely	e.g., 1-100 ng/L	no data	limited data
Nonylphenol	500-2500 ug/g	2-7 ug/g	no data	minimal	10-25
NPEO total	25-1000 ug/g	no data	no data	minimal	no data
PBDES total	1000-3000ng/g	0.01-650 ng/g	no data	1-20 in worms	no data
LAS	1,000-30000 ug/g	not persistent	no data	no data	7-8.5
BEHP	2000–200000 ng/g	300-500 ng/g	no data	no data	no data
BPA	100-10,000 ng/g	80- 150 ng/g	no data	nd in worms	no data
Perfluoro organics	<1 - 100 ng/g	no data	no data	no data	no data
Fragrances (polycyclic)	5,000-400,000 ng/g	nd-3000 ng/g	no data	<1-3 in worms	no data
Triclosan	1,000-40,000 ng/g	<1-50 ng/g	0.5-400 ng/L	27	18
QACs	20,000-100,000 ng/g	no data	no data	no data	no data
Estrogens	1-100 ng/g	not persistent	no data	no data	<1-7
Fluorescent whitening agents	5,000-100,000 ng/g	no data	no data	no data	no data
Quaternary ammonium compounds	20,000-100,000 ng/g	no data	no data	no data	no data
Siloxanes	no data	no data	no data	no data	no data
UV filters	1500-3,500 ng/g	no data	no data	no data	no data
PAHs	100-1500 ng/g	nd - 20 ng/g	no data	no data	no data
Total PCBs	1-300 ng/g	<1 ng/g	no data	up to 18	no data
Dioxins and Furans	0.001-0.1 ng TEQ/g TS dw	no data	no data	no data	no data
Pathogens	varies widely, can be less than 10 MPN/g TS dw for bacteria	varies widely depending on indigenous microbes	Varies widely based on local conditions	no data	varies widely depending on microbe

Table 143. Summary of Contaminant Research Class and Identified Knowledge Gaps

Contaminant or Class of Contaminant	Recommended Group	Identified Knowledge gaps	Research priority
Pharmaceuticals	II	1) persistence in soils; 2) mobility in soils; 3) toxicity to microbes and higher life forms in soil; 4) uptake by plants	high
APE/APEOs	I	1) toxicity to microbes and higher life forms in soil	secondary
Linear Alkylbenzene sulfonates (LAS)	I	1) toxicity to microbes and higher life forms in soil; 2) uptake by plants	secondary
Phthalates	I	1) toxicity to microbes and higher life forms in soil	secondary
Bisphenol A	II	1) mobility in soils; 2) toxicity to microbes and higher life forms in soil; 3) uptake by plants	high
Brominated Flame retardants	II	1) toxicity to microbes and higher life forms in soil; 2) uptake by plants	high
Perfluorinated organic compounds (PFOCs)	II	1) persistence in soils; 2) mobility in soils; 3) toxicity to microbes and higher life forms in soil; 4) uptake by plants	high
Synthetic Fragrances	II	1) contradictory evidence on persistence in soil; 2) toxicity to microbes in soil; 3) uptake by plants	high
Antimicrobials	II	1) importance of elevated bioaccumulation factors; 2) limited toxicity data to microbes higher life forms in soil; uptake by plants	high
Fluorescent whitening agents, QACs, Siloxanes, UV Filters	II	1) persistence in soils; 2) mobility in soils; 3) bioaccumulation in soils; 4) toxicity to microbes and higher life forms in soil; 5) uptake by plants	high
Hormones	I	1) mobility in soils; 2) toxicity to microbes and higher life forms in soil	secondary
Sterols	I	1) mobility in soils; 2) toxicity to microbes and higher life forms in soil; 3) uptake by plants	secondary
Non-regulated metals	II	1) mobility in soils; 2) toxicity to microbes and higher life forms in soil; 3) uptake by plants	high
Radionuclides	I	1) mobility in soils; 2) toxicity to microbes and higher life forms in soil; 3) uptake by plants	secondary
Dioxin, Furans, PCBs	I	1) mobility in soils; 2) toxicity to microbes and higher life forms in soil; 3) uptake by plants	secondary

continued

Table 143 cont'd

Contaminant or Class of Contaminant	Recommended Group	Identified Knowledge Gaps	Research Priority
Dioxin, Furans, PCBs	I	1) mobility in soils; 2) toxicity to microbes and higher life forms in soil; 3) uptake by plants	secondary
Polyaromatic hydrocarbons (PAHs)	I	1) bioaccumulation in soils; 4) toxicity to microbes and higher life forms in soil; 5) uptake by plants	secondary
Pathogens	II	1) persistence in soils; 2) mobility in soils; 3) toxicity to microbes and higher life forms in soil; 5) human health via drainage and runoff; 4) uptake by plants; 6) new pathogens identified	high

Studies recommended in the WEAO (2001) report were listed in Table 17.1 of that report. It is reproduced here as Table 144 with a summary of the current status.

Identification of concentrations of unregulated metals in Ontario soils is an issue that remains to be addressed. While measurements of pharmaceutical and estrogenic hormone concentrations in biosolids and soils are now published in the technical literature, some practitioners (Smyth, 2009) still regard adequate analytical methods for some of these contaminants as one of the highest priority issues. In a study of three advanced wastewater treatment plants near Raleigh-Durham, NC, Linden et al (2008) reported that recoveries of hormones and alkylphenols (weak estrogenic compounds) spiked into biosolids were low, on the order of 48%.

Because research funding is often difficult to obtain, there is a need to focus on those contaminants or research areas that would be considered of the "highest priority". Smith (2009b) has a technical publication in press (Environment International) that reviews international research on emerging contaminants of concern, assesses the significance of different groups of emerging compounds in terms of risk of human toxicity and ecological impacts, and then prioritizes the compounds based on identified research needs.

Prioritization is accomplished by assessing the human and environmental risks associated with the contaminants. LaGuardia (2009) has noted that a Biosolids Research Summit hosted by the Water Environment Research Foundation in 2003 concluded that the knowledge of chemical constituents within biosolids and their associated risks are largely unknown. He thus recommended that more effort is needed to address the risk issue as it is the basis for a complete risk assessment. Bastian (2009) regards a lack of environmental concentration end-points for organisms in different matrices (e.g., microbes, plants and wildlife for soils; algae, invertebrates and vertebrates for aquatic environment) as a principal research gap. There are many different acute and sublethal toxicity endpoints currently available for soil-dwelling microorganisms, Plants and animals, and wildlife and aquatic organisms beyond survival, reproduction and growth. In the soil ecotoxicology field alone (e.g. for organisms in direct contact with soil) there are a number of functionaland structural endpoints to assess the health of microbial populations, short and long-term survival, growth, reproduction, behaviour, multi-species microcosm tests, histological and physiological endpoints (e.g., for contaminants with endocrine disruption modes

of toxic action, for indications of exposure to metals, etc.) for invertebrates, survival, growth, reproduction, and population metrics as well as physiological endpoints for plants. Field, and controlled semi-field methods also exist, some of them standardized. Since Aquatic ecotoxicology is a more mature science then soil ecotoxicology the range of endpoints available for aquatic organisms is even greater.

The WEAO (2001) report, and by extension this current review, have focused on specific classes of contaminants (i.e., organic compounds, metals and radionuclides and pathogens). McCarthy (2009b) has noted that there is far less information available on the combined, interactive effect of all potential contaminants in biosolids incorporated into soil, and has suggested that studies of the potential ecotoxic effects of biosolids applied to soils are as important as investigating the knowledge gaps associated with the fate and transport of specific contaminants. Xia (2009) has also indicated that the ecotoxicity of pharmaceutical and personal care products in biosolids applied to land is a research gap that needs to be addressed.

Table 144. Recommended Studies and Action from WEAO (2001) Report and Current Status

Group II Contaminant	Recommended Studies/Action	Current Status
Unregulated metals	Conduct a survey of unregulated metal concentrations in Ontario sewage biosolids and agricultural soils	Survey in biosolids completed by Hale (2009); no corresponding survey of unregulated metals in Ontario soils (or elsewhere)
Pathogens	Form a committee with representatives from the wastewater treatment and medical communities, and the public to explore and build consensus on such issues as the principles that should be used to define risks and acceptable risks, develop and monitor studies that would confirm/recommend improvements to current application program	A substantial body of work on pathogen persistence and mobility of pathogens in biosolids when applied to Ontario soils has been published by agencies including Agriculture and Agri-Food Canada, OMAFRA, Ontario MOE and others. Microbial risk assessment work related to pathogens in biosolids have been published by the Ontario MOE and others in the U.S. and U.K.
Pharmaceuticals and estrogenic hormones	Develop analytical methods for measuring pharmaceutical and estrogenic hormones in sewage biosolids. Conduct a survey of pharmaceuticals and estrogenic hormones in Ontario sewage biosolids	Analytical methods for pharmaceuticals and estrogenic hormones in biosolids have been developed by AXYS Analytical Services in Sydney BC for the U.S. EPA's targeted National Sewage Sludge Survey. A focused survey of pharmaceuticals and estrogenic hormones in

		Ontario sewage biosolids has not been published, although certain Ontario treatment plants have been included in broader Canadian wastewater and biosolids surveys conducted separately by Environment Canada and the Canadian Council of Ministers of the Environment.

Knowledge gaps and research requirements were identified in the responses received from experts on biosolids applied to land, found tabulated in Appendix B, as well as from the expert reviewers. These knowledge gaps and research recommendations have been summarized in Table 145. In general, the major research focuses can be summarized as the fate of pathogens in the environment following biosolids application, ecotoxicity and bioaccumulation studies of the micro-constituents in biosolids applied to soil, and occurrence and analytical methods for micro-constituents in biosolids and soils. The same experts are pursuing research in the coming year to address these knowledge gaps.

Other knowledge gaps that may be addressed as resources permit include the type of biosolids applied (e.g., lime-stabilized vs. anaerobic vs. compost) vs. soil mobility, and the effect of soil structure (% sand and clay, pH, OC content, possibly cation exchange capacity) on the persistence and mobility of the contaminants, both chemical and pathogenic. Furlong (2009) recommends that the transport of biosolids-derived contaminants in soils over several growing seasons needs to be investigated.

This review identified on-going research by a number of organizations or agencies, much of which has overlap with the current interests of this review. These organizations and agencies included the Canadian Council of Ministers of the Environment, Environment Canada, Agriculture and Agri-food Canada, the U.S. National Biosolids Partnership, the Water Environment Research Federation, and the U.S. EPA. Contact should be made with these organizations to promote common research goals and to prevent unnecessary duplication of research efforts.

4.2 Recommendations

4.2.1 Recommendations based on Knowledge Gaps

Recommendations based on identified knowledge gaps include the following:

- Because the data characterizing the fate, persistence, mobility, and bioaccumulation of all classes of pharmaceuticals are sparse, studies are needed to further the scientific understanding of these compounds when applied to soils in biosolids.

- The transport of PBDEs in surface runoff or leachate, mineralization of PBDEs in soils, and studies of plant uptake and toxicity of PBDEs are poorly documented and studies on these issues are recommended.

- Because there are only sparse data on the fate, mobility and potential bioaccumulation of Bisphenol A (BPA), perfluorinated organic compounds (PFOCs), synthetic fragrances and the antimicrobial hexachlorophene in the terrestrial environment as a result of land application of biosolids, research should be initiated to address these knowledge gaps.

- The lack of knowledge of bioaccumulative effects resulting from the antimicrobial triclosan in biosolids, and the concern regarding the effects of triclosan on soil microbial health, warrant additional research.

- A wide variety of compounds used in personal care products, such as fluorescent whitening agents, quaternary ammonium compounds, siloxanes and UV filters are poorly characterized in biosolids, and there are virtually no published data that describe the fate, transport, bioaccumulation and environmental effects of these compounds in the terrestrial environment. Research studies are needed to respond to these diverse knowledge gaps.

- Recommendations from the WEAO (2001) report for studies on the mobility and effects of unregulated metals in biosolids applied to Ontario soils have not been addressed and should be a research focus.

- In addition to addressing the knowledge gaps of individual contaminants in biosolids when applied to soils, complementary investigations of potential ecotoxicological effects of biosolids on plants and animals in soils should be conducted.

- The importance of the magnitude of bioaccumulation factors in soil fauna and flora is not well understood and needs to be investigated.

- With respect to pathogens, studies to elucidate the following are recommended:
  - development of adequate analytical procedures for pathogens in biosolids, including viability of identified pathogens;
  - occurrence and fate of known pathogens such as *Helicobacter, Campylobacter* and *Yersinia*, and of newer pathogens (e.g. influenza viruses such as H1N1, H5N1 and H5 N2);
  - risk assessments are sensitive to soil persistence kinetics particularly for viruses and should be studied; and
  - the potential human health risks from transport of viruses and other pathogens in surface water runoff and in groundwater.

Table 145. Knowledge Gaps and Research Recommendations from Biosolids Experts[5]

Topic	Recommended Research	Expert
Fate of Pathogens in Environment from Soil Application of Biosolids	Low level pathogen survival in soils after biosolids application	J. Brooks
	Antibiotic resistance development in soils resulting from biosolids applications	J. Brooks
	Bacterial regrowth in biosolids and soils	J. Brooks
	Removal of infectious prions by treatment and survival after land application	C. Gerba
	Occurrence of *Ascaris* ova and more quantitative data on survival in the environment	C. Gerba
	Quantitative risk assessment of *Ascaris* after land application	C. Gerba
	Potential for wild animals to become infected with pathogens in biosolids after land application	C. Gerba
	Pathogens in irrigation return flows following irrigation of agricultural fields onto which biosolids have been applied	C. Gerba
	Migration of pathogens from fields that have tile drains fields beneath them in cold climates with high rainfall	C. Gerba
	Concentration of adenoviruses in biosolids (they may occur in greater concentrations than other enteric viruses)	C. Gerba
	Better methods for the recovery of viruses from biosolids	C. Gerba
	More data on infectivity of *Cryptosporidium* after biosolids treatment and occurrence in biosolids	C. Gerba
Ecotoxicity and Bioaccumulation Studies	Determination of end-point values to assess the effects of chemical micro-contaminants in different matrices (soils, wildlife, plants, aquatic species) receiving biosolids amendment	R. Bastian
	Ecotoxicity studies to determine if biosolids sustainable with respect to the organisms (animals and plants) in soil	L. McCarthy
	Identification chemical constituents within biosolids and their associated risks when applied to soils	M. LaGuardia
	Long-term persistence, fate and soil transport of contaminants in biosolids over multiple growing seasons	E. Furlong
	Bioavailability of biosolids-borne chemicals and of non-extractable residues that form.	G. O'Connor
	Bioaccumulation and ecotoxicity of PPCPs in biosolids that applied on land	K. Xia
Occurrence and	Chemical composition of biosolids and persistence of	R. Halden

[5] Reviewer experts included

Analysis	contaminants through wastewater treatment	
	Development of good analytical methods for chemical micro-contaminants in biosolids and soil	S.A. Smyth
General Research needs	research on nanoparticles	E. Topp
	modelling and risk assessment - a need for tools to predict environmental concentrations and knowledge to extrapolate from one chemical or exposure scenario to another	E. Topp
	soil persistence kinetics with respect to viruses	E. Topp
	evaluate effects of biosolids as a contaminant in media (biosolids as a whole) rather than effect of contaminants in biosolids as individual toxic agents	N. Feisthauser
	effects of individual contaminatns to organisms directly exposed and those furth up the food chain	N. Feisthauser
	more effects information of biosolids on terrestrial organisms	N. Feisthauser
	effects on aquatic organisms from runoff	N. Feisthauser
	environmental effects data for soil microorganisms, soil invertebrates, plants and other soil-dwelling wildlife	N. Feisthauser
	when characterizing issues related to metals , speciate metals and total concentrations in biosolids.	N. Feisthauser

4.2.2 Other Recommendations

Other recommendations resulting from this review included:

1. Much new data are being published in the literature as of this date, and so the review should be updated again in approximately 5 years.

2. WEAO should attempt to leverage biosolids research results by coordinating with other organizations or agencies that are active in biosolids research, such as the Canadian Council of Ministers of the Environment, the U.S. EPA, the U.S. National Biosolids Partnership, and the Water Environment Research Foundation.

3. Engage the soil ecotoxicology community in research and reviews on biosolids related issues.

4.2.3 Prioritization of Recommendations

Prioritization of the research efforts is properly accomplished by comparing the risks associated with the contaminants when loaded to the terrestrial environment in biosolids. Such assessments have not been completed. Otherwise any prioritization must be made based on professional judgement, which is a subjective interpretation of the compiled data herein.

Because the Biosolids Steering Committee has requested some prioritization of research efforts for contaminants in biosolids, and their fate in the terrestrial environment when applied to soils in biosolids, it seems reasonable to seek data for those contaminants where none currently exists on a multitude of issues. Using this approach, the priority efforts should be directed at the occurrence and concentrations in biosolids, and the fate, transport, accumulation and environmental effects of the following types of contaminants, in no preferential order:

- perfluorinated organic compounds;
- myriad personal care products including, but not limited to fluorescent whitening agents, quaternary ammonium compounds, siloxanes and UV filters;
- concentrations and viability of protozoans such as *Cryptosporidium* in biosolids and soils receiving biosolids applications;
- pathogens of recent concern such as H1N1 virus (swine influenza) and H5N1 and H5N2 viruses (avian influenza).

The above short list of contaminants is proposed based on the assumption that adequate analytical procedures exist to accomplish the research goals. If the analytical procedures do not exist, the greatest priority must be in the method development so that the research priorities identified can then be carried out.

It should also be stated that costs to continue to address single substances is prohibitative and efforts should be made to address mixures, their fate and significance to the environment and human health.

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Ying, GG., Yu, XY and Kookana, RS 2007. Biological Degradation of triclocarban and triclosan in a soil under aerobic and anaerobic conditions and comparison with environmental fate modeling. Environ. Poll. , 150, 300-305.

APPENDIX A: LIST OF EXPERTS ON BIOSOLIDS CONTAMINANT FATE

Table A-1. List of Experts on Biosolids Contaminant Fate

Name	Affiliation	Address	Tel	email	Context
Mr. Robert Bastian	U.S. EPA	Room 7329K EPA East, 1200 Pennsylvania Ave., NW, Washington, D.D. 20460	(202) 564-0653	bastian.robert@epa.gov	regulatory aspects of quality of biosolids
Dr. John Brooks	U.S. Dept. of Agriculture	USDA-ARS, 810 Hwy 12E, Mississippi State, MS 39762	(662) 320-7411	jbrooks@msa-msstate.ars.usda.gov	expert on pathogen fate in biosolids
Dr. Sally Brown	University of Washington	203 Bloedel Hall, Box 352100, Seattle, Washington 98195-2100	(206) 616-1299	slb@u.washington.edu	expert in fate of contaminants in land-applied biosolids
Mr. Jack Bryden	BC Ministry of Environment	2975 Jutland Road, Victoria, BC	(250) 387-9985	jack.bryden@gov.bc.ca	oversees biosolids issues in BC
Dr. Kent Burnison	Environment Canada	National Water Research Institute, 867 Lakeshore Road, Burlington, ONL7R 4A6	(905) 336-4407	Kent.Burnison@ec.gc.ca	Canadian expert on micro-constituents in wastewater and biosolids
Dr. Allison Cupples	Michigan State University	Dept. of Civil Engineering, East Lansing, MI 48824	(517) 342-3370	cupplesa@msu.edu	expert on micro-constituents in wastewater and biosolids
Mr. Robert Davis	European Union	66 Station Road, Chinnor, OXON, OX9 4PZ, England	011 441 844 352 771	robert.davis@wrcplc.co.uk	regulatory aspects of biosolids quality and beneficial use
Ms. Cecily Flemming	Ontario Ministry of the Environment	40 St. Clair Ave. W., 9th floor Toronto ON M4V1M2	(416) 327-6409	Cecily.Flemming@ontario.ca	Ontario MOE expert on pathogens and biosolids
Dr. Ed Furlong	U.S. Geological Survey	National Water Quality Laboratory, P.O. Box 25046, Denver Federal Center, Denver, CO 80225-0046	(303) 236-3941	efurlong@usgs.gov	expert on micro-constituents in wastewater and biosolids
Dr. Tom Granato	Metropolitan Water Reclamation District of Greater Chicago	Lue-Hing Research and Development Complex, 6001 West Pershing Road, Cicero, IL 60804, USA	(708) 222 4063	thomas.granato@mwrdgc.dst.il.us	expert in fate of contaminants in land-applied biosolids

continued

Table A-1 (cont'd)

Name	Affiliation	Address	Tel	email	Context
Dr. Rolf Halden	Arizona State University	Center for Environmental Biotechnology, The Biodesign Institute, 1001 S. McAllister Avenue, P.O. Box 875701, Tempe AZ 85287-5701	(480) 727 0893	Rolf.Halden@asu.edu	expert on micro-constituents in wastewater and biosolids
Dr. Rob Hale	Virginia Institute of Marine Science, The College of William and Mary	Dept of Aquatic animal Health, Gloucester Point, VA 23062	(804) 684-7228	hale@vims.edu	expert on micro-constituents in wastewater and biosolids
M. Marc Hébert	Ministère du Développement durable, de l'Environnement et des Parcs, Direction des politiques en milieu terrestre, Service agricole	675, boulevard René-Lévesque Est, 9e étage, boîte 71, Québec (Québec) G1R 5V7	(418) 521-3950 ext. 4826	marc.hebert@mddep.gouv.qc.ca	oversees biosolids issues in QC
Mr. Tony Ho	Retired, Ontario Ministry of the Environment	Richmond Hill, Ontario	(905) 770-0104	ho_tony@ymail.com	retired biosolids specialist, Ontario MOE
Dr. Sonya Kleywegt	Ontario Ministry of the Environment	40 St. Clair Ave. W., 9th floor Toronto ON M4V1M2	(416) 212-1525	sonya.kleywegt@ontatio.ca	Ontario MOE expert on micro-constituents in wastewater and biosolids
Dr. Mark LaGuardia	Virginia Institute of Marine Science, The College of William and Mary	Dept of Aquatic animal Health, Gloucester Point, VA 23062	(804) 684-7728	markl@vims.edu	expert on micro-constituents in wastewater and biosolids
Dr. David Lapen	Agriculture and Agri-Food Canada	960 Carling Ave Ottawa, Ontario K1A 0C6	(613) 759-1537	David.Lapen@agr.gc.ca	expert in fate of contaminants in land-applied biosolids

Continued

Table A-1 (cont'd)

Name	Affiliation	Address	Tel	email	Context
Dr. Hing-Biu (Bill) Lee	Environment Canada	National Water Research Institute, 867 Lakeshore Road, Burlington, ONL7R 4A6	(905) 336-6266	bill.lee@ec.gc.ca	Canadian expert on micro-constituents in wastewater and biosolids
Dr. Chris Metcalfe	Trent University	ESC A111, 1600 West Bank Drive, Peterborough, ON K9J 7B8	(705) 748-1011 ext 7272	cmetcalfe@trentu.ca	Analytical procedures for measuring PPCPs in biosolids, soils and drainage
Dr. George O'Connor	University of Florida	410 Newell Hall, PO Box 110510 Gainesville, FL 32611-0510	(352) 392-1781 ext 329	gao@ufl.edu	expert in fate of contaminants in land-applied biosolids
Mr. Chris Peot/ Dr. Sudhir Murthy	DC Water and Sewerage Authority	5000 Overlook Avenue SW, Washington, DC 20032	(202) 787-4329	chris_peot@dcwasa.com	Biosolids Division Manager/Research Engineer
Dr. Ian Pepper	The University of Arizona	2601 E. Airport Drive, Tucson, AZ 85756	(520) 626-3328	ipepper@ag.arizona.edu	expert on pathogen fate in biosolids especially in U.S. southwest
Mr. Frans Schulting	Global Water Research Coalition	c/o International Water Association, Alliance House, 12 Caxton Street, London SW1H 0QS, United Kingdom	+ 44 207 654 5545	f.lschulting@freeler.nl	point of contact for biosolids issues and research for the GWRC
Mr. Rick Stevens	U.S. EPA	USEPA - Office of Science and Technology ,EPA Connecting Wing, 1200 Pennsylvania Avenue, NW Washington, DC 20460	(202) 566-1135	stevens.rick@epa.gov	leader of US Targeted National Sewage Sludge Survey for EPA

Continued

Table A-1 (cont'd)

Name	Affiliation	Address	Tel	email	Context
Dr. Ed Topp, Angela Lorenzen, Ralph Chapman, Lyne Sabourin	Agriculture Canada	1391 Sandford St. London, Ontario N5V 4T3	(519) 457-1470 ext 235	ed.topp@agr.gc.ca	expert in fate of contaminants in land-applied biosolids
Dr. Adrian Unc	University of Ottawa	Centre for Research on Environmental Microbiology, 451 Smyth Rd., Ottawa, Ontario K1H 8M5	(613) 562-5800 ext. 8568.	aunc@uottawa.ca	Canadian expert on pathogens and biosolids
Mr. Mike Van Ham	Sylvis Environmental, Inc.	427 Seventh St., New Westminster, BC , V3M3L2	(604) 777-9788	mvanham@sylvis.com	biosolids beneficial use
Dr. Kang Xia	University of Georgia	Dept of Crop & Soil Sciences, 3111 Miller Plant Sciences Building, Athens, GA 30602	(662) 325 5896	kxia@uga.edu	expert on micro-constituents in wastewater and biosolids

APPENDIX B: RESPONSES OF BIOSOLIDS EXPERTS TO SURVEY QUESTIONS

QUESTIONNAIRE RESPONSE FOR 2009 WEAO "ASSESSING THE FATE AND SIGNIFICANCE OF SELECTED METALS, TRACE ORGANICS, AND PATHOGENS IN SEWAGE BIOSOLIDS APPLIED TO AGRICULTURAL LAND"

Mr. Robert Bastian (by telephone)
U.S. EPA, Washington, D.C. Tel: (202) 564-0653; email: Bastian.Robert@epamail.epa.gov

Question	Response
1. Please indicate what your research interests are with respect to contaminants in biosolids? What classes of contaminants?	How they affect regulatory issues and standards development; Also personal management of research projects developed under ear-marked Congressional funding.
2. Could you briefly summarize what you believe are the major observations and conclusions to date?	
3. What do you see as the major research gaps that need to be addressed?	End-point values are needed to assess the effects of these contaminants in different matrices (soils, wildlife, plants, aquatic species) receiving biosolids amendment.
4. Can you indicate in general terms what on-going or future research you have planned?	A national demonstration of reclaimed wastewater and effects on soil aquifers (ear-marked Congressional funding under Clean Water Act Section 104 b3).

QUESTIONNAIRE RESPONSE FOR 2009 WEAO "ASSESSING THE FATE AND SIGNIFICANCE OF SELECTED METALS, TRACE ORGANICS, AND PATHOGENS IN SEWAGE BIOSOLIDS APPLIED TO AGRICULTURAL LAND"

Question	Response
5. Do you have any publications in press (not yet published)? On what topic?	
6. Are you aware of any "gray" literature, such as unpublished data or papers that would add value to our report?	Risk assessment study on triclocarban by grad student of George O'Connor's at University of Florida [Elizabeth Hodges Snyder]; study on endocrine disrupting compounds in biosolids by Karl Linden of Duke University [now with Colorado School of Mines]; work by Metro Water Reclamation District of Greater Chicago
7. Are there other researchers you might suggest that we could contact to acquire additional information? Please provide contact info if possible.	see question 6 above

QUESTIONNAIRE RESPONSE FOR 2009 WEAO "ASSESSING THE FATE AND SIGNIFICANCE OF SELECTED METALS, TRACE ORGANICS, AND PATHOGENS IN SEWAGE BIOSOLIDS APPLIED TO AGRICULTURAL LAND"

Dr. John Brooks
U.S. Dept. of Agriculture Tel: (662) 320-7411 email: john.brooks@ars.usda.gov

Question	Response
1. Please indicate what your research interests are with respect to contaminants in biosolids? What classes of contaminants?	Most of my recent research interest centers around pathogens, specifically, bacterial and viral enteric pathogens in biosolids and manure. We are interested in antibiotic resistance and contaminating antibiotics and personal care products in biosolids and manure. Overall we conduct experiments with respect to persistence and transport (horizontally and vertically) through the soil profile, air, water, and vegetation contaminated by these residuals.
2. Could you briefly summarize what you believe are the major observations and conclusions to date?	To date, the scientific community is aware and has accepted that Class B biosolids has pathogens, albeit at relatively low levels as currently measured by our limited technologies. These low levels generally speaking do not present a major mathematical risk, however in situations such as the recent foodborne vegetable outbreaks, a similar assessment would have also been made, and yet 100s of cases and a few deaths resulted from our lack of understanding as it relates to low level pathogen survival in soil and crops... how did it get there, etc? Add in antibiotic resistance, at this point it also does not appear to be significantly influenced by biosolids use, however our grasp of the situation is only scratching the surface. However if the Part 503 rules are followed these risks are severely limited; it appears that they do function well.
3.What do you see as the major research gaps that need to be addressed?	Low level pathogen survival and antibiotic resistance are chief amongst my concerns. Included with low level pathogen survival I would also suggest bacterial regrowth as a concern as well. The concern with personal care products and pharmaceuticals is legitimate as once again we have a limited knowledge base, but the research that is out there seems to suggest that the levels are below threshold levels.

QUESTIONNAIRE RESPONSE FOR 2009 WEAO "ASSESSING THE FATE AND SIGNIFICANCE OF SELECTED METALS, TRACE ORGANICS, AND PATHOGENS IN SEWAGE BIOSOLIDS APPLIED TO AGRICULTURAL LAND"

Question	Response
4. Can you indicate in general terms what on-going or future research you have planned?	Currently, we are investigating the survival of bacterial and viral pathogens in manure vs. biosolids land application in field and bench level experiments. We have various projects involving composting in the poultry and swine industries and the influence of land applied manures/biosolids on antibiotic resistance in the soil population.
5. Do you have any publications in press (not yet published)? On what topic?	Yes, various manuscripts recently submitted on aerosols in CAFO environments, runoff of land applied manure, and soil nutrient/microbial quality as influenced by long term manure application. We also have a couple papers on long term biosolids application and its influence on microbial properties and activity in soil as well as microbial population influences.
6. Are you aware of any "gray" literature, such as unpublished data or papers that would add value to our report?	No
7. Are there other researchers you might suggest that we could contact to acquire additional information? Please provide contact info if possible.	Ian L. Pepper (University of Arizona); Charles P. Gerba (University of Arizona), Jordan Peccia (Yale University)

QUESTIONNAIRE RESPONSE FOR 2009 WEAO "ASSESSING THE FATE AND SIGNIFICANCE OF SELECTED METALS, TRACE ORGANICS, AND PATHOGENS IN SEWAGE BIOSOLIDS APPLIED TO AGRICULTURAL LAND"

Dr. Sally Brown
University of Washington Tel: (206) 616-1299; email: slb@u.washington.edu

Question	Response
1. Please indicate what your research interests are with respect to contaminants in biosolids? What classes of contaminants?	I have worked on nonylphenol, estrogens and triclosan in biosolids amended soils My previous work was on Pb, Zn and Cd in biosolids
2. Could you briefly summarize what you believe are the major observations and conclusions to date?	Biosolids reduce metal availability in contaminated soils NP, estrogens and triclosan are quickly degraded in biosolids amended soils- they do not appear to be of significant concern in terrestrial ecosystems
3. What do you see as the major research gaps that need to be addressed?	Benefits associated with land application of biosolids
4. Can you indicate in general terms what on-going or future research you have planned?	Carbon sequestration in biosolids amended soils

QUESTIONNAIRE RESPONSE FOR 2009 WEAO "ASSESSING THE FATE AND SIGNIFICANCE OF SELECTED METALS, TRACE ORGANICS, AND PATHOGENS IN SEWAGE BIOSOLIDS APPLIED TO AGRICULTURAL LAND"

Question	Response
5. Do you have any publications in press (not yet published)? On what topic?	no
6. Are you aware of any "gray" literature, such as unpublished data or papers that would add value to our report?	no
7. Are there other researchers you might suggest that we could contact to acquire additional information? Please provide contact info if possible.	The W2170 group- Greg Evanylo would be the contact person evanylo@vt.edu

QUESTIONNAIRE RESPONSE FOR 2009 WEAO "ASSESSING THE FATE AND SIGNIFICANCE OF SELECTED METALS, TRACE ORGANICS, AND PATHOGENS IN SEWAGE BIOSOLIDS APPLIED TO AGRICULTURAL LAND"

Dr. Ed Furlong (telephone interview Nov 12 2009)
U.S. Geological Survey Tel: (303) 236-3941; email: efurlong@usgs.gov

Question	Response
1. Please indicate what your research interests are with respect to contaminants in biosolids? What classes of contaminants?	• Pharmaceuticals, endocrine disrupting chemicals • Development of new methods of emerging contaminants • Studying the transfer of compounds to biosolids during wastewater treatment • Distribution fate effects after field application
2. Could you briefly summarize what you believe are the major observations and conclusions to date?	• These compounds are of importance in biosolids due to their magnification (i.e. concentration when forming biosolids from liquid) • Application to soils (semi-arid) can persist • Migration/movement is more difficult to assess • Susceptibility to transport offsite appears to be important as biosolids are exposed to meteorological conditions potentially into surface water
3. What do you see as the major research gaps that need to be addressed?	• Long-term persistence and fate (one and two seasons have been studied, but there has been no opportunity to study soil transport over multiple growing seasons)
4. Can you indicate in general terms what on-going or future research you have planned?	• Rearrangement on soil surface under heavy rainfall (semi-arid climate) • Off-site transport under extreme rainfall events under semi-arid conditions • Bioaccumulation in earthworms

QUESTIONNAIRE RESPONSE FOR 2009 WEAO "ASSESSING THE FATE AND SIGNIFICANCE OF SELECTED METALS, TRACE ORGANICS, AND PATHOGENS IN SEWAGE BIOSOLIDS APPLIED TO AGRICULTURAL LAND"

Question	Response
5. Do you have any publications in press (not yet published)? On what topic?	no
6. Are you aware of any "gray" literature, such as unpublished data or papers that would add value to our report?	US EPA has just published within the last 6-12 months (available on website) a national sludge survey
7. Are there other researchers you might suggest that we could contact to acquire additional information? Please provide contact info if possible.	Ed Topp (Agriculture Canada) Chris Metcalf (Trent University) Thomas Borch (Colorado State University) 970-491-6235 [Borch has worked with Furlong on research projects]

QUESTIONNAIRE RESPONSE FOR 2009 WEAO "ASSESSING THE FATE AND SIGNIFICANCE OF SELECTED METALS, TRACE ORGANICS, AND PATHOGENS IN SEWAGE BIOSOLIDS APPLIED TO AGRICULTURAL LAND"

Charles Gerba
University of Arizona Tel: (520) 621-6906; email: gerba@ag.arizona.edu

Question	Response
1. Please indicate what your research interests are with respect to contaminants in biosolids? What classes of contaminants?	Pathogen removal by treatment and fate after land application. Occurrence and concentration of pathogens in biosolids.
2. Could you briefly summarize what you believe are the major observations and conclusions to date?	Most pathogens have a limited lifetime time after land application. Some aerosol risk to on-site workers during spray application to biosolids
3. What do you see as the major research gaps that need to be addressed?	Removal of infectious prions by treatment and survival after land application. Better data on the occurrence of *Ascaris* ova and more quantitative data on survival in the environment. Quantitative risk assessment of *Ascaris* after land application. Potential for wild animals to become infected with pathogens in biosolids after land application. Pathogens in irrigation return flows from irrigated agriculture from fields onto which biosolids have been applied. Migration of pathogens from fields that have tile drains fields beneath them in cold climates with high rainfall. Concentration of adenoviruses in biosolids needed as they may occur in greater concentrations than other enteric viruses. Better methods for the recovery of viruses from biosolids. Current methods range from 0.1% to 20%. More data on infectivity of Cryptosporidium after biosolid treatment and occurrence in biosolids.

QUESTIONNAIRE RESPONSE FOR 2009 WEAO "ASSESSING THE FATE AND SIGNIFICANCE OF SELECTED METALS, TRACE ORGANICS, AND PATHOGENS IN SEWAGE BIOSOLIDS APPLIED TO AGRICULTURAL LAND"

Question	Response
4. Can you indicate in general terms what on-going or future research you have planned?	Removal of infectious prions by treatment and survival after land application. Occurrence and concentration of adenovirus on biosolids.
5. Do you have any publications in press (not yet published)? On what topic?	Many. Impact of biosolids on microbial genetic diversity of bacteria in soil. Fate of antibiotic resistant bacteria in soils to which biosolids have been applied. Nation wide survey on the occurrence of pathogens in biosolids in the United States.
6. Are you aware of any "gray" literature, such as unpublished data or papers that would add value to our report?	
7. Are there other researchers you might suggest that we could contact to acquire additional information? Please provide contact info if possible.	

QUESTIONNAIRE RESPONSE FOR 2009 WEAO "ASSESSING THE FATE AND SIGNIFICANCE OF SELECTED METALS, TRACE ORGANICS, AND PATHOGENS IN SEWAGE BIOSOLIDS APPLIED TO AGRICULTURAL LAND"

Rolf Halden
Arizona State University Tel: (480) 727-0893; email: halden@asu.edu

Question	Response
1. Please indicate what your research interests are with respect to contaminants in biosolids? What classes of contaminants?	Emerging organic contaminants. Unmonitored, persistent, organic high-production volume (HPV) chemicals Organohalogens in biosolids
2. Could you briefly summarize what you believe are the major observations and conclusions to date?	In 2004 we identified triclocarban as an overlooked environmental contaminant. In 2006 we used mass balances to demonstrate that the two antimicrobials triclosan and triclocarban are not effectively biodegraded during wastewater treatment, and that both substances accumulate in biosolids equivalent to 50% and 76%, respectively, of the contaminant mass arriving at the plant in raw sewage. We performed meta-analysis of existing mass balances and used them to predict the existence of other, yet unmonitored persistent compounds in biosolids. Our research indicates that biosolids are a repository of persistent chemistry.
3. What do you see as the major research gaps that need to be addressed?	More research should be conducted to determine the chemical composition of biosolids. Any compound that persists the optimized treatment process in the wastewater treatment plant likely will also persist in the environment and cause harm there due to its longevity.
4. Can you indicate in general terms what on-going or future research you have planned?	We conducted a screening of 2006 unmonitored organic hydrophobic HPV compounds and identified a list of substances that are projected to be toxic as well as persistent. We are planning to screen the U.S. nationwide biosolids repository we created at ASU to see whether these substances are indeed present.

QUESTIONNAIRE RESPONSE FOR 2009 WEAO "ASSESSING THE FATE AND SIGNIFICANCE OF SELECTED METALS, TRACE ORGANICS, AND PATHOGENS IN SEWAGE BIOSOLIDS APPLIED TO AGRICULTURAL LAND"

Question	Response
5. Do you have any publications in press (not yet published)? On what topic?	1. Deo, R. P. and **Rolf U. Halden.*** 2009. Effect of Filtration on the Quality of Monitoring Data Reported for Organic Compounds during Wastewater Treatment. *J. Environ. Monit.* (Accepted for Publication). 2. Deo, R. P. and **Rolf U. Halden.*** 2009. Empirical Model for Predicting Concentrations of Refractory Hydrophobic Organic Compounds in Digested Sludge from Municipal Wastewater Treatment Plants. *Environ. Chem.* (In Press). 3. Heidler J. and **R. U. Halden**.* 2009. Fate of Organohalogens in U.S. Wastewater Treatment Plants and Estimated Chemical Releases to Soils Nationwide from Biosolids Recycling. *J. Environ. Monit.* (In Press; Accessible online at: DOI:10.1039/B914324F). 4. McClellan, K. and R. U. Halden*. 2010. Pharmaceuticals and Personal Care Products in Archived U.S. Biosolids from the 2001 EPA National Sewage Sludge Survey. Water Research. In Revision. 5. Higgins, C. P., Z. J. Paesani, T. E. A. Chalew, and **R. U. Halden**. 2009. Bioaccumulation of Triclocarban in *Lumbriculus variegates*. *Environ. Toxicol. Chem.* 65:141-148. 6. I am the editor of a book on ACS book on Pharmaceuticals, Personal Care Products, and Organohalogens in the U.S. Environment. The book will appear online in July 2010.
6. Are you aware of any "gray" literature, such as unpublished data or papers that would add value to our report?	No.

QUESTIONNAIRE RESPONSE FOR 2009 WEAO "ASSESSING THE FATE AND SIGNIFICANCE OF SELECTED METALS, TRACE ORGANICS, AND PATHOGENS IN SEWAGE BIOSOLIDS APPLIED TO AGRICULTURAL LAND"

Question	Response
7. Are there other researchers you might suggest that we could contact to acquire additional information? Please provide contact info if possible.	Lakhwinder S. Hundal, Ph.D. Metropolitan Water Reclamation District of Greater Chicago, Research & Development Dep., 6001 W Pershing Rd., Cicero, IL 60804; Email: lakhwinder.hundal@mwrd.org; Tel: (708) 588-4201 Rob Hale, Professor Department of Environmental & Aquatic Animal Health Virginia Institute of Marine Science P.O. Box 1346 C/O Central Receiving 1208 Greater Road Gloucester Pt, VA 23062 Tel : (804) 684-7228; email hale@vims.edu Chad A. Kinney Department of Chemistry, Colorado State University at Pueblo, 2200 Bonforte Blvd, Pueblo, Colorado Email: chad.kinney@colostate-pueblo.edu; Tel (719) 549-2600 Ed Topp Ph.D. Principal Research Scientist Agriculture and Agri-Food Canada 1391 Sandford Str., London, ON, N5V 4T3 Canada Tel: 519-457-1470 e.235; email: toppe@agr.gc.ca

QUESTIONNAIRE RESPONSE FOR 2009 WEAO "ASSESSING THE FATE AND SIGNIFICANCE OF SELECTED METALS, TRACE ORGANICS, AND PATHOGENS IN SEWAGE BIOSOLIDS APPLIED TO AGRICULTURAL LAND"

Dr. Mark LaGuardia
Virginia Institute of Marine Science, The College of William and Mary Tel: (804) 684-7728; email: markl@vims.edu

Question	Response
1. Please indicate what your research interests are with respect to contaminants in biosolids? What classes of contaminants?	To understand the chemical constituents within biosolids and their fate. Contaminant interest includes brominated flame-retardants (BFRs). BFRs have been detected on biosolids (detected in every sample reported in 2008 USEPA's NTSSS). Some BFRs are considered endocrine disrupters, detected in human breast milk and been shown to disrupt behavioural development in laboratory studies. Other contaminants include personal care products and pharmaceuticals.
2. Could you briefly summarize what you believe are the major observations and conclusions to date?	Wastewater treatment by its nature collects and concentrates chemicals that enter its waste stream. During the treatment process some classes of chemicals have been shown to mineralize but others transform (metabolites) or persist the treatment process and reside in sludge. These chemicals then enter the environment with land-application but with the exception of metals little is understood about their environment fate.
3. What do you see as the major research gaps that need to be addressed?	In 1996 and 2002 the National Research Council (NRC) of the National Academy of Science, along with the Water Environment Research Foundation (WERF) Biosolids Research Summit of 2003 concluded that the knowledge of the chemical constituents within biosolids and their associated risks is largely unknown. I also believe much more needs to be done to address this issue, as it is the bases (knowing which chemicals reside in sludge) for a complete risk assessment.
4. Can you indicate in general terms what on-going or future research you have planned?	Continue to develop analytical methods to analyze constituents in biosolids and those constituents released to soil, air and water by its land application.

QUESTIONNAIRE RESPONSE FOR 2009 WEAO "ASSESSING THE FATE AND SIGNIFICANCE OF SELECTED METALS, TRACE ORGANICS, AND PATHOGENS IN SEWAGE BIOSOLIDS APPLIED TO AGRICULTURAL LAND"

5. Do you have any publications in press (not yet published)? On what topic?	BFR trends in biosolids.
6. Are you aware of any "gray" literature, such as unpublished data or papers that would add value to our report?	No
7. Are there other researchers you might suggest that we could contact to acquire additional information? Please provide contact info if possible.	

QUESTIONNAIRE RESPONSE FOR 2009 WEAO "ASSESSING THE FATE AND SIGNIFICANCE OF SELECTED METALS, TRACE ORGANICS, AND PATHOGENS IN SEWAGE BIOSOLIDS APPLIED TO AGRICULTURAL LAND"

Lynda McCarthy (telephone interview Nov 16 2009)
Ryerson University, Toronto, ON Tel: (416) 979-5000 ext 6378; email: l2mccart@ryerson.ca

Question	Response
1. Please indicate what your research interests are with respect to contaminants in biosolids? What classes of contaminants?	Stage 1: Environmental Assessment with respect to terrestrial organisms. Stage 2: What happens to adjacent bodies of water after heavy rain events. Interested in the impact on biological organisms.
2. Could you briefly summarize what you believe are the major observations and conclusions to date?	Very, very preliminary results indicate no acute impact on organisms with biosolids addition. (Studying earthworms, spring tails, plants)
3. What do you see as the major research gaps that need to be addressed?	No work is being done on the study of the organisms. Is the addition of biosolids sustainable with respect to the organisms.
4. Can you indicate in general terms what on-going or future research you have planned?	Continuing with this long-term work. Looking as well at acute toxicity. Are the organisms reproducing? Continue with reproductive/life-cycle tests. Also, in crops where are the organic contaminants being sequestered (i.e. are we getting ibuprofen in the corn?)

QUESTIONNAIRE RESPONSE FOR 2009 WEAO "ASSESSING THE FATE AND SIGNIFICANCE OF SELECTED METALS, TRACE ORGANICS, AND PATHOGENS IN SEWAGE BIOSOLIDS APPLIED TO AGRICULTURAL LAND"

Question	Response
5. Do you have any publications in press (not yet published)? On what topic?	WEAO September 2009 Conference Proceedings: peer review
6. Are you aware of any "gray" literature, such as unpublished data or papers that would add value to our report?	NO
7. Are there other researchers you might suggest that we could contact to acquire additional information? Please provide contact info if possible.	NO The people in charge are not providing funding for what is a logical study. Everything is concerned with fate & transport of 20,000 chemicals, but nothing is being done to study the impact on the organisms.

QUESTIONNAIRE RESPONSE FOR 2009 WEAO "ASSESSING THE FATE AND SIGNIFICANCE OF SELECTED METALS, TRACE ORGANICS, AND PATHOGENS IN SEWAGE BIOSOLIDS APPLIED TO AGRICULTURAL LAND"

George O'Connor
University of Florida Tel: (352) 392-7181 ext 329; email: gao@ufl.edu

Question	Response
1. Please indicate what your research interests are with respect to contaminants in biosolids? What classes of contaminants?	Yes, antimicrobials (TCS and TCC)
2. Could you briefly summarize what you believe are the major observations and conclusions to date?	Behaviour of biosolids-borne antimicrobials different than spiked (neat), added chemicals. Current models of fate, transport, and risk (especially models based on modeled parameters from Kow values) are insufficient.
3. What do you see as the major research gaps that need to be addressed?	Bioavailability of biosolids-borne chemicals and of non-extractable residues that form.
4. Can you indicate in general terms what on-going or future research you have planned?	Address bioavailability issues and seek to improve models of fate, transport, and risk assessment.

QUESTIONNAIRE RESPONSE FOR 2009 WEAO "ASSESSING THE FATE AND SIGNIFICANCE OF SELECTED METALS, TRACE ORGANICS, AND PATHOGENS IN SEWAGE BIOSOLIDS APPLIED TO AGRICULTURAL LAND"

Question	Response
5. Do you have any publications in press (not yet published)? On what topic?	Yes (5 papers), on various aspects of TCC fate, transport, and risk assessment. Original data described in dissertation by Elizabeth Hodges Snyder, 2009 Univ. FL.
6. Are you aware of any "gray" literature, such as unpublished data or papers that would add value to our report?	Snyder's dissertation (hardly "gray"), plus Metropolitan Water Reclamation District of Greater Chicago (MWRDGC) data (some are field data)
7. Are there other researchers you might suggest that we could contact to acquire additional information? Please provide contact info if possible.	Kang Xia (Mississippi), Thomas Young (UC, Davis), Ed Topp (Environ. Canada), Lakhwinder Hundal (MWRDGC), Chris Higgins (Colo. School Mines, Golden, CO)

QUESTIONNAIRE RESPONSE FOR 2009 WEAO "ASSESSING THE FATE AND SIGNIFICANCE OF SELECTED METALS, TRACE ORGANICS, AND PATHOGENS IN SEWAGE BIOSOLIDS APPLIED TO AGRICULTURAL LAND"

Shirley Anne Smyth (telephone interview Nov 19, 2009)
Environment Canada, Burlington, ON Tel: (905) 336-4509; email: ShirleyAnne.Smyth@ec.gc.ca

Question	Response
1. Please indicate what your research interests are with respect to contaminants in biosolids? What classes of contaminants?	Contaminant fate in municipal wastewater: bioaccumulation, biodegradation products (metabolites); mass balances. Municipal biosolids: determine occurrence and fate; what are we accomplishing with existing technologies? What other technologies could be examined?
2. Could you briefly summarize what you believe are the major observations and conclusions to date?	Observations are limited by analytical techniques available. Synthetic musk fragrances may be a problem in biosolids. Also need to track antimicrobials (triclosan and triclocarban) and polybrominated diphenyl ethers.
3. What do you see as the major research gaps that need to be addressed?	Development of good analytical methods is lacking. Need to identify fate and effects of micro-contaminants in the environment
4. Can you indicate in general terms what on-going or future research you have planned?	A program on surveillance of micro-contaminants in treatment plants including biosolids will continue this coming year, under the Chemicals Management Plan, funded by Environment Canada and Health Canada. It will include both cold and warm weather sampling components at 20 wastewater treatment plants representative of a broad cross-section of Treatment processes used in Canada

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Question	Response
5. Do you have any publications in press (not yet published)? On what topic?	No
6. Are you aware of any "gray" literature, such as unpublished data or papers that would add value to our report?	A workshop on pharmaceuticals and personal care products in wastewater was held in Niagara-on-the-Lake in 2007; A similar workshop was held in Toronto in June.
7. Are there other researchers you might suggest that we could contact to acquire additional information? Please provide contact info if possible.	Ed Topp, Agriculture and Agri-Food Canada Lynda McCarthy, Ryerson University

QUESTIONNAIRE RESPONSE FOR 2009 WEAO "ASSESSING THE FATE AND SIGNIFICANCE OF SELECTED METALS, TRACE ORGANICS, AND PATHOGENS IN SEWAGE BIOSOLIDS APPLIED TO AGRICULTURAL LAND"

Dr. Kang Xia
Mississippi State University Tel: (662) 325-5896; email: kx6@msstate.edu

Question	Response
Please indicate what your research interests are with respect to contaminants in biosolids? What classes of contaminants?	My research interests are: • Biotic and abiotic transformation products and pathways of PPCPs associated with biosolids • Persistence of PPCPs in biosolids-amended soils The class of contaminants in biosolids is PPCPs.
Could you briefly summarize what you believe are the major observations and conclusions to date?	Adsorption of PPCPs to biosolids may adversely affect their transformation in soils, an important factor that must be included in models predicting environmental fate of biosolids-associated PPCPs.
What do you see as the major research gaps that need to be addressed?	Bioaccumulation and ecotoxicity of PPCPs in biosolids that applied on land.
Can you indicate in general terms what on-going or future research you have planned?	On-going: • Biotic and abiotic transformation products and pathways of PPCPs associated with biosolids • Persistence of PPCPs in biosolids-amended soils Future: • Bioaccumulation of PPCPs in biosolids • Technologies capable of reducing PPCPs in biosolids

QUESTIONNAIRE RESPONSE FOR 2009 WEAO "ASSESSING THE FATE AND SIGNIFICANCE OF SELECTED METALS, TRACE ORGANICS, AND PATHOGENS IN SEWAGE BIOSOLIDS APPLIED TO AGRICULTURAL LAND"

Question	Response
Do you have any publications in press (not yet published)? On what topic?	4 publications are in press on topics: • Transformation of triclosan and triclocarban in soils and biosolids-applied soils • Occurrence and fate of PPCPs in soils receiving long-term biosolids application • Abiotic transformation of triclosan on mineral surfaces • Detection of triclosan using molecular imprint technique
Are you aware of any "gray" literature, such as unpublished data or papers that would add value to our report?	A recent oral presentation by Kuldip Kumar et al., entitled: "Uptake of pharmaceutical and personal care products by plants – potential Mechanisms" at the 2009 ASA-CSSA-SSSA International Annual Meetings.
Are there other researchers you might suggest that we could contact to acquire additional information? Please provide contact info if possible.	Dr. Kuldip Kumar of the Metropolitan Water Reclamation District of Greater Chicago (kuldip.kumar@mwrd.org).

Additional survey requests were submitted to:

Dr. Allison Cupples, Michigan State University
Dr. Thomas Granato, Metropolitan Water District of Greater Chicago
Mr. Alan Hais, Program Manager, Water Environment Research Foundation
Dr. Sonya Kleywegt, Ontario Ministry of the Environment (declined)
Dr. Bill Lee, Environment Canada
Dr. Murray McBride, Cornell University
Mr. Chris Peot, DC Water and Sewer Authority
Mr. Vince Pileggi, Ontario Ministry of the Environment (deferred to Dr. S. Kleywegt and Ms. S. Bonte-Gelok)
Dr. Adrian Unc, University of Ottawa