Beneficial Use of Municipal Biosolids in Agriculture – Literature Review and Recommendations Concerning the Impact of Iron and Aluminum Salts on Soil Phosphorus Availability

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ABSTRACT

Aluminum or iron salts added during municipal wastewater (sewage) treatment hydrolyze to form amorphous oxides that sorb organic matter, phosphorus (P) and other wastewater constituents. During effluent clarification they settle out of suspension and contribute to the sewage biosolids. Effects of the amorphous oxides on soil P solubility resulting from long-term, repeat applications of sewage biosolids are not well understood and the main concerns follow: (1) soil P solubility may increase, contributing to water pollution; and (2) soil P solubility may decrease, contributing to crop P deficiency and reduced yields. A literature review was conducted and the proposed Québec land application criteria were assessed. Findings indicated that P solubility in acid and noncalcareous neutral soils (i.e., most Québec soils) is closely related to the degree of P saturation of their amorphous oxides ($DPS_{M3}4$ = M3P / AlM3; concentrations in mg / kg soil), rather than the actual amounts of amorphous oxides in the soils. The critical $DPS_{M3}4$ values are 0.025 for heavy soils (> 30% clay) and 0.04 for light soils (≤ 30% clay), below which crop deficiency is likely to occur, and 0.075 for heavy soils and 0.15 for light soils, above which there is considerable risk of water contamination. Thus, it is recommended that:

1. Land application of sewage biosolids to Québec soils should be based on $DPS_{M3}4$ agri-environmental criteria. Soils should be monitored and land application discontinued if $DPS_{M3}4$ values increase to 0.15 for soils with ≤ 30% clay and to 0.075 for soils with > 30% clay, or if $DPS_{M3}4$ values decrease to 0.04 for soils with ≤ 30% clay and to 0.025 for soils with > 30% clay.

2. Research is required to determine whether Al / Fe rich sewage biosolids or other residues effectively reduce the risk of water pollution associated with $DPS_{M3}4$ values exceeding 0.15 for soils having ≤ 30% clay and 0.075 for soils having > 30% clay.

3. Whereas Fe amorphous oxide is not a significant contributor to P sorption in most acid and noncalcareous neutral Québec soils, it could become significant in soils with a history of repeat applications of biosolids rich in Fe. These conditions are unlikely to occur in Québec since:
    - biosolids containing Al or Fe salts are applied to < 0.3% of agricultural soils,

- few biosolids contain Fe salts,
- few soils receive long-term repeat loadings of biosolids, and
- few soils receiving Fe salt treated biosolids exhibit low $DPS_{M3}4$ values.

However, Mehlich-3 Fe analysis should be performed for Québec soils with low $DSP_{M3}4$ values and a history of repeat applications of biosolids rich in Fe.

4. All constraints in both the Canadian standards for pelletized biosolids and the Québec Provisional Criteria relating to Mehlich-3 extractable Al + 0.5 Fe (mg / kg) in soils and total Al + 0.5 Fe (mg / kg) in sewage biosolids and other fertilizing residuals should be deleted.

5. The equation for $P_{available}$ in the Québec Provisional Criteria should be maintained to estimate short-term P availability for land application of sewage biosolids.

6. Research is required to determine if the Pavailable equation should be modified to reflect the slow-release P fertilizer property of sewage biosolids.

ABBREVIATIONS

Al: Aluminum

Al_{ox}, Fe_{ox} and P_{ox}: Ammonium oxalate extractable Al, Fe and P

AlM3, FeM3: Mehlich-3 extravtable Al and Fe

cm: Centimetre

ds: Dry solids

DPS: Degree of soil P saturation

DPS_{M3}: Mehlich-3 degree of soil P saturation (M3P / AlM3)

$DPS_{M3}1$: Mehlich-3 degree of soil P saturation (M3P / AlM3); concentrations in mmol / kg soil

$DPS_{M3}2$: Mehlich-3 degree of soil P saturation (M3P / AlM3 + FeM3); concentrations in mmol / kg soil

$DPS_{M3}3$: Mehlich-3 degree of soil P saturation (M3P / P fixation capacity); concentrations in mg / kg soil

$DPS_{M3}4$: Mehlich-3 degree of soil P saturation (M3P / AlM3); concentrations in mg / kg soil

$DPS_{M3}5$: Mehlich-3 degree of soil P saturation (M3P / AlM3); concentrations in mg / L soil

DPS_{ox}: Ammonium oxalate degree of soil P saturation ($P_{OX} / [Al_{OX} + Fe_{OX}]$); concentrations in mmol / kg soil

$DPS_{ox}1$: Ammonium oxalate degree of soil P saturation ($P_{ox} / 0.61[Al_{ox} + Fe_{ox}]$); concentrations in mmol / kg soil

DRP: Dissolved reactive P

EPC_0: Equilibrium P concentration at zero sorption/desorption

Fe: Iron

FeO-P: Iron oxide strip extractable P = readily desorbable P

ha: Hectare

K: Potassium

kg: kilogram

L: Litre

M: Maximum soil P sorption capacity

M3P: Mehlich-3 extractable P

MCP: Monocalcium phosphate fertilizer

mg: milligram

Mg: Megagram = tonne

mmol: millimole

MRF: Residual fertilizing materials

N: Nitrogen

NH_3: Ammonia

NH_4Cl: Ammonium chloride

Olsen P: Sodium bicarbonate ($NaHCO_3$) extractable P

P: Phosphorus

P_{si}: P sorption index

SRP: Soluble reactive phosphorus

STP: Soil test P

TSP: Triple superphosphate fertilizer

WSP: Water-soluble P

WTR: Water treatment residual

yr: Year

1. INTRODUCTION

Aluminum (Al) or iron (Fe) salts may be added during municipal wastewater treatment to enhance removal of organic matter, phosphorus (P) and other constituents. Whereas Al is usually added as aluminum sulfate [$Al_2(SO_4)_3 \cdot 18\ H_2O$] or alum [$K_2SO_4 \cdot Al_2(SO4)_3 \cdot 24\ H_2O$], Fe may be added in various forms as chlorides ($FeCl_2$ or $FeCl_3$), sulfates ($FeSO_4$ or $Fe_3(SO_4)_2$) or an industrial byproduct such as pickle liquor.

In contact with water, these salts hydrolyze to form amorphous oxides that present large surface areas for sorption of phosphorus and other dissolved or suspended constituents. Subsequently, they settle out of suspension during effluent clarification and contribute to the wastewater treatment residuals (sewage biosolids).

Similarly, Al and Fe salts are used in drinking water treatment to remove color and turbidity and the residuals may be managed independently or transferred to wastewater treatment plants where they contribute to sewage biosolids production.

Adding Al or Fe salts during wastewater treatment is practiced in many Québec municipalities such as Montréal and Saguenay (Jonquière sector), where there are programs for beneficial use of sewage biosolids. However, spreading residuals containing Al- and Fe amorphous oxides on Québec soils is contentious because the effects on soil chemical properties and P availability to plants are not well understood.

2. OBJECTIVES

A comprehensive review of scientific information was undertaken to:

1. Develop an improved understanding of the short-term and long-term effects of sewage biosolids containing amorphous Al- and Fe oxides on plant-available P in soils.
2. Recommend appropriate modifications to Québec criteria for land application of the above-mentioned biosolids in order to avoid;
    - long-term reduction of P availability in low P soils, that may cause reduced crop yields and
    - long-term enhancement of P solubility in high P soils, that may cause water pollution.
3. Recommend a short-term P availability index for Québec municipal biosolids.

3. QUÉBEC REGULATIONS FOR BENEFICIAL USE OF RESIDUALS

Currently sewage biosolids recycling to land in Québec is affected by three sets of regulations as follows:

- Canadian standard (CAN/BNQ) for pelletized biosolids,
- Provisional criteria for the beneficial use of residual fertilizer materials and
- Canadian Fertilizers Act.

3.1 Canadian Standard (CAN/BNQ) for Pelletized Sewage Biosolids

A voluntary Canadian standard (BNQ 2002) was developed by the BNQ (Bureau de Normalisation du Québec) under the Canadian Standards Council. Municipal wastewater treatment plants may request certification of their sewage biosolid products according to the standard. Following certification, MENV Certificates of Authorization are not required for land application of the products.

It is recommended that total Al + 0.5 Fe in pelletized sewage biosolids for land application should not exceed 100 000 mg / kg dry solids (ds). (Note: Al and Fe both have +3 valences and 0.5 Fe is chemically equivalent to Al since the atomic weight of Fe is two times that of Al.) Pelletized biosolids with more than 75 000 mg / kg ds Al + 0.5 Fe should not be applied on soils with phosphorus saturation < 5% to avoid the risk of reducing P availability to crops. By contrast, pelletized biosolids with less than 75 000 mg / kg ds Al + 0.5 Fe should not be applied on soils with phosphorus saturation > 10% (> 15% for vegetables) to avoid risks of water pollution.

Currently, no Québec sewage biosolids products are BNQ certified, but one municipality is in the process of obtaining certification.

3.2 Québec Provisional Criteria

Land application of Québec sewage biosolids not certified by BNQ is subject to receipt of an MENV Certificate of Authorization and projects should meet the provisional criteria (MENV 2002) for residual fertilizing materials (MRF).

Two categories of MRF are defined based on criteria to prevent environmental contamination. Class C1 MRF have low contaminant concentrations and minimal spreading restrictions and Class C2 MRF have higher contaminant concentrations and significant spreading restrictions. Whereas no maximum solids loading rate is defined for land application of C1 MRF, the maximum solids loading rate for C2 MRF is 22 Mg dry solids (ds) / ha / 5 yr. Similarly, C1 MRF containing ≤ 25000 mg Al + 0.5 Fe / kg ds may be applied to any soil whereas C2 MRF containing between 25000 and 50000 mg Al + 0.5 Fe / kg ds must be applied to soils with ≤ 2000 mg/kg Mehlich-3 extractable Al + 0.5 Fe and C2 MRF containing between 50000 and 100000 mg Al + 0.5 Fe / kg ds must be applied to soils with ≤ 1600 mg/kg Mehlich-3 extractable Al + 0.5 Fe. The pH of soils before and after spreading C2 materials must be ≥ 6 for agriculture and ≥ 5 for other uses.

Recommended soil loadings for both Classes C1 and C2 MRF attempt to supply crop requirements for nitrogen (N), P and potassium (K) and avoid environmental contamination. But loadings are defined by the most restrictive parameter, which for sewage biosolids is usually P. Phosphorus loadings in sewage biosolids are based on crop needs and soil P availability (CRAAQ, 2003), and the percentage availability of biosolids P calculated according to the following equation (MENV 1995, MENV 2002) which has not been validated:

$$\%P_{\text{available}} = 70 - \{\text{concentration } (Al_{\text{total}} + 0.5\ Fe_{\text{total}}\ [\text{mg / kg}]) - 20000\} / 2000$$

The equation is based on several assumptions as indicated below (M. Hébert, MENV, personal communication):

- For biosolids not treated with Al or Fe salts, P availability is about 70% as compared to mineral fertilizers. This is equivalent to manure P availability that ranges from 65-80% compared with mineral fertilizers (CRAAQ (2003).
- With increasing Al and Fe content, biosolids P availability is assumed to decrease linearly to an arbitrary value of 5% for an Al + 0.5 Fe content of 150000 mg / kg ds.
- An Al + 0.5 Fe content of 20000 mg / kg ds represents the background content of biosolids with no Al or Fe salt added and is close to the C1 criterion of 25000 mg / kg) ds.

Because land application of municipal biosolids is often limited by the crop requirement for P, it is important to have a good index of the short-term availability of P in biosolids to avoid under fertilization of crops. However, long-term repeat applications of sewage biosolids may lead to P buildup particularly in agricultural soils and possible water contamination. This problem is recognized in the provisional criteria (MENV 2000) which define limits for P loadings to agricultural soils with > 150 kg P / ha as follows:

- The total P loading to soils (including complementary fertilizer) must be ≤ the amount removed by crop harvest, and
- The percentage phosphorus saturation of soils (S) must be ≤ 10% according to the equation S = 100 x P (Mehlich-3) / Al (Mehlich-3).

3.3 Canadian Fertilizers Act

Under the authority of the *Fertilizers Act and Regulations*, Agriculture and Agri-Food Canada introduced standards for metals in fertilizers and soil supplements (CFIA 1997). They were developed to insure that these materials, including processed sewage, would pose only a minimum risk of adverse effects due to metal contamination. Maximum acceptable concentrations of arsenic, cadmium, cobalt, mercury, molybdenum, nickel, lead, selenium and zinc in fertilizers and supplements and maximum acceptable cumulative additions of these metals to soil were defined but no specific environmental restrictions for P, Al or Fe were included.

4. SOIL PHOSPHORUS

“Only two mechanisms by which soils hold phosphate in the field have been proved to be of importance, namely, those involving calcium ions and those involving iron and aluminum ions” (Russell 1961, Tisdale et al. 1985). Calcium ions that hold phosphate in soil may be in solution, or exchangeable and form calcium phosphates on the surface of clay particles, or anchored on the surface of calcium carbonate crystals. The aluminum and iron ions may be in films of hydrated oxides, or the aluminum may be present as exchangeable cations if the soil is acid, or as a film of aluminum hydroxide in a limed formerly acid soil.

In the Soil Science literature aluminum and iron hydrated oxides are called by various names including; “hydrated oxides”, “hydrous oxides”, “oxides”, “hydroxides”, “oxyhydroxides”, and “sesquioxides”. “Sesquioxide” is a chemical term referring to an oxide containing three atoms or equivalents of oxygen to two other elements or radicals. Generally aluminum and iron hydrated oxides in soils are amorphous but particularly the iron hydrated oxides may be crystalline. Frequently the amorphous materials are referred to as “free (i.e., reactive) oxides”. To avoid confusion in the remainder of this report, aluminum and iron hydrated oxides will be referred to as “amorphous oxides” and “crystalline oxides”.

It is well established that soil Al and Fe components vary considerably in their ability to sorb P (Yuan and Lavkulich 1994, McLaughlin et al. 1981, Parfitt 1978). In general, the amorphous oxides adsorb considerably greater amounts of P than their crystalline counterparts that adsorb more than layer silicates (clay minerals). Allophanic materials (mixtures of amorphous aluminum and silicon oxides) also adsorb appreciable amounts of P. Differences in the P adsorption properties of these materials appear to be related to the number of functional M - OH groups presented at the liquid-solid interface.

Results of fractionation studies involving the principal soil groups throughout the world are consistent with the above information. In calcareous soils, or soils that have not been much weathered, most of the inorganic phosphate is present as calcium phosphates. In moderately weathered soils, the principal form of inorganic phosphate is that sorbed on aluminum and iron oxide films; and as weathering proceeds, an increasing proportion occurs inside iron oxide precipitates. In strongly weathered low humic latosols all of the inorganic phosphate is locked up in precipitates and concretions (Russell 1961).

Québec soils have developed under temperate climatic conditions and are moderately weathered. They include the following soil series; gleysols, luvisols, podzols, brunisols and regosols and generally exhibit neutral to acid pH values (Vézina et al. 2000). The principal form of inorganic phosphate in Québec soils is expected to be associated with aluminum and iron (amorphous) oxide films and considerable evidence to this effect has been presented (Giroux et Tran 1985, 1996, Vézina et al. 2000, Khiari et al. 2000).

5. ALUMINUM AND IRON AMORPHOUS OXIDES

The sorbing properties of Al- and Fe amorphous oxides are used to remove organic matter, P and other constituents during municipal wastewater treatment. The amorphous oxides flocculate and settle out of suspension during clarification and contribute to sewage biosolids production. Similarly, Al- and Fe amorphous oxides are used to remove colour and turbidity during drinking water treatment and the residuals (sludges) may be managed independently or transferred to wastewater treatment plants where they contribute to sewage biosolids production.

5.1 Amorphous Oxides and Soils

Beneficial use of manures and sewage biosolids based on crop N requirement usually supplies P in excess of crop needs. Excess soil P is not harmful to plants but off-site migration to surface waters is a major concern because P is the limiting nutrient for eutrophication of most freshwaters (Elliot et al. 2002a). Recently, there is considerable interest in using Al- and Fe-rich residues to immobilize P in soils and reduce or eliminate off-site migration of this nutrient.

For example, Haustein et al. (2000) compared Al-rich water treatment residuals (Al-WTR) and HiClay Alumina (HCA – a byproduct of commercial alum production) for decreasing P in run-off from fields excessively high in soil-test P. The P adsorption capacity of the Al-WTR was 20 times higher than HCA and it increased the total recoverable Al in the soil whereas HCA had no effect. High rates (up to 18 Mg / ha) of both materials reduced Mehlich–3 soil test P (M3P). Both 9 and 18 Mg / ha rates of WTR decreased runoff P levels significantly below those of control plots throughout the 4-month experimental period, whereas the same rates of HCA decreased P levels only up to 1 month. Differences between these two materials were attributed to the higher Al content (46.7 vs. 15.9 g / kg) and greater P adsorption capacity (1750 vs. 86 mmol / kg) of the WTR.

Hyde and Morris (2000) incubated up to 60 g / kg (≅ 120 Mg / ha) dry solids (ds) of raw, dry and frozen Al- and Fe-WTR with two soils having above-optimum M3P concentrations (833 and 630 mg / kg) at 26^{o}C for 21 days and reported 64%, 28% and 23% average reductions of M3P, respectively. Similarly, Peters and Basta (1996) incubated 30 and 100 g / kg (≅ 60 and 200 Mg / ha) ds of two WTR (HS1 and HS2), cement kiln dust (CKD) and treated bauxite red mud (RM) with a slightly acid soil having 533 mg M3P / kg soil and a calcareous soil having 296 mg M3P / kg soil at 25^{o}C for 9 weeks. Reductions from 533 to 250 mg M3P / kg soil followed the trend HS2 = CKD ≥ HS1 ≥ RM for the acid soil and from 296 to 110 mg M3P / kg soil followed the trend HS2 > HS1 > RM > CKD for the calcareous soil. The treatments caused no serious pH, soluble soil Al, or soil salinity problems.

Elliot and Dempsey (1991) caution that water treatment sludges may favourably modify the pH and water holding capacity of soils but generally have little fertilizer value. Supplemental phosphorus fertilizer will usually be needed to offset the strong P-binding capacity of these sludges.

5.2 Amorphous Oxides and Other Soil Amendments

Poultry litter contains $\cong$ 20 g P / kg ds of which $\cong$ 2 g P / kg is water-soluble. A laboratory study was conducted in which poultry litter was amended with alum, sodium aluminate, quick lime, slaked lime, calcitic limestone, dolomitic limestone, gypsum, ferrous chloride, ferric chloride, ferrous sulfate and ferric sulfate and incubated in the dark at 25^{o}C for 1 week (Moore and Miller 1994). Results indicated that water-soluble P was reduced from > 2000 mg P / kg litter to < 1 mg P / kg litter by all of the amendments except gypsum and sodium aluminate (50 to 60% reduction) and the limestones.

Alum application (0.091 kg / bird of $Al_2(SO_4)_3$?14 H_2O) lowered the pH of poultry litter, particularly during the first 3 wk of each growout (Moore et al. 2000). Reductions in litter pH reduced ammonia (NH_3) volatilization and atmospheric NH_3 in the alum treated houses. Broilers grown on alum treated litter were significantly heavier than controls (1.73 kg vs. 1.66 kg). Soluble reactive phosphorus (SRP) concentrations in runoff from pastures fertilized with alum treated litter averaged 73% lower than from normal litter throughout a 3-yr period. These results indicated that alum-treatment of poultry litter is a very effective best management practice to increase agricultural productivity and reduce non-point source P pollution.

Codling et al. (2000) reported that incorporating Al-WTR or an Fe-rich residue substantially reduced the water-soluble P and the Bray and Kurtz no.1-extractable P in poultry litter and long-term litter amended soils. It was suggested that these residues may be useful for reducing P runoff and leaching from poultry litter and litter amended fields.

Elliot et al. (2002b) compared the ability of water treatment residuals {aluminum sulfate (AL-WTR), and ferric sulfate (Fe-WTR), a lime softening residual (Ca-WTR) and pure hematite} to alter P solubility and leaching in low P-sorbing, Immokalee sandy soil amended with dewatered biosolids and triple superphosphate (TSP) fertilizer. In the absence of WTRs, 21% of TSP total P and 11% of biosolids total P leached from laboratory columns during 4 months. With co-applied WTRs, the losses from TSP treated columns were reduced to 3.5% (Fe-WTR), 2.5% (Ca-WTR) and < 1% (Al-WTR) of applied P. For the biosolids treatments all WTRs retarded downward P flux such that leachate P was not statistically different than for the control (soil only) columns. It was suggested that oxalate extraction be used to obtain an index of the P-fixing capacity of Al and Fe amorphous oxides in WTRs and potentially releasable P in biosolids using thePhosphorus Saturation Index $\{DPS_{ox} = P_{ox} / (Al_{ox} + Fe_{ox})\}$. Conceptually, DPS_{ox} is the molar ratio of total sorbable P to the Al and Fe components capable of P fixation. $DPS_{ox} < 1$ indicates excess P adsorption sites in materials and no leaching problem whereas $DPS_{ox} > 1$ indicates a potential problem. However, limitations of the DPS_{ox} are that it applies only to materials in which Al- and Fe amorphous oxides determine the P fixing capacity, and it is most useful for systems in which the characteristics of the amendment dominate P chemistry.

5.3 Amorphous Oxides and Crop Growth

Ippolito et al. (1999) conducted a greenhouse study to investigate the efficacy of co-application of Al-WTR and sewage biosolids to two native shortgrass species (blue gama and western wheatgrass). Results with blue gama indicated a positive linear relationship between increasing WTR rate and yield and a negative relationship between increasing WTR rate and shoot P and Al concentrations ($P < 0.10$). With western wheatgrass, there was a negative quadratic relationship between increasing WTR rate and shoot Al concentration ($P < 0.10$). No P deficiency symptoms were observed. All soluble biosolids P was adsorbed when WTR and biosolids were mixed at an 8 : 1 ratio and it was suggested that higher ratios of these materials might result in some soil P adsorption.

Exchangeable P was measured for soils amended with sewage biosolids and WTR in a 7-year field experiment (Naylor and Carr 1997). The Al-WTR (11.6% Al ds basis) amendment reduced exchangeable P level in the soils but did not limit plant growth, suggesting that WTRs may be useful for reducing P solubility in high P soils.

Adding air-dried Al-WTR to soils at rates of 2 and 20 g / kg improved aggregation but the high application rate led to germination problems and decreased P uptake by maize (Rengasamy et al. 1980).

Yields of fescue grass grown in the greenhouse decreased with increasing Al-WTR application rates (0, 1, 2, and 4%) to soil and this trend was attributed to reductions in plant-available P because it was corrected with supplemental P fertilizer (Lucas et al. 1994).

Basta et al. (2000) evaluated three Al-WTRs as soil substitutes and the ability of soil tests to predict P adequacy for bermudagrass. Soil tests indicated P deficiency for two of the WTRs and a control soil. Phosphorus concentrations in tissue grown on the unfertilized WTRs and soil were below adequate levels. Fertilizing with (50, 100 and 200 mg P / kg) increased bermudagrass yield and tissue P concentration for the soil but not for the WTRs. Water-soluble P and Olsen P provided information on the ability of WTRs to support growth but not on P adequacy. The M3P soil test overestimated plant availability of P in WTRs due to the dissolution of P adsorbed by amorphous Al. Water extracts were the best predictor of P adequacy in WTR and were recommended for determining P fertilizer additions to these materials.

Cox et al. (1997) conducted a greenhouse study to determine Al-WTR effects on inorganic forms of P and availability to wheat (*Triticum aestivum* L.) in a thermic Aquic Hapludults soil. Surface applied Al-WTR exhibited little effect on P availability to wheat but incorporation into the entire soil caused a decrease in P availability. Reduced availability resulted from a decrease in loosely bound P due to retention on Al compounds in the WTR. Of the inorganic P fractions studied, loosely-bound (1 M NH_4Cl-extractable) P was the best predictor of P availability in Al-WTR amended soil but Mehlich-1 P was also a good indicator. Thus, the fertilizer P requirement is higher on alum sludge amended than on unamended soil but traditional soil testing methods (Mehlich-1 P) can be used to determine it.

5.4 Summary

Aluminum and Fe amorphous oxides usually added as WTRs or other industrial byproducts reduce P solubility in soils and losses of this nutrient in runoff and leachates.

They also reduce P solubility in soil amendments such as poultry litter and in litter and commercial fertilizer amended soils. However, WTRs have little fertilizer value and are not satisfactory soil substitutes. For example, bermudagrass grown on WTRs was P deficient and fertilizer P addition increased neither the yield nor P concentration of the plant material. WTRs applied to the soil surface had little effect on P availability to wheat but incorporation into the entire soil decreased P availability. Thus, Al- and Fe amorphous oxides can effectively reduce P solubility and water quality problems associated with P-rich soils but they may increase the fertilizer P requirement for optimum crop production on other soils.

6. SEWAGE BIOSOLIDS

As indicated in the previous section, the sorbing properties of Al- and Fe amorphous oxides are used to remove organic matter, P and other constituents during municipal wastewater treatment. The amorphous oxides contribute to sewage biosolids production and there is recognition that they may significantly affect the chemical nature and plant availability of soil P. Studies to investigate these potential effects are summarized below.

6.1 Soil Effects

The Water Environment Research Foundation evaluated ten long-term (9 - 23 years) sewage biosolids reuse programs and identified significant increases in plant available soil P (WERF 1993). It was recommended that soil P levels be monitored where biosolids are used continuously over time and that future biosolids application rates may need to be determined by crop P requirement rather than crop N requirement.

Most sewage treatment in Ontario involves the addition of Al or Fe salt for P removal and approximately one-third of the biosolids (120000 Mg / year ds) are spread on agricultural land. The effect of Ontario biosolids on soil P availability was investigated at 36 sites that had received either 2 or 3 biosolids applications at the rate of 8 Mg / ha ds (OMAFRA 1995). Results indicated significantly more available P in biosolids treated than in untreated soils (mean $NaHCO_3$-extractable P_2O_5 values of 29 and 9 mg / kg, respectively) but levels in the treated soils were well below the 60 mg / kg P_2O_5 maximum for biosolids application.

Soon et al. (1978) reported on three years of field experiments with anaerobically digested sewage biosolids treated with $Ca(OH)_2$, $Al_2(SO_4)_3$ and $FeCl_3$. Biosolids supplied

260 to 4560 kg P / ha / yr and increased $NaHCO_3$-extractable (plant-available) soil P. The P additions to soil were in the order Fe-biosolids > Al-biosolids > Ca-biosolids but $NaHCO_3$-extractable P was in the order Ca-biosolids > Fe-biosolids > Al-biosolids indicating that the P in Ca-biosolids amended soil was more labile than in Fe- and Al-biosolids amended soil. Phosphorus adsorption was associated with increased calcium carbonate and amorphous Al- and Fe oxide contents in the biosolids amended soils and decreased in the order: Ca-biosolids >> Al-biosolids = Fe-biosolids > untreated soil (Lee et al. 1981). Phosphorus fractionation showed that just more than 50% of inorganic P in the Ca-biosolids amended soil and about 70% in the Al- and Fe-biosolids amended soil was Al- and Fe-P (Soon and Bates 1982) but there was no evidence of P deficiency in corn (*Zea mays L.*) and bromegrass (*Bromus inermis Leyess*) grown on any of the Al- and Fe-biosolids amended soils.

Similarly, Chang et al. (1983) fractionated P in soils from experimental plots that had received composted and liquid sewage biosolids at rates up to 90 Mg / ha / yr and 15 cm / yr, respectively, for 5 years. Results indicated increased water-soluble P (WSP) and Al- and Fe-bound P in all biosolids amended soils. Whereas Ca-bound P accounted for 50 - 60% of total P in the control soil, Al- and Fe-bound P accounted for > 60% of total P in surface (0-15 cm) soils that had received the high rate of composted biosolids. There was little change in the soil P distribution three years after biosolids applications were terminated indicating that the biosolids effects were persistent.

Soil samples from 11 biosolids application sites and adjacent setback areas that had never received biosolids were analyzed for oxalate-extractable P (P_{ox}), aluminum (Al_{ox}) and iron (Fe_{ox}); degree of phosphorus saturation {$DPS_{ox}1 = (P_{ox} / 0.61[Al_{ox} + Fe_{ox}]$ mmol / kg)}; Mehlich-1 P; desorbable P (Fe-oxide strip [FeO-P]); and WSP (Maguire et al. 2000). Biosolids application sites had significantly greater P_{ox} in topsoils (0-20 cm) when averaged for all sites but biosolids application also increased $[Al_{ox} + Fe_{ox}]$, which meant that DPS was not always increased. The data suggest that adding biosolids according to current N-based guidelines will lead to an accumulation of P in soils, but its availability/solubility may not increase due to associated increases in soil $[Al_{ox} + Fe_{ox}]$.

Eight biosolids generated by different treatment processes with respect to digestion and Fe, Al and lime (Ca) addition and a poultry litter (PL) were incubated with a silt loam and sandy loam soil for 51 days (Maguire et al. 2001). Biosolids and PL amendments increased extractable P in the soils generally in the order: [biosolids produced without Al or Fe addition] > [biosolids produced with Al or Fe and Ca addition= PL] > [biosolids produced with Al or Fe addition]. Total P, P_{ox} and Mehlich-1 P in the biosolids were poor indicators of change in water-soluble P, desorbable P (Fe-oxide strip [FeO-P]) and Mehlich-1 P in biosolids amended soils. However, M3P and the molar ratio of P to [Al + Fe], by either USEPA 3050 digestion or oxalate extraction of the biosolids, were good predictors of changes in soil extractable P following biosolids but not PL amendment. Thus, testing biosolids for P availability rather than total P may be a useful tool for predicting extractable P from biosolids amended soils.

Soil incubation studies were conducted to measure P availability in raw and anaerobically digested sewage biosolids from activated wastewater treatment plants using four different methods of phosphorus removal: alum addition, ferric chloride addition, anaerobic/oxic biological P removal and no provision for excess P removal (Kyle and McClintock 1995). Bray-1 P testing of biosolids and fertilizer-amended soils and ortho-P testing of leachates indicated that the P in Al- and Fe-biosolids was less available than in non-chemical biosolids.

6.2 Crop Effects

Bicarbonate-extractable (Olsen) P was larger with monocalcium phosphate (MCP) fertilizer than with Ca-, Al-, Fe- and untreated sewage biosolids applied to acid, neutral and alkaline soils at rates up to 500 kg P / ha (Gestring and Jarrell 1982). Yield was relatively unaffected by biosolids application rate for all treatments indicating that P availability was not limiting for plant growth in any of the soils. Moreover, no discernible trends in P uptake were observed for any of the fertilizer treatments or application rates. Phosphorus was equally available from the biosolids and MCP added to soils.

Phosphorus availability in Ca-, Al- and Fe-treated sewage biosolids was measured by growing rape in treated soil in the greenhouse (Kuile et al. 1983). Ca-biosolids was a slightly better source of P than MCP fertilizer, however, the Fe- and Al-biosolids were less than 50% as effective as MCP. It was concluded that tertiary treated biosolids generally appear to be unsuitable substitutes for soluble P fertilizers under practical farming conditions (No measurements of extractable P, Al or Fe were reported for the biosolids or treated soil in this study).

Sewage biosolids produced without Al or Fe addition and MCP were applied to two P-deficient sesquioxic soils (Typic Haplorthox and Tropeptic Haplorthox) at rates up to 1000 kg P / ha, and Italian ryegrass (*Lolium multiflorum*) was grown for 209 days (McLaughlin and Champion 1987). Biosolids exhibited the characteristics of a slow-release fertilizer. Whereas rates of P uptake declined rapidly with time in MCP treated soils, they increased or declined only slowly in biosolids treated soils. The relative efficiency of biosolids compared with MCP as a P source increased from 44 to 90% and 64 to over 100% with time in the respective soils.

6.3 P Leaching and Runoff

Sewage biosolids P leaching from soil with a very low P-sorption capacity was related to the degree of P saturation $DPS_{ox} = ([P_{ox}] / [Al_{ox}+Fe_{ox}]$ concentrations in mmol / kg soil) based on oxalate extraction of the pre-applied biosolids (Elliot et al. 2002a). Biosolids with $DPS_{ox} \leq \sim 1.1$ exhibited no appreciable P leaching whereas biosolids cake ($DPS_{ox} = 1.4$) and pellets ($DPS_{ox} = 1.3$) exhibited significant leaching losses. It was concluded that the biosolids DPS_{ox} appears useful for identifying biosolids with potential to enrich leachate P when applied to low P-sorbing soils. However, soil with even a modest P-sorption capacity may mask the differences in biosolids-P leachability.

Three acid soils (pH 5.3 - 6.1) were amended with 50 g / kg ds of digested sewage biosolids (Al- or Fe-precipitated) in a laboratory study Rydin and Ottabong (1997). During continuous leaching with artificial rainwater, approximately 15% of total P leached from unamended soils whereas 20% of total P leached from Fe-biosolids amended soils and up to 43% of total P leached from Al-biosolids amended soils. Fractionation indicated that P adsorbed to Fe and Al was more or less exhausted, declining from 35% of total P at the start of the leaching experiment to 5% at the end. The released P was considered to be potentially plant-available.

The leaching potential of P from a range of sewage biosolids- or MCP fertilizer amended soils was evaluated (Siddique et al. 2000). In most cases, more P was released from the fertilized- than the biosolids-treated soils. Increasing $NaHCO_3$ (Olsen)-extractable P from 15 to 62 mg / kg had negligible effect on P release but there was a sharp increase in P leached between 92 and 134 mg / kg. At all depths in all leached soils, bicarbonate resin P decreased in the order: P fertilized > sludge > control. At the lowest depth (16-20 cm) of the leached soils, the degree of P saturation (resin P / Langmuir P sorption maximum) decreased in the same order and was related curvilinearly ($P < 0.001$) to cumulative P leached. The more rapid rate of P saturation and P leaching in fertilized than biosolids-treated soils emphasizes the role of the P source in adsorption-desorption processes.

Biosolids additions in the field had little effect on P retention during 4 years in a soil with abundant oxalate-extractable Al and Fe and a correspondingly large native P-sorbing capacity (Lu and O'Connor, 2001). However, biosolids significantly increased P retention in a soil with low oxalate-extractable Al and Fe and low native P-sorbing capacity. The effects lasted 1 to 3 years after application, depending on biosolids source and rate of application, and generally mimicked the persistence of increased extractable Al and Fe concentrations in the poorly P-sorbing soil. It was suggested that P in biosolids containing (or tailored to contain) abundant Al and / or Fe would be expected to behave as a slowly available P source, and to be less subject to leaching losses than completely soluble P sources.

Water-soluble P was compared for 42 biosolids representing a variety of wastewater and biosolids treatment processes, 13 manures and manure composts from different livestock and 2 commercial fertilizers (Brandt et al. 2002). The mean percent WSP (WSP / total P x 100) for all biosolids was significantly lower than for all manures and fertilizers tested. This difference was attributed primarily to higher levels of Fe and Al in biosolids that tend to fix P in water-insoluble forms. Among the biosolids tested, those from facilities with biological P removal exhibited the highest mean WSP%. It was concluded that policies for P-based nutrient management should be designed to reflect the substantially different potential for soluble P losses in runoff and leachates from biosolids, livestock manures and commercial fertilizers.

Phosphorus transfer in surface runoff from field plots receiving no P, TSP fertilizer, liquid cattle manure (LCS), liquid anaerobically digested sewage biosolids (LDB), or dewatered sewage biosolids cake (DBC) was compared over a 2-year period (Withers et al. 2001). Phosphorus release from the different sources was related to P extracted by either water or Olsen-P in the order TSP > LCS > LDB > DBC. Results indicated a lower risk of P transfer in surface runoff following biosolids application compared with the other agricultural amendments at similar P rates.

A study was conducted to determine the effect of wastewater treatment process on the forms and amounts of P in biosolids, biosolids-amended soils and in runoff from biosolids amended soils (Penn and Sims 2002). Two soil types were amended with eight biosolids and a poultry litter at equal rates of total P (200 kg / ha); unamended soils were used as controls. Biosolids produced with a biological nutrient removal process caused the largest increases in extractable soil P and runoff dissolved reactive P (DRP). Alternatively, biosolids produced with ferric chloride had the least extractable P and caused the smallest increases in extractable soil P and runoff DRP when added to soils. The differences in soil and biosolids extractable P levels as well as runoff losses were related to inorganic P forms in the biosolids.

6.4 Summary

Sewage biosolids application to soils according to N-based guidelines leads to an accumulation of P in topsoils. However, release of this P may be mitigated by associated increases in Al- and Fe-amorphous oxides. Mehlich-3 P and the molar ratio of P to [Al + Fe], appear to be good indicators of soil P availability following sewage biosolids amendment. Crop effects generally indicate lower P availability from Al- and Fe-treated sewage biosolids than from Ca-treated sewage biosolids or fertilizer. However, Al- and Fe-treated sewage biosolids added to P-deficient sesquioxic soils behaved like slow-release fertilizer and their relative efficiencies compared with MCP increased significantly with time. In general, P leaching and runoff from sewage biosolids treated soils are less than from animal manure and fertilizer treated soils and the differences are attributed to higher levels in sewage biosolids of Al and Fe that tend to fix P in water-insoluble forms.

7. PHOSPHORUS AND ENVIRONMENTAL SOIL TESTING – EXCEPT QUÉBEC

Soil testing for P is a well-established agricultural practice, recognized worldwide to identify P deficient soils requiring fertilization or manuring to attain economically optimum crop yields. More recently, soil P testing to identify agricultural soils that contribute to nonpoint-source pollution of surface waters is of increasing importance, particularly in areas with high animal densities (Sims et al. 2000, Sims et al. 1998, Daniel et al. 1998, Sharpley et al. 1996). A summary of international (except Québec) soil P testing studies reflecting agronomic and environmental concerns follows.

The degree of P saturation (DPS) of soil is the molar ratio of P already sorbed (e.g., oxalate extractable P) to the total P sorption capacity (e.g., oxalate extractable Al + Fe) of the soil (i.e., $DPS_{ox} = P_{ox} / Al_{ox} + Fe_{ox}$). A model-based approach involving DPS_{ox} was developed to predict the impact of soil P losses by fixation, immobilization, and subsurface runoff/leaching on soil test P levels for flat, noncalcareous sandy soils in the Netherlands (Schoumans and Groenendijk 2000). Assuming that the concentration of ortho-P at the mean highest water table should not exceed 0.01 mg / L to avoid groundwater contamination, it was determined that DPS_{ox} of the soils should not exceed a critical value of 0.25. Furthermore, changes in soil test P values with time were estimated using the model and it was demonstrated that many decades would be required to reduce present high P levels in the soils to environmentally acceptable levels.

In 213 observations across a range of soils and managements for corn production systems in Wisconsin, agronomic soil P testing was as effective as environmentally oriented soil P testing for predicting WSP concentrations in runoff following filtration through 0.45 µm pore diameter. Good relationships occurred between the Bray-1 soil test P level and WSP concentration in runoff for most of the tests and sampling depths used (Andraski and Bundy 2003). These relationships were not improved using alternative environmentally oriented soil P extraction techniques (Mehlich-3, distilled water, Fe-oxide strip, DPS_{ox}) or shallower sampling depths compared with the soil test methods currently in use. Results indicated that high corn residue surface cover, recent additions of manure, and low soil permeability can alter the relationship between soil test P level and WSP concentration in runoff and may need to be accounted for when interpreting potential P losses in runoff using soil P tests.

The surface 5 cm of 23 high P soils (85-419 mg / kg M3P) in Oklahoma and Texas which had received beef feedlot, poultry or swine manure (90-1880 kg P / ha / yr for up to 35 yr) were successively extracted with Fe-oxide strips in the laboratory to investigate residual soil P availability (Sharpley 1996). Decreasing Fe-oxide strip P with successive extractions followed the equation: FeO-P = a^{-b} (r^2 of 0.88 - 0.98) where “a” is the extraction number (DPS also accounted for 85% of the variation in total P released to strips during 15 successive extractions). The equation also described the annual decline in soil P following P application in several field studies indicating that successive Fe-oxide strip extraction of high-P soils may provide a realistic representation of soil P release under field conditions.

Equilibrium P concentrations at zero sorption / desorption (EPC_0) were determined to assess the tendency for soils in the Fraser Basin of British Columbia to gain or release P when they are placed in contact with natural waters (Yuan and Lavkulich 1995). Soils with high EPC_0 showed a greater tendency to release P into waters than soils with low EPC_0. DPS_{ox} was highly correlated with EPC_0 indicating that it is the proportion of surface occupied by phosphate rather than the absolute amounts of P fractions that determines the movement of P from soil to water. DPS_{ox} is easier to measure than EPC_0 and was suggested as an index for managing manure application to prevent over-application and resulting water pollution in the Fraser Basin of British Columbia.

The A and E horizons of Florida spodosols heavily impacted by cattle manure (intensive and holding areas) for both active and abandoned dairies generally had higher DPS values than pasture, forage, and native areas which were minimally impacted (Nair and Graetz 2002). DPS was significantly (P = 0.0001) related to WSP for all soil horizons, suggesting that it can be used as an indicator for P loss potential from soil.

Relationships between agronomic soil test P (STP = Mehlich-1) and environmentally oriented tests proposed to measure the potential for P loss by erosion, runoff and leaching were determined for 127 soils [122 mainly acid sands from Delaware and 5 acid sands from the Netherlands] (Pautler and Sims 2000). STP was significantly correlated with total P (r = 0.57***), 0.01 M $CaCl_2$-soluble “soluble” P (r = 0.71***), FeO-P (r = 0.84***), and P_{ox} (r = 0.84***). FeO-P was a better predictor of soluble P than STP (r^2 = 0.76***). In addition, DPS of the soils was determined by three methods: Langmuir P sorption isotherms; oxalate extraction of P, Al and Fe; and STP plus a single-point P sorption index. Soluble P, STP and FeO-P increased for DPS > 0.3, as was observed for upper DPS limits in the Netherlands and Belgium (0.25 - 0.4). Soils rated agronomically excessive in STP (> 50 mg P / kg) had higher ratios of soluble P, FeO-P, and P_{ox} to total P than those in agronomically optimum or lower categories.

Agronomic and environmental soil tests for predicting P leaching losses from undisturbed soils were evaluated using intact soil columns from five soils with a wide range of soil test procedures (Maguire and Sims 2002). The columns were leached with deionized water, the leachates analyzed for DRP, and the soils analyzed for Mehlich-1 and Mehlich-3 extractable P, Al, and Fe. $DPS_{M3}1$ of the soils was calculated as the molar ratio of Mehlich-3 extractable P / [Al + Fe]. Leachate DRP was frequently above concentrations associated with eutrophication. For the relationship between DRP in leachate and all of the soil tests used, a change point was determined below which leachate DRP increased slowly per unit increase in soil test P, and above which leachate DRP increased rapidly. The environmental soil tests (WSP, 0.01 M $CaCl_2$-soluble P, FeO-P) were slightly better at predicting leachate DRP than the agronomic soil tests (Mehlich-1 P, Mehlich-3 P, and $DPS_{M3}1$). But $DPS_{M3}1$ was as good as the environmental soil tests if two outliers were omitted. Results supported the development of M3P and $DPS_{M3}1$ categories for profitable agriculture and environmental protection.

Sims et al. (2002) evaluated the Mehlich-3 extraction as an environmental soil P test using 465 soils typical to the Mid-Atlantic region and found that it (M3P) accurately predicted WSP, FeO-P, and total sorbed P (oxalate P). $DPS_{M3}2$ = (M3P / AlM3 + FeM3) was linearly related to DPS_{ox} and a $DPS_{M3}2$ range of 0.10 to 0.15 corresponded to reported environmental limits for DPS_{ox} of 0.25 – 0.40. Rainfall simulation and column leaching studies showed $DPS_{M3}2$ predicted runoff and leachate P concentrations better than M3P. The following approach now used in Delaware for agri-environmental interpretation of M3P and $DPS_{M3}2$ was proposed for use in the Mid-Atlantic region of the USA:

- Below optimum: crop response likely; M3P ≤ 50 mg/kg; $DPS_{M3}2 < 0.06$,
- Optimum: economic crop response to P unlikely, recommendations for P rarely made; M3P = 51–100 mg/kg; $DPS_{M3}2$= 0.06–0.11,
- Above Optimum: soil P will not limit crop yields, no P recommended; M3P > 100 mg/kg; $DPS_{M3}2 > 0.11$,

- Environmental: implement improved P management to reduce potential for nonpoint P pollution; M3P > 150 mg/kg; $DPS_{M3}2 > 0.15$,
- Natural Resource Conservation: no P applied even if the potential water quality impact is low - to conserve P, a finite natural resource.

7.1 Summary

Identification of agricultural soils that contribute to non-point source P pollution of waters is increasingly important and there has been considerable effort to use both agronomic soil P tests (e.g., Bray-1, Mehlich-1 and -3, Olsen) and environmentally oriented soil P tests (e.g., distilled water extraction, Fe, P sorption index, DPS) for this purpose. In general, agronomic soil tests have proven satisfactory for soils with similar properties but for soils with widely different properties, tests such as water-soluble P and the DPS are much more satisfactory. Critical $DPS_{ox} = 0.25 – 0.40$ for soils in the Netherlands, Belgium and Germany, above which P losses are considered to be environmentally unacceptable are consistent with $DPS_{M3}2 > 0.11$ currently adopted for soils in Delaware and proposed for soils in the Mid-Atlantic region of the USA.

8. PHOSPHORUS AND ENVIRONMENTAL SOIL TESTING – QUÉBEC

Areas in Québec with intensive animal production have soil test P values well above those needed for optimum crop yields, and agriculture is a major cause of elevated P levels in river waters. Soil P tests to predict fertilizer needs are agronomically efficient but not necessarily suited to assessing the risks of water contamination (Sims et al. 1998, Leclerc et al. 2001). Considerable Québec research has been directed toward developing environmentally oriented tests to assess the risks of water contamination by soil P and the results are summarized below.

The maximum P sorption capacities (M) of 30 soil samples from the A, B and C horizons of five main soil series taken from sites under forest, dairy farms, and farms with a known surplus of manure in the Beaurivage watershed of Québec were closely related to their P sorption indices (P_{si}; $r > 0.97^{**}$) in all horizons (Simard et al. 1994). The M and P_{si} parameters were related to organic carbon (OC), M3P, and Fe_{ox} and Al_{ox} in the A horizon; to M3P, Al_{ox} and sand content in the B horizon; and to OC and Al_{ox} in the C horizon. Water-soluble P was related to pH, OC, M3P and exchangeable Ca in the A horizon, to M3P and sand content in the B horizon; and to pH, M3P and Fe_{ox} in the C horizon. It was concluded that soil test M3P can be used in conjunction with other readily available soil data to predict the potential for water contamination from soil P loss.

The A, B and C horizons of a Typic Humaquept were sampled from a forest (F) and from hay fields of farms with no surplus of manure (D) or a known surplus of manure (SN) (Beauchemin et al. 1996). Leaching experiments with 0.01 M KCl containing 5 mg P / L for the sorption phase and a P-free electrolyte solution for the desorption phase, were conducted. It was estimated that available P sorption capacities were 50% lower in the A horizon of agricultural soils than in the A horizon of forest soils. In the B horizon, P sorption capacities were comparable for all soils. In the C horizon, available P sorption capacity was 75% lower in the agricultural SN than in other soils. After P saturation, potential amounts of desorbable P in the A and B horizons of agricultural soil were 2-fold greater than in forested soil. A significant relationship ($P < 0.05$) was established between soil Al_{ox} and the number of pore volumes necessary to decrease the effluent concentration to 1 mg P / L.

Ryegrass (*Lolium multiflorum* L.) was grown in the greenhouse on 58 surface soils from different regions of Québec and relative yields ([yield without P / yield with P] x 100) were determined (Giroux et Tran 1996). Relationships between the relative yields and M3P, WSP and DPS_{M3}, calculated on a weight (mg / kg soil) basis as M3P / P fixation capacity ($DPS_{M3}3$) and M3P / AlM3 ($DPS_{M3}4$), were established for the soils. $DPS_{M3}3$ exhibited a wide range of values (0.005 to 0.47) and was highly correlated with the relative yields of ryegrass (41 to 99%) and WSP (0.07 to 15.6 mg P / kg soil) indicating importance as both an agronomic and environmental index. However, the $DPS_{M3}3$ and $DPS_{M3}4$ values were approximately equal and very highly correlated (r = 0.98**). Since $DPS_{M3}4$ can readily be obtained from the Mehlich-3 soil test, it was recommended as the routine index. An environmental risk classification was constructed based on M3P, $DPS_{M3}4$ and WSP content of soils as follows:

- Very low: crop response likely; M3P $\leq$ 60 kg / ha; $DPS_{M3}4 < 0.01$, WSP < 1 mg / L,
- Low: M3P = 61-150 kg / ha; $DPS_{M3}4$ = 0.01 - 0.05; WSP $\leq$ 1 mg / L,
- Optimum: M3P = 151-250 kg / ha; $DPS_{M3}4$ = 0.05 - 0.10; WSP = 1 - 2.5 mg / L,
- Above optimum: M3P = 250 - 490 kg / ha; $DPS_{M3}4$ = 0.10 - 0.20; WSP = 2.5 - 6 mg / L,

- Excessive: M3P > 490 kg / ha; $DPS_{M3}4$ = > 0.20; WSP > 6 mg / L.

Data from 78 field experiments on acid coarse-textured Québec soils was used to develop a reliable and unifying criterion for making environmentally and agronomically efficient fertilizer P recommendations to sustain potato (*Solanum tuberosum* L.) production (Khiari et al. 2000). The degree of P saturation, calculated on a weight / volume (mg / L soil) basis as M3P / AlM3 ($DPS_{M3}5$) was more closely related to crop response and P dissolution in P enriched soils than soil test M3P. Five fertility and environmental risk soil groups were constructed as follows:

- Extremely low fertility and extremely low environmental risk; $DPS_{M3}5 < 0.02$,
- Very low fertility and very low environmental risk; $DPS_{M3}5 = 0.02 - 0.04$,
- Low fertility and low environmental risk group; $DPS_{M3}5 = 0.04 - 0.08$,
- Medium fertility and medium environmental risk group; $DPS_{M3}5 = 0.08 - 0.15$, and
- High fertility and high environmental risk group; $DPS_{M3}5 > 15$.

The critical crop response value was $DPS_{M3}4 = 0.08$ and the environmental threshold was $DPS_{M3}5 = 0.15$, thus defining the limits of a medium soil fertility group. Recommended P addition to high fertility soils ($DPS_{M3}5 > 0.15$) was 21 kg P / ha, the amount of P exported by a tuber harvest of approximately 42 Mg / ha.

Recently, Beauchemin et al. (2003) reported results for Montreal Lowland soils that were consistent with the environmental risk categories proposed by Giroux et Tran (1996) and Khiari et al. (2000). Three noncalcareous gleysols and two noncalcareous brunisols with higher P sorbing properties exhibited a mean A horizon $DPS_{M3}4$ of 0.08 and the tile-drainage P concentrations were mainly less than the surface water quality standard of 0.03 mg total P / L, whereas four calcareous gleysols with lower P sorbing properties exhibited a mean A horizon $DPS_{M3}4$ of 0.17 and consistently gave tile-drainage P concentrations exceeding the provincial surface water quality standard.

Studies involving 182 soil series included in an inventory of problem agricultural soils from diverse regions of Québec (Vézina et al. 2000) and 66 Montreal Lowlands area soils (Leclerc et al. 2001) showed that the maximum P sorption capacity (M) of surface soils is related primarily to pedogenic (soil-forming) processes and texture. Three major soil groups differentiated on the basis of M were identified as: (1) gleysols and luvisols; (2) podzols and (3) brunisols and within these groups the M values generally decreased with lighter soil textures. It was suggested that physico-chemical properties available from soil survey data banks in combination with soil P sorption-desorption characteristics could be used to develop a system for assessing the potential for water contamination through loss of soil P. For example, Gleysolic clay soils with high M have a low risk for P loss whereas coarse textured soils with low M and near neutral pH values have a high risk for P loss.

Recently, CRAAQ (2003) provided new fertilizer recommendations for corn based on DPS_{M3} studies involving 98 fertilization plots and a wide range of soil types. A distinction was made between soils with more than 30% clay (heavy soils) and soils with less than or equal to 30% clay (light soils). The critical environmental limits relative to the Dutch criterion of 0.10 mg / L P in soil solution were established at $DPS_{M3}4 = 0.076$ for heavy soils and $DPS_{M3} = 0.13$ for light soils. CRAAQ also provided new fertilizer recommendations for potatoes based on $DPS_{M3}4$ but didn't define separate soil classes because this crop is produced mainly on sandy (light) soils. The critical environmental limit of $DPS_{M3}4 = 0.15$ derived by Khiari et al. (2000) relative to the Dutch criterion of 0.10 mg / L P in soil solution was adopted. Since this value is consistent with the value of 0.13 for corn production in light soils, it may be assumed that these critical environmental criteria are applicable to all types of Québec soil / crop production. These criteria would be approximately $DPS_{M3}4 = 0.075$ for heavy soils and $DPS_{M3}4 =$ 0.13 - 0.15 for light soils.

8.1 Summary

The DPS is highly correlated with WSP in Québec soils and appears to be an important environmentally oriented test for assessing the risk of water contamination through soil P loss. The ratio of Mehlich-3 extractable P to Al (M3P / AlM3) is highly correlated with, and appears to be a suitable index for DPS since it can be derived with existing datasets from routine soil testing. Based on a considerable body of field experimental evidence, the critical environmental criteria relative to the Dutch criterion of 0.10 mg / L P in soil solution are 0.075 for heavy soil (> 30% clay) and 0.13 – 0.15 for light soils (≤ 30% clay).

9. SYNTHESIS AND RECOMMENDATIONS

9.1 Introduction and Objectives

In many Québec municipalities such as Montréal and Saguenay (Jonquière sector), Al or Fe salts are added to enhance removal of organic matter, P and other constituents during wastewater treatment. However, land application of the sewage biosolids containing Al and Fe amorphous oxides is contentious because the effects on soil chemical properties and P availability to plants are not well understood.

A comprehensive review of scientific information was undertaken to:

1. Develop an improved understanding of the short-term and long-term effects of sewage biosolids containing amorphous Al and Fe oxides on plant-available P in soils.
2. Recommend appropriate modifications to Québec criteria for land application of the above-mentioned biosolids in order to avoid;
    - long-term reduction of P availability in low P soils, that may cause reduced crop yields and
    - long-term enhancement of P availability in high P soils, that may cause water pollution.
3. Recommend a short-term P availability index for Québec municipal biosolids.

9.2 Land Application – P Effects

In many areas of the world (including parts of Québec) with high animal densities, long-term application of manure based on crop N requirements has increased soil test P values well beyond levels needed for optimum crop yields and has enhanced runoff and leaching losses of P. Less information is available for long-term use of sewage biosolids but similar trends in soil P availability have been reported (Sims et al. 2000).

Sewage biosolids P is generally less mobile with respect to leaching and runoff and less plant available than manure and fertilizer P (Siddique et al. 2000, Brandt et al. 2002, Soon et al. 1978, Kuile et al. 1983). Reduced availability of sewage biosolids P has been attributed to their Al and Fe amorphous oxide contents and the effects are larger for Al or Fe salt treated biosolids than for untreated biosolids. Phosphorus deficiency in crops has not been reported following land application of Al or Fe salt treated sewage biosolids but there is concern that it could result from long-term repeat applications, depending upon the biosolids loading and soil characteristics. Evidence for this concern is that P deficiency in crops has been observed following land application of specific Al-rich residues (Basta et al. 2000, Cox et al. 1997, Lucas et al. 1994, Rengasamy et al. 1980) and Al salts added to manure reduce the P solubility (Moore and Miller 1994, Moore et al. 2000, Codling et al. 2000) and soils (Haustein et al. 2000, Hyde and Morris 2000, Peters and Basta 1996, Elliot and Dempsey 1991).

9.3 Land Application – P Concerns

Thus, the main P related concerns with land application of Al and Fe salt treated sewage biosolids are as follows:

- Reduced soil P availability and reduced crop yields resulting from long-term repeat applications of Al / Fe rich biosolids to soil.
- Buildup of available P in soils beyond critical environmental limits resulting from long-term repeat applications of biosolids with low Al / Fe amorphous oxide contents applied at rates exceeding crop P requirements.

Presently these concerns are addressed in Québec's provisional criteria for beneficial use of residual fertilizer materials (MENV 2002) and the Canadian standard for pelletized sewage biosolids (BNQ 2002) mainly by restricting sewage biosolids solids, nutrient (usually P) and amorphous oxide loadings to soils.

9.4 Québec Soils

Québec soils are mainly podzols, brunisols, luvisols and gleysols developed under temperate climatic conditions and are moderately to highly weathered. They generally exhibit acid to neutral pH values with large amounts of Al and Fe amorphous oxides in the podzols (more acid) and medium to low amounts in the others (less acid). Oxalate-extractable (amorphous) Al concentrations in 58 Québec plough layer soils ranged from 0.06 – 2.7% with a mean of 0.36% and Fe concentrations ranged from 0.06 – 1.3% with a mean of 0.52% (Giroux et Tran 1996). Most values for Québec soils, except the luvisols and gleysols, exceeded approximate mean values of 0.08% (30 mmol / kg) Al and 0.08% (15 mmol / kg) Fe for 122 Delaware soils, mean values of 0.09% Al and 0.24% Fe for 84 Dutch soils and mean values of 0.13% Al and 0.15% Fe for 301 Belgian soils (Pautler and Sims 2000). There is convincing evidence that inorganic phosphorus in Québec podzols and brunisols is associated mainly with Al and Fe amorphous oxides (e.g., Khiari et al. 2000, Beauchemin and Simard 1999, Giroux et Tran 1996, Simard et al. 1994). But in luvisols and gleysols, calcium and magnesium phosphates are often the main forms with Al and Fe phosphates present in lesser amounts (M. Giroux, MAPAQ, personal communication).

9.5 Amorphous Oxides - Soil P Effects

Aluminum and Fe amorphous oxides are naturally occurring soil constituents resulting from weathering processes that slowly but continuously degrade aluminosilicate clays and other minerals. Frequently, they occur in combination with organic matter and clay minerals as coatings on soil particles and contribute significantly to nutrient, particularly anion retention. The Al and Fe amorphous oxides in sewage biosolids and other industrial byproducts are chemically (Al_2O_3, Fe_2O_3) and mineralogically indistinguishable from those in soils and studies show that their soil P effects are related to their P contents. Sewage biosolids have significant P contents and exhibit moderate effects on soil P availability (e.g., Soon et al. 1978, Chang et al. 1983, Maguire 2000, Kuile et al. 1983, Mc Laughlin and Champion 1987), whereas water treatment residues contain little P and drastically reduce soil P availability (e.g., Haustein et al. 2000, Elliot and Dempsey 1991, Ippolito et al. 1999, Cox et al. 1997).

9.6 Soil P Testing

Soil testing for P is an accepted agricultural management practice to identify soils in which P deficiency must be corrected by fertilization or manuring to attain optimum crop yields. Plant availability of soil P has traditionally been measured using single extraction techniques such as Bray-1, or -2, Mehlich-1 or -3, North Carolina DA (dilute acid) -4 or -10, Morgan’s and Olsen-P (Sims et al. 2000, Giroux et Tran 1985). Most are dilute solutions of strong acids, bases or chelates and were developed to dissolve or desorb an amount of soil P proportional to that available to plants during the growing season.

However, with many soils showing high to excessive P contents for agricultural crop production the impact of soil P on water quality is a major concern and methods to identify these soils are of increasing importance. Because agronomic soil tests were designed to extract soluble and labile P and to reflect the buildup of P in soils, many studies have shown them to be reasonably well correlated with the loss of soluble and biologically available P in agricultural soils (Sims et al. 2000). But recent studies show that some new soil tests, such as WSP, FeO-P, P flux (measured in situ with ion exchange membranes), and the degree of soil P saturation (DPS) can better predict the potential for P loss to surface and groundwater than agronomic soil tests.

9.7 The Québec Situation

Areas in Québec with intensive animal production have soil test P values well above those needed for optimum crop yields, and agriculture is a major cause of elevated P levels in river waters (Leclerc et al. 2001, Sims et al. 1998). Thus, considerable research has been directed toward understanding soil P availability and developing tests to assess the risks of water contamination.

Studies have involved numerous agronomic soil P tests including Mehlich-3 and several environmentally oriented tests including WSP, P_{ox}, Al_{ox}, Fe_{ox}, DPS_{M3} and DPS_{OX}. The DPS is defined as the proportion of binding sites in soil that are covered with P. Mehlich-3 is the routine laboratory soil P test used in Québec.

Results indicated that $DPS_{M3}4$ (concentrations in mg / kg soil) and DPS_{OX} (concentrations in mmol / kg soil) were highly correlated with WSP in Québec soils and that they appeared to be important indices for assessing the risks of water contamination. But $DPS_{M3}4$ was the preferred index because it can be derived with existing datasets from routine soil testing.

Study has shown that the relationship between DPS_{M3} and P solubility is not unique for all Québec soils and that adoption of a single saturation index may require definition of specific critical levels for distinct groups of soils based on pH, pedogenic processes and texture (Vézina et al. 2000, Beauchemin and Simard 1999). However, fertility and environmental (agri-environmental) risk categories have been proposed for Québec soils and are shown in Table 1.

Recently, CRAAQ (2003) provided fertilizer recommendations for corn and potatoes based on $DPS_{M3}4$ critical environmental limits (Table 1). For corn, a distinction was made between soils with more than 30% clay (heavy soils) and soils with less than or equal to 30% clay (light soils). Separate soil classes were not defined for potatoes because this crop is produced mainly on sandy (light) soils. Critical environmental limits for corn, relative to the Dutch criterion of 0.10 mg / L P in soil solution, were established at $DPS_{M3}4 = 0.076$ for heavy soils and $DPS_{M3}4 = 0.13$ for light soils and for potatoes at $DPS_{M3}4 = 0.15$; the value derived by Khiari et al. (2000). These CRAAQ values are in agreement with but somewhat less conservative than values proposed by Giroux et Tran (1996) for a wide range of Québec soils and values adopted in Delaware and proposed for soils in the Mid-Atlantic region of the USA (Sims et al. 2002). $DPS_{M3}4$ values ranging from 0.10 - 0.15 correspond with reported environmental limits for DPS_{OX} of 0.25 - 0.40 for the Netherlands, Belgium and Germany (Sims et al. 2002).

9.8 Long-Term Soil P Availability

9.8.1 Recommendation #1

There is convincing evidence that P solubility in acid and non calcareous neutral Québec soils determines both plant availability of P and the risk of water contamination and is related to the DPS of amorphous oxides rather than the actual amounts of these oxides in soil. Although DPS_{OX} (P_{OX} / [Al_{OX} + Fe_{OX}]) is considered to be the reference index, $DPS_{M3}4$ (M3P / AlM3; concentrations in mg / kg soil) is highly correlated with DPS_{OX} for Québec soils and can be derived with existing data from routine soil testing. Thus, **it is recommended that land application of sewage biosolids to Québec soils be based on the CRAAQ (2003) $DPS_{M3}4$ criteria presented in Table 1. Soils should be monitored and land application discontinued if $DPS_{M3}4$ values increase to 0.15 for soils with £ 30% clay and to 0.075 for soils with > 30% clay or if $DPS_{M3}4$ values decrease to 0.04 for soils with £ 30% clay and to 0.025 for soils with > 30% clay.** The risk of water pollution is increased if $DPS_{M3}4$ values exceed 0.15 and 0.075, and the risk of crop P deficiency is increased if $DPS_{M3}4$ values fall below 0.04 and 0.025 for the respective soil groupings.

9.8.2 Recommendation #2

Research is required to determine if Al / Fe rich sewage biosolids or other residues effectively reduce the risk of water pollution associated with soils exhibiting $DPS_{M3}4$ values exceeding 0.15 for soils with ≤ 30% clay and 0.075 for soils with > 30% clay.

9.8.3 Recommendation #3

Whereas Fe amorphous oxide is not a significant contributor to P sorption in most acid and noncalcareous neutral Québec soils, it could become significant in soils with a history of repeat applications of biosolids rich in Fe. These conditions are unlikely to occur in Québec since:

- biosolids containing Al or Fe salts are applied to < 0.3% of agricultural soils,
- few biosolids contain Fe salts,
- few soils receive long-term repeat loadings of biosolids, and
- few soils receiving Fe salt treated biosolids exhibit low $DPS_{M3}4$ values.

However, **it is recommended that Mehlich-3 Fe analysis should be performed for Québec soils with low $DSP_{M3}4$ values and a history of repeat applications of biosolids rich in Fe.**

9.8.4 Recommendation #4

Detailed information concerning regulations for beneficial use of sewage biosolids in Québec is presented in Section 3 of this report. Since P solubility is related to DPS rather than the actual amounts of amorphous oxides in Québec soils, **it is recommended that all constraints in both the Canadian standards for pelletized biosolids (BNQ 2002) and the Québec Provisional Criteria (MENV 2002) relating to Mehlich-3 extractable Al + 0.5 Fe (mg / kg) in soils and total Al + 0.5 Fe (mg / kg) in sewage biosolids and other fertilizing residuals should be deleted.**

However, measurement of Al + 0.5 Fe in biosolids is required to calculate short-term P availability (see Recommendation #5 below).

Table 1. Proposed P fertility and environmental (agri-environmental) risk categories for acid and noncalcareous neutral soils

Fertility and Environmental Risk Category	Giroux et Tran (1996)[a]			Khiari et al. (2000)[b]	Sims et al. (2002)[c]		CRAAQ (2003)[d]			
	WSP (mg / L)	M3P (kg / ha)[e]	DPS$_{M3}$4	DPS$_{M3}$5	M3P (kg / ha)	DPS$_{M3}$2	WSP (mg / L)	DPS$_{M3}$4		
								Potato Soil	Corn Soil	
									≤ 30% clay	> 30% clay
Extremely low				< 0.02						
Very low	< 1	< 60	< 0.01	0.02-0.04						
Low	< 1	61-150	0.01-0.05	0.04-0.08	≤ 112	< 0.06				
Optimum	1-2.5	151-250	0.05-0.10	0.08-0.15	112-224	0.06-0.11	≤ 0.10	0.08 - 0.15	0.04 - 0.13	0.025 - 0.075
Above optimum	2.5-6	251-490	0.10-0.20	> 0.15	> 224	> 0.11				
Excessive	> 6	> 490	> 0.20		> 336	> 0.15				

Categories were developed with data for [a]: 58 soils; [b]78 soils; [c]: 465 soils; [d]: 98 soils; [e]: mg / kg x 2.24
M3P: Mehlich-3 extractable P; WSP: Water-soluble P; DPS$_{M3}$4: M3P / AlM3, concentrations in mg / kg soil; DPS$_{M3}$5: M3P / AlM3, concentrations in mg / L soil; DPS$_{M3}$2: M3P / AlM3, concentrations in mmol / kg soil

9.9 Short-Term Sewage Biosolids P Availability

9.9.1 Recommendation #5

Aluminum- and Fe-amorphous oxides sorb P and reduce its solubility in sewage biosolids and soils. Moreover, widely variable amorphous oxide contents in Al- and Fe-biosolids (e.g., 1 - 3% total Al and 0.8 - 8.5% total Fe; Elliot et al. 2002a) are expected to affect the short-term P availability of these materials. The Québec Provisional Criteria propose to regulate biosolids application to soils based on crop needs and soil P availability (CRAAQ 2003), and the percentage availability of biosolids P calculated according to the following equation (MENV 1995, MENV 2002) that has not been validated:

$$\%P_{available} = 70 - \{concentration\ (Al_{total} + 0.5\ Fe_{total}\ [mg / kg]) - 20000\} / 2000$$

Assuming average total Al (1.5%) and Fe (4%) contents in sewage biosolids the $\%P_{available}$ calculated according to the equation is 62% and assuming maximum total Al (3%) and Fe (8.5%) contents in sewage biosolids the $\%P_{available}$ is 44%. These values are in agreement with < 50% for Al- and Fe-treated biosolids (Kuile et al. 1983), 44% to 64% short-term availability for untreated biosolids (McLaughlin and Champion 1987) and 40% for Ontario biosolids, most of which are Al- or Fe treated (OMOE & OMAFRA 1996). **It is recommended that the proposed equation be maintained to estimate short-term P availability for land application of Québec sewage biosolids.**

9.9.2 Recommendation #6

However, it is noted that biosolids may act a slow release fertilizer whose P availability compared with inorganic fertilizer can increase considerably over the long-term (McLaughlin and Champion 1987). **It is recommended that research should be conducted to determine if the $P_{available}$ equation requires modification to reflect the slow-release P fertilizer properties of sewage biosolids.**

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