Organic Pollutants in Australian Biosolids

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Public Health Risks From Organic Pollutants



Reproduction, Impaired Immune System & Neurological Damage

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Keywords:

p-p′ DDE Sperm count

Thyroid hormones

PBDE

PCB

Available online 18 February 2011



In Vitro exposure reproductive health problems



Methods: Fifty-two men were recruited in a fertility clinic. Semen counts were done for each participant. Serum thyroid hormone and PBDE, PCB and *p*-*p*' DDE levels were measured. Sociodemographic questionnaire were administered to each participant and all medical data were obtained from medical record.

Results: Semen mobility was negatively related to BDE-47, BDE-100 and Σ BDE. No relations were observed with other semen parameters. Thyroxin levels were negatively associated to serum BDE-47, BDE-99, Σ BDE and p-p' DDE and positively related to Σ PCB. No relations were observed between T3, TSH and any of the chemicals measured.

Conclusion: These findings increased the evidence that PBDE may interfere with semen quality and thyroid status in general population.

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Are We THREATENING per Fertility, Intelligence and Serviced ? - A Scientific Detective Story

iron. Health Persp. 1998, 106, 347-353

• • • Australian Organic Regulations

Australia National	NSW	Vic	SA	Qld	Tas	WA	NZ	EU	USA
C1	A	C1	A	A	A	C1	а		
	В		В	В					
C2	С	C2	С	С	В	C2	b	1	A
	D			D				2	В
	E	C3		E	С	C3			

- Each state has slightly different guidelines
- Inevitable confusion

Australian Organic Regulations (mg/kg)

	Minimum						Maximum				
Compound	Nat.	Vic	WA	SA	NSW & Qld	Nat.	Vic	WA	SA	NSW & Qld	NEPC
ΣDDT	0.5	0.5	0.5	-	0.5	1	1	1	-	1	200
Aldrin	-	-	0.02	-	0.02	-	-	0.5	-	1	10
Chlordane	-	-	0.02	0.02	0.02	-	-	0.5	0.5	1	50
Dieldrin	_	-	0.02	0.02	0.02	-	-	0.5	0.5	1	10
Heptachlor	-	-	0.02	-	0.02	-		0.5	-	1	10
НСВ	-	-	0.02	-	0.02	-		0.5	-	1	
Lindane	-	-	-	-	0.02	-		-	-	1	
∑OCPs	0.05	0.05	-	-	-	0.5	1	-	-	-	
PCBs	0.05-0.3	0.2	0.3	-	0.3	0.5	1	0.5	-	1	10

Category A – 'Standard' residential with garden/accessible soil (home-grown produce contributing less than 10% of vegetable and fruit intake; no poultry): this category includes *children's day-care centers, kindergartens, preschools and primary schools*

• • International Organic Guidelines

	AOX mg kg ⁻¹	DEHP mg kg ⁻¹	LAS mg kg ⁻¹	NP/NPE mg kg ⁻¹	OCPs mg kg ⁻¹	PAH mg kg ⁻¹	PCBs mg kg ⁻¹	PCDD/Fs ng WHO ₀₅ TEQ kg ⁻¹	Other mg kg ⁻¹
Austria	500					6	0.2 -1	50 - 100	
Australia					₩DDT		0.5-1	50	
					1 OCPs 1				
Denmark		50	1300	10		3			
EC (2000)a	500	100	2600	50		6	0.8	100	
EC (2003)a			5000	450		6	0.8	100	
France						1.5 - 4	0.8		
Germany (2002)	500					1	0.1	100	
Germany Proposed (2007)	400					1	0.1	30	MBT+OBT: 0.6 Tonalid: 15 Galaxolide: 10
USA								300	

Biosolids Regulations in Australia

How were they derived?

- Sound science
- Risk assessment
- Protection of public health and the environment
- Best guess
- Achievable targets
- Detection limits









Are biosolids contaminant limits for OCPs/PCBs necessary for the protection of public health & the environment?

- 1. Empirical Data
- 2. Risk Assessment
- 3. Regulatory Limits

• • OCP/PCB Data 2004 - 2006

	Overall	2004	2005	2006
Overall	829 (58)	221 (17)	335 (33)	273 (36)
NSW	539 (22)	169 (8)	181 (11)	189 (14)
Qld	191 (24)	11 (3)	151 (14)	65 (13)
Tas	6 (2)	0 (0)	0 (0)	6 (2)
Vic	48 (7)	10 (3)	28 (5)	10 (4)
WA	45 (3)	31(3)	11 (3)	3 (3)

No of biosolids; () = No of WWTP

CLARKE et al (2010) Environment International, 36, 323-329.

• • OCPS/PCBs Summary Statistics

Variable	Det	<dl< th=""><th>X</th><th>Mean mg kg⁻¹</th><th>StDev mg kg⁻¹</th><th>Min mg kg⁻¹</th><th>Max mg kg⁻¹</th></dl<>	X	Mean mg kg ⁻¹	StDev mg kg ⁻¹	Min mg kg ⁻¹	Max mg kg ⁻¹
Σ DDT	112	717	14	0.04	0.05	0.01	0.27
Aldrin	3	826	0	0.03	0.03	0.01	0.07
Chlordane	227	602	27	0.03	0.03	0.01	0.30
Dieldrin	567	262	68	0.05	0.06	0.01	0.77
Heptachlor	16	813	2	0.05	0.04	0.02	0.17
НСВ	22	807	3	0.04	0.06	0.01	0.30
Lindane	0	829	0	*	*	*	*
PCBs	10	819	1	0.26	0.14	0.02	0.41

Group 1

Commonly detected >10%; dieldrin 68%, chlordane 27%, DDE 13%

<u>Group 2</u>

Infrequently detected < 5%; HCB 3%, heptachlor 2%, PCBs 1%

<u>Group 3</u>

Rarely detected <1%; DDT 0.3%, DDD 0.5%, aldrin 0.4%, lindane 0%

CLARKE et al (2010) Environment International, 36, 323-329

• • OCPs/PCBs 2004 - 2006

C2 Unsuitable for Beneficial Reuse



CLARKE et al (2010) Environment International, 36, 323-329

OCPs/PCBs 2004 - 2006



C2 Unsuitable for Beneficial Reuse

C1 Restricted Use

CLARKE et al (2010) Environment International, 36, 323-329

• Time Series Data 1995 – 2006

Cmps	Det	<dl< th=""><th>X</th><th>Mean mg kg⁻¹</th><th>StDev mg kg⁻¹</th><th>Min mg kg⁻¹</th><th>Max mg kg⁻¹</th></dl<>	X	Mean mg kg ⁻¹	StDev mg kg ⁻¹	Min mg kg ⁻¹	Max mg kg ⁻¹
DDT	29	2237	1.30	0.05	0.05	0.01	0.17
DDD	89	2177	3.93	0.06	0.15	0.01	1.04
DDE	129	2137	5.69	0.02	0.02	0.01	0.13
ΣDDT	174	2092	7.68	0.05	0.11	0.01	1.04
Aldrin	6	2260	0.26	0.10	0.16	0.01	0.41
Dieldrin	1554	712	68.58	0.10	0.08	0.01	0.49
Chlordane	1016	1250	44.84	0.11	0.10	0.01	0.73
Heptachlor	9	2257	0.40	0.13	0.08	0.04	0.25
НСВ	175	2091	7.72	0.07	0.09	0.01	0.48
Lindane	0	2266	0.00	*	*	*	*
PCBs	126	2140	5.56	0.30	0.20	0.06	1.40

<u>Group 1</u> Commonly detected dieldrin 69%, chlordane 45%

<u>Group 2&3</u> All other compounds detected in less than 10% samples

CLARKE et al (2010) Environment International, 36, 323-329





CLARKE et al (2010) Environment International, 36, 323-329

PCBs Time Series 1995 - 2006



CLARKE et al (2010 Environment International, 36, 323-329.

Time Series Analysis 1995 - 2006





OCPs and PCBs can be removed from biosolids regulations in Australia because:

- 1. They are infrequently detected
- 2. Almost never above highest contaminant limit
- 3. The contaminant limit is not based upon protection of public health/environment
- 4. Is a poor use of money (>\$200 per sample)



'Emerging' Organic Pollutants

Thousands of Potential Contaminants





• • • Assessment Matrix

	Persistence 2 – Yes 1 - Uncertain 0 – No	Food chain 2 – Possible 1 - Uncertain 0 - No	Ecological	Soil Ecotoxicity 2 - Yes 1 - Uncertain 0 - No	Research 3 - Lack of data 2 - Few studies 1 - Consistent 0 - Many & similar	Score (/11)
Antibiotics	0	2	0	1	2	5
Benzothiazoles	1	1	0	1	3	6
Bisphenol A	0	0	0	0	2	2
Organotins	1	1	2	1	2	7
Phthalates	0	0	0	0	1	1
PBDEs	2	2	2	1	0	7
PCAs	2	2	1	1	3	9
PCNs	2	2	1	1	3	9
Siloxanes	0	0	0	0	1	1
PFCs	2	2	2	1	3	10
QACs	0	0	0	0	2	2
Steroids	0	0	0	0	2	2
Synthetic Musks	1	0	1	0	1	3
Triclosan	1	0	2	2	2	7
Triclocarban	1	0	2	2	2	7

Polybrominated diphenyl ethers (PBDEs)

Used as fire retardantElectronics

Recently included as UN POPEnvironmental contaminant



More classes – BFRs, PFCs & PCAs

Cougoi et al / Environment Inte Occurrence of perfluorinated compounds (PFGs) in drinking water of North Rhine-Westphalia, Germany and new approach to assess drinking water on Land and Content weinesstephan for ther Levels of Chiorinated Paraffins in Water he Universität München lichaei Witherman Sabine Berghan PF Hermann H. Dieter^{c,*} HCDBCO Hygiene, Social and Environmental Medicine, Run-Thyperofessor, Harun Parlar on the occasion of his 65th birthday espinalia State Agency for Nature, Brithment and Consumer Protection (TANYV-NRW), Recklinghausen, Germany ment Agency (Umweltbundownen) of Grynnik Genetion (TANYV-NRW), Recklinghausen, Germany endeu Berling Germany, Constant Genetion (TANYV-NRW), Recklinghausen, Sollwarts, Welther and State Parlanet (State Refue Berling Germany, Sollwarts, State (State) (North Rhi Federal Envi 844 Dessa Rlau Rerlin Cermany lvzed for chlorinated paraffins (CPs). CPs were not detected in river water samples negative ion mass spectrometry (GC-ECNI-MS) (LOQ = 100 ng/L). However, middle cl influents while short chain chlorinated paraffins (SCCPs) were detected only in 2 of Loug-chain perfluorinated permicals in digested sources sludges circ Switzerdand And Fease Correcke ", Walter Ciger ", Alfredo Calder " Br Et Keywords: Chlorinated parafilins: Defermination: Occurrence: Polychlorinated malkanes; Ky Laboratory of Pollution Processes and Environmentator Science and Engineering. Nankai University. Tomin China wiss Federal Laboratories for Maternals Testing and Research, CH-8600 Dubendoff, Switzerland Br Br wiss rederal Laboratories for Materials testing and research, Cr-Bobb Dubendor, Switzerland ger Research Consulting, CH-8049 Aurich, Switzerlawded: February 5, 2010; revised: March 16, 2010; accepted: March 21, 2010 Swiss Federal Institute of Aquatic Science and Technology, CH-8600 Dibendorf, Switzerland trations of long-chain PFCs in dige statistical science and science and the Trends PERFI JORINATED PHOSPHONIC ACIDS IN CANADIAN SURFACE WATERS AND ASTEWATER TREATMENT PLANT EFFLUENT: DISCOVERY OF A NEW CLASS OF ccurrence, Tate and anal D'EOR, PAPRICK W CROZIER, VASILE I. EUROUI, † ERIC J. REINER, ‡ E. LAURENCE LIBELO, § rvice Branch, Ontario Ministry of the Environment, 125 Resource Road, Egyppio, Ontario M9P³V6, Canada ental Protection Regress, Office of Pollution Prevention and Toxics, Mail Code 7406C, 1200 Pennsylvania Avenue. environmen -сн=сн Fig. 1. Chemical structures of most important NBFRs.

Novel Brominated Fire Retardants

Perfluorochemicals (PFCs): Short Chain, Long Chain, phosphonic acid

> Polychlorinated alkanes (mixed bromo/chloro alkanes)

Do organic pollutants in biosolids pose a risk to public health and the environment?



Human Health Risk Assessment

Hazard Identification + Dose-Response Image: Construction + Risk Characterization

MAXIMUM RESIDUE LIMITS (MRLs)

- Equating TDI with typical quantities of ingested material (US EPA 1997)
- 200 g plant material
- 300 mL milk that is 4% fat
- 50 g animal fat ingested daily

• • Exposure Pathways



• • Pathway 3 - *Grazing Animal*



Percentage Exposure

< 5% for chronic dose exposure & worst-case scenarios

Cmps.	P1 – Direct Exposure		P2 -	P3 - Grazing Animal				P4 -	
				Plant	Past	ture	Gra	zing	water
	Child	Adult	Child Pica		Meat	Milk	Meat	Milk	
Dioxins	0.05	0.02	4.90	1.05	1.47	2.94	0.88	1.59	2.83
WPBDEs	< 0.01	< 0.01	0.01	< 0.01	0.11	0.17	0.06	0.10	0.58
BB-153	0.01	0.01	1.12	0.31	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
ΣDDT	< 0.01	< 0.01	0.08	0.21	0.06	0.10	0.04	0.05	0.56
Dieldrin	0.02	0.01	2.38	1.23	0.67	1.15	0.40	0.63	2.74
Chlordane	< 0.01	< 0.01	0.20	0.71	0.04	0.05	0.02	0.03	0.40
W PCBs	< 0.01	< 0.01	0.01	0.01	0.01	0.01	< 0.01	< 0.01	0.19

¹ Soil exposure is child of 15 kg and adult of 70 kg ingests 100 mg soil day⁻¹ and 50 mg soil day⁻¹ respectively; pica exposure 10 g day⁻¹ ² Daily plant consumption by humans assumed to be 200 g

³ Daily grazing animal consumption is 50 g fat and 300 mL that is 4 % fat; pasture animals assumed to ingest 10 kg fodder grown on sewage sludge amended soil and grazing animals assumed to ingest 10 kg pasture with 500 g associated soil

• • • Solutions ??

- Deal with the issue
- Review of potential pollutants in catchment
- Source control
- Risk assessment
- Bioanalytical tools

This is long-term problem!!



Bioanalytical Tools

Final Report

Monitoring Strategies for Chemicals of Emerging Concern (CECs) in Recycled Water

Recommendations of a Science Advisory Panel

Panel Members Paul Anderson, Nancy Denslow, Jörg E. Drewes (*Chair*), Adam Olivieri, Daniel Schlenk, and Shane Snyder



Convened by the
State Water Resources Control Board

June 25, 2010 Sacramento, California

- Recommended strategy by US EPA
- Generalized toxicity
 testing
- Compliment to traditional chemical testing
- Represent a paradigm shift for biosolids managers



	Current
Human promoters	18,000
Human 3' UTRs	12,000

- Hypoxia
- p53
- NFkB
- STAT1
- CREB
- Cholesterol biosynthesis
- Glucocorticoid receptor
- PPAR
- Estrogen receptor
- Androgen receptor
- more...

Pilot Study with Wastewater Treatment:



- Sample name: Site_Treatment
- Green_Valley_E2 spike = Green Valley water sample to which we added 10nM bestradiol (E2) as a control

Conclusions:

- Significant ER activation from Roger Rd site but not Green Valley site
 - Artificially adding 10nM E2 to Green Valley sample activates ER pathway
- Significant and unexpected GR activity from both sites
- GR activity is removed by UV treatment

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Comments/Questions

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