



Monitoring and prioritisation of organic contaminants in sewage sludges using specific chemical analysis and predictive, non-analytical methods

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Abstract

Municipal sludge application on agricultural land (land utilization) is practised widely and accounts for between 30–40% of production in Canada and the UK. Land utilization is subject to public concerns over the potential for deleterious effects of organic contaminants on agricultural productivity and uptake into the foodchain. Consequently, reliable data on the concentrations of organic contaminants in sludge are required to assess risks associated with land use. A detailed monitoring survey has been carried out by WTC to determine the concentrations of a range of industrial organic contaminants in 11 Canadian sewage sludges and one sludge compost. Volatile, base-neutral and acid extractable contaminants seldom exceeded 5 mg kg⁻¹ dry wt., organochlorine pesticides and polychlorinated biphenyls did not exceed 1 mg kg⁻¹ dry wt. and toxaphene and *N*-nitrosodimethylamine were not detected in the materials analyzed. Mean total PCDD and PCDF concentrations were $\leq 36 \mu\text{g kg}^{-1}$ dry wt. (median 6.7 $\mu\text{g kg}^{-1}$ dry wt.) and mean toxic equivalents were $\leq 0.12 \mu\text{g kg}^{-1}$ dry wt. (median 0.02 $\mu\text{g kg}^{-1}$ dry wt.). It was concluded that in many Canadian sludges the aforementioned organic contaminants represent no significant risk to agriculture and the environment. However, other organic contaminants potentially present in sewage sludge may not be amenable to analysis by the target compound techniques widely used. Consequently, WRc have applied a non-analytical approach to assess which contaminants may occur in sewage sludges and persist in treated soils. Predictions of physicochemical properties using quantitative structure activity relationships (QSARs) have been used to aid the screening and prioritisation of a range of high production volume chemicals (HPVCs) that may enter sewage treatment works. Analytical surveys for organic residues are expensive and this type of approach may assist in identifying further contaminants which should be analyzed in sewage sludges and treated soils.

Keywords: Organic contaminants; Sewage sludge; VOC; Non-analytical methods; Ranking

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1. Introduction

Municipal sludge application on agricultural land (land utilization) is practised widely in Canada and the UK. It accounts for approximately one-third (120 000 tonnes year⁻¹ dry wt.) of Canadian sludge production and 40% (~400 000 tonnes year⁻¹ dry wt.) of UK sludge production.

Land utilization is desirable for a variety of reasons. For agriculture it represents an inexpensive nitrogen and phosphorus fertilizer and soil conditioning material; for the environment it represents resource recovery and reuse; and for wastewater treatment authorities it frequently represents the most economic sludge management method. Sludge may contain pathogens, heavy metals and organic contaminants that constitute risks to agriculture. Considerable pathogen and heavy metal research has been conducted and land utilization guidelines have been formulated to account for these constituents in sludges. However, data is inadequate to assess the need for land utilization guidelines for organic contaminants.

Organic contaminant data for 15 Canadian sludges analyzed during 1980–1985 were reported by Webber and Lesage (1988). A few of the samples were 1-week composites but most were grabs and several different analytical protocols were employed. Subsequently, analysis of 37 Ontario sludges was conducted as part of the Ontario Ministry of the Environment, Municipal-Industrial Strategy for Abatement program (MOE, 1988). Raw and stabilized sludges were analyzed and samples were 5-day flow proportioned composites. A minimum of three grab aliquots was collected, at least 2 h apart, each day but not all samples contained sufficient sludge solids to yield reliable results.

The future of land utilization in Canada is subject to public concerns about deleterious effects on agriculture and the foodchain of organic contaminants in sludges. Available information concerning the concentrations of organic contaminants in Canadian sludges is limited and of questionable reliability. Reliable information is needed to assess the risks associated with land utilization and to respond to the public concerns.

A preliminary monitoring study involving two

Ontario sludges and carefully controlled sampling and analytical protocols yielded highly reproducible polynuclear aromatic hydrocarbon, organochlorine pesticide and polychlorinated biphenyl data during a 5-month period (Webber, 1994). Based on this information, it was concluded that reliable organic contaminant information could be obtained for a wide range of Canadian municipal sludges.

A monitoring study of Canadian municipal sludges was undertaken and the objectives were to: (1) monitor a wide range of organic contaminants in Canadian municipal sludges; (2) assess sampling and analytical variability associated with the measurements; (3) monitor changes in the measurements during a 6-month sampling period; and (4) assess the suitability of Canadian municipal sludges for land utilization.

2. Experimental

2.1. Sludge and compost

Liquid sludges were obtained from 11 locations in Canada; two from British Columbia, three from Alberta, one from Saskatchewan, one from Manitoba and four from Ontario. In addition, one sludge compost was obtained from British Columbia. All but three of the sludges were anaerobically digested mixed primary and waste activated materials. One from British Columbia was aerobically digested mixed primary and waste activated sludge, one from Saskatchewan was anaerobically digested primary sludge and one from Ontario was raw primary sludge. The compost resulted from a mix of raw primary sludge and wood waste (hog fuel). Six different piles of compost varying in age from 1 to 10 years were sampled.

2.2. Sample handling

Sludges were sampled the first Monday or Tuesday of the month during a 6-month period beginning in September 1993. Samples were taken three times within a 4-h period, at 0, 2 and 4 h, from a sludge digester or transport line. Lines were flushed to ensure that samples were obtained directly from the digestors. Several 1-l bottles filled to 0.75 l with sludge were collected at each sampling time. Concurrently, three vials filled headspace-free

with sludge for VOC analysis were collected at each sampling time. The samples were placed in a picnic cooler with ice packs and shipped air express to the WTC. Usually, they arrived within 24 h and VOC analysis was completed within a fur-

ther 48 h. For each location, the sludge in 1-l bottles was composited in a stainless steel bucket and duplicate subsamples were analyzed. The subsamples were maintained at 4°C prior to analysis.

Compost was obtained with a spade used to dig

Table 1
Volatile organic (VOC) and base neutral and acid extractable (BN&A) analytes

VOC	BN&A	BN&A	
1,1,1-Trichloroethane	Polynuclear Aromatic Hydrocarbons (PAH) Naphthalene Acenaphthylene Acenaphthene Fluorene Phenanthrene Anthracene Fluoranthene Pyrene Benzo[a]anthracene Chrysene Benzo[b]fluoranthene Benzo[k]fluoranthene Benzo[a]pyrene Indeno[1,2,3-c,d]pyrene Dibenzo[a,h]anthracene Benzo[g,h,i]perylene	Nitrosamines N-Nitrosodiphenylamine N-Nitrosodi-n-propylamine	
1,1,2,2-Tetrachloroethane		Phthalate Esters Dimethylphthalate Diethylphthalate Di-n-butylphthalate Butylbenzylphthalate Bis-2-ethylhexylphthalate Di-n-octylphthalate	
1-1,2-Trichloroethane		Acid Group Phenol 2-Chlorophenol 2-Nitrophenol 2,4-Dimethylphenol 2,4-Dichlorophenol p-Chloro-m-cresol 2,4,6-Trichlorophenol 2,4-Dinitrophenol 4-Nitrophenol 4,6-Dinitro-o-cresol Pentachlorophenol	Other Compounds Nitrobenzene Isophorone Hexachloroethane Hexachlorobutadiene Hexachlorocyclopentadiene 2-Chloronaphthalene 2,6-Dinitrotoluene 2,4-Dinitrotoluene 1,2-Diphenylhydrazine 3,3'-Dichlorobenzidine
1,1-Dichloroethane			
1,1-Dichloroethylene			
1,2,4-Trimethylbenzene			
1,2-Dibromoethane			
1,2-Dichlorobenzene			
1,2-Dichloroethane			
1,2-Dichloropropane			
1,2-Diethylbenzene			
1,3,5-Trimethylbenzene			
1,3-Dichlorobenzene		Haloethers Bis-2-chloroethylether Bis-2-chloroisopropylether Bis-2-chloroethoxymethane 4-Bromophenylphenylether 4-Chlorophenylphenylether	
1,3-Diethylbenzene			
1,4-Dichlorobenzene			
1,4-Diethylbenzene			
2-Ethyltoluene			
3-Ethyltoluene			
4-Ethyltoluene			
Benzene			
Bromodichloromethane			
Bromoform			
Chlorobenzene	Chlorinated Benzenes 1,3-Dichlorobenzene 1,4-Dichlorobenzene 1,2-Dichlorobenzene 1,2,4-Trichlorobenzene Hexachlorobenzene		
Chlorodibromomethane			
Chloroform			
Cis-1,2-dichloroethylene			
Cumene			
Cyclohexane			
Dibromomethane			
Dichloromethane			
Ethylbenzene			
Hexane			
Nonane			
<i>o</i> -Xylene			
Octane			
Propylbenzene			
Styrene			
Tetrachloroethylene			
Tetrachloromethane			
Toluene			
<i>trans</i> -1,2-Dichloroethylene			
Trichloroethylene			
<i>m/p</i> -Xylene			

at least 60 cm into the base of each pile at 10 approximately evenly spaced locations. Subsamples from each pile were composited and three vials and 1 l of each composite sample were prepared for VOC and the other analyses, respectively. The vials were filled 'as nearly as possible' headspace-free. Transport and analysis were as for the sludges.

Hereafter the sludges and sludge compost included in this study are referred to as 'sludges' or 'Canadian municipal sludges'.

2.3. Analytical

A complete listing of the analytes is presented in Tables 1 and 2. Analyses were conducted at the WTC except for the polychlorinated dibenzo(*p*)dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) which were analyzed at Environment Canada's River Road Environmental Technology Centre, Ottawa, ON. Volatile organic contaminants (VOCs) were recovered from sludges by the purge and trap method and were measured by combined gas chromatographic-mass selective detector (GC-MSD) analysis. The method detection limits (MDLs) ranged from <10–1700 $\mu\text{g kg}^{-1}$ dry wt. Base-neutral and acid extractable compounds (BN&As) were extracted with acetone-hexane and measured by combined gas chromatographic-mass spectrometric (GC-MS) analysis. The MDLs ranged from <1–14 mg kg^{-1} dry wt. Organochlorine pesticides (OCs), polychlorinated biphenyls (PCBs) and toxaphene were extracted with acetone-hexane and measured by gas chromatographic (GC) analysis following florisil clean-up. *N*-Nitrosodimethylamine (NDMA) was extracted with dichloromethane and measured by GC-MS analysis. The MDLs for OCs ranged from 1–10 $\mu\text{g kg}^{-1}$ dry wt., for PCBs was 500 $\mu\text{g kg}^{-1}$ dry wt., for toxaphene was 1 mg kg^{-1} dry wt. and for NDMA was 400 ng kg^{-1} dry wt. Polychlorinated dibenzo(*p*)dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) were extracted with toluene following sulphuric acid digestion and measured using a high resolution gas chromatograph coupled to a high resolution mass spectrometer. Analyses were conducted for 17 2,3,7,8-substituted PCDD and PCDF congeners, and for the tetra-, penta-, hexa-, hepta- and octa-

Table 2
Other organic analytes

Organochlorine pesticides (OC)	Polychlorinated dibenzo-dioxins (PCDD) Congeners
Aldrin	
Alpha BHC	
Alpha chlordane	2378-TCDD
Alpha endosulfan	12378-P5CDD
Beta endosulfan	123478-H6CDD
Dieldrin	123678-H6CDD
Endrin	123789-H6CDD
Gamma BHC	1234678-H7CDD
Gamma chlordane	OCDD
Heptachlor	
Heptachlorepoxyde	Homologues
Hexachlorobenzene	TCDD
Methoxychlor	P5CDD
Mirex	H6CDD
<i>o,p'</i> -DDT	H7CDD
<i>p,p'</i> -DDE	OCDD
<i>p,p'</i> -DDT	
	Polychlorinated dibenzofurans (PCDF) Congeners
Polychlorinated biphenyls (PCB)	2378-TCDF
	12378-P5CDF
Toxaphene	23478-P5CDF
	123478-H6CDF
<i>N</i>-Nitrosodimethylamine (NDMA)	123678-H6CDF
	234678-H6CDF
	123789-H6CDF
	1234678-H7CDF
	1234789-H7CDF
	OCDF
	Homologues
	TCDF
	P5CDF
	H6CDF
	H7CDF
	OCDF

chlorinated dioxin and furan homologues. The MDLs for homologues ranged from 0.04–5 ng per analyte peak. MDLs varied depending upon the amount of sludge analyzed and the degree of dilution of extracts.

3. Results and discussion

3.1. VOCs

The sludges were analyzed for 44 VOC compounds (Table 1). Recoveries of check standards (known amounts of analytes treated like a sample) and two surrogate compounds (Table 3) added to samples ranged from 75 to 110% with most >90%. Method blanks were 'no-detection' or 'trace' (i.e. <MDL). Measurements were not adjusted for method blanks or the surrogate recoveries.

In general, VOCs were not detected or they occurred at low $\mu\text{g kg}^{-1}$ dry wt. concentrations in

the sludges. Sixteen compounds were not detected or occurred infrequently and at very low concentrations. Summary data for the VOCs observed regularly are presented in Table 4. Mean values for 13 did not exceed $500 \mu\text{g kg}^{-1}$ dry wt. and for an additional four did not exceed $1000 \mu\text{g kg}^{-1}$ dry wt. (i.e. 1 ppm). Except for toluene, mean values for the remaining VOCs in Table 4 ranged up to $7368 \mu\text{g kg}^{-1}$ dry wt. (i.e. 7.4 ppm). Mean toluene concentrations for most sludges ranged from 3.7 to $1810 \mu\text{g kg}^{-1}$ dry wt. but for three Ontario sludges were 36, 38 and 42 ppm. Concentrations in two of these sludges exhibited wide ranges but in the third

Table 3

Mean volatile organic contaminant (VOC) concentrations ($\mu\text{g/kg}$ dry wt.) in Canadian municipal sludges and sludge compost, September 1993–February 1994

	BC	BC	BC (com- post)	AB	AB	AB	SK	MB	ON	ON	ON	ON
1,2,4-Trimethylbenzene	27	4678	ND	5660	5068	1215	6752	6979	6608	2176	7865	3130
1,2-Dichlorobenzene	10	46	ND	421	80	134	76	307	59	131	126	192
1,2-Diethylbenzene	2	120	ND	300	102	71	319	268	106	78	199	93
1,3,5-Trimethylbenzene	17	1817	0.4	1582	1632	373	1937	1929	3296	714	2493	971
1,3-Dichlorobenzene	12	19	ND	77	8	71	3	25	18	29	52	16
1,3-Diethylbenzene	3	342	ND	563	277	148	534	510	493	193	504	231
1,4-Dichlorobenzene	33	265	2.2	560	202	352	354	670	488	870	845	740
1,4-Diethylbenzene	5	795	ND	2070	1006	374	2137	2196	1172	608	2215	696
2-Ethyltoluene	6	1048	ND	1046	932	267	1158	1310	2171	430	1538	632
3&4-Ethyltoluene	31	3061	0.9	3146	3202	686	4431	4035	7368	1289	4658	1961
Benzene	24	134	4.6	483	39	84	45	52	58	75	58	54
Chlorobenzene	3	21	ND	62	42	56	21	91	64	83	197	75
Chloroform	111	151	7.2	148	94	179	72	119	95	216	186	94
Cis-1,2-dichloroethylene	ND	302	ND	760	61	26	269	367	814	29	50	59
Cumene	3	124	ND	140	126	33	153	143	257	103	191	80
Cyclohexane	103	44	ND	90	70	119	35	63	45	110	88	43
Ethylbenzene	21	127	1.3	390	336	105	617	549	518	499	421	119
Nonane	8	1002	ND	1200	1241	216	1805	1465	1996	378	902	633
<i>o</i> -Xylene	24	352	1.3	464	832	129	1552	1006	1504	422	707	268
Octane	23	5	ND	10	222	ND	150	112	383	19	32	10
Propylbenzene	3	562	ND	595	597	139	687	727	845	218	751	365
Styrene	0.3	1.6	ND	29	ND	5.9	ND	ND	ND	1.9	1.3	ND
Tetrachloroethylene	39	202	ND	111	27	115	192	59	231	95	80	65
Toluene	196	628	3.7	1290	923	383	740	1542	38 218	35 964	42 437	1810
Trichloroethylene	126	238	0.3	176	136	229	233	167	380	252	246	165
<i>m/p</i> -Xylene	45	423	3.1	802	2332	247	3520	2061	2786	1319	1265	422
Surrogate (% recovery)												
1,4-Difluorobenzene	151	100	98	96	98	97	94	99	97	99	96	99
1-Bromo-4-fluorobenzene	98	94	80	91	93	93	87	91	84	96	92	96

ND, no detection; AB, Alberta; MB, Manitoba; BC, British Columbia; SK, Saskatchewan; ON, Ontario.

Table 4
Organic contaminants (mg/kg dry wt.) in agricultural soil and Canadian municipal sludges and sludge compost

Parameter	Agricultural soil ^a		Maximum permissible addition to background soil (kg/ha)	Maximum permissible sludge concentration ^b	Observed mean sludge concentrations ^c	
	Background	Clean-up			High	Median
VOCs						
1,2-Dichlorobenzene	0.002	0.88	1.76	44	0.42	0.1
1,4-Dichlorobenzene	0.002	0.32	0.64	16	0.87	0.42
Benzene	0.002	0.06	1	25	0.48	0.06
Chlorobenzene	0.002	2.4	5.6	140	0.2	0.06
Chloroform	0.006	0.13	0.25	6.2	0.22	0.12
Ethylbenzene	0.002	0.5	1	50	0.62	0.36
<i>o/m/p</i> -Xylene	0.002	1	2	50	5.1	1.5
Tetrachloroethylene	0.002	0.45	0.9	22	0.23	0.09
Toluene	0.002	1	2	50	42	1.1
Trichloroethylene	0.004	0.39	0.77	19	0.38	0.23
BN&As						
1,2-Dichlorobenzene	0.002	0.88	1.76	44	0.32	0.08
1,4-Dichlorobenzene	0.002	0.32	0.64	16	2.6	0.52
2-Chlorophenol	0.1	0.1	0	—	0.15	0.06
Acenaphthene	0.05	15	30	750	1.6	0.53
Acenaphthylene	0.23	100	200	5000	3.4	0.05
Anthracene	0.05	28	56	1400	1.7	0.23
Benzo[<i>a</i>]anthracene and chrysene	0.28	13.2	26	650	19	1.1
Benzo[<i>a</i>]pyrene	0.1	1.2	2.2	55	6.8	0.33
Benzo[<i>b,k</i>]fluoranthene	0.05	12	24	600	4.9	0.76
Benzo[<i>g,h,i</i>]perylene	0.2	35	70	1750	5.2	0.24
Bis-2-ethylhexylphthalate	< 5 ^d	100	190	4750	244	160
Dibenzo[<i>a,h</i>]anthracene	0.15	1.2	2.1	52	3.9	0.03
Fluoranthene	0.24	40	80	2000	5	1.04
Fluorene	0.05	340	680	17 000	2.5	0.63
Indeno[1,2,3- <i>c,d</i>]pyrene	0.11	12	24	600	1.8	0.15
Naphthalene	0.05	4.6	9.1	230	13	2
Phenanthrene	0.19	40	80	2000	11	2.3
Phenol	0.1	40	80	2000	9.4	2
Pyrene	0.19	1.3	2.2	55	14	1.2
OCs & PCBs						
Hexachlorobenzene	< 0.05 ^d	0.66	1.2	30	0.033	0.001
<i>p,p'</i> -DDE	0.12 ^e	1.6	3	75	0.013	ND
Total PCBs	0.3	0.5	0.4	10	0.28	ND
PCDD + PCDF (µg/kg dry wt.)						
Total TEQ	0.007	0.01	0.006 ^f	0.15	0.12	0.02

ND, no detection; TEQ: toxic equivalents as 2,3,7,8-TCDD using International Toxic Equivalency Factors.

^aSource, MOEE (1994).

^bAssuming maximum permissible addition in 40 Mg dry wt. of sludge.

^cSource; Tables 3, 5 and 6, except OCs and PCBs.

^dData not available; numbers are large estimates.

^eData not available; used number for DDT.

^fValues in g/ha.

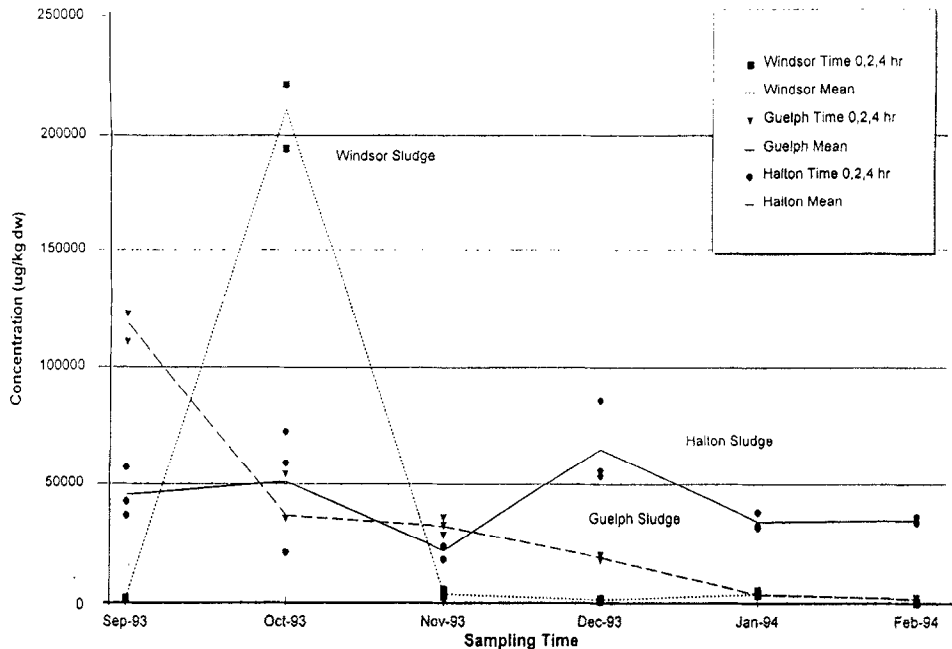


Fig. 1. Changes in toluene concentration with time during municipal sludge sampling.

were approximately constant throughout the 6-month sampling period (Fig. 1). There was generally good reproducibility of VOC analyses for sludges taken at 0, 2 and 4 h within each sampling period. With some exceptions, the most notable being toluene in Ontario sludges, VOCs did not exhibit large variations in concentrations during the 6-month study period.

These results are similar to previous reports for Ontario (MOE, 1988) and USA sludges (Jacobs et al., 1987) because many analytes were not detected or occurred at very small $\mu\text{g kg}^{-1}$ dry wt. concentrations. Other analytes exhibited considerable ranges of concentration and a few (e.g. toluene) occurred at $>100\,000\ \mu\text{g kg}^{-1}$ dry wt. (i.e. >100 ppm). Generally higher frequencies of occurrence for observed analytes in the present than in previous studies probably reflect reduced MDLs associated with improved analytical techniques.

Except for 1,4-dichlorobenzene, the VOCs observed in Canadian municipal sludges at mean concentrations $>1000\ \mu\text{g kg}^{-1}$ dry wt. (Table 3)

were alkylbenzenes which are derived from coal and petroleum (Morrison and Boyd, 1976). They probably gained entry to the sewer systems in automotive fuel and lubricants or as a result of industrial activity. The very large concentrations of toluene observed in Ontario sludges likely resulted from industrial activity. Toluene is used widely as a solvent and to manufacture other organic compounds. The 1,4-dichlorobenzene (Paramoth®) is used for killing moths and their larvae, roaches, some other insects, peach tree borers and for preserving furs, carpets, woollen clothes and rugs (Merck, 1989). Also, it is used widely as a deodorant in institutional washrooms.

To place sludge organic contaminant loadings to land into an agricultural perspective, Jacobs et al. (1987) drew a parallel with pesticide use. Many pesticides are organic chemicals that are applied to soil-plant systems at rates of 0.2–4 kg ha^{-1} of active ingredient. Assuming an agronomic sludge application rate of 8 Mg ha^{-1} dry wt., the loadings for sludges with organic contaminant concentrations of 1, 10 and 100 mg kg^{-1} dry wt.

are 0.008, 0.08 and 0.8 kg ha⁻¹. It was concluded that sludges with contaminant concentrations approaching 100 mg kg⁻¹ dry wt. must be viewed as potentially having an impact on the soil-plant system, depending on the chemical/toxicological properties of the contaminant.

Recently, guidelines for the clean-up of contaminated sites were proposed for Ontario (MOEE, 1994). They were developed to ensure protection of human health and the natural environment from adverse effects associated with exposure to contaminated soil, sediment and groundwater. Using criteria contained in these guidelines, maximum permissible loadings of several VOCs to agricultural land were calculated (Table 4). Assuming maximum permissible metal concentrations in sludge and mean background concentrations in soil (OMAF/MOE, 1992), land application is limited by molybdenum and the maximum permissible loading of this metal is supplied in approximately 40 Mg ha⁻¹ dry wt. of sludge. Assuming this loading, calculated maximum permissible VOC concentrations in sludge (Table 4) greatly exceeded concentrations observed in the Canadian municipal sludges, except for toluene. Although limited, these data indicate that VOCs in Canadian sludges are unlikely to represent a significant risk to agriculture and the environment.

VOCs volatilise and degrade and disappear rapidly from sludge-soil systems (WTC, unpublished information). A study of 10 VOCs including trichloroethylene, benzene, chloroform, 1,1-dichloroethane, toluene, *o*-xylene, 3-ethyltoluene, ethylbenzene, 1,3-diethylbenzene and 1,4-dichlorobenzene indicated that persistence increased with increasing VOC boiling point and increasing soil organic matter content. However, the maximum observed half-life ($t_{0.5}$) for VOCs was 322 h and for toluene was 76 h in sludge-treated mineral soil. Ryan et al. (1988) classified anthropogenic organic compounds on the basis of $t_{0.5}$ in soil as follows: class A, <10 days (i.e. <240 h); class B, 10–50 days; and class C >50 days. It was pointed out that class A compounds are reduced to <0.1% of their original concentration in soil within 100 days. Gillett (1983) considered compounds with $t_{0.5}$ > 336 h in soil sufficiently stable to be of environmental concern.

It is concluded that, with the possible exception of toluene in Ontario sludges, VOCs in Canadian municipal sludges represent no significant risk to agricultural production. Even at concentrations observed in the above-mentioned sludges, it is unlikely that toluene represents a significant risk to agricultural production because of its short half-life (<76 h) in soil. However, the concentrations in Ontario sludges are indicative of undesirable industrial discharges and local authorities may wish to identify the sources and implement controls.

3.2. BN&As

The sludges were analyzed for 55 BN&A compounds (Table 1). It was impossible to resolve some chromatographic peaks and values are reported for benzo[*a*]anthracene and chrysene and for benzo[*b,k*]fluoranthene. Occasionally no MDL and/or sludge measurement was obtained. Method blank measurements generally were 'no-detection' or 'trace' and recoveries of five surrogate compounds (Table 5) added to samples ranged from <50% to >100%. Measurements were not adjusted for method blanks or the surrogate recoveries.

Detailed data indicated that BN&As frequently were not detected in sludges or that they occurred at concentrations less than the MDLs, most of which were <2 mg kg⁻¹ dry wt. Also, there was general agreement between replicate analyses and among sampling periods. Twenty-six compounds were not detected or occurred infrequently and at very low concentrations in the sludges. Summary data for 29 BN&As observed regularly in the sludges are presented in Table 5. Mean concentrations for six were <1 mg kg⁻¹ dry wt. and for 16 were <5 mg kg⁻¹ dry wt. Mean concentrations for the phthalate esters and polynuclear aromatic hydrocarbons (PAHs) frequently exceeded 5 mg kg⁻¹ dry wt. In particular, concentrations of PAH compounds such as benzo[*a*]anthracene and chrysene, benzo[*a*]pyrene, benzo[*b,k*]fluoranthene and pyrene were elevated in the Saskatchewan sludge probably because of heavy steel industry in the sewerage district. Mean total PAH concentrations in the sludges ranged from 2.2 to 79 mg kg⁻¹ dry wt., with a median value of 11 mg kg⁻¹ dry wt.

Table 5

Mean base neutral and acid extractable (BN&A) contaminant concentrations (mg/kg dry wt.) in Canadian municipal sludges and sludge compost, September 1993–February 1994

	BC	BC	BC (com- post)	AB	AB	AB	SK	MB	ON	ON	ON	ON
1,2-Dichlorobenzene	ND	ND	ND	0.2	0.08	0.03	0.07	0.32	0.11	0.08	0.04	0.11
1,4-Dichlorobenzene	0.26	2.55	ND	0.44	0.27	0.22	0.42	0.82	1.32	0.81	0.93	0.63
2,4-Dimethylphenol	ND	0.06	ND	ND	ND	ND	ND	ND	ND	ND	0.67	0.21
2,6-Dinitrotoluene	ND	0.14	ND	0.34	ND	ND	ND	ND	0.57	0.26	0.28	0.07
2-Chlorophenol	0.06	0.02	0.01	0.03	0.04	0.06	0.03	0.08	0.06	0.15	0.12	0.12
Acenaphthene	0.17	1.45	ND	0.09	0.57	0.4	1.6	0.85	1.32	0.14	0.49	0.36
Acenaphthylene	0.03	3.38	0.01	0.16	0.06	0.19	0.22	0.04	0.01	ND	0.05	0.11
Anthracene	0.01	0.97	0.003	0.25	0.53	0.11	1.71	0.2	0.3	0.07	0.7	0.12
Benzo[a]anthracene and chrysene	0.63	1.17	0.17	1.91	0.94	0.48	19.39	1.33	1.03	0.32	0.97	1.41
Benzo[a]pyrene	0.21	0.32	0.05	0.73	0.3	0.08	6.83	0.35	0.35	0.2	0.35	0.55
Benzo[b,k]fluoranthene	0.54	0.73	0.15	1.24	0.78	0.41	4.9	0.9	0.83	0.48	0.62	1.05
Benzo[g,h,i]perylene	0.11	0.25	0.06	0.75	0.12	0.08	5.21	0.33	0.37	0.2	0.23	0.35
Bis-2-ethylhexylphthalate	64	96	1.61	244	182	161	150	221	171	115	159	230
Butylbenzylphthalate	1.1	6.1	0.05	4.1	0.4	0.8	10.1	3.2	6	0.3	0.3	2.1
Di-n-butylphthalate	5.3	7.7	0.78	6.7	11	9.8	7.5	7.6	12.3	5.7	3.6	4.1
Di-n-octylphthalate	1.25	4.09	ND	6.85	3.85	3.36	7.27	8.08	8.47	3.78	3.15	5.75
Dibenzo[a,h]anthracene	ND	0.59	ND	0.24	0.01	ND	3.89	0.02	0.02	0.07	0.06	0.04
Diethylphthalate	0.27	0.65	0.06	0.14	0.19	0.42	0.03	0.18	0.25	0.24	0.15	0.16
Dimethylphthalate	0.06	0.13	ND	0.09	0.03	ND	ND	ND	ND	0.01	ND	ND
Fluoranthene	0.76	4.99	0.25	1.75	1.04	0.63	4.69	1.3	0.96	0.57	1.04	1.35
Fluorene	0.45	1.27	ND	1.15	0.81	0.2	2.52	0.97	0.34	0.21	0.67	0.59
Indeno[1,2,3-c,d]pyrene	0.14	0.1	0.03	0.44	0.14	0.01	1.84	0.22	0.29	0.07	0.15	0.31
Naphthalene	0.5	13	0.08	2.5	1.5	0.7	2.2	2.8	1.8	0.9	2.6	1.2
Nitrobenzene	4.1	2.4	ND	2.1	ND	ND	0.7	0.2	5.2	0.8	0.2	ND
Phenanthrene	2.4	10.7	0.14	4	2.3	0.9	9.9	3.6	2.3	0.5	2.1	2.3
Phenol	5.5	9.4	0.01	5.4	1.9	1.2	1.6	2.7	2.4	0.7	2.2	1.6
Pyrene	1.1	4.9	0.26	2.2	1.3	0.6	14	1.7	0.9	0.6	1.2	1.6
Surrogate (% recovery)												
2-Fluorobiphenyl	89	92	107	92	92	91	87	93	96	96	98	95
Nitrobenzene-d5	71	77	96	79	78	75	76	74	86	72	69	70
P-terphenyl-d14	91	94	103	99	101	101	89	97	91	96	99	98
Phenol-d5	53	62	42	61	57	53	64	65	71	56	63	63
Tri-fluoro- <i>m</i> -cresol	69	82	63	79	78	74	82	89	88	85	94	88

ND, no detection; AB, Alberta; MB, Manitoba; BC, British Columbia; SK, Saskatchewan; ON, Ontario.

Base-neutral and acid extractable contaminant concentrations in Canadian municipal sludges observed during the present study are similar to previous reports (Jacobs et al., 1987; MOE, 1988; Webber and Lesage, 1988; Webber, 1994). Most compounds were not detected or occurred at very small concentrations. Similar data sets were obtained for three compounds, 1,2-, 1,3- and 1,4-dichlorobenzene, by both VOC and BN&A analyses. In general, only the polynuclear aromatic

hydrocarbons (e.g. benzo[a]anthracene and chrysene, benzo[a]pyrene, pyrene and etc.) and phthalate esters (e.g. bis-2-ethylhexylphthalate) exceeded 1 mg kg⁻¹ dry wt. Polynuclear aromatic hydrocarbons (PAHs) are fossil fuel combustion products and phthalate esters lend flexibility to plastics and are ubiquitous in the environment.

According to the Jacobs et al. (1987) rationale, phthalates in Canadian municipal sludges are a potential concern for agriculture but PAHs are

not. However, calculations based on guidelines for the clean-up of contaminated sites in Ontario (MOEE, 1994) indicated that observed bis-2-ethylhexylphthalate and PAH concentrations (Table 4) do not represent a significant risk to agriculture and the environment. Benzo[a]pyrene and pyrene are the most limiting PAHs but maximum permissible concentrations of these compounds exceeded the observed mean concentrations in Canadian municipal sludges by at least fourfold.

Phthalate esters degrade rapidly in soil (Ryan, 1986; Huddleston et al., 1986; WTC, unpublished information). By contrast, high molecular weight polynuclear aromatic hydrocarbons are persistent in soil but the mean concentrations in Canadian municipal sludges are much smaller than 10 mg kg⁻¹ dry wt. and loadings to soil during land application would be small. Moreover, there is considerable evidence that polynuclear aromatic hydrocarbons are not taken up by growing crops (Overcash et al., 1986; Witte et al., 1988; O'Connor et al., 1991; Goodin and Webber, 1995).

According to the guidelines for clean-up of contaminated sites in Ontario (MOEE, 1994) two BN&As, 2-methylnaphthalene and 2-chlorophenol, are not allowed to exceed the background levels for agricultural land use in soil overlying potable groundwater. Although 2-methylnaphthalene was not measured in this study it is probable that its concentrations approximated those of the other low molecular weight PAHs (i.e. <5 mg kg⁻¹ dry wt.). The mean concentrations of 2-chlorophenol were <0.2 mg kg⁻¹ dry wt. Since the amounts of these compounds in an agronomic application rate of sludge (e.g. 8 Mg ha⁻¹ dry wt.) are small and both degrade aerobically (U.S.EPA RREL), it is unlikely that land application of them in Canadian municipal sludges represents a significant risk for potable groundwater quality.

3.3. OCs, PCBs, toxaphene and NDMA

All sludges were analyzed for 17 OCs (Table 2) and total PCBs, and four sludges, not including the compost, were analyzed for toxaphene and NDMA. Recoveries of check standards were 80-105% and method blank measurements were 'no-detection' or 'trace'.

Several OCs including aldrin, alpha BHC, alpha

chlordane, alpha endosulfan, beta endosulfan, dieldrin, endrin, heptachlor, heptachlorepoxyde, mirex, and *o,p'*-DDT (MDLs; $\leq 10 \mu\text{g kg}^{-1}$ dry wt.) were not detected in sludge or were observed infrequently at concentrations approaching the MDLs. Others did not exceed 1 mg kg⁻¹ dry wt. in sludge and, except for *p,p'*-DDE which occurred in all six compost samples, they occurred infrequently. Toxaphene (MDL, 1 mg kg⁻¹ dry wt.) and NDMA (MDL, 0.4 $\mu\text{g kg}^{-1}$ dry wt.) were not detected in the four sludges analyzed. Polychlorinated biphenyls (MDL, 0.5 mg kg⁻¹ dry wt.) were detected in five sludges but concentrations did not exceed 0.8 mg kg⁻¹ dry wt.

Large concentrations of organochlorine pesticides are not expected to occur in Canadian municipal sludges and compost because production and use of these compounds, except for endosulfan (Thiodan®), have been banned in Canada since the mid-1970s. Endosulfan is a non-persistent stomach insecticide used on field crops. The study results were consistent with this expectation and with other reports (Jacobs et al., 1987; Webber and Lesage, 1988). Most were 'no detection' and observations were sporadic and usually much <1 mg kg⁻¹ dry wt. Considering that past agricultural use of organochlorine pesticides was at rates up to approximately 5 kg ha⁻¹, the concentrations observed in sludge are considered trivial. Similarly, large concentrations of PCBs are not expected to occur in Canadian municipal sludges because production and use of these compounds have been banned in Canada since the mid-1970s. The study results were generally smaller than previously reported values for sludge (Jacobs et al., 1987; Webber and Lesage, 1988). They were 'no detection', 'trace' or approximately the 0.5 mg dry wt. MDL. A recent study (Webber, 1994) indicates that background PCB concentrations in Canadian agricultural soils approximate those in sludges. Concentrations in the soils ranged from approximately 0.015 to 0.24 mg kg⁻¹ dry wt. Calculations based on guidelines for the clean-up of contaminated sites (MOEE, 1994) indicate that observed hexachlorobenzene, *p,p'*-DDE and total PCB concentrations in Canadian municipal sludges represent no significant risk to agriculture and the environment (Table 4).

Toxaphene and NDMA were among the 16 organic contaminants considered during the round one review of U.S. EPA Part 503 Regulations (U.S.EPA, 1993). NDMA is a potent carcinogen formed by the reaction of nitrite with dimethylamine and by the action of nitrate reducing bacteria (Merck, 1989). Toxaphene is a complex but reproducible mixture of at least 175 C₁₀ polychlorinated derivatives with an overall approximate empirical formula of C₁₀H₁₀Cl₈ (Merck, 1989). It is a non-carcinogenic stomach insecticide used against a variety of crop pests. Neither NDMA nor toxaphene was detected in the Canadian municipal sludges.

3.4. PCDDs and PCDFs

Single analyses were conducted of the September, October, November and December 1993 sludge samples and the six compost samples. Elaborate quality assurance/quality control procedures ensured the accuracy of results. They included proof rinsing all glassware, a method blank with each batch of 10 samples and surrogate additions to the samples. The method blank results were 'no detection' except for minor amounts of octa- and heptachlorinated dioxins and furans,

and recoveries of the nine ¹³C₁₂-labelled surrogate compounds were almost always <100%. Sample results were adjusted for the surrogate recoveries.

The notorious 2,3,7,8-TCDD was observed at concentrations ranging from 0.0007 to 0.0027 μg kg⁻¹ dry wt. in the September 1993 samples of four sludges but was not detected in other samples of these sludges or in any other sludges. Other dioxin and furan congeners were observed in most of the sludge samples. In general, concentrations of the dioxin and furan homologues increased with increasing molecular weight. Mean total dioxin and furan concentrations in the materials ranged from 2.0 to 36 μg kg⁻¹ dry wt. (median 6.7 μg kg⁻¹ dry wt.) and dioxins exceeded furans by approximately five times (Table 6). The mean total toxic equivalents as 2,3,7,8-TCDD (mean TEQ) calculated using International Toxic Equivalent Factors, for the sludges ranged from 0.005 to 0.12 μg kg⁻¹ dry wt. (median 0.025 μg kg⁻¹ dry wt.). With two exceptions, the total toxic equivalents for each material exhibited good agreement among samples. One sample each of one sludge and the compost exhibited much larger concentrations than other samples of those materials.

Results of the present study compare favourably

Table 6

Mean dioxin polychlorinated dibenzo(p)dioxin (PCDD) and furan (PCDF) contaminant concentrations (μg/kg dry wt.) in Canadian municipal sludges and sludge compost Sept.–Dec. 1993

	BC	BC	BC (com- post)	AB	AB	AB	SK	MB	ON	ON	ON	ON
Total TEQ	0.01	0.1	0.005	0.12	0.03	0.08	0.01	0.02	0.01	0.01	0.1	0.01
Total PCDD	2.6	22	1.8	11	5.5	4.7	3.6	5.8	2.1	4.8	32	4
Total PCDF	0.4	2.4	0.2	4.2	1.2	2.6	0.5	0.9	0.5	0.5	4	0.6
Total PCDD + PCDF	3	25	2	15	6.7	7.3	4.1	6.7	2.6	5.3	36	4.6
Surrogate (% recovery)												
13C12-TCDD	62	62	81	60	62	63	61	59	66	61	52	56
13C12-TCDF	68	67	88	66	69	70	66	64	67	66	57	60
13C12-P5CDD	42	44	70	41	40	43	66	46	56	47	39	48
13C12-P5CDF	48	50	82	47	46	50	58	50	55	49	40	47
13C12-H6CDD	76	75	95	71	77	78	60	70	73	73	64	66
13C12-H6CDF	85	85	110	82	88	88	71	78	77	80	73	73
13C12-H7CDD	55	51	76	52	51	53	60	54	62	57	45	54
13C12-H7CDF	60	62	91	59	60	64	64	58	66	60	48	55
13C12-OCDD	37	45	56	40	36	40	57	41	46	38	35	38

TEQ, toxic equivalents as 2,3,7,8 TCDD using International Toxic Equivalency Factors; PCDD, polychlorinated dibenzodioxin; PCDF, polychlorinated dibenzofuran; AB, Alberta; MB, Manitoba; BC, British Columbia; SK, Saskatchewan; ON, Ontario.

with other reports. Geometric mean total concentrations of dioxins and furans in 37 Ontario sludges ranged from 2.5 to 7.2 $\mu\text{g kg}^{-1}$ dry wt. (MOE, 1988). Median total TEQ concentrations for 200 USA sludges included in a 1988 national survey were between 0.009 and 0.05 $\mu\text{g kg}^{-1}$ dry wt. depending on how the calculation was done (Rubin, 1994). The concentrations of dioxins and furans in 16 UK sludges increased with degree of chlorination and the hepta- and octa-dioxins predominated (Stuart et al., 1993). Average concentrations of tetra- to octa-dioxins and furans in the UK sludges were about 20 $\mu\text{g kg}^{-1}$ dry wt. Jacobs et al. (1987) reported generally small ($< 60 \mu\text{g kg}^{-1}$ dry wt.) concentrations of dioxins and no detectable furans in four USA sludges and no detectable 2,3,7,8-TCDD in 431 USA sludges. Other reports indicate a 31 $\mu\text{g kg}^{-1}$ dry wt. TEQ concentration in a Swedish sludge (Naf et al., 1989), and a mean total TEQ concentration of 22 $\mu\text{g kg}^{-1}$ dry wt. in three Netherlands sludges (H.B. Bols, Rijkswaterstaat, private communication).

There are few guidelines/regulations for dioxins and furans in soils and those available are conservative. For example, both the CCME (1991) interim assessment criterion for total TEQ concentration in soil and the interim remediation criterion for total TEQ concentration in agricultural soil are 0.01 $\mu\text{g kg}^{-1}$ dry wt. Similarly, the MOEE (1994) background TEQ concentration in Ontario agricultural soil is 0.007 $\mu\text{g kg}^{-1}$ dry wt. and the proposed agricultural clean-up TEQ concentration is 0.01 $\mu\text{g kg}^{-1}$ dry wt. Based on the latter criteria it was calculated that observed TEQ concentrations in some Canadian municipal sludges approximate maximum permissible levels for land application (Table 4).

The USEPA has conducted a thorough review of dioxins and furans in the environment and has concluded that even very small concentrations represent significant risks. Consequently, a recent voluntary agreement between the U.S.EPA and American Forest and Paper Association places tight controls on the quality of paper mill sludges for land application. It provides for unrestricted use of paper mill sludge with $< 0.01 \mu\text{g kg}^{-1}$ dry wt. TEQ concentration and regulated use of paper

mill sludge with > 0.01 but $< 0.05 \mu\text{g kg}^{-1}$ dry wt. TEQ concentration. Total TEQ concentrations in arable land receiving the sludge may not exceed 0.01 $\mu\text{g kg}^{-1}$ dry wt. and in pasture land may not exceed 0.001 $\mu\text{g kg}^{-1}$ dry wt. Total TEQ concentrations in several of the Canadian municipal sludges included in this study exceeded the 0.05 $\mu\text{g kg}^{-1}$ dry wt. maximum value for USA paper mill sludges.

Under this approach to assessing the organic contaminant inputs to land it is concluded that dioxins and furans in Canadian municipal sludges may represent a limiting factor to agriculture and the environment. However, information concerning the fate and effects of dioxins and furans in sludge treated soils is limited and must be expanded to assess the need for land application guidelines/regulations.

4. Non-analytical methods of prioritising organic contaminants in sewage sludges

EC and USEPA lists of priority chemicals provide an indication of which chemicals should be considered of particular concern in the environment. The above survey of a wide range of specific contaminants in Canadian sludges provides valuable data on which to make assessments of the environmental impact of disposal practices. Although it appears extensive, the database covers only a relatively small number of the organic chemicals that may enter sewage treatment works and persist in sewage sludges for disposal. For example, it does not include organic chemicals on the EC list of approximately 1800 High Production Volume Chemicals (HPVCs) which could occur in sewage sludges for disposal (EC, 1993), since these chemicals are used or produced in the EU in quantities in excess of 1000 tonnes per annum.

In order to assess the potential risks of these organic contaminants it will be necessary to: (a) Carry out further analytical surveys of sewage sludges for target compounds of potential concern, and/or (b) Use non-analytical methods to screen organic chemicals and assess their propensity for accumulation in sewage sludge for disposal.

The main obstacle to using method (a) and the identification of, and screening for organic con-

taminants in sewage sludges is the prohibitive expense of developing specific analytical methods in order to provide reliable survey data. This problem arises because of the highly complex nature of sewage sludges and the presence of other analytically interfering co-contaminants (e.g. PCBs need to be fractionated from PCCD/Fs during sludge extract clean-up to avoid analytical interference/misquantification of residue concentrations). The approach of using target compound analysis also pre-supposes a knowledge of which chemicals will be present in sewage sludge. It should be noted that some contaminants may not be amenable to analysis by the target compound techniques widely used. Consequently, a non-analytical approach to assess which contaminants may occur in sewage sludges and persist in treated soils could be a cost-effective means of prioritising further contaminants which should be determined analytically in sewage sludges in treated soils. One such approach is to use predictive data on physicochemical and loss processes in order to assess the persistence and fate of chemicals which are likely to reach sewers. Such an approach may also aid the identification of persistent residues in both sewage sludge and sewage effluent discharges.

The behaviour of organic contaminants during wastewater treatment and their potential environmental effects after disposal of sewage sludge depend on their physicochemical properties and their susceptibility to sorption, volatilisation, chemical degradation (hydrolysis) and biodegradation.

Physicochemical properties such as vapour pressure, aqueous solubility and octanol-water partition coefficient can be used to predict the propensity for loss during sewage treatment by volatilisation or partitioning into sewage sludge and for some chemicals such data are readily available. However, for very many chemicals such data may be incomplete, of dubious quality or not available. The susceptibility to biodegradation for many chemicals during aerobic or anaerobic treatment processes has not been studied and only few data are available. Consequently, a predictive approach was used to generate information on both physicochemical properties and susceptibility to biodegradation using structure activity relationships.

As the behaviour of a molecule is primarily dependent on its chemical structure it is possible in many instances to predict many properties and effects using structure-activity relationship models, which relate a particular property (e.g. oxidation rate) to one or more physicochemical descriptors. This simple predictive method has been used to categorise a selection of HPVC compounds in a largely qualitative manner in order to determine its utility for contaminant prioritisation. The compounds were selected at random from the HPVC list, except that any chemicals which have been previously reported to occur in sludge were excluded.

The following qualitative ranking system was used to score chemicals according to their propensity to persist in sewage sludge. The score allocated is highest for those chemicals with highest tendency to persist in sewage sludges for disposal.

4.1. Volatility

The partitioning of a chemical between air and water is described by the Henry's Law constant (HLC). The HLC values were estimated using a bond-contribution method of Hine and Mookerjee (1975) and this parameter was used as an indicator of the likelihood of loss via volatilisation during sewage treatment by allocating a score dependent on the band into which the estimated HLC fell as follows:

HLC < 10 ⁻⁷	Involatile	Score 3
HLC 10 ⁻⁷ –10 ⁻³	Moderate tendency to volatilise	Score 2
HLC > 10 ⁻³	Volatile	Score 1

4.2. Organic carbon-partition coefficient

The partitioning of a chemical between water and suspended sediment or sludge is described by the organic carbon partition coefficient, log K_{oc} , and this was used as an indicator of partitioning/association with solids during treatment. Log K_{oc} values were estimated using the method of Meylan et al. (1992). The estimated log K_{oc} was allocated a score of 1–3 dependent on the band of values into which it fell as follows:

Log K_{oc} < 2.5	Low tendency to partition	Score 1
Log K_{oc} 2.5–4	Moderate tendency to partition	Score 2
Log K_{oc} > 4	High tendency to partition	Score 3

4.3. Biodegradation

The biodegradation of a chemical can be estimated by consideration of its chemical structural features and a method developed by Howard et al. (1987) was used for this purpose. A score of 0 and 2 was allocated dependent on whether the chemical was predicted to undergo fast or slow biodegradation.

Biodegradation probability < 0.5	Slow biodegradation	Score 2
Biodegradation probability > 0.5	Fast biodegradation	Score 0

4.4. Hydrolysis

Susceptibility to hydrolysis was predicted using the method of Mill et al. (1987) which is suitable for only a limited range of chemical compound types, namely esters, epoxides, halomethanes and alkyl halides.

A score of 0 or 1 was allocated dependent on prediction of low or high susceptibility to hydrolysis.

Susceptible to hydrolysis	Score 0
Not susceptible to hydrolysis	Score 1

An overall score of 2–9 is possible. High overall scores provide an indication that a chemical may persist in sewage sludges during treatment processes. However, it should be noted that such a generic approach is only qualitative. The procedure was calibrated using two model chemicals, acetic acid and benz[a]anthracene, which would be expected to show widely different behaviour during sewage treatment. Acetic acid has a relatively low overall score of 4 which reflects its tendency to biodegrade, low organic carbon partition coefficient, high volatility with high water solubility. In contrast, benz[a]anthracene, which is resistant to hydrolysis and biodegradation, has an intermediate volatility with low water solubility and a high organic carbon partition coefficient shows the second highest overall rating of 8. Previous target compound analyses (Aichberger and Reifener, 1983) and the recent WTC Canadian sludge survey have shown that benz[a]anthracene is a ubiquitous contaminant in sewage sludges.

The predictions for a range of 34 HPVCs are shown in Table 7. The ranking procedure shows all of the 34 selected HPVC compounds to be more likely than acetic acid to persist in sewage sludge. Several compounds have rankings equivalent to benz[a]anthracene, for example 4-amino-3-sulphonic acid and edetic acid. One of the selected HPVCs, namely bis-(pentabromophenyl)ether (PBE), has the maximum ranking of 9, suggesting that it is likely to reach sewage sludge. This prediction is in agreement with existing knowledge of the composition of sewage sludge, since PBE shows many structural features in common with the PCBs and PCDD/DFs. The ranking of these selected HPVCs suggests that many compound classes which have not yet, to our knowledge, been determined in sewage sludge may indeed be present. One such class of compounds is the aryl sulphonic acids which are widely used in dyestuffs and have recently been reported to occur in sewage effluents and river waters (Lange et al., 1995). However, little is known about the ecotoxicity of the aryl sulphonic acids. The ranking approach outlined here appears to have some merit for assessing which industrial organic compounds may persist in sewage sludge and for which analytical methods should be developed. It would be worthwhile applying the procedure to all of the HPVC chemicals to determine which of these should be quantified in sewage sludge. Only then can a proper assessment of their significance be undertaken.

5. Development of the ranking scheme

The proposed approach considers volatilisation, sorption to solids, hydrolysis and biodegradation, but does not consider chemical oxidation. The latter is one of the more commonly applied methods for removal of organic specific chemicals in industrial process effluents. One way of incorporating a measure of 'oxidisability' using a predictive approach is to consider the molecular orbital energy of the organic chemicals. Chemical oxidation is a process in which electrons are lost from the oxidised molecule and consequently the energy of the highest occupied molecular orbital E_{HOMO} can be a useful measure of the availability of electrons for

Table 7
 Predicted physicochemical properties for selected HPVCs and ranking (scores shown in parentheses)

Chemical	Use	HLC (atm m ³ mol ⁻¹)	Log K _{oc}	Biodegradation probability	Hydrolysis	Rank score
Nitrilo-trimethylene tris-phosphonic acid	Limescale/soap scum cleaners	1.65 × 10 ⁻³⁴ (3)	2.5 (1)	0.39 (2)	1	7
N,N-Dicyclohexyl-benzothiazole-2-sulphenamide	Accelerator in rubber vulcanizing	2.63 × 10 ⁻⁹ (3)	5.04 (3)	0.58 (0)	1	7
Pentadecyl methacrylate	Used in copolymers in video/compact disk manufacture, concrete curing agent	7.65 × 10 ⁻³ (1)	4.73 (3)	0.89 (0)	0	4
Tetrachlorotoluene	Chemical intermediate used in manufacture of pentachlorobenzyl chloride	1.93 × 10 ⁻⁴ (2)	3.28 (2)	-0.06 (2)	1	7
2,2'-Dimethyl-4,4'-methylene-(cyclohexyl) amine	Chemical intermediate	8.0 × 10 ⁻⁹ (3)	3.26 (2)	0.94 (0)	1	6
Vinylpyrrolidone	Organic synthesis	5.53 × 10 ⁻⁸ (3)	1.61 (1)	0.91 (0)	1	5
4-Aminotoluene-3-sulphonic acid	Azo dye intermediate	9.81 × 10 ⁻¹³ (3)	2.72 (2)	0.26 (2)	1	8
Benzenesulphonyl chloride	Catalyst, chemical intermediate for sulphonamides	8.76 × 10 ⁻⁶ (2)	3.07 (2)	0.79 (0)	1	5
Anilazine	Fungicide	3.40 × 10 ⁻⁷ (2)	3.16 (2)	-0.16 (2)	1	7
4,4'-Methylenediphenyl diisocyanate	Preparation of polyurethanes, rubber bonding to rayon/nylon	8.95 × 10 ⁻⁷ (2)	5.58 (3)	0.68 (0)	0	5
2-Chloroanthraquinone	Insect/bird repellent	2.36 × 10 ⁻⁹ (3)	2.48 (1)	0.46 (2)	1	7
Bis(pentabromophenyl) ether	Flame retardant	1.19 × 10 ⁻⁸ (3)	5.61 (3)	-0.68 (2)	1	9
6-Aminopenicillanic acid	Intermediate in synthetic penicillin manufacture	2.81 × 10 ⁻¹⁴ (3)	1.07 (1)	0.89 (0)	1	5
2,3,5,6-Tetrachloropyridine	Intermediate in pesticide/herbicide production	8.46 × 10 ⁻³ (1)	2.37 (1)	-0.24 (2)	1	5
Nitrofen	Herbicide	2.55 × 10 ⁻⁷ (2)	3.89 (2)	0.62 (0)	1	5
Formaldehyde	Disinfectant, manufacture of phenolic resin, explosives, dyes, pesticides, etc.	9.29 × 10 ⁻⁵ (2)	-0.04 (1)	1.01 (0)	1	4
o-Acetyl salicylic acid	Pharmaceutical	1.30 × 10 ⁻⁹ (3)	0.81 (1)	1.01 (0)	0	4
Parathion	Pesticide	2.96 × 10 ⁻⁷ (2)	3.25 (2)	0.62 (0)	1	5
Edetic acid	Food antioxidant/chelating agent	1.17 × 10 ⁻²³ (3)	3.18 (2)	0.49 (2)	1	8
Phenazone	Pharmaceutical	6.65 × 10 ⁻¹⁰ (3)	2.34 (1)	0.79 (0)	1	5
2-Mercaptoethanol	Synthetic chemical	1.27 × 10 ⁻⁷ (2)	0.12 (1)	0.87 (0)	1	4
Sulphanilamide	Pharmaceutical	1.49 × 10 ⁻¹⁰ (3)	2.51 (1)	0.43 (2)	1	7
N,N-Dimethyl formamide	Solvent for organic synthesis	7.38 × 10 ⁻⁸ (3)	0.38 (1)	0.92 (0)	1	5
Methanethiol	Intermediate in manufacture jet fuel, pesticides, fungicides, plastics	2.61 × 10 ⁻³ (1)	1.15 (1)	0.73 (0)	1	3
t-Butylamine	Intermediate for pharmaceuticals, dyestuffs, rubbers, synthetic tanning agents, insecticides	1.77 × 10 ⁻⁵ (2)	1.56 (1)	0.68 (0)	1	4
Pivalic acid	Organic intermediate	1.28 × 10 ⁻⁶ (2)	0.44 (1)	0.59 (0)	1	4

Table 7 (Continued)

Chemical	Use	HLC (atm m ³ mol ⁻¹)	Log K _{oc}	Biodegradation probability	Hydrolysis	Rank score
Tris(2-ethylhexyl)phosphate	Flame retardant/defoaming agent/corrosion inhibitor	9.56 × 10 ⁻⁵ (2)	6.36 (3)	1.18 (0)	1	6
Methacrylic acid	Manufacture of methacrylate resins	4.53 × 10 ⁻⁷ (2)	0.28 (1)	0.78 (0)	1	4
Methyloxirane	Chemical intermediate	1.6 × 10 ⁻⁴ (2)	0.37 (1)	0.37 (2)	0	5
Acrylic acid	Plastics manufacture	2.89 × 10 ⁻⁷ (2)	0.08 (1)	0.79 (0)	1	4
1-Aminoanthraquinone	Manufacture of dyestuffs and pharmaceuticals	1.12 × 10 ⁻¹² (3)	1.71 (1)	0.42 (2)	1	7
9,10-Dioxoanthracene-1-sulphonic acid	Dye intermediate	1.48 × 10 ⁻¹⁵ (3)	3.13 (2)	0.40 (2)	1	8
2,4-Chlorobenzoyl benzoic acid	Chemical intermediate	2.90 × 10 ⁻¹¹ (3)	2.19 (1)	0.62 (0)	1	5
Acetic acid	Manufacture of cellulose acetate, acetate rayon, plastics, rubbers, printing, solvent/gums/inks	5.5 × 10 ⁻⁷ (2)	-0.21 (1)	0.79 (0)	1	4
Benz[a]anthracene	Combustion product	5.0 × 10 ⁻⁶ (2)	5.36 (3)	-0.02 (2)	1	8

reaction i.e. release in oxidation. For intermolecular reactions, each reagent has its own pair of Highest Occupied Molecular Orbitals (HOMO) and Lowest Unoccupied Molecular Orbitals (LUMO), and these frontier orbitals are where the most important reactions take place. Molecular orbital energy of the HOMO is likely to be important in determining both the likelihood and rate of

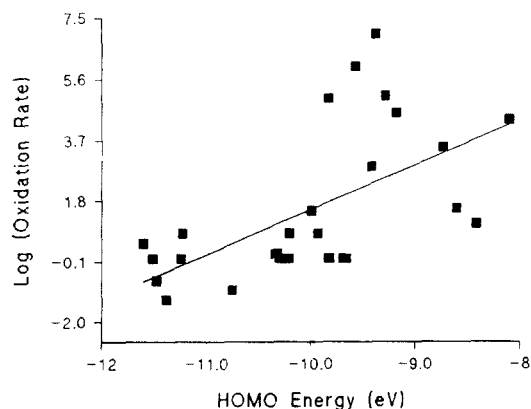


Fig. 2. Relationship between Log(oxidation rate) with RO₂ radicals and HOMO energy for a range of organic compounds.

an oxidation reaction. The VAMP software package (Oxford Molecular Ltd.) was used to calculate HOMO energies and the importance of these energies was assessed using a set of experimental oxidation rates for a range of 41 organic chemicals obtained from the literature (Mabey et al., 1982).

Initial results indicate the E_{HOMO} is an indicator of propensity of contaminants to oxidation, and there is a weak but positive correlation between E_{HOMO} and oxidation rate (Fig. 2). Such a positive relationship of this type is in agreement with the linear relationship between polarographic oxidation half-wave potentials for organic compounds and energies of highest occupied molecular orbitals recognised by Streitweiser (1961).

Further work is required before this tentative relationship between E_{HOMO} and oxidation rate can be used to derive a structure activity relationship for predicting oxidation rates of organic chemicals, but it does offer some promise.

6. Summary and conclusions

Municipal sludge and sludge compost are

valuable agricultural soil amendments. They contain significant amounts of nitrogen and phosphorus which are important plant nutrients, and organic matter which is a valuable soil conditioner. But they also contain substances such as pathogens, metals and organic contaminants which may reduce soil quality for agricultural production.

It is widely accepted that land utilization must be regulated to minimize the risks associated with buildup of deleterious constituents in agricultural soil. Considerable pathogen and metal research has been conducted and guidelines have been formulated to account for these constituents in sludges. However, data were inadequate to assess the need for organic contaminant guidelines.

The present study provides detailed industrial organic contaminant data for 11 Canadian municipal sludges and one sludge compost collected between September 1993 and February 1994. The sludges were obtained from wastewater treatment plants representing wide ranges of size and degree of industrialization in sewerage districts. However, most were from cities thought to represent worst-case Canadian situations for sludge contamination.

Results exhibited generally good agreement among replicate analyses and sampling times. There were no consistent changes in the concentrations of organic contaminants with time. With a few exceptions (e.g. toluene), organic contaminant concentrations in the sludges were low. Calculations based on proposed guidelines for the cleanup of contaminated sites in Ontario indicated that the only organics likely to limit land application of Canadian municipal sludges are toluene and dioxins and furans. However, these proposed guidelines are preliminary and further study of the fate and effects of toluene and dioxins and furans in sludge treated soils is required to confirm this finding. It is concluded that many Canadian sludges represent no significant organic contaminant risk to agriculture and the environment.

However, current approaches are limited by our understanding of what chemicals may be present in sludges and the availability of appropriate analytical methods. A ranking approach based on a range of physicochemical parameters predicted

solely from chemical structure provides a potential way of assessing which other compounds may be present. Application of the ranking procedure to a select group of HPVCs not previously reported to be present in sewage sludge indicated that many may occur. Novel classes of chemicals which should be analyzed for in sewage sludge have been predicted and the approach should be applied to all of the HPVCs. A tentative approach to predicting the oxidizability of organic chemicals during sewage treatment has shown promising results.

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