EMERGING SUBSTANCES OF CONCERN IN BIOSOLIDS: CONCENTRATIONS AND EFFECTS OF TREATMENT PROCESSES

Final Report – Literature Review

CCME Project # 447-2009

September 11, 2009

Submitted to:

CANADIAN COUNCIL OF MINISTERS OF THE ENVIRONMENT
123 Main Street, Suite 360
Winnipeg, MB
R3C 1A3

Submitted by:

Hydromantis, Inc.
Hamilton, ON

University of Waterloo
Waterloo, ON

Trent University
Peterborough, ON

*This report was prepared by **Hydromantis, Inc., University of Waterloo and Trent University**, under contract to the Canadian Council of Ministers of the Environment (CCME). It contains information which has been prepared for, but not approved by, CCME. CCME is not responsible for the accuracy of the information contained herein and does not warrant, or necessarily share or affirm, in any way, any opinions expressed therein.*

PN 1440

ACKNOWLEDGEMENTS

This report was prepared for the Biosolids Task Group (BTG) of the Canadian Council of Ministers of the Environment (CCME). The authors appreciate the valued comments received from Task Group members from their review of the draft manuscript.

This report was prepared for CCME's BTG by Hydromantis, Inc. of Hamilton, ON.
Hugh Monteith, P.Eng. (Project Manager)
Lars Sterne, P.Eng.
Shujun Dong, P.Eng.

The electronic literature search was completed by:
Wayne J. Parker, Ph.D., P.Eng., Dept. of Civil and Environmental Engineering, University of Waterloo, ON

Contributions to the literature review and helpful comments and were contributed by:
Wayne J. Parker, Ph.D., P.Eng., Dept. of Civil and Environmental Engineering, University of Waterloo, ON
Chris Metcalfe, Ph.D., Environmental and Resource Studies, Trent University, Peterborough, ON

ACRONYMS

ADBI	polycyclic musk fragrance, trade name Celestolide
AHMI	(or AHDI) polycyclic musk fragrance, trade name Phantolide
AHTN	polycyclic musk fragrance, trade name Tonalide
AMX	derivative nitro musk fragrance, amino Musk xylene
AP	alkylphenol
APE	alkylphenol ethoxylate
ATII	polycyclic musk fragrance, trade name Traesolide
BEHP	bis(2-ethylhexyl) phthalate
BLS	fluorescent whitening agent
BPA	Bisphenol A
BFR	brominated flame retardants
DAF	dissolved air flotation
DAS 1	fluorescent whitening agent
DDE	dichlorodiphenyldichloroethylene
DDT	dichlorodiphenyltrichloroethane
DPE	diphenyl ether
DPMI	polycyclic musk fragrance, trade name Cashmeran
DSBP	fluorescent whitening agent
EE2	17α-ethinylestradiol
E1	estrone
E2	17β-estradiol
E3	estriol
EO	ethoxylate
ESOC	emerging substance of concern
HBCD	hexabromocyclododecane
HCH	hexachlorocyclohexane
HHCB	polycyclic musk fragrance, trade name Galaxolide
IFAS	integrated fixed-film activated sludge
LAS	linear alkylbenzene sulphonates
MA	nitro musk fragrance, trade name Musk ambrette
MEE2	mestranol
MGD	million gallons per day
MK	nitro musk fragrance, trade name Musk ketone
MM	nitro musk fragrance, trade name Musk moskene
MT	nitro musk fragrance, trade name Musk tibetene
MX	nitro musk fragrance, trade name Musk xylene
na	not analysed
nd	not detected
ng/g	nanograms/gram
N-MePFOSAA	2-(N-methylperfluorooctanesulfonamido)acetate
N-EtPFOSAA	2-(N-ethylperfluorooctanesulfonamido)acetate
NP	nonylphenol
NPE	nonylphenol ethoxylate

OP	octylphenol
PBDE	polybrominated diphenyl ethers
PCP	pentachlorophenol or personal care product
PFDA	perfluorodecanoic acid
PFDS	perfluorodecane sulfonate
PFDoDA	perfluorododecanoic acid
PFHxS	perfluorohexanesulfonate
PFNA	perfluorononanoic acid
PFOA	perfluorooctanoic acid
PFOS	perfluorooctanesulfonate
PFOSA	perfluorooctane sulfonamide
PFOSSA	perfluorooctanesulfonamidoacetate
PFTA	perfluotetradecanoic acid
PFUnDA	perfluoroundecanoic acid
RAS	return activated sludge
SRT	solids retention time
TBBPA	tetrabromobisphenol A
TNSSS	Targeted National Sewage Sludge Survey
TS	total solids
WAS	waste activated sludge

EXECUTIVE SUMMARY

INTRODUCTION

The Biosolids Task Group (BTG) established by the Canadian Council of Ministers of the Environment (CCME) is mandated to study and make recommendations on biosolids management at the national level. Wastewater treatment facilities (WWTF) across Canada generate residual wastewater solids (sewage sludge) that require treatment for safeguarding human health and the environment prior to their use or disposal. Options for disposal, recovery or recycling of biosolids include energy, nutrient or material recovery, landfilling, incineration, managed land application, land reclamation, and commercial product recovery (compost and pellets).

In this report, the term sludge or raw sludge is most closely identified with the European Union definition “sewage sludge”, which is a “mixture of water and solids, separated from various types of water as a result of natural or artificial processes at urban wastewater treatment plants”. The European concept of “treated sludge” can more closely be identified with the material called “biosolids” in this report. In this report, the tern biosolids is applied to a treated material produced from raw sludge by processes such as anaerobic and aerobic digestion, composting, thermal or air drying, and alkaline stabilization with additives such as lime or cement kiln dust.

The end use of the biosolids is often governed by the constituent quality of the biosolids, such as nutrients, metals, pathogens and trace constituents. Concentrations of nutrients and metals in biosolids have been widely documented in the past, as have some trace organic constituents such as dioxins and furans, polyaromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs). Conversely, there is a notable lack of a database regarding the presence in Canadian biosolids of a certain class of wastewater constituents termed emerging substances of concern (ESOCs). These ESOCs include an array of pharmaceuticals, personal care products, brominated flame retardants and industrial contaminants (such as plasticizers and surfactants).

At the present time, the ability to detect ESOCs in biosolids at the ng/L or ng/g TS (dry wt) exceeds the understanding of the scientific and public communities of any potential risk associated with their detected presence. Thus the detection ESOCs in biosolids does not automatically imply that there is a risk for human health or the environment associated with proper biosolids management. The data presented in the review may contribute to further risk assessments, which consider other factors such as the persistence in the soil, the bioaccumulation in the food-chain and the toxicity of the compounds to humans and animals, to determine if these ESOCs should be regulated in the future.

While there is documentation in the literature of ESOCs in biosolids, especially in America and Europe), no focused study has been completed yet on a complete and recent inventory of ESOCs in Canadian biosolids. This literature review documents the occurrence of ESOCs and other selected compounds in sludges and biosolids with a focus on the effectiveness of sludge treatment processes to reduce concentrations. It will provide a basis for conducting a targeted sampling program which CCME can use to evaluate and manage the risks associated with

ESOCs in biosolids destined for managed land application, land reclamation, production of commercial soil amendments and energy production.

METHODOLOGY

Following a computerized literature search, a citation review template was created in MS-Excel to capture the relevant data extracted form each citation. Two major categories were identified for the concentration data provided, namely for "occurrence" purposes, and for "process removal efficiency" purposes. Data classified for occurrence assessment were those in raw sludge or in treated biosolids streams which had not been adjusted in any manner, such as by spiking to elevate concentrations. Removal efficiencies reported in the original literature were used when reported. Data identified for assessment of process removal efficiencies included reported removal efficiencies based on processes deliberately spiked prior to treatment, as well as non-spiked treatment processes. The scale of the tests was identified in the spreadsheet summaries to allow assessment of possible differences between laboratory or pilot-scale studies, and those conducted at full-scale.

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

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

At the start of the literature review, other potential categories were identified, such as nanoparticles and prions. Although publications involving risk assessments or laboratory spiking studies of prions were identified, no citations were found in the literature regarding the concentration of these substances in biosolids. Consequently and thus they were dropped from the literature review.

Categories of biosolids treatment processes in this review include:

- Anaerobic digestion
- Aerobic digestion
- Composting
- Lime addition
- Heat drying
- Other drying (e.g. air or solar drying)
- Other treatment
- Unknown

LITERATURE REVIEW SUMMARY

Industrial Chemicals

The compounds included in the industrial category in this review are diverse in their chemical properties and uses. The occurrence data are found more readily than are removal efficiency data. The plasticizer bis(2-ethylhexyl)phthalate has been characterized more frequently than have other phthalate esters or similar compounds. Limited data suggest it can be removed by some sludge treatment processes, including anaerobic digestion. The plastic-associated chemical BPA is detected in most raw and digested sludges. Limited data reviewed herein indicate it is relatively unchanged by most biosolids treatment processes, based on a comparison with concentrations in other sludges. Although perfluorooctanoic acid (PFOA) and perfluorooctanesulfonate (PFOS) are the dominant species of the most frequently reported perfluorinated organic compounds, other less well recognized compounds may well be present at similar concentrations as well. Biotransformation of PFOS and PFOA in both aerobic and anaerobic environments may play a role in the presence of the compounds such as 2-(N-methylperfluorooctanesulfonamido)acetate and 2-(N-ethylperfluorooctanesulfonamido)acetate.

Relative to the other ESOCs discussed in this review, which are often observed in the ng/g TS concentration range, linear alkylbenzene sulfonates (LAS) are present at concentrations that are order of magnitude higher. In limited data, sludges aerobically digested sludge from Germany and untreated sludges from Spain had lower concentrations of LAS than did anaerobically digested sludges from the same and other countries. The most commonly reported phenolic compound was pentachlorophenol (PCP). Data reviewed indicated that PCP concentrations in sludge can be reduced during anaerobic digestion. Pesticide residues in the µg/g TS range were reported in a variety of sludge types in France by Ruel *et al*. (2008), demonstrating the persistence of these compounds. A comprehensive comparison of pesticide concentrations in sludges from other countries is lacking. Solvent data were limited but were generally identified at the ng/g TS concentration level in sludge samples. In general, there was almost a complete lack of removal efficiency data by different biosolids treatment processes for the industrial chemicals.

Alkylphenols and their Ethoxylates

There appear to be differences in alkylphenol (AP) and their associated ethoxylate (APE) concentrations between biosolids samples collected from different countries, possibly due to different regulations for detergent product formulation. In raw sludges or aerobically digested sludges, concentrations of mono- and di-ethoxylated species of nonylphenol (NP) may occur at concentrations approximately equal to or even slightly greater than the parent nonylphenol. Of the biosolids treatment processes examined, anaerobic digestion consistently has the highest concentrations of 4-NP, as a result of anaerobic biotransformation processes converting mono- and di-ethoxylated species to the parent compound. Composting appears to result in lower concentrations of APs and APEs than does drying or lime treatment. Limited data suggest that lime treatment may result in lower reduction of APEs compared to composting or drying processes. A composting period of between 40 and 70 days is needed to reduce the starting level of 4-NP by over 90%.

Brominated Flame Retardants

The main group of compounds in the brominated flame retardant (BFR) category is the polybrominated diphenyl ethers (PBDEs). There are apparent differences in concentrations of different PBDE isomers in North America and other countries (e.g., Europe, Kuwait, and Australia). The isomer decabromodiphenyl ether (decabromo DPE, or BDE 209) was observed in all the samples at the highest concentration of any of the isomers, followed by the penta BDE99 and tetra BDE47 isomers. Available data indicate that the concentrations of the PBDE isomers are substantially lower in the solids streams prior to secondary treatment (e.g. primary sludge), and more concentrated in the solids streams following secondary treatment (i.e., return activated sludge, and dewatered secondary or mixed sludge). Anaerobic digestion may result in a reduction of decabromodiphenyl ether, but concentrations of lower brominated congeners may increase due to this biotransformation. There was insufficient information to determine if other biosolids treatment processes can result in reduction of PBDEs. Few occurrence data were identified for other BFRs such as tetrabromobisphenol A (TBBPA) and hexabromocyclododecane (HBCD). No reduction efficiency data for the BFRs in biosolids treatment processes were observed in the literature.

Pharmaceutical Compounds

This class of ESOCs in sludges and biosolids includes many different sub-classes with different therapeutic uses. There is a wide range of data available for the different pharmaceuticals that may be present in sludges and biosolids. Some compounds like the anti-epileptic carbamazepine have been widely characterized, while others have only one or two references in the literature. As a result of there being limited occurrence data for many pharmaceuticals, there are even fewer data available investigating the reduction of these drugs in biosolids treatment processes. Anaerobic digestion is the treatment process for which most data on pharmaceutical concentrations prior to and after treatment have been recorded. Reduction of the compounds appears to be highly specific to each class of pharmaceutical.

Hormones and Sterols

The hormones 17α-ethinylestradiol (EE2), estrone (E1) and 17β-estradiol (E2) are among the most frequently characterized compounds of this category in sludges and biosolids. Estrone (E1) is higher in concentration than these other common estrogenic compounds. The concentration of the natural hormone progesterone was the highest of the other estrogens observed. Concentrations of androgens in sludges were reported less frequently than estrogens. Concentrations of plant sterols in sludges and biosolids were among the highest observed in this literature review, with concentrations in the tens of thousands of ng/g TS. Composting and heat drying resulted in lower concentrations of the phytosterols in the biosolids; anaerobic digestion treatment had the highest concentrations of the four treatment methods. Concentrations of the animal sterols reported in sludges varied substantially from one reference or source to the next, but were in any case among the highest concentrations observed in this review. Composting resulted in the lowest observed concentrations of both cholesterol and 3β-coprostanol in different biosolids treatment processes. Removal efficiencies up to 85% were recorded for both 17α-ethinylestradiol (EE2) and a mixture of estrone (E1) and 17β-estradiol (E2) in both thermophilic and mesophilic anaerobic digestion. Removal efficiency data for hormones and sterols in other biosolids treatment processes are scarce.

Personal Care Products

The publications reviewed have centred almost exclusively on the presence of the anti-bacterials triclosan and triclocarban, synthetic musk fragrance compounds, and limited data on fluorescent whitening agents, quaternary ammonium compounds and siloxanes. There is negligible focus on other personal care products (PCP) compounds, such as parabens, sunscreen agents or insect repellents, identified in CCME's Review of the State of Knowledge of Municipal Effluent Science and Research: Review of Effluent Substances. Triclosan is found in sludge and biosolids samples at a concentration approximately an order of magnitude higher than is hexachlorophene.

Concentration data for triclocarban in sludges and biosolids are extremely sparse. There is no apparent reduction of triclosan by anaerobic digestion or other biosolids treatment processes such as composting, lime addition or heat treatment.

Polycyclic musks are present at higher concentrations than nitro musks. HHCB and AHTN are the predominant polycyclic musks, followed by ATII. The two main nitro musks identified in sludge samples were Musk ketone and Musk xylene. Full-scale anaerobic digestion does not appear to reduce concentrations of polycyclic musks in sludges, with concentrations in the digested sludges higher than in the raw sludge. Laboratory spiked anaerobic digestion studies indicate reductions in AHTN and HHCB concentrations are possible. Aerobic treatment appears to cause a reduction in concentrations of polycyclic musks. There are insufficient data reported in the literature to determine the effectiveness of the different biosolids treatment processes for reductions of the compounds.

Documentation of the occurrence of the disinfectant quaternary ammonium compounds in sludges and biosolids is limited, but reported concentrations of the compounds are significantly higher than for many of the other types of ESOCs. Occurrence and concentrations of siloxanes in sludges and biosolids are poorly documented.

There are insufficient data reported in the literature to determine the effectiveness of the different biosolids treatment processes for reductions of most of the personal care products.

Metals and Metalloids

The substances included in this review include a number of elements that include both metals and metalloids, such as arsenic and selenium, which will be referred to as “metals” for simplicity. The concentration database for metals and metalloids is limited because this review was focused on data from the year 2000 on, and much of the documented research on metals occurred previously. After iron and aluminum, the metals of highest concentration are zinc and copper, two metals commonly used in household plumbing. There are few data characterizing concentrations of elements such as antimony, beryllium, thallium, titanium, and vanadium in biosolids. Organotin compounds are present in sludges at low concentrations of less than 1 mg/kg TS (less than 1,000 ng/g TS). Limited data suggest the organotin compounds are not reduced in concentration by anaerobic digestion.

Other Substances

This section brings together compounds which were not readily included in the previous sections. The major groupings include the polyaromatic hydrocarbons (PAHs) and polychlorinated polyaromatic compounds (biphenyls (PCBs); dibenzofurans (PCDFs); and dibenzo-p-dioxins (PCDDs). The upper range of naphthalene, methylnaphthalene isomers and benzo(a)anthracene were at or above 100,000 ng/g TS in the literature review of Harrison *et al*. (2006), although a survey of Canadian sludges resulted in median concentrations typically lying in the range of 100 to 1,500 ng/g TS. The simplest PAHs, naphthalene and phenanthrene, consisting of two and three fused benzene rings, respectively, have the highest median concentrations of the PAHs in a survey of Canadian sludges. Data on the effect of biosolids treatment processes on reducing concentrations of PAHs are very limited. For the lower molecular weight PAHs anthracene and phenanthrene, composted and air dried biosolids have apparent lower concentrations than biosolids produced by heat drying or after anaerobic digestion. Anaerobic digested sludge had the highest concentrations of the PAHs examined in the biosolids from different treatment processes. For the literature surveyed, the range and means of the PCDDs and PCDFs reported from different countries appear to be very similar, with mean values in the range of 0.020 ng TEQ/g TS. More recent data from Québec and Ontario (unpublished) indicate a median of 0.008 ng TEQ/g TS for land applied biosolids.

ANALYSIS OF LITERATURE REVIEW

The interpretation of the published results on occurrence, concentrations and removal efficiencies of contaminants in sludges and biosolids is complex. Terminology of residual wastewater solids, as used by the different authors in the publications, is not consistent. References to “sludge” in the publications reviewed are construed to mean “untreated sewage sludge”. Often, however, the word sludge may be used when in fact the more appropriate term may be “biosolids”, as the residual solids have been subjected to a stabilization process. In much of the data reviewed, including other literature reviews, the sludges or biosolids are not specified by type (raw or treated, primary or secondary, etc) which makes the effort of determining if some processes are more beneficial than others in minimizing the concentrations of these substances. Some reviews, which summarize concentration data, group different types of sludges together without regard to the nature of the sludges.

There is a great disparity in published literature in the attention devoted to the occurrence of different ESOCs in sludges and biosolids. Some compounds have been examined comprehensively, and there is a substantial database on occurrence of these substances. Examples of the well-documented substances include the plasticizer bis(2-ethylhexyl)phthalate, the surfactant nonylphenol and some of its ethoxylates, the synthetic musk fragrances HHCB and AHTN, the flame retardants polybrominated diphenyl ethers, and the bacteriostat triclosan. In other cases however, there is a significant lack of information on concentrations of other substances in sludges and biosolids, including many antibiotics and other pharmaceuticals. CCME’s report on the State of Knowledge of Municipal Effluent Science and Research identified many classes of personal care products in treated effluents, including parabens (anti-microbial preservatives), sunscreen agents and insect repellents, for which no occurrence data in sludges or biosolids were found. Lack of adequate analytical protocols may hinder this effort.

In much of the data reviewed, including other literature reviews, the sludges or biosolids are not specified by type (raw or treated, primary or secondary, etc.) which makes the effort of determining if some processes are more beneficial than others in minimizing the concentrations of these substances. Some reviews, which summarize concentration data, group different types of sludges together without regard to the nature of the sludges. There appeared in the review to be evidence that sludges from some countries have lower concentrations than others, which may be reflective of manufacturing or use restrictions.

The concentrations of different ESOCs reviewed in this report can vary widely in sludges and biosolids, from the low part per billion (ng/g TS) (e.g. estrogens and androgens to the part per thousand level, for plant and animal sterols, and from literature in the 1990s, linear alkylbenzene surfactants. LAS concentrations may now be lower, but there is a scarcity of recent data for these compounds.

High concentrations (e.g., mg/g TS range) of substances identified in the sludges and biosolids are not necessarily a cause for concern. The plant and animal sterols for example are natural products that may serve as an anthropogenic indicator or marker. Conversely, very low (e.g., ng/g TS range) concentrations of substances such as hormones, polybrominated diphenyl ethers and perfluorinated organic compounds that may be found in biosolids destined for land application are likely to be of greater concern due to their potential for endocrine disruption or persistence, bioaccumulation or toxicity.

With respect to different biosolids treatment processes, in most publications only the final treated biosolids concentrations are typically documented. Without the accompanying raw sludge concentrations, an evaluation of the effectiveness of the processes becomes more tenuous. In the data provided by Kinney *et al*. (2006), there appears to be evidence of some reduction in ESOC concentrations resulting from certain biosolids treatment processes such as composting or drying, based only on differences in concentrations between the treated biosolids. Without raw sludge data, however, no firm conclusions can be drawn.

The treatment process most characterized for ability to reduce contaminant concentrations is the anaerobic digestion process. For example in the studies by Carballa *et al*. (2006, 2007a, 2007b), concentrations of a variety of contaminants are provided for both raw sludge and sludges digested under different temperature regimes and retention times. From this review it appears that certain ESOCs can be reduced by anaerobic digestion, while others are recalcitrant (e.g., Bisphenol A, musk fragrances, triclosan), or perhaps even increased in concentration (e.g., 4-nonylphenol) by anaerobic biotransformation processes.

It is evident from this review that published knowledge of the potential for reduction of specific ESOCs in wastewater sludges by composting, alkaline stabilization or drying processes is incomplete

There is a major lack of published data regarding ESOC occurrence, concentration and removal in septage. Only one study published after the year 2000 was identified here, making a comparison of concentrations in septage relative to other wastewater sludges or biosolids difficult. No studies on the effectiveness of treatment of septage for reduction of ESOC concentrations were identified.

Many ESOCs are hydrophilic, such as many drugs and does not tend to remain in biosolids but rather in the treated water. However, many of the ESOCs examined in this review are hydrophobic, they concentrate in the residual wastewater solids (sludges). The understanding of the fate of these compounds by different biosolids processes is largely unknown. Because land application of biosolids is an important management technique in Canada, it is desirable to minimize any potential adverse effects to the terrestrial environment due to amendment of soils with biosolids. Consequently, there is a need to understand whether certain biosolids treatment processes are better than others at reducing concentrations of ESOCs in wastewater sludges. Should it be determined from literature studies or actual testing that certain types of ESOCs remain unaffected by biosolids treatment processes, then other means of limiting the concentrations of these recalcitrant compounds in biosolids should be explored, such as by source control, pretreatment and sewer use limits, or more extreme measures such as product re-formulations or outright bans on manufacture or use.

RECOMMENDATIONS

Based on the literature review and above assessment, the following recommendations are offered:

1. There is a need to define criteria for what is an adequate database for characterization of contaminants in sludges and biosolids, then to apply the criteria to the compiled data. An example of the review criteria might consist of a minimum number of qualified references (e.g., n=6), and specified relative standard deviation about a mean concentration (e.g. RSD = 25%).
2. Where there are insufficient data, the availability of adequate analytical protocols for the ESOCs of interest needs to be determined by qualified analytical personnel. If adequate analytical procedures are not available, then method development should be set as a priority.
3. If acceptable analytical protocols are available, the sampling survey proposed as part of this study to investigate the ability of biosolids treatment processes to reduce concentrations of ESOCs in sewage sludge and biosolids should be .initiated. Assessment of biosolids treatment effectiveness requires both raw and treated biosolids samples, as well as any potential process sidestreams to aid in mass balance closures.
4. As part of the biosolids treatment survey, sites with septage treatment should be included so that a database of ESOCs in septage can be expanded.
5. In the proposed survey of biosolids treatment processes, within budgetary limits, different types of pharmaceuticals, synthetic musk fragrances and Bisphenol A should be included as primary target analytes. Secondarily, as budgetary limitations permit, classes of ESOCs such as human hormones, brominated flame retardants, perfluorinated organic compounds, quaternary ammonium compounds, and siloxanes should be analysed.
6. Should it be determined from literature studies or actual testing that certain types of ESOCs remain unaffected by biosolids treatment processes, then other means of limiting the concentrations of these recalcitrant compounds in biosolids should be explored, such as by source control, pretreatment and sewer use limits, or more extreme measures such as product re-formulations or outright bans on manufacture or use. Such actions should b consistent across Canada. With respect to non-persistent ESOCs in biosolids applied to land, a mitigating approach may be to prescribe an interim period between the time of land application and the beginning of seeding or grazing to allow soil microbes time to degrade the compounds.
7. Lastly, data produced by this and similar reviews, and by the forth-coming field investigation, need to be transferred out to appropriate agencies and researchers.

Table of Contents

List of Tables

1.0 INTRODUCTION

1.1 BACKGROUND

The Biosolids Task Group (BTG) established by the Canadian Council of Ministers of the Environment (CCME) is mandated to study and make recommendations on biosolids management at the national level. Wastewater treatment facilities (WWTF) across Canada generate residual wastewater solids (biosolids) that require treatment for safeguarding human health and the environment prior to their use or disposal. Options for disposal, recovery or recycling of biosolids include energy, nutrient or material recovery, landfilling, incineration, managed land application, land reclamation, and commercial product recovery (compost and pellets).

This report examines the occurrence of wastewater constituents termed emerging substances of concern (ESOCs) in residual solids from municipal wastewater treatment. The residual solids in various usages have been termed simply as "sludge" or alternatively as "biosolids". The Final Report of the recent US. EPA Targeted National Sewage Sludge Survey (U.S. EPA, 2009) began with this definition:

> "Sewage sludge is the solid, semisolid, or liquid organic material that results from the treatment of domestic wastewater by municipal wastewater treatment plants, also known as publicly owned treatment works (POTWs). The U.S. Environmental Protection Agency (EPA) uses the terms sewage sludge and biosolids interchangeably, but others often refer to biosolids as sewage sludge that has had additional processing for land application."

The ambiguity with respect whether the raw unprocessed material has been subjected to further processing or treatment can be observed in this definition. By contrast, the European Union (EU, 2000) differentiates between sludge, sewage sludge and treated sludge.

> **Sludge**: "mixture of water and solids separated from various types of water as a result of natural or artificial processes."
> **Sewage sludge**: "sludge from urban water treatment plants", whereby 'urban wastewater' is understood as: "domestic wastewater or the mixture of domestic wastewater with industrial wastewater and/or run-off rain water". The definition of "domestic wastewater" is: "wastewater from residential settlements and services, which originates predominantly from the human metabolism and from household activities".
> **Treated sludge**: Sludge which has undergone a treatment process so as to significantly reduce its biodegradability and its potential to cause nuisance as well as health and environmental hazards when it is used on land.

In this report, the term sludge or raw sludge is most closely identified with the European Union definition "sewage sludge", which is a "mixture of water and solids, separated from various types of water as a result of natural or artificial processes at urban wastewater treatment plants". The European concept of "treated sludge" can more closely be identified with the material called "biosolids" in this report. In this report, the tern biosolids is applied to a treated material produced from raw sludge by processes such as anaerobic and aerobic digestion, composting, thermal or air drying, and alkaline stabilization with additives such as lime or cement kiln dust.

The end use of the biosolids is often governed by the constituent quality of the biosolids, such as nutrients, metals, pathogens and trace constituents. Concentrations of nutrients and metals in biosolids have been widely documented in the past, as have some trace organic constituents such as dioxins and furans, polyaromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs). Conversely, there is a notable lack of a database regarding the presence in Canadian biosolids of a certain class of wastewater constituents termed emerging substances of concern (ESOCs). These ESOCs include an array of pharmaceuticals, personal care products, brominated flame retardants and industrial contaminants (such as plasticizers and surfactants).

At the present time, the ability to detect ESOCs in biosolids at the ng/L or ng/g TS (dry wt) exceeds the understanding of the scientific and public communities of any potential risk associated with their detected presence. Thus the detection ESOCs in biosolids does not automatically imply that there is a risk for human health or the environment associated with proper biosolids management. The data presented in the review may contribute to further risk assessments, which consider other factors such as the persistence in the soil, the bioaccumulation in the food-chain and the toxicity of the compounds to humans and animals, to determine if these ESOCs should be regulated in the future.

While there is documentation in the literature of ESOCs in biosolids, especially in America and Europe, no focused study has been completed yet on a complete and recent inventory of ESOCs in Canadian biosolids. Consequently, CCME has issued a Request for Proposals to document the occurrence of ESOCs in biosolids and to conduct a targeted sampling program which will provide a basis for CCME to understand the current state of knowledge and to determine whether Canadian approaches to biosolids management are sustainable.

1.2 PROJECT OBJECTIVES

The objectives of this project are to:

1. Prepare a comprehensive review of research on ESOCs in biosolids within Canada and elsewhere based on technical literature and wastewater sector contacts;
2. Complete a survey and analyze biosolids samples with respect to ESOCs;
3. Identify those ESOCs of potential concern in Canadian biosolids;
4. Review and recommend treatment technologies that mitigate EC concentrations in biosolids;
5. Suggest Best Management Practices (BMPs);
6. Identify knowledge gaps and research needs for ESOCs with respect to biosolids;
7. Produce a final report of the project to the Contract and Project Authorities by October 30, 2009.

This report responds to Objective 1.

2.0 METHODOLOGY OF REVIEW

2.1 LITERATURE SEARCH AND IDENTIFICATION

In December of 2008, a computerised literature search was executed by Dr. Wayne Parker at the University of Waterloo with the objective of identifying citations pertaining to biosolids and contaminants.

The computerised literature search was supplemented with telephone calls to experts on the topic of ESOCs in biosolids. Telephone discussions were held with:

- Dr. Mel Webber of Webber Environmental, Burlington, ON
- Shirley Anne Smythe of Environment Canada, Burlington, ON
- Dr. George O'Connor of the Dept. of Soil and Water Science, the University of Florida at Gainesville
- Dr. Sally Brown of the University of Washington.

2.2 LITERATURE COMPILATION

A citation review template was created in MS-Excel to capture the relevant data extracted from each citation. An initial data review session with Hydromantis and Dr. Parker assessed the nature and quality of the information extracted to mid-January. Two major categories were identified for the concentration data provided, namely for "occurrence" purposes, and for "process removal efficiency" purposes. Data classified for occurrence assessment were those in raw sludge or in treated biosolids streams which had not been adjusted in any manner, such as by spiking to elevate concentrations. Removal efficiencies reported in the original literature were used when reported. The Project Team decided not to calculate removal efficiencies from any of the original data after it appeared that values of the efficiencies calculated by the Team might differ form those in the original literature. Data identified for assessment of process removal efficiencies included reported removal efficiencies based on processes deliberately spiked prior to treatment, as well as non-spiked treatment processes. The scale of the tests was identified to allow assessment of possible differences between laboratory or pilot-scale studies, and those conducted at full-scale.

During the data review, it became clear that a number of issues needed to be addressed in interpreting the data. Analytical procedures needed to be checked to determine the basis of the matrix reported. For example, in some cases, only the liquid fraction of the sample was analyzed, while in other cases the analysis was performed on the whole sample including solids. In yet other cases, the total concentration was estimated using the analysed liquid concentration, to which was added a contaminant mass associated with the solids, estimated from a solids partition coefficient, to obtain the total concentration.

A second issue was consistency in the reported use of units of concentration. The units of measurement were variously reported on a volumetric liquid basis (e.g., ng/L), a solids mass basis (e.g., ng/g dry solids), or in other units such as ng/g of organic carbon.

The research team determined that because of the large number of potential contaminants to report, and the number of citations for reviewing, that data entry consistency was necessary. A principal concern was the manner in which non-detectable concentrations were entered in the master spreadsheet. If a compound was included in the analytical test group, but was reported in the original reference as non-detected, it was so classified in the spreadsheet. If a contaminant was not included in the analytical test group, the cell was left blank. The distinction is necessary to differentiate between compounds that were looked for but were not detected (affects the occurrence interpretation) and those that were not included for identification (no impact on occurrence assessment).

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

Presentation of the data in a publication required another decision regarding presentation. Mean or median values were also entered in the spreadsheet if reported in the original citations. When several concentrations within a category were documented within the same citation, a range could then be reported (e.g. n.d. – 20 ng/L).

2.3 CLASSIFICATION OF SUBSTANCES

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

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

At the start of the literature review, other potential categories were identified, such as nanoparticles and prions. No literature citations were found for these substances, and thus they were dropped from the literature review.

2.4 CLASSIFICATION OF BIOSOLIDS TREATMENT PROCESSES

Categories of biosolids treatment processes in this review include:

- Anaerobic digestion
- Aerobic digestion
- Composting
- Lime addition
- Heat drying
- Other drying (e.g. air or solar drying)
- Other treatment
- Unknown

3. CONTAMINANTS IN SLUDGES AND BIOSOLIDS

3.1 INDUSTRIAL COMPOUNDS

3.1.1 Introduction

The compounds included in this section are those which are produced or used as industrial chemical products or intermediates. This review is not intended to provide a complete historical record of concentrations of all industrial compounds in sludges and biosolids, as past surveys completed through the 1970s and through 1990s have documented these as "legacy" contaminants from the U.S. EPA's Priority Pollutant List. The intent of this review is to provide more recent data from approximately 2000 onward to the present.

The main categories of industrial compounds examined in this Section include:

- Plasticizers and Bisphenol A
- Perfluorinated organic acid and derivative compounds
- Pesticides
- Surfactants (excluding alkylphenol and ethoxylates, discussed separately)
- Chlorophenols
- Solvents, and
- Miscellaneous compounds not covered elsewhere.

3.1.2 Plasticizers and Metabolites

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

Concentrations of phthalate esters found recently in the literature are provided in Table 1. Data for an array of phthalate esters provided by Harrison *et al*. (2006) in their sludge literature review and by Tan *et al*. (2007) for return activated sludge samples, clearly shows that bis(2-ethylhexyl) phthalate (BEHP) is the predominant compound in this class, at concentrations several orders of magnitude higher than the other phthalate esters. Concentration data from several nations provided in Table 1 focus almost exclusively on BEHP, without analysis or reporting of the other phthalate compounds. The mean concentration of BEHP in Swedish sludges at 24,500 ng/g TS appeared to be lower than the concentrations reported in sludges from other countries.

In addition to phthalate esters, other similar types of compounds are used as plasticizers. Concentrations of the compounds bis(2-ethylhexyl) terephthalate and bis(2-ethylhexyl) adipate are shown in Table 2 for two sludge samples from a chemically enhanced primary treatment facility in Montreal (Barnabé *et al*., 2008).

Table 1. Concentrations of Phthalate Esters in Municipal Wastewater Solids

Sludge Source	Concentration (ng/g TS)[c]						Reference
	Dimethyl phthalate	Diethyl phthalate	Di-n-butyl phthalate	Butylbenzyl phthalate	Bis (2-ethylhexyl) phthalate	Di-n-octyl phthalate	
U.S.A. Biosolids (n=9)					3,460 – 31,700 (10,500)[b,h]		Kinney *et al*. (2006)
Not specified (literature review)	26	18	393	201	62,480	570	Harrison *et al*. (2006)
Return activated sludge (plant 1)	not analysed	39.9±24.3[a]	149±80.4	25.7±9.4	9,910 ± 2,770	not analysed	Tan *et al*. (2007)
Return activated sludge (plant 2)	not analysed	17.2±12.0	12.6±3.4	11.0±9.5	2,200 ± 1,480	not analysed	
Norway sewage sludges[d]					27,000 - 115,000 (83,000)[b,g]		Jaganyi (2007)
Sweden sewage sludges[d]					25,000 - 661,000 (170,000) [b,g]		
Denmark sewage sludges[d]					3,900 - 170,000 (24,500) [b,g]		
Canadian sludge (1995-1998)e					1,600 - 245,000 (160,000) n=6?		Webber and Nichols (1995)
Homogenized sludge[f]					80,000 ± 10,000[g]		Barnabé *et al*. (2008)
Dewatered sludge[f]					90,000 ± 12,000 [g]		

[a] mean ± standard deviation [b] range (median) [c] equivalent to parts per billion

[d] based on definition of sewage sludge used in Jaganyi (2007), this material is believed to be an untreated or "raw" sludge

[f] from chemically assisted primary treatment only [g] number of samples not specified in citation [h] ng/g OC

Table 2. Concentrations of Other Plasticizers and Metabolites in Primary-Assisted Clarifier Sludge

Sludge Source	Concentration (ng/g TS)					Reference
	Bis (2-ethylhexyl) terephthalate	Bis (2-ethylhexyl) adipate	2-ethyl-hexanol	2-ethyl-hexanal	2-ethyl-hexanoic acid	
Homogenized sludge	45,000 ± 2,300[a]	34,000 ± 1,000	12,500 ± 900	34,000 ± 1,400	20,700 ± 400	Barnabé *et al*. (2008)
Dewatered sludge	104,000 ± 5,00	340,000 ± 10,000	4,500 ± 300	85,000 ± 3,400	14,600 ± 300	

[a] mean ± standard deviation based on minimum of 3 replicate analyses

Comparing concentrations of these two compounds with those of BEHP in the same sludges in Table 1 indicate that the terephthalate and adipate esters are present in similar concentrations to the BEHP. The chemicals 2-ethylhexanol and 2-ethylhexanal are metabolites of the bis(2-ethylhexyl) organic acid esters (phthalates, adipates, terephthalates, etc.). The aldehyde (2-ethylhexanal) was observed at a higher mean concentration than was the alcohol (2-ethylhexanol) in the data of Barnabé *et al*. (2008), particularly in the dewatered sludge sample.

Concentrations of plasticizer and chemical intermediate compounds in treated biosolids samples are presented in Table 3. The highest concentration of BEHP was observed in the group of biosolids treatment data developed by Ruel *et al*. (2008), consisting of anaerobically digested, limed and dried biosolids. BEHP concentrations in the other reported literature were in the range of 15,000 to 53,000 ng/g TS.

Table 3. Concentrations of Plasticizers and Chemical Intermediates following Biosolids Treatment Processes

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

nd = not detected
[a] mean ± standard deviation based on minimum of 3 replicate analyses
[b] mean ± standard deviation from literature database; number not specified

Barnabé *et al*. (2008) reported on concentrations of three plasticizers in dried sludge from the Montreal QC, chemically-assisted primary treatment plant. Gibson *et al*. (2007) provided concentrations of BEHP at the inlet and outlets of composting and heat drying processes. Composting appeared to result in lower concentrations than heat drying, but the data are limited.

Removal in Biosolids Treatment Processes

Removal efficiency data in biosolids treatment processes were only found for BEHP (Table 4). Composting appeared to result in effective reduction of BEHP, with removal efficiencies of 64% and 70% reported by Gibson *et al*. (2007) and Williams (2007), respectively. The limited data suggested heat drying and anaerobic digestion were less effective at reducing the concentration of BEHP in feed sludge than was composting.

Table 4. Removal of the Plasticizer BEHP in Biosolids Treatment Processes

Treatment Process	Removal Efficiency (%)	
composting	64%	70%
heat dry	23%	
anaerobic digestion		32%
Reference	Gibson *et al*. (2007)	Williams (2007)

3.1.3 Bisphenol A

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

Bisphenol A has received considerable attention in wastewater sludges and biosolids. Lee and Peart (2002) included BPA as a target analyte in a survey of Canadian raw and digested sludges. The data are summarized in Table 5. The highest concentration of BPA in that survey (39,800 ng/g TS) was observed in raw sludge from the Toronto Highland Creek Wastewater Treatment Plant, whereas the minimum concentration was noted in a digested sludge sample from the North Toronto sewage treatment facility. Other high concentrations of BPA were observed on the digested sludges of highly urbanized centres such as Windsor (ON), Galt (ON), Hamilton (ON) and Edmonton (AB). Median concentrations of BPA in the raw and digested sludge samples were 280 and 555 ng/g TS, leading to the conclusion that BPA is not removed during sludge anaerobic digestion.

Concentrations of BPA in other sludge samples are summarized in Table 6. The range of concentrations in this table from minimum to maximum is very broad, as indicated by the range supplied by Harrison *et al*. (2006). The observed minimum value of 0.1 ng/g TS recorded by Harrison *et al*. (2006) is lower than the values of 3 – 4 ng/g TS reported by Tan *et al*. (2007) for return activated sludges. The high value of 32,100,000 ng/g TS from Harrison *et al*. (2006) is several orders of magnitude higher than maximum values found in the other literature cited in Table 5.

Table 5. Concentrations of Bisphenol A in Canadian Sludges (Lee and Peart, 2002)

Municipal Treatment Plant and Sludge Type	Bisphenol A (BPA) concentration (ng/g TS)
Edmonton (Goldbar) Raw	310
Regina Raw	280
Adelaide Raw	250
Burlington Raw	190
Ottawa Raw	450
Toronto (Ashbridges Bay) Raw	180
Toronto (Highland Creek) Raw	39,800
Toronto (Humber) Raw	1,710
Toronto (North) Raw	320
Montreal (MUC-PSI) Raw	1,060
Quebec City Raw	160
Quebec City Raw	130
Vancouver Digested	300
Vancouver Digested	440
Calgary (Bonnybrook) Digested	800
Calgary (Fish Creek) Digested	790
Edmonton (Goldbar) Digested	3,180
Regina Digested	490
Saskatoon Digested	260
Saskatoon Digested	1,170
Burlington Digested	1,860
Galt Digested	9,560
Guelph Digested	460
Hamilton Digested	4,440
Ingersoll Digested	470
Kitchener Digested	230
Ottawa Digested	640
Waterloo Digested	2,540
Windsor Digested	11,100
Toronto (Ashbridges Bay) Digested	620
Toronto (Humber) Digested	280
Toronto (North) Digested	100
Granby Digested	240
Moncton Digested	130
Truro Digested	300
Median raw	280
Median digested	555

Table 6. Concentrations of Bisphenol A in Other Sludges and Biosolids

Sludge Source	Sludge Type	Concentration (ng/g TS)	Reference
Toronto sewage sludge	raw sludge	70 – 11,000 (680)[a]	Webber and Sidwha (2005)
	digested sludge	120 – 13,000 (1090)	
(Literature review)	not specified	0.10 – 32,100,000	Harrison *et al*. (2006)
Greek sludge	dewatered secondary or anaerobic digested sludge	560 – 1,750 (530)	Stasinakis *et al*. (2008)
Return activated sludge	Plant A	3.8±4.3[b]	Tan *et al*. (2007)
	Plant B	3.1±1.2	
Various	Not specified	4 – 1,363	Williams (2007)
Plant G	Waste activated sludge	1,620[c]	Kinney *et al*. (2006)
Plant H	Dewatered	1,090[c]	

[a] range (median); n=16 (raw sludge); n=18 (digested sludge) [b] mean ± standard deviation
[c] ng/g organic carbon

<u>Biosolids Treatment Processes</u>

Only limited data were identified which characterised the concentrations of BPA resulting from biosolids treatment processes. BPA concentrations in several treatment processes documented by Kinney *et al*. (2006) are summarised in Table 7. Of the various treatment processes, the concentration of BPA was lowest in the heat dried biosolids and highest in the anaerobically digested sludge. Additional data are needed to determine if these trends can be extrapolated on a more universal basis.

Table 7. Concentrations of Bisphenol A following Biosolids Treatment Processes (Kinney et al., 2006)

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

3.1.4 Perfluorinated Organic Acid and Derivative Compounds

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

Concentrations of the perfluorinated compounds in various sludges and biosolids are provided in Table 8. There are many compounds in this class as is evident from the table. In many other sludges, the predominant compounds are the perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS). The maximum concentration of PFOA found in this review was 241 ng/g TS found in a sample of a sludge from New York state (Sinclair and Kannan, 2006) and the maximum for PFOS was 160 ng/g TS in a sample of Oregon sludge (Schultz *et al*., 2006). Concentrations of perfluorodecanoic acid (PFDA) and perfluoroundecanoic acid (PFUnDA) were found at higher mean concentrations of 52 and 60 ng/g TS, respectively in sludge from Plant A in NYS in the testing by Sinclair and Kannan (2006), although in most other studies these compounds had much lower concentrations. In the only study in this review with perfluorodecane sulfonate (PFDS) as a target compound, Schultz *et al*. (2006) observed concentrations of a similar magnitude as those for PFOS. Perfluorohexane sulfonate (PFHxS) and perfluorododecanoic acid (PFDoDA) were found in relatively low concentrations compared to the predominant compounds identified above.

Several other perfluorinated organic compounds were identified by Schultz *et al*. (2006) in the study of sludges from an Oregon treatment plant. Data for most of these compounds are provided in Table 9. The magnitude of these compounds, with the exception of the perfluotetradecanoic acid (PFTA), is at least as great as for the more commonly analyzed PFOA and PFOS compounds. The presence of the compounds 2-(N-methylperfluorooctanesulfonamido)acetate (N-MeFOSAA) and 2-(N-ethylperfluorooctanesulfonamido)acetate (N-EtFOSAA) are thought to occur as metabolites of parent sulfonamido alcohols during aerobic secondary treatment with adsorption on the settled mixed liquor (Schultz *et al*., 2006). These data indicate that more compounds can be detected in sludge samples when the target analyte list is expanded.

No removal efficiency data in biosolids treatment processes were found for these chemicals. The data presented by Schultz *et al*. (2006) indicate that biotransformation of these compounds and precursor compounds can occur in both aerobic and anaerobic environments, complicating efforts to quantify “removals” through the treatment processes.

Table 8. Concentrations of More Common Perfluorinated Organic Acids and Derivatives in Sludges and Biosolids

Compound	Concentration (ng/g TS)									Reference
	Perfluoro-octanoic acid (PFOA)	Perfluoro-octane sulfonate (PFOS)	Perfluoro-octane sulfonamide (PFOSA)	Perfluoro-hexane sulfonate (PFHxS)	Perfluoro-nonanoic acid (PFNA)	Perfluoro-decanoic acid (PFDA)	Perfluoro-decane sulfonate (PFDS)	Perfluoro undecanoic acid (PFUnDA)	Perfluoro-dodecanoic acid (PFDoDA)	
Sewage sludge - Denmark	0.7-19.7 (4)[a]	4.8-74.1 (18.4)	0.5-3.6 (0.8)	0.4-10.7 (3.6)	0.4-8.0 (1.5)	1.2-32.0 (7.2)		0.5-4.4 (1.2)		Bossi *et al*., (2008)
Bossi literature review	0.3-0.7 (0.5)	0.3-1.0 (0.6)		0.09-0.01 (0.01)	<0.6-0.2 (0.1)					
Plant A: dewatered cake	39	154	24	<2.5	<13	47		6.9	12	Loganathan *et al*., (2007)
Plant A: solar dried sludge	8.3-219	8.2-110	<2.5-21	<2.5	<2.5-4.4	2.5-34		<2.5-7.7	<2.5-28	
Plant B: dewatered cake	15	20	<2.5	<2.5	<2.5-11	19-41		<2.5	<2.5-10	
Plant B: Ash	7.0 - 35	<2.5 - 50	<2.5 - 7.0	<2.5	<2.5	7.0 - 35		<2.5	<2.5	
NYS Plant A	69 - 241 (144)	26 - 65 (37)		<10 - 18 (<10)		25 - 91 (52)		35 - 115 (60)		Sinclair and Kannan (2006)
NYS Plant B	18 - 89 (80)	<1-0 - 34 (25)		<10		<25 - 39 (27)		<25		
Primary Sludge	<6 - 12 (7.1)	18 - 3.8 (53)		nd - 12 (3.4)	nd - 10 (4.2)	1.6 - 3.9 (2.8)	14 - 2.9 (19.4)	2.0 - 4.2 (2.6)	1.3 - 1.6 (1.5)	Schultz *et al*., (2006)
Return Activ. Sludge	<6 - 8.2 (6.7)	31 - 55 (43)		nd	3.1 - 4.9 (3.8	7.2 - 0.8 (9.1)	94 - 140 (130)	7.7 - 0.5 (9.2)	6.1 - 7.8 (7.1)	
Thickened Sludge	<6	20 - 18 (42)		nd	nd	3.4 - 5.3 (3.9)	57 - 71 (62)	3.9 - 5.0 (4.4)	4.1 - 5.1 (4.3)	
Anaerobic Digested Sludge	<3	81 - 160 (100)		nd	9.2 - 0.3 (9.9)	5.4 - 6.4 (5.9)	90 - 93 (91)	5.9 - 8.4 (6.8)	3.6 - 4.2 (3.8)	

nd = not detected

[a] range (mean)

Table 9. Concentrations of Additional Perfluorinated Organic Acids and Derivatives in Sludges and Biosolids (Schultz et al., 2006)

Sludge Type	Concentration (ng/g TS)			
	PFOSAA	N-MePFOSAA	N-EtPFOSAA	PFTA
Primary Sludge	<3 - 3.4 (<3)[a]	5.2 - 8.9 (6.3)	15 - 5.8 (20)	nd
Return Activated Sludge	14 - 23 (19)	99-61 (140)	90 -140 (120)	<3
Thickened Sludge	6.2 - 7.6 (6.9)	35 - 52 (41)	43 - 52 (48)	0.9 - 1.3 (1.2)
Anaerobic Digested Sludge	9.4 - 12.4 (11)	130 - 140 (130)	91 - 100 (98)	<3

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

3.1.5 Surfactants

Linear alkylbenzene sulphonates are a class of surfactants widely used in commercial products, but especially in detergent formulations. In wastewater treatment, because of relatively high solid:liquid partition coefficients, these surfactants tend to sorb onto wastewater solids and thus concentrate in the residual solids. There are two main concerns related to these compounds in biosolids destined for land application. The first issue is the potential adverse effects on soil biota, with reported effective concentrations of 1,143 to 1437 µg/g DM in soil, causing an adverse effect to 50% of several microbial species (Jacobsen *et al*., 2004). The second concern is that the surfactants can increase the mobilization of other hydrophobic contaminants in the soil, resulting in higher concentrations of the contaminants in leachate and drainage water (Jacobsen *et al*., 2004).

Because of the significant body of data on alkylphenols and their ethoxylates, a separate section has been devoted to those compounds. Otherwise, data identified in the more recent literature examine the linear alkylbenzene sulphonates (LAS). Concentration data for this class of surfactants is presented in Table 10. Relative to the other ESOCs discussed in this review, LAS are present at very high concentrations. Note that concentration units are expressed as µg/g TS (equivalent to parts per million), rather than the more usual concentration units of ng/g TS (equivalent to parts per billion) for ESOCs. In the review by Jaganyi (2007), aerobically digested sludge from Germany and untreated sludges from Spain had lower concentrations of LAS than did anaerobically digested sludges from the same and other countries. Similarly, in the review by Angelidaki *et al*. (2004), the concentrations range of LAS in aerobically digested sludges was much lower than the range in anerobically digested sludges.

Other data presented by Cavalli (2004) indicated that LAS was much less likely to be biodegraded in an anaerobic sludge environment than in aerobic sludge. Use of the OECD biodegradability screening test indicated that LAS was not biodegradable in anaerobic tests after 28 days. Further inhibition concentrations of LAS in anaerobic sludge digestion were identified in Cavalli (2004) as 25 mg/L, corresponding to 17 µg/g TS on a dry weight basis. In summarising removal of LAS in wastewater treatment, the data suggest that aerobic digestion can result in lower concentrations of LAS in the treated sludge than anaerobic digestion.

Table 10. Concentrations of Linear Alkylbenzene Sulfonates in Sludges and Biosolids

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

3.1.6 Phenolic Compounds

Compounds included in this category include chlorinated phenols and para-cresol, a simple alkylphenol. Chlorinated phenols are used as disinfectants, biocides, preservatives, dyes, pesticides and industrial and medical organic chemicals (CCREM, 1987). Pentachlorophenol (PCP) is used as a wood preservative. Cresol solutions are used as household cleaners, disinfectants and deodorizers as well as chemical intermediates in insecticide production. Chlorophenols in general have been implicated in epidemiological studies to contribute to soft tissue sarcomas, Hodgkin’s disease and leukemia (Health Canada, 2009c). Pentachlorophenol (PCP) is classified by the International Association on Cancer Research (IARC) as a possible human carcinogen, with suggested links to non-Hodgkin lymphoma. Acute effects of PCP can include fever and respiratory distress (Carex Canada, 2009). Cresols are largely removed by secondary biological treatment, with little predicted to be sorbed to residual solids (UNEP, 2009).

This literature review has not focused on the longer-term historical data of phenolic compounds in sludges and biosolids because, as legacy contaminants, much has been published on their concentrations prior to 2000. A substantial body of occurrence data of phenolics in sludges was compiled by Monteith (1987). The focus of this review is directed more at ESOCs or compounds of emerging concern rather than on the legacy contaminants.

In a survey of Canadian municipal raw sludge and anaerobically digested biosolids (Table 11), PCP concentrations ranged from a high value of 131 ng/g TS in Edmonton raw sludge to a low value of 7.1 ng/g TS in a digested sludge sample from the Toronto Ashbridges Bay Wastewater Treatment Plant (Lee and Peart, 2002).

Table 11. Pentachlorophenol (PCP) Concentrations in Canadian Municipal Sludges (Lee and Peart, 2002)

Municipal Treatment Plant and Sludge Type	Pentachlorophenol (PCP) concentration (ng/g TS)
Edmonton (Goldbar) Raw	131
Regina Raw	16.4
Adelaide Raw	56.6
Burlington Raw	27.7
Ottawa Raw	28.9
Toronto (Ashbridges Bay) Raw	45.8
Toronto (Highland Creek) Raw	22.9
Toronto (Humber) Raw	44.5
Toronto (North) Raw	20.1
Montreal (MUC-PSI) Raw	28.9
Quebec City Raw	80
Quebec City Raw	27.9
Vancouver Digested	99.4
Vancouver Digested	239
Calgary (Bonnybrook) Digested	10.5
Calgary (Fish Creek) Digested	71.9
Edmonton (Goldbar) Digested	119
Regina Digested	15.6
Saskatoon Digested	19.7
Saskatoon Digested	35.6
Burlington Digested	12.5
Galt Digested	8.4
Guelph Digested	15.1
Hamilton Digested	10.6
Ingersoll Digested	18.3
Kitchener Digested	17.8
Ottawa Digested	15.1
Waterloo Digested	85.1
Windsor Digested	13.5
Toronto (Ashbridges Bay) Digested	7.1
Toronto (Humber) Digested	11.1
Toronto (North) Digested	88.8
Granby Digested	54.5
Moncton Digested	58.3
Truro Digested	99.4
median raw	28.9
median digested	18.1

Median concentrations in the raw and digested solids samples were 29 and 18 ng/g TS, indicating the potential for a reduction in the PCP concentrations by anaerobic digestion.

Concentrations of phenolic compounds in other sludges and biosolids are presented in Table 12. The mean concentration of PCP in a variety of sludges and biosolids reported by Ruel *et al.* (2008) is substantially higher than the range of values reported by Lee and Peart (2002). The mean concentration of trichlorophenols, used as a chemical intermediate in pesticide production, was much higher at 70,400 ng/g TS, although this value may be skewed upward by one or two high concentrations, based on the very high value of the standard deviation of the mean.

Table 12. Concentrations of Phenolic Compounds in Sludges and Biosolids

Compound	Sludge or Biosolids Source	Concentration (ng/g TS)	Reference
Para-cresol	African - Sewage sludges	350 - 5,370	Jaganyi (2007)
Trichlorophenols	anaerobic digestion, limed, drying	70,400 ± 297,000[a]	Ruel *et al*. (2008)
pentachlorophenol	anaerobic digestion, limed, drying	600 ± 1,800[a]	

[a] mean ± standard deviation from literature database; number not specified

3.1.7 Pesticides

Pesticides are applied to eliminate unwanted target species of insects or plants. Although their toxic nature is thus intended to act on the target species, other organisms may be similarly affected. Unintended biological effects have also occurred, such as the decline of herring gulls in the Great Lakes through the 1970s and 1980s. Gull eggshells became highly fragile as a result of DDT accumulated in the parent bird (Environment Canada, 2009a). Because of the high degree of chlorination, these compounds tend to be very persistent and bioaccumulative. Several of the pesticides included in the review below, including aldrin, dieldrin and hexachlorobenzene are included in Tier I of the Canada-Ontario Agreement respecting the Great Lakes Basin as target compounds for virtual elimination (Green Ontario 2009).

This literature review has not focused on the longer-term historical data of pesticides in sludges and biosolids because, as legacy contaminants, much has been published on their concentrations prior to 2000. A substantial body of occurrence data of pesticides in sludges was compiled by Monteith (1987). The focus of this review is directed more at ESOCs or compounds of emerging concern rather than on the legacy contaminants.

Pesticide concentration data from a number of review papers are summarized in Table 13. Note that these are predominantly chlorinated hydrocarbon insecticides. Concentrations of the pesticides appear to vary widely in the different source sludges. The review data presented by Ruel *et al*. (2008) are among the highest observed. The limited data from Canadian sources for hexachlorobenzene and total DDT and metabolites (XCG, 2007) indicate that pesticide concentrations in sludges are lower than reported elsewhere, while the concentration of aldrin was of a similar magnitude as in the other reported study.

Table 13. Concentrations of Pesticide Compounds in Sludges and Biosolids

Compound	Concentration (ng/g TS)					
	34 Canadian stabilized sludges (1987)	Canadian sludge (1995-1998)	anaerobic digestion, limed, drying	Swiss sludges	UK sludges	French sludges
Aldrin	300		4100 ± 7000[a]		10 - 200 (30)[b]	
Chlorpyrifos			500[c]			
Dieldrin			26,300 ± 30,000[a]	100 - 2,000	10 - 5,300 (500)	
Diuron						11.2 - 46.6
Total pp'-DDT & op'-DDT & pp'-DDE		17		100 - 500		
Endosulfan			300[c]			
Endrin			500 ± 500[a]		10 - 700 (100)	
Heptachlor			4,900 ± 3,300[a]			
Hexachloro-benzene	10	5.4	1,200 ± 1,500[a]			
Hexachloro-cyclohexane; Lindane; γ-HCH			12,300 ± 22,000[a]	100 - 900	10 - 70,000 (400)	
Reference	XCG (2007)		Ruel *et al*. (2008)	Fent (1996)	Rogers (1996)	Ghanem *et al*. (2007)

[a] mean ± standard deviation from literature database; number not specified [b] range (mean)
[c] no standard deviation calculated due to analytical difficulties

3.1.8 Solvents

As with the pesticide group, many solvents were included in the original U.S. EPA Priority Pollutant list of the 1980s and have received significant attention previously. Because the focus of this review is directed more at ESOCs or compounds of emerging concern in sludges and biosolids than on the legacy contaminants, the review is limited in scope.

Concentration data for some common industrial solvents in sludge and biosolids are presented in Table 14. Concentrations of solvents reported in Canadian sludges (XCG, 2007) are less than 500 ng/g TS. Concentrations reported in different treated biosolids by Ruel *et al*. (2008) were present at substantially higher concentrations than those reported by XCG (2007).

Table 14. Concentrations of Solvents in Sludges and Biosolids

Compound	Concentration (ng/g TS)		
	Canadian sludges (1995-1998)	34 Canadian stabilised sludges (1987)	anaerobic digestion, limed, drying
Benzene	0.04 - 483 (45)[a]		1,000
1-2-Dichloroethane	nd		
Dichloromethane	5 - 19 (8)		
Carbon tetrachloride	nd		
Trichloroethylene	0.3 - 380 (167)		
1,1,1- Trichloroethane	nd	200	
Tetrachloroethylene	nd - 231 (59)	300	8,100
Reference	XCG (2007)		Ruel *et al*., (2008)

nd = not detected
[a] range (mean)

3.1.9 Miscellaneous Compounds

Few compounds are included in this group. The substance 4-chloroaniline (PCA) is used as a chemical intermediate in the production of a number of products, including agricultural chemicals, azo dyes and pigments, and pharmaceutical and personal care products. In aerobic aquatic environments, PCA is determined to be inherently biodegradable, but exhibits no appreciable biodegradation under anaerobic conditions. It has a relatively low affinity for sorbing to soils, and so leaching of PCA from biosolids to groundwater may occur, especially in soils of low organic matter content and elevated pH. Bioaccumulation in aquatic organisms is considered unlikely (WHO, 2003). Health effects in exposed occupational workers include development of methemoglobinemia and anemia. Other effects include damage to kidneys and liver (WHO, 2003).

In the U.S. EPA’s TNSSS, 4-chloroaniline was found at a median concentration of 513 ng/g TS (U.S. EPA, 2009).

3.1.10 Section Summary

The compounds included in this review are diverse in their chemical properties and uses. The occurrence data are found more readily than are removal efficiency data. The main summary points follow.

1. The plasticizer BEHP has been characterized more frequently than have other phthalate esters or similar compounds. Limited data suggest it can be removed by some biosolids treatment processes, including anaerobic digestion.
2. The plastic-associated chemical BPA is detected in most raw and digested sludges. Limited data reviewed indicate it is relatively unchanged by most biosolids treatment processes, based on a comparison with concentrations in other sludges.
3. Although the perfluorinated organic compound perfluorooctanoic acid (PFOA) and perfluorooctanesulfonate (PFOS) are found in the highest concentrations of those reported

most frequently, other less well recognized compounds may well be present at high concentrations as well. Biotransformation in both aerobic and anaerobic environments may play a role in the presence of the compounds such as 2-(N-methylperfluorooctanesulfonamido)acetate and 2-(N-ethylperfluorooctanesulfonamido)acetate.

4. Relative to the other ESOCs discussed in this review, linear alkylbenzene sulfonates are present at very high concentrations. The data reviewed indicate that aerobic digestion can result in lower concentrations of LAS in the treated biosolids than can anaerobic digestion.
5. The most commonly reported phenolic compound was pentachlorophenol. Data reviewed indicated that PCP concentrations in sludge can be reduced during anaerobic digestion.
6. Very high pesticide residues were reported in a variety of sludge types by Ruel *et al*. (2008), demonstrating the persistence of these compounds. A comprehensive comparison of pesticide concentrations in sludges from other countries is lacking.
7. Solvent data were limited but were generally identified at low concentrations in sludge samples.
8. In general, there was almost a complete lack of removal efficiency data by different biosolids treatment processes for the industrial chemicals.

3.2 ALKYLPHENOL AND THEIR ETHOXYLATES

3.2.1 Introduction

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

Under the appropriate conditions, APEs are biologically transformed to the AP intermediate, which has been implicated in aquatic toxicity responses in fish, mammals, invertebrates and algae, although it was not found to be bioaccumulative (Environment Canada, 2009b). The APs have also been implicated as weakly estrogenic compounds, in particular capable of inducing feminization of male fish.

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

3.2.2 Occurrence Data

Raw and anaerobically digested municipal sludges from Canadian municipalities were surveyed for alkylphenols (AP) and their ethoxylates by Lee and Peart (2002). The results are provided in Table 15. Concentrations of the alkylphenols and their ethoxylates are observed at higher concentrations than many of the other ESOCs. Concentration units reported for these compounds are in the μg/g TS range, rather than in the ng/g TS range. In raw sludges, concentrations of 4-nonylphenol (NP) tended to dominate, but in a number of samples, the mono-ethoxylated NP and di-ethoxylated NP were of similar or greater magnitude (e.g., London Adelaide, Quebec City, Montreal). After anaerobic digestion, the concentration of 4-NP was substantially increased compared to levels in corresponding raw sludges. The median value of 4-NP in digested sludge samples was 413 μg/g TS, compared to a median concentration of 91 μg/g TS in the raw sludge samples. Concentrations of the di-ethoxylated NP and higher congeners were lower in digested sludges than in the raw sludges, suggesting transformation of the higher-ethoxylated species to the parent 4-NP and the mono-ethoxylated NP. Another AP compound, 4-tert-octyl phenol was reported in the study. The median concentration of 10.4 μg/g TS in the digested sludge was higher than the median value of 4.75 μg/g in the raw sludge.

Concentrations of APs and their ethoxylates in Toronto sludges reported by Webber and Sidwha (2005) are presented in Table 16. Concentrations of 4-NP were higher in digested sludges than in the raw sludge samples. Data from another Canadian survey (XCG Consultants, 2007) reported that 4-NP in mixed raw and digested sludges was the predominant form, approximately an order of magnitude higher than the mono-ethoxylated form of higher ethoxylated species (Table 16).

Table 15. Concentrations (µg/g TS) of Alkylphenol (AP) and Ethoxylates (EO) in Canadian Municipal Sludges and Biosolids (Lee and Peart, 2002)

Municipal Treatment Plant and Sludge Type	4-nonyl phenol (NP)	NP mono-EO (NP1EO)	NP di-EO (NP2EO)	NP tri-EO (NP3EO)	Higher NP-EOs NP(4-17)EO	4-tert-octyl phenol
Edmonton (Goldbar) Raw	237	107	22	5.3	28.4	6.9
Regina Raw	97.7	26.9	11.8	20.1	194	4
Adelaide Raw	20.1	60.9	60.2	23.3	10.6	2.9
Burlington Raw	90.3	98.7	38.5	9.6	44.7	8
Ottawa Raw	53.6	13.9	10.6	8.1	43.5	4.3
Toronto (Ashbridges Bay) Raw	126	129	73.7	11.9	3.5	8.6
Toronto (Highland Creek) Raw	112	94.9	40.5	13.8	15.7	13.6
Toronto (Humber) Raw	125	62.9	91.7	28.9	13	5.2
Toronto (North) Raw	92.7	69.4	34.6	<2	<2	5.4
Montreal (MUC-PSI) Raw	11.3	27.9	35.7	43.1	467	2.6
Quebec City Raw	12.4	24.6	19.8	15.1	141	2.9
Quebec City Raw	33.1	20.5	24.1	12.4	145	3.3
Vancouver Digested	457	124	26.6	17.7	47.6	10.7
Vancouver Digested	468	74.1	31.6	7.7	4.5	10.4
Calgary (Bonnybrook) Digested	413	154	33.1	<2	8.1	6.2
Calgary (Fish Creek) Digested	393	154	20.5	16.5	5.1	6
Edmonton (Goldbar) Digested	848	160	36.8	6	11.1	11.3
Regina Digested	568	228	1.8	1.9	11.5	10.8
Saskatoon Digested	26.5	39.3	39.3	6.8	2.1	1.9
Saskatoon Digested	139	97.2	24.8	4.5	<2	3.8
Burlington Digested	435	66	3.2	<2	17.7	13.1
Galt Digested	1210	126	24.1	12.4	23	20.5
Guelph Digested	1230	130	36.4	8.4	120	43.9
Hamilton Digested	403	114	26.4	6.9	5.5	15.6
Ingersoll Digested	232	32	6.7	3.9	67	8.5
Kitchener Digested	617	19.8	3	<2	<2	11.6
Ottawa Digested	298	83.7	11	2	<2	7.2
Waterloo Digested	518	146	38	4.1	5.9	8.2
Windsor Digested	203	307	127	34.7	139	13
Toronto (Ashbridges Bay) Digested	450	36.8	4.7	1.5	<2	12.8
Toronto (Humber) Digested	495	53.2	16.8	4.6	25.1	12.3
Toronto (North) Digested	233	28	2.2	<2	<2	6.5
Granby Digested	18.3	46.8	64.8	8.1	7.7	1.3
Moncton Digested	4.6	29.8	17.8	10.9	55.7	0.8
Truro Digested	18.3	30.4	68	15.8	9.9	2.1
Median raw	91.5	61.9	35.15	13.8	43.5	4.75
Median digested	413	83.7	24.8	6.9	11.3	10.4

Table 16. Supplementary Concentration Data for APEs in Canadian Sludges and Biosolids

Sludge or Biosolids Source	Sludge Type	Parameter	Concentrations (µg/g TS)				Reference
			4-nonyl phenol (NP)	NP1EOs and NP2EOs	Nonylphenol (1-17) ethoxylates[a] NP(4-17)EO[b]	4-tert-octyl phenol	
Toronto	raw sludge	range	15-311	not anal.	57-497[a]	0.8-14	Webber and Sidwha (2005)
		mean	55	not anal.	187[a]	3.7	
	digested biosolids	range	85-514	not anal.	18-342[a]	1.9-13	
		mean	244	not anal.	83[a]	6.7	
Guelph	stabilized (not specified)		450	not anal.	325[b]	not anal.	XCG (2007)
Canadian residuals (1995-1998)	Raw and digested sludges	Range	4.6 – 1,230	2.1 – 467	1.5 – 43[b]	not anal.	
		Mean	305	58	12[b]	not anal.	
		Median	232	18	9[b]	not anal.	

Surveys of nonylphenol in sludges from other countries have been summarized in other literature reviews. Concentrations of NP for many types of sludges fall in the range of 500 to 2,500 µg/g TS, with the highest maximum value of 7,214 reported from Sweden although minimum levels may be as low as approximately 25 µg/g TS (Table 17). One very low value of 0.0195 µg/g TS for Norwegian final sludge was reported by Soares *et al*. (2008). The data in the table appear to indicate there may be differences in concentrations of 4-NP in biosolids samples, with some countries such as Italy (Soares *et al*., 2008), Denmark (Jaganyi 2007) and France (Ghanem *et al*., 2007) having lower concentration ranges than other countries. Changes in formulation of household laundry detergents may be responsible; Ahel *et al*. (2000) reported that effluent concentrations of NPEs declined after Switzerland imposed a ban on use of NPEs in laundry detergents. Data provided by Tan *et al*. (2007) for return activated sludge indicated the concentration of 4-NP in this solids steam was low in comparison to other sludges.

Ruel *et al*. (2008) reported concentrations of total polyethoxylated nonylphenols in French biosolids as 44 µg/g TS, but noted analytical problems with the sludge matrix. These difficulties were reflected in the high standard deviation value of 970 µg/g TS (Table 18). In the same sampling survey, the mean value of total octylphenols was only 2.6 µg/g TS. Low concentrations of the mono- and di-ethoxylated forms of nonylphenol (maximum values of 41 and 25 µg/g TS, respectively) were found by Stasinakis *et al*. (2008). The literature survey of Harrison *et al*. (2006) however, indicated concentrations of alkylphenol ethoxylates were observed at up to 7,214 µg/g TS. Very low concentrations of 4-tert-octylphenol and 4-cumylphenol (less than 0.05 µg/g TS each) were documented by Tan *et al*. (2007) in return activated sludge samples.

Table 17. Concentrations of Nonylphenol in Sludges and Biosolids from Other Countries

Country	Sludge Treatment	4-nonylphenol (µg/g TS)	Reference
Switzerland	Anaerobic Digestion	450-2530	Soares *et al*. (2008)
	Aerobic Digestion	120-650	
	Final sludge	540-1000	
Germany	Aerobic Digestion	80-500	
	Unidentified	128.2	
USA	Anaerobic Digestion	754	
	Heat treatment	496	
	Lime treatment	470	
	Composting	64	
Italy	Raw Sludge before anaerobic digestion	242	
	Sludge after anaerobic digestion	308	
Norway	Final sludge	0.0195	
Norway	Biosolids	25-2298	Jaganyi (2007)
Sweden	Biosolids	23-7214	
Denmark	Biosolids	0.3-537	
Africa	Biosolids	0.15-2790	
Australia	Return Activated sludge Plant #1	0.429±0.238 [a]	Tan *et al*. (2007)
	Return Activated sludge Plant #2	0.0205±0.005	
France	Mixed sludge sources (anaerobically digested, composted, limed or dried) in different conventional secondary or tertiary plants	132 ± 730	Ruel *et al*. (2008)
U.S.A.	Aerobically digested biosolids	nd-180	Xia *et al*. (2005)
	Anaerobically digested biosolids	300-1300	
Greece	Dewatered anaerobically digested or dewatered secondary sludge	<0.04 -0.45	Stasinakis *et al*. (2008)
France	Unknown/not specified prior to pelletization	16.5 – 125	Ghanem *et al*. (2007)
	Unknown/not specified prior to composting	75.6-173	
	Unknown/not specified prior to lime treatment (Plant 2)	49.6-136	
	Unknown/not specified prior to lime treatment (Plant 3)	89.8-217	
U.S.A.	Digested sludge (aerobic and anaerobic)	13-898	Heidler and Halden (2008)
Mexico and UK	Anaerobically digested sludge before composting	114	Gibson *et al*. (2007)

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

Table 18. Concentrations of Nonylphenol Ethoxylates and Other Alkylphenol in Sludges and Biosolids

Biosolids Type	Concentration (μg/g TS)						Reference
	Nonylphenol monoethoxylate (NP1EO)	Nonylphenol diethoxylate (NP2EO)	Nonylphenol (1-17) ethoxylates NP(1-17)EO	Alkylphenol carboxylates	4-tert-octylphenol	4-Cumylphenol	
dewatered anaerobically digested or dewatered secondary sludge	1.01 - 41.3	<0.96 - 24.7					Stasinakis *et al*. (2008)
mixed sludge sources (anaerobically digested, composted, limed or dried) in different conventional secondary or tertiary treatment plants			44 ± 970 [a]		2.6 ± 4 (as Octyl phenols)		Ruel *et al*. (2008)
Unknown/not specified			nd–7214	10–14			Harrison *et al*. (2006)
Return activated sludge Plant #1					0.035±0.0029 [a]	0.0015±0.0013	Tan *et al*. (2007)
Return activated sludge Plant #2					0.0056±0.0024 [a]	BDL	

nd=not detected; BDL=below detection limit.

[a] mean ± standard deviation

3.2.3 Effect of Sludge Treatment Processes on Occurrence of Alkylphenols and Ethoxylates

A number of published studies have compared concentrations of the alkylphenols resulting from different types of sludge treatment processes (Table 19). The different studies reviewed here have been grouped by the biosolids treatment process.

In Kinney *et al*. (2006), concentrations are expressed μg/g OC, rather than the more common units of μg/g total solids (TS). Assuming that carbon in the solids is organic carbon, and that C is approximately 50 % of activated sludge biomass (Metcalf & Eddy, 1991), then concentrations expressed on an organic carbon basis would be approximately halved if expressed on a total solids basis. Concentrations of 4-nonylphenol are substantially higher following anaerobic digestion than after other forms of treatment (e.g., Kinney *et al*., 2006). Giger *et al*. (1984) were among the early researchers to propose that the hydrophobic NP1EO and NP2EO compounds associated with wastewater solids were degraded biologically to NP in anaerobic digestion. Studies by Hale and LaGuardia (2002) and LaGuardia *et al*. (2004) indicate that composting and drying result in lower levels of nonylphenol and ethoxylates, but that concentrations following lime treatment may not be much different than after anaerobic digestion. Composting appeared to result in the most consistent low concentrations of the tested alkylphenols and surfactants, presumably due to a prolonged retention time for aerobic biodegradation at elevated temperatures during the curing period.

3.2.4 Removal Efficiencies of Biosolids Treatment Processes

Fewer studies actually reported removal efficiencies of APs and their ethoxylates. The effect of different durations of the composting period on the reduction of 4-nonylphenol has been studied by Xia *et al*. (2005) and Das and Xia (2008). Their results, summarised in Table 20, indicate that a composting period of between 40 and 70 days is needed to reduce the starting level of 4-NP by over 90%. A higher proportion of wood shavings mixed with the biosolids resulted in a lower initial concentration of the 4-NP and a faster rate of reduction of the 4-NP.

In Table 21, Gibson *et al*. (2007) found that composting resulted in a higher removal efficiency of 4-NP than did heat drying, in general agreement with most other observed data in Table 19. Conversely, Ghanem *et al*. (2007) noted only an 18% reduction in 4-NP with composting, compared to removal efficiency of 72% for drying by pelletization. Removals by lime treatment were variable.

Table 19. Concentrations of Alkylphenols and their Ethoxylates after Biosolids Treatment

Biosolids Treatment	Concentration (μg/g TS unless otherwise specified)					Reference
	4-nonylphenol (NP)	Nonylphenol mono-ethoxylate (NP1EO)	Nonylphenol diethoxylate (NP2EO)	Total of nonylphenols (NPs), NP1EOs and NP2EOs	Octylphenols (OP)	
Anaerobically digested WAS	1,520	79.4	0.793		3.50 μg/g OC	Kinney *et al*. (2006)
anaerobically digested biosolids				758-981		Hale and LaGuardia (2002)
Anaerobically digested biosolids-A	683	28.4	<1.5		9.9	LaGuardia *et al*. (2004)
Anaerobically digested biosolids-B	720	25.7	<1.5		12.6	
Anaerobically digested biosolids-C	779	102	32.6		11	
Anaerobically digested biosolids-D	701	55.8	<1.5		11.7	
Anaerobically digested biosolids-E	887	64.9	22.7		6.7	
Fresh biosolids (anaerobic)	300-1300					Xia *et al*. (2005)
Anaerobically digested biosolids STP 1 (n=3)	1840 ± 61 [a]					Pryor *et al*. (2002)
Anaerobically digested biosolids STP 2 (n=6)	1790 ± 68					
Anaerobically digested biosolids STP 3 (n=3)	1480 ± 38					
Anaerobically digested biosolids STP 4 (n=6)	1240 ± 161					
Anaerobically digested biosolids STP 5 (n=3)	1130 ± 188					
anaerobically digested biosolids	900					Brown *et al*. (in press)
composted WAS	2.18-491 μg/g OC	3.96-17.2 μg/g OC	2.85-7.01 μg/g OC		0.90-4.21 μg/g OC	Kinney *et al*. (2006)
composted biosolids				6.1-176		Hale and LaGuardia (2002)
Composted biosolids-A	5.4	0.7	<1.5		<0.5	LaGuardia *et al*. (2004)

Table 19 (cont'd)

Biosolids Treatment	Concentration µg/g TS unless otherwise specified					Reference
	4-nonylphenol (NP)	Nonylphenol mono-ethoxylate (NP1EO)	Nonylphenol diethoxylate (NP2EO)	Total of nonylphenols (NPs), NP1EOs and NP2EOs	Octylphenols (OP)	
Composted biosolids-B	172	2.5	<1.5		1.5	LaGuardia *et al*. (2004)
Composted biosolids-C	14.2	<0.5	<1.5		<0.5	
Anaerobically digested sludge after composting	14					Gibson *et al*. (2007)
Composted biosolids	nd-120					Xia *et al*. (2005)
Unknown/not specified, after composting (n=3)	119.9 ± 14.4					Ghanem *et al*. (2007)
air dried WAS	229 µg/g OC	23.9 µg/g OC	44.6 µg/g OC		2.71 µg/g OC	Kinney *et al*. (2006)
Unknown/not specified, after drying to pellets (n=11)	17.3 ± 6.2					Ghanem *et al*. (2007)
Heat dried WAS	261 µg/g OC	44.6 µg/g OC	89.0 µg/g OC		0.414 µg/g OC	Kinney *et al*. (2006)
Heat dried biosolids				nd-544		Hale and LaGuardia (2002)
Heat dried biosolids-A	496	33.5	7.4		7.5	LaGuardia *et al*. (2004)
Anaerobically digested sludge after heat drying	212					Gibson *et al*. (2007)
Limed biosolids				529-932		Hale and LaGuardia (2002)
Limed biosolids-A	820	81.7	25.3		5.3	LaGuardia *et al*. (2004)
Limed biosolids-B	119	154	254		2	
Unknown/not specified after lime treatment (Plant 2) (n=12)	62.5 ± 14.1					Ghanem *et al*. (2007)
Unknown/not specified after lime treatment (Plant 3) (n=9)	130 ± 35.8					

nd=not detected

[a] mean ± standard deviation

Table 20. Removal Efficiencies of 4-NP by Biosolids Composting

Biosolids:Wood shaving ratio	% Reduction of 4-NP after Time of Composting in Days			
	8	20	40	70
43:57	76%	80%	90%	no data
65:35	22%	70%	78%	92%
84:16	7%	60%	70%	92%
Reference	Xia *et al*. (2005)	Das and Xia (2008)		

Table 21. Removal Efficiencies of APs and Ethoxylates by Biosolids Treatment Processes

Constituent	Sludge Type	Removal Efficiency %	Reference	Country
4-nonylphenol	Unknown/not specified, after drying to pellets	72	Ghanem *et al*. (2007)	France
	Unknown/not specified, after composting	18		
	Unknown/not specified after lime treatment (Plant 2)	31		
	Unknown/not specified after lime treatment (Plant 3)	19		
	Composted anaerobically digested sludge	88	Gibson *et al*. (2007)	Mexico and UK
	Heat dried anaerobically digested sludge	39		
AP Polyethoxylates	Aerobic/Anaerobic	40-100	Lindberg (2005)	Sweden

3.2.3 Section Summary

The important points from this section follow.

1. There appear to be differences in APE and AP concentrations between biosolids samples collected from different countries, possibly due to different regulations for detergent product formulation.
2. In raw sludges or aerobically digested sludges, concentrations of mono- and di-ethoxylated species of NP may occur at concentrations approximately equal to or even slightly greater than nonylphenol.
3. Of the biosolids treatment processes examined, anaerobic digestion consistently has the highest concentrations of 4-NP, as a result of anaerobic biotransformation processes converting mono- and di-ethoxylated species to the non-substituted AP.
4. Composting appears to result in lower concentrations of APs and APEs than does drying or lime treatment. Limited data suggest that lime treatment may result in lower reduction of APEs compared to composting or drying processes.
5. A composting period of between 40 and 70 days is needed to reduce the starting level of 4-NP by over 90%.

3.3 BROMINATED FLAME RETARDANTS

3.3.1 Introduction

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

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

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

3.3.2 Occurrence Data

Among the most detailed concentration data of PBDEs in Canadian wastewater solids is that of Rayne and Ikonomu (2005) for the Kelowna, BC wastewater treatment plant. Isomer concentrations were documented for primary sludge, anaerobically fermented primary sludge, return activated sludge dissolved air flotation float solids, and dewatered centrifuge cake. The data are produced in Table 22, converted to a dry solids basis for comparison with other literature concentration data. The isomer decabromo DPE (BDE 209) was observed in all the samples at the highest concentration of any of the isomers, followed by the penta BDE99 and tetra BDE47 isomers. The data indicate that the concentrations of the PBDE isomers are substantially lower in the solids streams prior to secondary treatment (primary sludge before and after anaerobic fermentation), and more concentrated in the solids streams following secondary treatment (i.e., return activated sludge, dissolve air flotation (DAF) float and centrifuge cake).

Table 22. PBDE Concentrations in Kelowna, BC Wastewater Solids Streams (from Rayne and Ikonomou, 2005)

BDPE Isomer	Concentration (ng/g TS)				
	Primary sludge	Fermented Primary sludge	Return Activated Sludge	DAF sludge	Biosolids
2,4-Dibromodiphenyl Ether (di BDE7)	0.0070	0.0059	0.0620	0.0898	0.0806
2,4' + 3,3'- Dibromodiphenyl Ether (di BDE8/11)	0.0070	0.0151	0.0728	0.0820	0.0764
3,4'- Dibromodiphenyl Ether (di BDE13)	0.0070	0.0189	0.0661	0.0980	0.0753
4,4'- Dibromodiphenyl Ether (di BDE15)	0.0651	0.0551	0.477	0.408	0.348
2,2',4- Tribromodiphenyl Ether (tri BDE-17)	0.379	0.343	5.70	8.57	4.88
2,3',4- Tribromodiphenyl Ether (tri BDE25	0.0279	0.0415	0.326	0.422	0.279
2,4,4'-Tribromodiphenyl Ether (tri BDE 28)	1.15	1.05	8.71	10.74	7.67
2,2',4,4'-Tetrabromodiphenyl Ether (tetra BDE47)	58.46	57.97	469.50	553.22	401.95
2,2',4,5'-Tetrabromodiphenyl Ether (tetra BDE49)	1.67	1.67	13.80	17.10	11.82
2,3',4,4'-Tetrabromodiphenyl Ether (tetra BDE66)	1.33	1.35	11.21	12.63	9.17
2,3',4',6-Tetrabromodiphenyl Ether (tetra BDE-71)	0.160	0.132	1.72	3.76	1.47
3,3',4,4'-Tetrabromodiphenyl Ether (tetra BDE77)	0.0070	0.0164	0.0459	0.0258	0.106
2,2',4,4',5-Pentabromodiphenyl Ether (penta BDE85)	3.19	2.44	25.47	30.53	22.16
2,2',4,4',5-Pentabromodiphenyl Ether (penta BDE99)	71.81	61.70	603.46	738.35	523.98
2,2',4,4',6-Pentabromodiphenyl Ether (penta BDE100)	10.65	10.67	87.50	111.50	79.64
2,3,3',4,4'-Pentabromodiphenyl Ether (penta BDE105)	0.0139	0.0065	0.129	0.0426	0.118
2,3',4,4',6-Pentabromodiphenyl Ether(penta BDE119)	0.0488	0.0474	0.503	0.608	0.437
3,3',4,4',5-Pentabromodiphenyl Ether (penta BDE126)	0.0581	0.0384	0.167	0.0426	0.192
2,2',3,4,4',5'-Hexabromodiphenyl Ether (hexa BDE 138)	0.990	0.842	8.04	8.63	6.73
2,2',3,4,4',6'-Hexabromodiphenyl Ether (hexa BDE140)	0.204	0.206	1.99	2.19	1.67
2,2’,4,4’,5,5’-Hexabromodiphenyl Ether (hexa BDE 153)	10.89	8.90	86.29	98.47	78.06
2,2’,4,4’,5,6’-Hexabromodiphenyl Ether (hexa BDE 154)	5.61	4.99	51.18	57.36	43.89
2,2’,4,4’,6,6’-Hexabromodiphenyl Ether (hexa BDE155)	0.265	0.228	2.08	2.54	1.82
2,2',3,4,4',5,6-Heptabromodiphenyl Ether (hepta BDE181)	0.0163	0.0242	0.0796	0.0949	0.1214
2,2’,3,4,4’,5’,6-Heptabromodiphenyl Ether (hepta BDE 183)	2.41	1.35	9.43	10.72	8.16
2,3,3‘,4,4‘,5,6-heptabromodiphenyl ether (BDE-190)	0.100	0.080	0.442	0.512	0.480
2,2',3,3',4,4',5,5',6-Nonabromodiphenyl Ether (nona BDE206)	2.04	2.31	11.91	14.93	11.06
2,2',3,3',4,4',5,6,6'-Nonabromodiphenyl Ether (nona BDE207)	2.17	2.99	14.64	18.94	14.44
2,2',3,3',4,5,5',6,6'-Nonabromodiphenyl Ether (nona BDE208)	0.251	0.407	2.03	2.30	1.93
2,2',3,3',4,4',5,5',6,6'-Decabromodephenyl Ether (deca BDE209)	122.44	146.15	553.46	691.20	558.66
TOTAL PBDEs	300.10	310.65	1989.45	2421.57	1809.15

Data for PBDEs in wastewater solids from the Windsor Little River treatment plant are provided by Song *et al*. (2006). The concentrations of eight major isomers monitored in the study are summarized in Table 23.

Table 23. Concentrations of Major PBDE Isomers in Windsor Little River WW Solids (Song et al., 2006)

PBDE Isomer	Concentration, ng/g TS mean ± std. dev.[a]	
	Primary sludge	Waste activated sludge
2,4,4'-Tribromodiphenyl Ether (tri BDE 28)	8.0 ± 3.1	14 ± 6
2,2',4,4'-Tetrabromodiphenyl Ether (tetra BDE47)	586 ± 207	963 ± 415
2,2',4,4',5-Pentabromodiphenyl Ether (penta BDE99)	757 ± 272	1247 ± 516
2,2',4,4',6-Pentabromodiphenyl Ether (penta BDE100)	122 ± 42	167 ± 129
2,2',3,4,4',5'-Hexabromodiphenyl Ether (hexa BDE 138)	9.1 ± 4.3	17 ± 6
2,2’,4,4’,5,5’-Hexabromodiphenyl Ether (hexa BDE 153)	84 ± 27	109 ± 82
2,2’,4,4’,5,6’-Hexabromodiphenyl Ether (hexa BDE 154)	49 ± 19	71 ± 54
2,2’,3,4,4’,5’,6-Heptabromodiphenyl Ether (hepta BDE 183)	12 ± 6	22 ± 10

[a] mean ± standard deviation of 3 samples

Decabromo (BDE209) was not monitored in this study. The two isomers detected at the highest concentrations in both sludge types were the penta BDE99 and the tetra BDE47. As was observed with the data from Rayne and Ikonomou (2005), the WAS sample exhibited higher concentrations of the monitored isomers than did the primary sludge.

One of the more comprehensive studies on PBDEs in municipal biosolids was completed in Australia (Clarke *et al*., 2008), comparing concentrations in eight urban and eight rural biosolids samples. Table 24 presents the concentration data for the different PBDE isomers included in the analytical method for the urban wastewater treatment plants sampled. Decabromo DPE (BDE209) was present at the highest concentration (mean 881 ng/g TS). It is of interest that three of the four plants identified as having anaerobic digestion as part of the treatment have concentration of decabromo DPE, and indeed many of the isomers, higher than the mean value. Because of the limited sample size, however, it is not clear whether this represents an actual phenomenon that occurs with anaerobic digestion, or whether it is an artifact of the limited sample size. The apparent higher concentration of the decabromo DPE in the anaerobically digested sludge samples is contrary to expected dehalogenation reaction which occurs under anaerobic conditions. For example, Shin *et al*. (2006) observed a decline of decabromo DPE (BDE209) under batch anaerobic test at both 35 and 55 ^{o}C, with concomitant increases in lower brominated congeners. Because the concentrations of many of the lower brominated isomers in anaerobically digested sludges are higher than the mean value of urban biosolids samples, it is likely the observation is due to the randomness of the samples rather than due to higher levels attributed to the anaerobic digestion process.

Results for the eight rural samples in the Australian survey are provided in Table 25. Only one of the rural plants utilized anaerobic digestion as a biosolids treatment process, while most relied instead on dewatering and drying of the biosolids. Decabromo DPE was present in all the

Table 24. PBDE Concentrations in Sludges and Biosolids from Australian Urban Municipalities (Clarke et al., 2008)

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

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

Table 25. PBDE Concentrations in Sludges and Biosolids from Australian Rural Municipalities (Clarke et al., 2008)

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

rural biosolids samples at the highest concentration of any isomer, as was the case with the urban biosolids samples. The sample derived for solar drying had the highest concentrations of almost all isomers in the rural biosolids samples. There are insufficient data to determine whether it is the sludge itself or the treatment method that results in the high concentrations relative to the other rural samples.

Based on statistical analysis, Clarke *et al*. (2008) concluded that the sum of the PBDE isomers were not statistically different between the urban and rural biosolids. The authors further concluded that the lower brominated isomers, representative of the Penta-DPE commercial formula were consistent between urban and rural biosolids, and thus were likely of domestic sources. Greater variability between the concentrations of decabromo DPE in urban and rural biosolids was observed however, suggesting to the authors that industrial sources were likely the main contributors to the presence of decabromo DPE in biosolids.

The recently published US EPA's Targeted National Sewage Sludge Survey documented concentrations of many target analytes including PBDEs. Biosolids from a total of 74 municipal treatment plants in 35 states were included in this comprehensive national survey. The data were statistically analyzed to determine median, mean and standard deviations for the target contaminants. The results for the PBDEs are presented in Table 26. The sludges represent a wide range of process types, geographic locations and treatment plant capacities, although all facilities tested had a treatment capacity greater than 3780 m^3/d (1 MGD) with a minimum of secondary treatment (US EPA 2009).

Table 26. PBDE Concentrations in Sludges and Biosolids Based on U.S. EPA's Targeted National Sewage Sludge Survey (US EPA 2009)

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

Number of POTW samples = 78

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

Occurrence data retrieved from the literature for other countries are summarized in Table 27.

Table 27. Occurrence data for PBDEs in Biosolids Samples from Other Countries

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

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

The data indicate that the isomer concentrations are much higher in biosolids samples from the U.S. than from samples from European facilities or from the sited in Kuwait. The mean concentration data from the US EPA's sludge survey in Table 26 are similar to the U.S. concentration values in Table 27. Canadian concentration data presented in Tables 22 and 23 are more similar to the U.S. values, while the Australian data found in Tables 24 and 25 lie between the North American and European/Kuwaiti data.

3.3.3 Effect of Treatment Processes

LaGuardia *et al*. (2004) compared PBDE concentrations in four biosolids treatment processes, including composting, lime treatment, heat drying, and anaerobic digestion. The concentration data from these treatments are provided in Table 28.

Table 28. Comparison of PBDE Concentrations in Four Biosolids Treatment Processes (LaGuardia et al., 2004).

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

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

A study be Gerecke *et al*. (2006) at a full-scale Swiss treatment plant was of interest because it compared samples of PBDEs before and after anaerobic digestion, and also investigated two other type of brominated flame retardant. Data are provided in Table 29.

All three classes of flame retardants were reduced by full-scale anaerobic digestion. The decabromo isomer was present at much higher concentrations than the other two flame retardants. The tetrabromobisphenol A (TBBPA) class was reduced by the largest extent while the decabromo DPE was reduced by the least extent. In laboratory studies, Gerecke *et al*. (2006) determined compound half-lives of less than a day for the hexabromocyclododecane (HBCD) and TBBPA, compared to 700 days for the decabromo DPE. Shin *et al*. (2006) also found in laboratory studies with batch reactors that concentrations of decabromo DPE were reduced by anaerobic treatment, with a faster reduction occurring at thermophilic than at mesophilic temperatures. Such observations may well explain why anaerobic treatment resulted in lower concentration in biosolids than did composting, heat treatment or liming in the study by LaGuardia *et al*. (2004).

Table 29. Concentrations of Brominated Flame Retardants in Sludge Before and After Anaerobic Digestion (Gerecke et al., 2006)

Flame retardant	Concentration nmol/L		Concentration ng/g	
	raw	digested	raw	digested
2,2',3,3',4,4',5,5',6,6'-Decabromodephenyl Ether (BDE209)	76	49	2,490	1,605
Hexabromocyclododecane (HBCD) (6 stereoisomers)	2.1	1.2	66.32	37.89
Tetrabromobisphenol A + Tetrabromobisphenol (dimethyl) (TBBPA)	1.9	0.3	34.20	5.40

No reduction efficiency data for the PBDEs in biosolids treatment processes were observed in the literature.

3.3.4 Section Summary

The main points of interest for this section follow.

1. There are apparent differences in concentrations of PBDE isomers in North America and other countries (e.g., Europe, Kuwait, and Australia).
2. The isomer decabromo DPE (BDE 209) was observed in all the samples at the highest concentration of any of the isomers, followed by the penta BDE99 and tetra BDE47.
3. Available data indicate that the concentrations of the PBDE isomers are substantially lower in the solids streams prior to secondary treatment (e.g. primary sludge), and more concentrated in the solids streams following secondary treatment (i.e., return activated sludge, and dewater secondary or mixed sludge).

4. Anaerobic digestion may result in a reduction of decabromo DPE, but concentrations of lower brominated congeners may increase.
5. There is insufficient information to determine if other biosolids treatment processes can result in reduction of PBDEs.
6. Few occurrence data were identified for other BFRs such as HBCD and TBBPA.
7. No reduction efficiency data for the PBDEs or other brominated flame retardants in biosolids treatment processes were observed in the literature.

3.4 PHARMACEUTICAL COMPOUNDS

3.4.1 Introduction

This class of ESOCs in sludges and biosolids includes many different sub-classes with different therapeutic uses. This report will follow to a great extent the classification used by Gielen (2007) for investigating interactions of pharmaceuticals in New Zealand sludge with soils. The classes of pharmaceuticals investigated and reported herein are provided in Table 30. By far, the most compounds identified belonged to the categories of antibiotics.

3.4.2 Antibiotics

Antibiotic pharmaceuticals consist of many classes of compounds applied to inhibit or kill pathogenic bacteria. The main classes of antibiotics observed in this literature review are found in Table 31.

Tetracycline Antibiotics

Data on the occurrence of tetracycline compounds in sludge and biosolids are sparse. The recent U.S. EPA Targeted National Sewage Sludge Survey (TNSSS) (EPA, 2009) provides one of the most complete pictures of the compounds there, as indicated in Table 32. Tetracycline and its metabolite 4-epitetracycline, doxycycline and minocycline were found in the highest concentrations. Other than the EPA data, few other studies have reported concentrations.

Earlier studies by Lindberg *et al*. (2005) and the review by Harrison *et al*. (2006) indicate a high Limit of Quantitation (LOQ) for doxycycline (approx. 1200 – 1500 ng/g TS). The more recent EPA (2009) study cites a median concentration of 424 ng/g TS, suggesting a significant improvement in analytical procedures in the interim.

Table 30. Categories and Pharmaceuticals Identified in this Review

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

Table 31. Classes of Antibiotics and Compounds Noted in Literature Review of Biosolids

Tetracyclines	Sulfonamides	Fluoroquinolones	Macrolides	Beta-lactams
Tetracycline	Sulfadimethoxine	Norfloxacin	Clarithromycin	Cloxacillin
4-Epitetracycline[a]	Sulfamerazine	Enrofloxacin	Erythromycin	Oxacillin
4-Epianhydrotetracycline[a]	Sulfamethazine/ Sulfametazine	Lomefloxacin	Azithromycin	Penicillin G
Anhydrotetracycline[a]		Sarafloxacin	Ormetoprim	Penicillin V
Chlortetracycline	Sulfadiazine	Flumequine	Virginiamycin	Dicloxacillin
4-Epichlortetracycline[b]	Sulfisoxazole	Ciprofloxacin	Tylosin	
4-Epianhydrochlortetracycline[b]	Sulfachloropyridazine	Ofloxacin	Roxithromycin	
Anhydrochlortetracycline[b]	Sulfanilamide	Clinafloxacin		
Isochlortetracycline[b]	Sulfadimidine			Bacteriostats
Oxytetracycline	Sulfonamide	Quinolones		Trimethoprim
4-Epioxytetracycline[c]	Sulfamethizole	Oxolinic acid	Lincosamides	Chloramphenicol
Demeclocycline			Clindamycin,	Hexachlorophene
Doxycycline		Cephalosprins	Lincomycin	Triclosan
Minocycline		Cefotaxime		Triclocarban

[a] metabolite of Tetracycline [b] metabolite of Chlortetracycline [c] metabolite of Oxytetracycline

Table 32. Concentrations of Tetracycline Antibiotics in Sludges and Biosolids

Tetracycline Compound	Not specified (sludge survey)	Not specified (literature survey)	Unknown sludge (An urban WWTP)	Unknown sludge (A rural WWTP)	Anaerobic & aerobic digested
Tetracycline	1278 (630) [a]		<LOQ - 15.8	19.8	
4-ETC	1135 (620)				
4-Epianhydro-tetracycline	251 (140)				
Anhydrotetracycline	263 (153)				
Chlortetracycline	55.1 (39.7)		<LOQ - 14.7		
4-Epichlortetracycline	119 (100)				
4-Epianhydrochlortetracycline	421 (397)				
Anhydrochlortetracycline	126 (105)				
Isochlortetracycline	83.4 (39.6)				
Oxytetracycline	57.9 (43.2)				
4-Epioxytetracycline	45.3 (41.5)				
Demeclocycline	106 (99.2)				
Doxycycline	877 (424)	<1200–1500			<LOQ - 1500
Minocycline	660 (432)				
Reference	U.S. EPA (2009)	Harrison *et al*. (2006)	Spongberg and Witter (2008)		Lindberg *et al*. (2005)

[a] mean (median) LOQ = limit of quantitation

Wu *et al*. (2008) observed the reduction of concentrations of tetracycline and doxycycline over time in aerobically digested biosolids held under different storage conditions (Table 33). Concentrations of tetracycline declined so readily that the tests were terminated after 8 days. Conditions of aerobic or anaerobic storage had no effect on the reduction in tetracycline, nor did the presence or absence of daylight. The data indicated that doxycycline required a substantially longer time for reduction in concentration than did tetracycline, with aerobic conditions providing a more favourable environment for reduction of doxycycline than anaerobic conditions. Presence or absence of daylight made no appreciable difference in the reduction of doxycycline.

Table 33. Effect of Storage Treatment on Tetracyclines in Aerobically Digested Biosolids (Wu et al., 2008)

Storage Treatment	Storage Time (days)	Concentration (ng/g TS)	
		Tetracycline	Doxycycline
Dark, Anaerobic	0	1500	1500
	7	900	1400
	35	no data [a]	1000
	77	no data	1100
Dark, Aerobic	0	1600	1500
	7	800	1500
	35	no data [a]	750
	77	no data	600
Daylight, Aerobic	0	1600	1500
	7	700	1600
	35	no data [a]	800
	77	no data	700

[a] study terminated after 8 days

<u>Sulfonamide Antibiotics</u>

Occurrence data for the sulphonamide class of drugs is scattered through the technical literature, with most attention devoted to one or two compounds (sulfamethoxazole). The most complete data set is derived for the U.S. EPA's TNSSS, in which sulfanilamide was detected at the highest concentration, approximately one to two orders of magnitude higher than the remaining drugs in this class (Table 34). In the literature survey by Jones-Lepp and Stevens (2007), maximum concentrations of sulfametazine and sulfapyridineb were 160 and 197 ng/g TS, respectively. Many of the sulphonamide class tested by Spongberg and Witter (2008) were beneath the limit of quantitation.

Several researchers included analysis of sulfamethoxazole in anaerobically digested sludge samples, but reported it at non-detectable levels (Göbel *et al*., 2005; Heidler and Halden 2008).

Treatment

Sulfamethoxazole was found to be highly amenable to anaerobic digestion in several laboratory-scale studies by Carballa and colleagues. This sulfa drug was so readily degradable in anaerobic digestion (99% removal) that no difference in removal efficiency due to operating temperature or

Table 34. Concentrations of Sulfonamide Antibiotics in Sludges and Biosolids

Sulfonamide Compound	Concentration (ng/g TS)						
	Survey of biosolids	Unknown sludge (An urban WWTP)	WAS (5 WWTPs)	Biosolids class A + sludge	Anaerobic digested biosolids	Primary Sludge	Anaerobic Sludge
Sulfadiazine	13.6 (9.8) [a]						
Sulfachloropyridazine	12.0 (9,8)						
Sulfadimethoxine	3.57 (2.01)	< LOQ - 8.15					
Sulfametazine	7.38 (4.0)	<LOQ - 26.7		nd-160			
Sulfamethizole	4.72 (3.97)	<LOQ					
Sulfamethoxazole	21.59 (4.32)					10±10[b]	5 ±5
Sulfanilamide	536 (99.2)						
Sulfathiazole	10.7 (9.8)	<LOQ					
Sulfapyridine				nd-197	1,000±100		
Sulfisoxazole		<LOQ - 21.9					
Sulfadimidine			nd - 31				
Sulfonamide			nd - 20				
Reference	U.S. EPA (2009) (n = 77)	Spongberg and Witter (2008)	Xu *et al*. (2007)	Jones-Lepp and Stevens (2007)	Göbel *et al*. (2005) (n=3)	Radjenovic *et al*. (2009) (n=9)	

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

solids retention time could be discerned (Carballa *et al*. 2006, 2007a) (Table 35). Similarly, no difference in the effect of pre-ozonating the sludge prior to digestion could be observed because the compound was effectively eliminated completely (Carballa *et al*., 2007b).

Table 35. Effect of Anaerobic Digestion Conditions on Removal Efficiency of Sulfamethoxazole

Anaerobic Temperature	Condition	Removal Efficiency %)	Reference
mesophilic	SRT = 20 d	(99 ± 1)[a]	Carballa *et al*. (2006)
mesophilic	SRT = 30 d	99	Carballa *et al*. (2007a)
mesophilic	SRT = 20 d	99	
mesophilic	SRT = 10 d	99	
thermophilic	SRT = 20d	98	
thermophilic	SRT = 10 d	99	
thermophilic	SRT = 6 d	99	
mesophilic	Non-ozonated	(100 ± 1)	Carballa *et al*. (2007b)
mesophilic	Ozonated	(100 ± 1)	
thermophilic	Non-ozonated	(100 ± 1)	
thermophilic	Ozonated	(100 ± 1)	

[a] mean ± standard deviation
SRT = solids retention time

Fluoroquinoline and Quinoline Antibiotics

The most complete identification of fluoroquinolone compounds in biosolids comes from the U.S. EPA TNSSS (Table 36). The drugs found at the highest levels were ciprofloxacin and ofloxacin, at median concentrations of 5,370 and 3,110 ng/g TS, respectively. These two pharmaceuticals have been identified most frequently in the literature, along with norfloxacin. The remaining fluoroquinolines and quinolines in the EPA survey had median concentrations under 50 ng/g TS.

Table 36. Concentrations of Fluoroquinolone and Quinolone Antibiotics in Sludges and Biosolids

Fluoroquinoline /Quinoline	Concentration (ng/g TS)					
	Sludge Survey	Anaerobic digestion (n=5 WWTPs)	Aerobic digestion (n=1 WWTP)	Literature Review	Unknown sludge (An urban WWTP)	Unknown sludge (A rural WWTP)
Ciprofloxacin	10,500 (5,370) [a]	1,400 – 4,800	500 - 900	50 – 4,800	<LOQ - 46.3	8.3
Clinafloxacin	75.6 (40.4)					
Enrofloxacin	27.9 (19.8)					
Flumequine	10.6 (9.87)					
Lomefloxacin	22.9 (19.8)					
Norfloxacin	275 (109)	900 – 4,200	100 - 400	10 – 4,200		
Ofloxacin	8,570 (3,110)	<LOQ–2,000	100 - 700	<10 – 2,000		
Oxolinic acid	4.7 (4.0)					
Sarafloxacin	294 (91.9)					
Reference	U.S. EPA (2009) (n = 78)	Lindberg *et al.* (2005)		Harrison *et al.* (2006)	Spongberg and Witter (2008)	

[a] mean (median)

Concentrations of the three main identified fluoroquinolones in raw and digested sludge samples are summarized in Table 37. Many of the publications reviewed indicate that the concentrations of ciprofloxacin and norfloxacin in the sludge samples are similar in magnitude on the order of 2,000 to 6,000 ng/g TS. Lindberg *et al.* (2005) tracked the concentrations of ciprofloxacin and norfloxacin through the residual solids stream of a wastewater treatment plant in Umea, Sweden. The concentrations increased as the sludge was combined, digested and dewatered, but then dropped significantly after drying by pelletization. It appears that these fluoroquinolone compounds are relatively unaffected by the anaerobic digestion process, as concentrations are in many cases higher in the digested sludge than in the raw sludge.

Treatment

When aerobically digested sludge containing ciprofloxacin was stored under different light and redox environments, there was no reduction in concentration from the initial starting level after 77 days of storage (Wu *et al.*, 2008).

Table 37. Concentrations of Three Fluoroquinolones in Sludge and Biosolids

Sludge Type	Source	Concentration (ng/g TS)			Reference
		Ciprofloxacin	Norfloxacin	Ofloxacin	
Primary sludge		2,900	2,900		Lindberg *et al*. (2006)
Secondary sludge		2,500	1,500		
Raw sludge to digester		6,600	5,100		
Digested biosolids		6,000	7,000		
Dewatered digested biosolids		10,600	9,800		
Dried biosolids (Pellets)		2,600	3,400		
Raw sludge, Zurich	WWTP1	1,400 ± 120 [a]	1,540 ± 30		Golet *et al*. (2002) (n=2)
	WWTP2	2,030 ± 200	1,960 ± 150		
Digested biosolids, Zurich	WWTP3	2,420 ± 60	2,370 ± 70		
	WWTP4	2,720 ± 200	2,130 ± 190		
Waste activated sludge, Zurich		2,500 ± 100	2,600 ± 100		Golet *et al*. (2003) (n=2)
Raw sludge, Zurich		2,200± 400	2,100 ± 200		
Anaerobic digested biosolids, Zurich		3,100 ± 400	2,900 ± 400		
Raw sludge		1,000-2,000	1,500–2,000		Jones-Lepp and Stevens (2007)
Digested biosolids		2,300–2,400	2,100–2,400		
Digested sludge		3,100-5970	2,900-6970		Heidler and Halden (2008)
Waste activated sludge, China	Plant A		301± 89	227 ± 46	Xu *et al*. (2007) (n=4)
	Plant B		40 ± 165	886 ± 222	
	Plant C		187 ± 38	165 ± 71	
	Plant D		372 ± 97	835 ± 186	
Primary Sludge, Spain				190±280	Radjenović *et al*., 2009) (n=9)
Anaerobic Digested biosolids, Spain				80 ±30	

[a] mean ± standard deviation

Macrolide Antibiotics

In Table 38, the data generated by the U.S. EPA's TNSSS suggest that azithromycin, tylosin and virginiamycin are present at the highest concentrations of the macrolide antibiotics, with mean values of 831 and 138 ng/g TS, respectively. Concentration data from an anaerobically digested sludge by Göbel *et al*. (2005) exhibited some of the highest concentrations of this class of antibiotics. Otherwise, concentration data for this class of antibiotics were sparse.

Treatment

Only limited data were found on the removal of a macrolide antibiotic by biosolids treatment. Studies by Carballa *et al*. (2006, 2007a) indicated that roxithromycin was highly degradable in laboratory-scale anaerobic digesters. The combination of thermophilic operation and longer retention times appeared to contribute to higher removal efficiency (Table 39).

Table 38. Concentrations of Macrolide Antibiotics in Sludges and Biosolids

Sludge Type	Concentration (ng/g TS)						Reference
	Azithro-mycin	Clarithro-mycin	Erythro-mycin	Roxithro-mycin	Virginia-mycin	Tylosin	
Not specified (sludge survey)	831 (278)[a]	41.58 (13.4)	36 (19)	8.1 (4.7)	138 (73.3)	269 (128)	U.S. EPA (2009)
Activated and digested	1.3-158	0.3-63		nd-131			Jones-Lepp and Stevens (2007)
Anaerobic digestion	2,500± 1,000[b]	700 ± 400					Göbel *et al*. (2005)
Unknown sludge (urban WWTP)		<LOQ - 30.2					Spongberg and Witter (2008)
Unknown sludge (rural WWTP)		<LOQ					
Primary sludge			105±50				Radjenović *et al*. (2009)
Anaerobically digested			70 ±30				
Not specified (2 plants)				<LOQ – 1,800		300 – 4,000	Nieto *et al*. (2007)
Waste activated sludge (Plant A)			76 ± 25	40 ± 23			Xu *et al*. (2007)
Waste activated sludge (Plant B)			195 ± 56	64 ± 16			
Wasted activated sludge (Plant C)			38 ±14	32 ± 9			
Waste activated sludge (Plant D)			62 ± 24	44 ± 10			

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

Table 39. Effect of Temperature and Retention Time on Removal of Roxithromycin in Anaerobic Digestion

Anaerobic Temperature	Retention Time (days)	Removal Efficiency (%)	Reference
mesophilic	20	(85 ± 15)[a]	Carballa *et al*. (2006)
mesophilic	30	99	Carballa *et al*. (2007a)
mesophilic	20	95	
mesophilic	10	no data	
thermophilic	10	(95 ± 5)	Carballa *et al*. (2006)
thermophilic	20	99	Carballa *et al*. (2007a)
thermophilic	10	98	
thermophilic	6	no data	

[a] mean ± standard deviation (n=2 or 3)

When aerobically digested sludge containing the macrolides clarithromycin and erythromycin was stored under different light and redox environments, both antibiotics declined from between 2,000 and 2,500 ng/g TS to non-detectable concentrations from between 7 and 35 days (Wu *et al*., 2008) (Table 40). Neither storage under anaerobic or aerobic conditions, nor the presence or absence of daylight appeared to affect the removal rates.

Table 40. Effect of Storage Treatment on Macrolides in Aerobically Digested Biosolids (Wu et al., 2008)

Storage Treatment	Storage Time (days)	Concentration (ng/g TS)	
		Clarithromycin	Erythromycin
Dark, Anaerobic	0	2,500	2,000
	7	300	1,200
	35	0	800
	77	0	250
Dark, Aerobic	0	2,500	2,200
	7	200	800
	35	0	400
	77	0	200
Daylight, Aerobic	0	2,500	2,200
	7	200	800
	35	0	300
	77	0	200

<u>Beta-Lactam Antibiotics</u>

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

Table 41. Concentrations of Beta-Lactam Antibiotics in Sludges and Biosolids (U.S. EPA, 2009)

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

[a] mean (median)

No data on removal efficiencies in biosolids treatment processes were found in this review.

<u>Lincosamide Antibiotics</u>

Only limited occurrence data in biosolids or sludges were found for this class of compounds (Table 42). In the EPA's TNSSS (U.S. EPA, 2009), lincomycin and clindamycin were found at median concentrations of 19.9 and 13.4 ng/g TS, respectively. In Ohio, clindamycin in sludges of three urban treatment plants ranged from 3.7 to 154 ng/g TS, while in sludge from a rural treatment facility, the concentration was18.2 ng/g TS (Spongberg and Witter, 2008).

Table 42. Concentrations of Lincosamide Antibiotics in Sludges and Biosolids

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

[a] mean (median) (n=78)

The effect of different storage conditions on the removal of clindamycin in aerobically digested solids was examined by Wu *et al*. (2008). The antibiotic declined rapidly in the first seven days of storage in both aerobic and anaerobic conditions and with daylight either present or absent in the aerobic samples (Table 43). Removal of the clindamycin was much slower in the remaining 70 days of the study. All test conditions produced approximately the same test results.

Table 43. Effect of Storage Treatment on Clindamycin in Aerobically Digested Biosolids (Wu et al., 2008)

Storage Treatment	Storage Time (days)	Clindamycin Concentration (ng/g TS)
Dark, Anaerobic	0	2,500
	7	1,000
	35	800
	77	800
Dark, Aerobic	0	2,500
	7	800
	35	700
	77	500
Daylight, Aerobic	0	2,500
	7	900
	35	700
	77	600

3.4.3 Nervous System

Anti-Epileptics (Anti-Convulsants)

Occurrence Data

Anti-epileptic drugs are used in the control of epilepsy. Occurrence data were primarily found for carbamazepine. The only reference to a second anti-epileptic drug, Primidone, stated the concentrations in sludge samples from three Ohio treatment plants were lower than the level of quantitation (Spongberg and Witter, 2008). Concentrations of carbamazepine in biosolids and sludge samples fell into a relatively narrow range (Table 44), from non-detectable to a maximum of 850 ng/g TS as reported by Jones-Lepp and Stevens (2007).

Table 44. Occurrence Data for Carbamazepine in Sludges and Biosolids

Sludge or Biosolids Source	Concentration (ng/g TS)	Reference
Raw sludge	69.6 ±2.2[a]	Miao *et al*. (2005) (n=3)
Anaerobically digested biosolids	258 ±4.7[a]	
Waste Activated Sludge	150 ng/g OC	Kinney *et al*. (2006)
Dewatered sludge	64 ng/g OC	
Not specified (Sewage treatment plant 1)	nd - 78	Nieto *et al*. (2007)
Not specified (Sewage treatment plant 2)	50 - 165	
Not specified (An urban WWTP)	4.8 - 12.9	Spongberg and Witter (2008)
Not specified (A rural WWTP)	21.1	
Not specified (sludge survey)	135 (55)[b]	U.S. EPA (2009) (n=78)
Primary sludge	70 ±60[a]	Radjenović *et al*. (2009) (n=2)
Biosolids class A + sludge	nd-850	Jones-Lepp and Stevens (2007)

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

Concentrations of carbamazepine following biosolids treatment processes are presented in Table 45. Kinney *et al*. (2006) compared several treatment processes. Other than anaerobic digestion, which exhibited a very high carbamazepine concentration of 1200 ng/g OC, concentrations were less than 180 ng/g TS. Other samples of anaerobically digested sludge ranged up to 281 ng/g TS. Carbamazepine concentrations observed in the treated biosolids were similar in magnitude to those of the other biosolids samples presented in Table 45.

Table 45. Concentrations of Carbamazepine in Treated Biosolids

Treatment Process	Concentration ng/g TS	Reference
compost	15-180 ng/g OC	Kinney *et al*. (2006)
heat dried	140 ng/g OC	
air dried	51 ng/g OC	
Anaerobic digested sludge	1,200 ng/g OC	
Digested sludge	281	Heidler and Halden (2008)
Anaerobic digested sludge	80 ±10[a]	Radjenović *et al*. (2009) (n=2)

[a] mean ± standard deviation OC = organic carbon

Metabolites of carbamazepine were monitored in the raw and digested solids of the Peterborough (ON) wastewater treatment plant (Miao *et al*., 2005) (Table 46). Concentrations of the metabolites included for analysis were either non-detected or present at very low concentrations (e.g., 2 -4 ng/g TS), compared to the concentrations of the parent compound in raw sludge (70 ng/g TS, or digested biosolids (258 ng/g TS, Table 44).

Table 46. Metabolites of Carbamazepine in Sludge (Miao et al., 2005)

Carbamazepine Metabolite	Concentration (ng/g TS)	
	Raw sludge	Anaerobic digested sludge
10,11-dihydro-10,11-epoxycarbamazepine	nd	nd
10,11-dihydro-10-hydroxycarbamazepine	nd	nd
2-hydroxycarbamazepine	1.9 ±1.1 [a]	3.4 ±0.9
3-hydroxycarbamazepine	1.6 ±0.8	4.3 ±0.9

[a] mean ± standard deviation (n=3) nd = not detected

<u>Removal of Carbamazepine in Biosolids Treatment Processes</u>

Only a limited set of tests have examined the removal of carbamazepine by biosolids treatment processes. Trials with anaerobic digestion documented by Carballa *et al*. (2007a) at laboratory scale indicated that carbamazepine was not reduced by the treatment at time up to 30 days at mesophilic conditions, and up to 20 days at thermophilic conditions (Table 47). Ternes *et al*. (2005) also reported that batch anaerobic digestion tests resulted in no removal of carbamazepine.

Table 47. Effect of Anaerobic Digestion Treatments on Removal of Carbamazepine (Carballa et al., 2007a)

Anaerobic Sludge Type	Solids Retention Time (d)	Removal Efficiency (%)
mesophilic	30	0
	20	0
	10	12
thermophilic	20	0
	10	0
	6	22
Average		0

Carballa *et al*. (2007b) also investigated the effect of pre-ozonation prior to anaerobic digestion under mesophilic and thermophilic conditions at laboratory scale (Table 48). The pre-ozonation treatment had a beneficial effect on the removal of carbamazepine, with up to a 60% reduction after 10 days at thermophilic temperatures. The authors considered the beneficial effect of the ozone was due to the carbamazepine existing primarily in the liquid phase, making it more susceptible to attack by the ozone (Carballa *et al*., 2007b).

Wu *et al*. (2008) examined the effects of storage methods on the reduction of carbamazepine and other pharmaceuticals in aerobically digested sludge. Treatment methods consisted of aerobic and anaerobic treatment in dark containers, and aerobic treatment subjected to solar radiation. There was no reduction from the initial carbamazepine concentration of approximately 2,500 ng/g TS in any of the three treatments after 77 days of storage.

Table 48. Effect of Pre-Ozonation on Anaerobic Digestion of Carbamazepine (Carballa et al., 2007b)

Sludge Type	Operating condition and SRT	Removal Efficiency, %
anaerobic digestion - mesophilic	Non-ozonated 20 d	0
anaerobic digestion - mesophilic	Ozonated 20 d	18± 5[a]
anaerobic digestion - thermophilic	Non-ozonated 10 d	0
anaerobic digestion - thermophilic	Ozonated 10 d	60 ± 3

[a] mean ± standard deviation

Mood-altering Pharmaceuticals

This section includes four different categories of pharmaceuticals including anti-anxiety (Amitriptyline, Diazepam and Paroxetine), anti-depressants (Fluoxetine), anti-psychotics (Chlorpromazine and Thioridazine), and psycho-stimulants (amphetamine, methamphetamine and caffeine). Data concerning these drugs in biosolids are generally scarce. The concentration data for fluoxetine in sludges indicate it is found typically in a range between 100 and 1,000 ng/g TS (Table 49). Concentrations of fluoxetine and paroxetine in a sample of primary sludge were of approximately the same magnitude (Radjenović *et al*., 2009).

Table 49. Concentrations of Representative Anti-Anxiety and Anti-Depressants in Sludges and Biosolids

Sludge Source	Concentration (ng/g TS)		Reference
	Fluoxetine	Paroxetine	
Waste Activated Sludge	370 ng/g OC		Kinney *et al*. (2006)
Dewatered Sludge	830 ng/g OC		
Primary Sludge	100±50[a]	70±50	Radjenović *et al*. (2009) (n=2)
Biosolids class A + sludge (literature review)	nd-59		Jones-Lepp and Stevens (2007)
Not specified (sludge survey)	245 (147)[b]		U.S. EPA (2009) (n=76)
Heat drying	480 ng/g OC		Kinney *et al*. (2006)
Composting	255-705 ng/g OC		
Air drying	2,800 ng/g OC		
Anaerobic digestion	4,700 ng/g OC		
Anaerobic digestion	150 ±60 [a]	50 ± 20	Radjenović *et al*. (2009) (n=2)

[a] mean ± standard deviation [b] mean (median) OC = organic carbon

Concentrations of two anti-depressants in the product of biosolids treatment processes are also provided in Table 49. Although some of the treated samples exhibit concentrations similar to untreated sludge samples, the values reported by Kinney *et al*. (2006) for other drying and anaerobically digested sludge are an order of magnitude higher than for the other treated biosolids and sludge samples. The disparity emphasizes the variability that can be observed in the different sludge matrices and locations.

One study attempted to detect these compounds, as part of a suite of target compounds, using different analytical extraction procedures (Gielen, 2007). The data are useful to indicate that concentrations of the pharmaceuticals are lower than the limit of quantitation. Results of this testing is presented in Table 50.

Table 50. Concentrations of Mood-altering Pharmaceuticals in Sludges and Biosolids (Gielen, 2007)

Extraction Procedure	Biosolids Source	Concentration (ng/g TS)		
		Amitriptyline	Chlorpromazine	Thioridazine
Soxhlet extraction	compost	<1	<14	<70
	WAS	not detected	not detected	not detected
	primary sludge	<1	not detected	not detected
Supercritical fluid extraction	compost	<5	<5	<259
	WAS	<5	<5	<259
	primary sludge	<5	<5	<259

Only a few studies provided any data on concentrations of psycho-stimulants in sludges or biosolids. The occurrence data appear in Table 51. The data indicate that caffeine and its metabolite can be present in variable concentrations from 5 to 5,000 ng/g TS. Gielen (2007) demonstrated that different extraction procedures in the analysis of caffeine in sludges can have a significant effect on the concentration reported. The data for amphetamine and methamphetamine are limited, with amphetamine exhibiting a higher concentration range than methamphetamine.

Table 51. Concentrations of Psycho-Stimulants in Sludges

Constituent	Sludge Type	Concentration (ng/g TS)	Ref
Amphetamine	Biosolids class A + sludge (literature review)	5-300	Jones-Lepp and Stevens (2007)
Methamphetamine	Biosolids class A + sludge (literature review)	0-4	
Caffeine	Unknown sludge (WWTP 1)	57 - 69	Nieto *et al*. (2007)
	Unknown sludge (WWTP 2)	<LOQ - 65	
	Unknown sludge (An urban WWTP)	<LOQ - 5.2	Spongberg and Witter (2008)
	Unknown sludge (A rural WWTP)	4.8	
	compost	7.4/43 [a]	Gielen (2007)
	Waste activated sludge	238/1,888	
	primary sludge	4,530/1,585	
1,7-Dimethylxanthine	Not specified (sludge survey)	1,180 (987) [b]	U.S. EPA (2009)

LOQ = limit of quantitation

[a] Soxhlet extraction/Supercritical fluid extraction

[b] mean (median) (n=78)

3.4.4 Analgesics and Anti-Inflammatory Drugs

Occurrence

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

The only analgesic compound identified in this review is acetaminophen (also called paracetamol in other countries). Several NSAIDs were identified in sludge and biosolids samples, including diclofenac, ibuprofen, naproxen, ketoprofen, indometacin and mefenamic acid. Occurrence data for these pharmaceuticals is found in Table 52. Compilation of data in this table reveals that the different analytical surveys have different suites of pharmaceuticals of interest. Only the NSAID Diclofenac appears on the target list of most publications examined, but was not an analyte of the recent EPA (2009) survey. Compounds that appear in the target lists of different research teams appear to be a function of pharmaceutical consumption (which in itself may be country-specific) and the analytical procedures used.

Removal of Analgesics and NSAIDs

There are few data reported in the literature on removal efficiencies of the analgesic and NSAID compounds. With laboratory-scale anaerobic digesters, Carballa *et al*. (2007a) observed that naproxen was readily removed under both mesophilic and thermophilic conditions, even at the shortest retention times tested (Table 53). Ibuprofen was more resistant to removal during anaerobic digestion, with slightly improved reductions at thermophilic over mesophilic operation (Carballa *et al*., 2006, 2007a). Diclofenac was relatively more resistant to removal in anaerobic digestion than either naproxen or ibuprofen. The relative removal efficiencies of the three NSAIDs were confirmed in laboratory batch anaerobic digestion tests completed by Ternes *et al*. (2005).

The effect of pre-ozonation prior to anaerobic digestion under mesophilic and thermophilic conditions at laboratory scale was examined by Carballa *et al*. (2007b) (Table 54). The pre-ozonation treatment had no beneficial effect on the removal of the NSAIDs tested, with perhaps even a slightly negative impact on reduction by anaerobic digestion when preceded by ozonation.

Table 52. Occurrence of Analgesics and Non-Steroidal Anti-Inflammatory Drugs (NSAIDs) in Sludges and Biosolids

Biosolids Source	Concentration (ng/g TS)								Reference
	Acetaminophen	Codeine	Diclofenac	Ibuprofen	Indomet-acin	Ketoprofen	Naproxen	Mefen-amic acid	
Not specified (Sewage treatment plant 1) (n=5)	nd - 34		nd - 65		70 - 99		nd - 242		Nieto *et al*. (2007)
Not specified (Sewage treatment plant 2) (n=5)	nd - 42		nd - 183		nd - 75		nd - 87		
Not specified (literature survey)	0.0006–4535								Harrison *et al*. (2006)
Not specified (An urban WWTP) (n=3)			<LOQ - 23.1						Spongberg and Witter (2008)
Not specified (A rural WWTP) (n=1)			28.5						
Not specified (sludge survey)	462 (396)[a]	30.6 (19.9)		653 (143)			86.2 (31.6)		EPA (2009)
Primary sludge			215±130[b]	535±193		220±110		10±5	Radjenović *et al*. (2009)
Anaerobic digested sludge			190±130	300 ±70		40±40		50±15	
Biosolids class A + sludge	nd-1400								Jones-Lepp and Stevens (2007)
Compost				<5					Gielen (2007)
Waste Activated Sludge				<1 - 41					
Primary sludge				153 - 299					

LOQ = Limit of Quantitation nd = not detected

[a] mean (median) (n=78) [b] mean ± standard deviation (n=2)

Table 53. Effect of Anaerobic Digestion Treatments on Removal of NSAIDs

Sludge Type	Condition	Removal Efficiency (%)			Reference
		Diclofenac	Ibuprofen	Naproxen	
anaerobic digestion - meso			40 ± 15 [a]	87± 5	Carballa *et al*. (2006)
anaerobic digestion - thermo			47 ± 10	91 ± 5	
anaerobic digestion - meso	SRT=30 d	5	30	80	Carballa *et al*. (2007a)
anaerobic digestion - meso	SRT=20 d	0	40	90	
anaerobic digestion - meso	SRT=10 d	80	60	90	
anaerobic digestion - thermo	SRT=20d	30	40	92	
anaerobic digestion - thermo	SRT=10 d	15	50	92	
anaerobic digestion - thermo	SRT=6 d	80	55	85	
anaerobic digestion		0	40	>80	Ternes *et al*. (2005)

[a] mean ± standard deviation (n=2 or 3)

Table 54. Effect of Pre-Ozonation on Anaerobic Digestion of NSAIDs (Carballa et al., 2007b)

Sludge Type	Condition	Removal Efficiency (%)	
		Diclofenac	Ibuprofen
anaerobic digestion - meso	Non-ozonated	80 ± 1 [a]	40 ± 10
anaerobic digestion - meso	Ozonated	75 ± 0	20 ±8
anaerobic digestion - thermo	Non-ozonated	75 ± 3	50 ± 10
anaerobic digestion - thermo	Ozonated	70 ± 1	45 ± 7

[a] mean ± standard deviation (n=2 or 3)

3.4.5 Bacteriostat Antibiotics

Two pharmaceuticals with bacteriostatic properties were identified, including trimethoprim often used for fighting urinary tract infections and chloramphenicol, mainly used in eye drops or ointment for bacterial conjunctivitis. Concentrations of trimethoprim in sludges are generally low (less than 100 ng/g TS) as indicated in Table 55. Chloramphenicol concentrations were beneath the limit of quantitation in waste activated sludges analysed by Xu *et al*. (2007).

Table 55. Concentrations of Trimethoprim in Sludges and Biosolids

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

nd = not detected
[a] mean (median) (n=78)
LOQ = limit of quantitation
[b] mean ± standard deviation (n=2)

3.4.6 Cardiovascular Pharmaceuticals

This class of pharmaceuticals is that which affect the cardiovascular system. Drugs in this class have generic actions including beta-blockers (atenolol, propanolol), calcium-channel blockers (diliatazem), thiazides (hydrochlorothiazide) and digoxin, These pharmaceuticals are used to control heart arrhythmia and hypertension (high blood pressure). Hydrochlorothiazide is prescribed as an anti-diuretic, which ultimately helps to reduce hypertension. Dehydronifedipine is a metabolite of the calcium-channel blocker nifedipine.

The compounds in this class that were identified in the literature review are provided in Table 56. The range of concentrations for pharmaceuticals in this class appears to be on the order of 10 to 400 ng/g TS. Based on the data provided by Radjenović *et al*., (2009), treatment of primary sludge by anaerobic digestion appears to result in a reduction of this class of compounds, with atenolol having a mean concentration notably lower in digested sludge compared to the level in primary non-digested sludge.

Table 56. Concentrations of Cardiovascular Pharmaceuticals in Sludges and Biosolids

Compound	Concentration (ng/g TS)				
	Not Specified (Sludge Survey)	Biosolids class A + sludge	Primary Sludge	Anaerobically Digested Sludge	Not specified (2 plants)
Atenolol			90±30[b]	10±2	
Digoxin	208 (99.4)[a]				
Diltiazem	40.2 (14.8)	nd-26			<LOQ - 12.8
Hydrochlorothiazide			40±20	15±10	
Propranolol			40±20	30±15	
Dehydronifedipine	5.03 (4.04)	8-390			
Reference	U.S. EPA (2009)	Jones-Lepp and Stevens (2007)	Radjenović *et al*. (2009)		Spongberg and Witter (2008)

nd = not detected
[a] mean (median) (n=78)
LOQ = limit of quantitation
[b] mean ± standard deviation (n=2)

3.4.7 Alimentary Tract Pharmaceuticals

<u>Occurrence</u>
This class of pharmaceuticals includes anti-diabetic drugs, and anti-dyspeptics or acid reflux inhibitors. The latter group has technical names including hydrogen receptor agonists or proton pump inhibitors. In Table 57, the anti-diabetic drug metformin is higher in concentration than its alternate glibenclamide. Cimetidine was identified at the highest concentration (1,330 ng/g TS) of gastric reflux inhibitors by a wide margin. Studies involving testing of sludges revealed non-detectable concentrations of cimetidine (Spongberg and Witter, 2008) and the proton pump inhibitor omeprazole (Nieto *et al*., 2007).

Table 57. Concentrations of Alimentary Tract Pharmaceuticals in Sludges and Biosolids

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

nd = not detected
[a] mean ± standard deviation (n=2)   [b] mean (median) (n=77)

Treatment

Data provided in Radjenović *et al*. (2009) in Table 57 are useful for comparing the effect of anaerobic digestion on concentrations of glibenclamide and famotidine. The concentrations of these two pharmaceuticals were higher following anaerobic digestion than in the raw primary sludge, indicating that the drugs are not amenable to reduction by anaerobic digestion.

3.4.8 Blood-Modifying Pharmaceuticals

This class of drugs includes anti-lipid (cholesterol lowering) (e.g., gemfibrozil, bezafibrate and clofibric acid) and anti-coagulants (e.g. Warfarin). Gemfibrozil was the compound reported most frequently in the literature, with concentrations ranging as high as 1,500 ng/g TS (Table 58). Maximum concentrations of the other pharmaceuticals in this class were substantially lower. The study completed by Radjenović *et al*., (2009) indicated that gemfibrozil was not likely to be removed by the anaerobic digestion process. No other data on removal efficiencies in biosolids treatment processes were found.

3.4.9 Respiratory and Anti-Allergenic Pharmaceuticals

Antihistamine drugs are used to prevent the formation of histamine as a result of allergic reactions to triggers such as pollens and insect stings. Occurrence data in sludges and biosolids are limited (Table 59) and generally focus on the compound diphenylhydramine. The data provided by Jones-Lepp and Stevens (2007) suggest the concentrations can be quite variable, although collectively the literature would indicate concentrations in the range of 100 to 1,000 ng/g TS might be expected. The mean concentration of loratidine in primary sludge at 50 ng/g TS (Radjenović *et al*., 2009) was lower than those observed for diphenylhydramine.

Table 58. Concentrations of Blood-Modifying Pharmaceuticals in Sludges and Biosolids

Sludge Source	Concentration (ng/g TS)				Reference
	Bezafibrate	Clofibric Acid	Gemfibrozil	Warfarin	
Not specified (sludge survey)			214 (101)^{a}	10.5 (9.9)	U.S. EPA (2009)
Literature review			nd - 1500	nd - 92	Jones-Lepp and Stevens (2007)
Literature review			nd - 1190		Harrison *et al*. (2006)
Unknown sludge (An urban WWTP)		<LOQ - 8.1	<LOQ - 3.4		Spongberg and Witter (2008)
Unknown sludge (A rural WWTP)			18.3		
Two treatment plant sludges	<LOQ - 88	<LOQ - 64			Nieto *et al*. (2007)
Primary sludge			50±50^{b}		Radjenović *et al*. (2009)
Anaerobic digested sludge			140 ±80		

nd = not detected

LOQ = limit of quantitation

[a] mean (median) (n=78)

[b] mean ± standard deviation (n=2)

Table 59. Concentrations of Anti-Allergenic Pharmaceuticals in Sludges and Biosolids

Compound	Sludge Source	Concentration (ng/g TS)	Reference
Diphenylhydramine	Not specified (sludge survey)	871 (541)^{a}	U.S. EPA (2009)
	Biosolids class A + sludge	15-7,000	Jones-Lepp and Stevens (2007)
	Waste activated sludge	150 ng/g OC	Kinney *et al*. (2006)
	Dewatered sludge	170 ng/g OC	
Loratidine	Primary sludge	50±40^{b}	Radjenović *et al*. (2009)
Albuterol	Not specified (sludge survey)	5.23 (5.29)^{a}	U.S. EPA (2009)
	Literature review	nd – 1,400	Jones-Lepp and Stevens (2007)

[a] mean (median) (n=77)

[b] mean ± standard deviation (n=2)

OC = organic carbon

Although the anti-bronchospasm drug albuterol was found at relatively low concentrations of 5 ng/g TS in the EPA's TNSSS (Table 59), the literature review by Jones-Lepp and Stevens (2007) indicated much higher concentrations have been observed in sludges and biosolids.

Concentrations of the anti-allergenic drugs in treated biosolids are provided in Table 60. Concentrations of diphenylhydramine in the data provided by Kinney *et al*. (2006) are highly variable. As noted above, the sludge and biosolids occurrence data, concentrations of this drug are quite variable, and so it is not possible to determine of the different concentrations in the processes result from the variability inherent in the sludge, or due to the process treatments. The data of Radjenović *et al*., (2009) for mean concentrations of loratidine in primary sludge (50 ng/g TS) and anaerobically digested sludge (160 ng/g TS) suggest that there is no reduction of the compound during anaerobic digestion.

Table 60. Concentrations of Two Anti-Allergenics following Biosolids Treatment Processes

Compound	Biosolids Process	Concentration (ng/g TS)	Reference
Diphenylhydramine	heat drying	2,900 ng/g OC	Kinney *et al*. (2006)
	compost	32 – 550 ng/g OC	
	air drying	810 ng/g OC	
	anaerobic digestion	22,000 ng/g OC	
Loratidine	anaerobic digestion	160 ± 40[a]	Radjenović *et al*. (2009)

[a] mean ± standard deviation (n=2)   OC = organic carbon

3.4.10 Anti-Parasitic and Anti-Fungal Pharmaceuticals

Anti-parasitic pharmaceuticals are used to control parasitic protozoa, helminths and other similar pathogens. The anti-fungal agent identified in the survey, miconazole, is used for treating athlete's foot, jock itch and vaginal yeast infections.

Occurrence data for these compounds were identified in two sources as indicated in Table 61. Of the three anti-parasitics identified in sludges in this review, carbadox was present at the highest concentration with a median value on 103 ng/g TS. The median concentration of miconazole was 207 ng/g TS. Considerable variability was associated with this substance in the survey as the mean value is approximately six times the median value.

Table 61. Concentrations of Anti-Parasitics and Anti-Fungals in Sludges and Biosolids

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

[a] mean (median) (n=78)   nd = not detected

3.4.11 Miscellaneous Pharmaceuticals

The drugs included here depart from the classification provided by Gielen (2007) due to the limited number of compounds for each use or presence in sludges. Concentrations of the compound salicylic acid were present at a wide range in the literature on sludges reviewed by Harrison *et al*. (2006) (Table 62). Cotinine is a metabolite of nicotine and is a marker of human presence in wastewaters and sludges. Digoxigenin is used to induce an immune system response in humans. The median concentration of this marker compound, at 39.8 ng/g TS, was relatively low in the EPA TNSSS, as was the median concentration of 19.9 ng/g TS for the ovulation inhibitor norgestimate.

No biosolids treatment data were found for these pharmaceuticals

Table 62. Concentrations of Miscellaneous Pharmaceuticals in Sludges and Biosolids

Compound	Use/Presence	Sludge source	Concentration (ng/g TS)	Reference
Digoxigenin	steroid immunohisto-chemical marker	Not specified (sludge survey)	57.2 (39.8) [a]	U.S. EPA (2009)
Norgestimate	ovulation inhibitor	Not specified (sludge survey)	27.5 (19.9)	
Salicylic Acid	skin-care	Literature review	0.002–13,740	Harrison *et al*., (2006)
		Unknown sludge (An urban WWTP)	<LOQ - 253	Spongberg and Witter (2008)
		Unknown sludge (A rural WWTP)	253	
Cotinine	nicotine metabolite	Not specified (sludge survey)	58.0 (13.2)	U.S. EPA (2009)

nd = not detected LOQ = limit of quantitation

[a] mean (median) (n=78)

3.4.12 Section Summary

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

1. There is a wide range of data available for the different pharmaceuticals that may be present in sludges and biosolids. Some compounds like carbamazepine have been widely characterized, while others have only one or two references in the literature.
2. As a result of there being limited occurrence data for many pharmaceuticals, there are even fewer data available investigating the reduction of these drugs in biosolids treatment processes.
3. Anaerobic digestion is the treatment process for which most data on pharmaceutical concentrations prior to and after treatment have been recorded. Reduction of the compounds appears to be highly specific to each class of pharmaceutical.

3.5 HORMONES AND STEROLS

3.5.1 Hormones

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

Natural and synthetic estrogens found most regularly in wastewater sludges are summarized in Table 63. Concentrations of these compounds in sludges are typically less than 50 ng/g TS, although in the U.S. EPA's Targeted National Sewage Sludge Survey (TNSSS, U.S. EPA 2009) the concentration of the natural hormone estrone (E1) had a mean concentration of 106 ng/g TS. The data suggest that estrone (E1) is higher than most of the other common estrogenic compounds. In an analysis of New Zealand Sludge, Gielen reported a mean value of 185 ng/g TS for the synthetic hormone 17α-ethinylestradiol (EE2), however the standard deviation of the mean was also very high indicating a wide spread of experimental values.

Table 63. Concentrations of Common Estrogenic Compounds in Sludges and Biosolids

Sludge Source	Concentration (ng/g TS)				Reference
	17α-ethinylestradiol (EE2)	17β-estradiol (E2)	Estriol (E3)	Estrone (E1)	
Sludge Survey	24.9 (25)[a]	34.3 (21.5)	38.7 (24.8)	106 (51.2)	U.S. EPA (2009)
Return activated sludge (2 plants)		nd	nd	nd - 17.5	Tan *et al*. (2007)
Literature review	<1.5 – 17	4.9 – 49		16 – 27.8	Harrison *et al*. (2006)
Compost	<5				Gielen (2007)
Waste activated sludge (lit. review)	<5				
Primary sludge (lit. review)	185 ± 185[b]				
Waste activated sludge	3	1.7		7	Andersen *et al*. (2003)
Primary sludge	<1.5	30		30	
Return activated sludge	<1.5	2.2		5.6	

nd = not detected
[a] mean (median) (n=73-78) [b] mean ± standard deviation (number not specified)

There are other natural and synthetic estrogenic compounds present in biosolids as well as those listed in Table 63. Additional estrogens detected in sludges and biosolids in the EPA's TNSSS

(EPA, 2009) are provided in Table 64. The concentration of the natural hormone progesterone was the highest of the others observed, with a median concentration of 139 ng/g TS. The median concentrations of the other estrogens were less than 50 ng/g TS.

Table 64. Concentrations of Other Estrogenic Compounds in Sludges and Biosolids (U.S. EPA, 2009)

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

[a] mean (median) (n= 73 to 78)

Removal of Estrogens

The effect of anaerobic digestion on the removal of the common estrogens in sludge has been investigated by Carballa *et al*. (2006, 2007a). Data are summarised in Table 65.

Table 65. Effect of Anaerobic Digestion Conditions on Removal Efficiency of Estrogenic Compounds

Anaerobic Temperature	Condition	Removal Efficiency (%)		Reference
		Estrone (E1) + 17β-estradiol (E2)	17α-ethinylestradiol (EE2)	
Mesophilic	SRT=20 d	(85 ± 10)%[a]	(85 ± 5)%	Carballa *et al*. (2006)
Mesophilic	SRT=30 d	70%	40%	Carballa *et al*. (2007a)
Mesophilic	SRT=20 d	no data	no data	
Mesophilic	SRT=10 d	95%	90%	
Thermophilic	SRT=10 d	(85 ± 5)%	(75 ± 15)%	Carballa *et al*. (2006)
Thermophilic	SRT=20d	80%	35%	Carballa *et al*. (2007a)
Thermophilic	SRT=10 d	no data	no data	
Thermophilic	SRT=6 d	90%	90%	
Mesophilic	Non-ozonated	(90 ± 10)%	(90 ±1)%	Carballa *et al*. (2007b)
Mesophilic	Ozonated	(80±1)%	(85 ±1)%	
Thermophilic	Non-ozonated	(90 ± 1)%	(90 ±1)%	
Thermophilic	Ozonated	(88±1)%	(85 ±1)%	

[a] mean ± standard deviation (n=2 or 3)

Data from Carballa *et al*. (2006) comparing mesophilic and thermophilic digestion indicates that the processes were approximately the same in their ability to remove the estrogens, based on a comparison of the standard deviations of the mean values. Removal efficiencies up to 85% were recorded for both 17α-ethinylestradiol (EE2) and a mixture of estrone (E1) and 17β-estradiol (E2). A second study comparing different solids retention times at the two operating temperatures yielded the unexpected result that a longer retention time provided lower removal efficiencies (Carballa *et al*., 2007a).

Carballa *et al*. (2007b) investigated the effect of pre-ozonation of the sludge prior to either mesophilic or thermophilic digestion. At both temperature regimes, the non-ozonated sludge exhibited higher removals of the estrogens than did the pre-ozonated sludge (Table 65).

Concentrations of androgens in sludges were reported less frequently than estrogens (Table 66). Results from the EPA TNSSS U.S. EPA, 2009) reported three androgens with mean values ranging from a low of 85 ng/g TS for androstereone to a high of 158 for androstenedione. Tan *et al*. (2007) reported that two target androgens androsterone and the metabolite etiocholanolone were both below detection limits in return activated sludge samples from two different plants.

Table 66. Concentrations of Androgenic Compounds in Sludges and Biosolids

Androgens	Concentration (ng/g TS)	
	Sludge Survey	Return Activated Sludge
Androstenedione	327 (158)[a]	
Androsterone	120 (84.9)	nd
Testosterone	163 (95.2)	
Etiocholanolone (androgen metabolite)		nd
Reference	U.S. EPA (2009)	Tan *et al*. (2007)

nd = not detected [a] mean (median) (n=73)

3.5.2 Sterols

Concentrations of plant sterols in sludges and biosolids (Table 67) were among the highest observed in this literature review, with concentrations in the tens of thousands of ng/g TS, and the median concentration of 207,000 ng/g TS reported for β-sitosterol in the EPA's TNSSS (U.S. EPA, 2009). The concentrations for the plant sterols reported in the literature review by Harrison *et al*. (2006) were much lower than those found in the EPA's TNSSS (U.S. EPA, 2009), and lower even than values reported for return activated sludge and waste activated sludge by Tan *et al*. (2007).

The concentrations of plant sterols in treated biosolids were documented in Kinney *et al*. (2006). Composting and heat drying resulted in lower concentrations of the phytosterols in the biosolids than did alternate drying methods or anaerobic digestion (Table 68). For both the β-sitosterol and β-stigmastanol, anaerobic digestion treatment had the highest concentrations of the four treatment methods examined.

Table 67. Concentrations of Plant Sterols in Sludges and Biosolids

Compound	Concentration (ng/g TS)		Concentration (ng/g OC)	
		not specified		
	Literature review	Sludge Survey	WAS	Dewatered
Campestanol (5α+5β)	3,000 – 14,000			
Campesterol	6,300	100,900 (46,500)[a]		
Desmosterol		15,650 (10,800)		
Ergosterol		19,830 (12,600)		
Sitostanol (5α-β+5β-β)	14,100 – 93,900			
Sitosterol (β-)	29,600 – 31,100	291,400 (207,000)	138,000	112,000
Stigmastanol; β-Stigmastanol; Stigmastanol (5α+5β)	1,900 – 12,900	168,100 (62,500)	44,600	40,500
Stigmasterol	6,700	321,200 (41,500)		
Reference	Harrison *et al.* (2006)	EPA (2009)	Kinney *et al*. (2006)	

[a] mean (median) (n=78) OC = organic carbon

Table 68. Concentrations of Plant Sterols following Biosolids Treatment Processes (Kinney et al., 2006)

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

OC = organic carbon

Concentrations of the animal sterols reported in sludges varied substantially from one reference or source to the next, but were in any case among the highest concentrations observed in this review, as shown in Table 69. The literature review of Harrison *et al*. (2006) reported the lowest concentrations of the compounds, while the highest values were documented in the EPA's TNSSS (U.S. EPA, 2009), with the fecal indicator 3β-coprostanol having a median concentration of 827,000 ng/g TS. Concentrations of two animal sterols by Kinney *et al*. (2006) in waste activated sludge and dewatered sludge were intermediate between the EPA data and the review data of Harrison *et al*. (2006).

Concentrations of animal sterols in biosolids treated by different processes are limited to two compounds in the work by Kinney *et al*. (2006) (Table 70). The results are not consistent for the two compounds. The highest concentration of cholesterol was found in biosolids treated by heat drying, whereas the highest concentration of 3β-coprostanol was observed following anaerobic digestion. For both compounds, however, composting resulted in the lowest concentrations.

There are too few data to determine whether composting would produce the lowest concentrations of these compounds.

Table 69. Concentrations of Animal Sterols in Sludges and Biosolids

Compound	Concentration (ng/g TS)		Concentration (ng/g OC)	
	Literature review	Not specified (Sludge Survey)	Waste Activated Sludge	Dewatered
Cholestanol (5α-); Cholestanol	22,700	680,000 (187,200) [a]		
Cholesterol	57,400		386,000	333,000
Coprostanol; 3β-Coprostanol	216,900	4,367,000 (827,100)	355,000	325,000
Epicoprostanol		1,703,000 (108,000)		
Reference	Harrison *et al.* (2006)	U.S. EPA (2009)	Kinney *et al.* (2006)	

[a] mean (median) (n=78) OC = organic carbon

Table 70. Concentrations of Animal Sterols following Biosolids Treatment Processes (Kinney et al., 2006)

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

3.5.3 Section Summary

The main points of interest in this section follow.

1. The hormones 17α-ethinylestradiol (EE2), estrone (E1) and 17β-estradiol (E2) are among the most frequently characterized compounds of this category in sludges and biosolids. Estrone (E1) is higher in concentration than the other common estrogenic compounds.
2. The concentration of the natural hormone progesterone was the highest of the other hormones observed, with a median concentration of 139 ng/g TS.
3. Concentrations of androgens in sludges were reported less frequently than estrogens, with median concentration of three identified androgens from the EPA sludge survey ranging from 85 to 158 ng/g TS.
4. Concentrations of plant sterols in sludges and biosolids were among the highest observed in this literature review, with concentrations in the tens of thousands of ng/g TS. Composting and heat drying resulted in lower concentrations of the phytosterols in the biosolids; anaerobic digestion treatment had the highest concentrations of the four treatment methods.

5. Concentrations of the animal sterols reported in sludges varied substantially from one reference or source to the next, but were in any case among the highest concentrations observed in this review.
6. Composting resulted in the lowest observed concentrations of both cholesterol and 3β-coprostanol in different biosolids treatment processes.
7. Removal efficiencies up to 85% were recorded for both 17α-ethinylestradiol (EE2) and a mixture of estrone (E1) and 17β-estradiol (E2) in both thermophilic and mesophilic anaerobic digestion.
8. Removal efficiency data for hormones and sterols in other biosolids treatment processes are scarce.

3.6 PERSONAL CARE PRODUCTS

3.6.1 Introduction

In the Review of the State of Knowledge of Municipal Effluent Science and Research: Review of Effluent Substances (Hydromantis *et al*., 2005), a number of different types of personal care products (PCP) were identified including synthetic musk fragrances, parabens (anti-microbial preservatives), sunscreen agents and insect repellents. In the current literature review focusing on occurrence and removal in biosolids, data were decidedly more limited. The information retrieved has centred primarily on the presence of the anti-microbials and synthetic musk compounds, with more limited data on fluorescent whitening agents, quaternary ammonium compounds and volatile methyl siloxanes.

3.6.2 Antimicrobials

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

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

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

Lee and Peart (2002) assessed the concentrations of triclosan and hexachlorophene as two of a suite of ESOCs in Canadian sludges, both raw and digested biosolids (Table 71).

Table 71. Occurrence of Triclosan and Hexachlorophene in Canadian Municipal Sludges and Biosolids (Lee and Peart, 2002)

Municipal Treatment Plant and Sludge Type	Triclosan (ng/g TS)	Hexachlorophene (ng/g TS)
Edmonton (Goldbar) Raw	14,800	102
Regina Raw	7,160	216
Adelaide Raw	3,430	308
Burlington Raw	8,900	797
Ottawa Raw	17,900	208
Toronto (Ashbridges Bay) Raw	10,600	138
Toronto (Highland Creek) Raw	17,100	502
Toronto (Humber) Raw	16,500	397
Toronto (North) Raw	12,500	181
Montreal (MUC-PSI) Raw	14,200	562
Quebec City Raw	6,100	113
Quebec City Raw	5,500	72.6
median raw	10,600	208
Vancouver Digested	8,410	477
Vancouver Digested	24,700	420
Calgary (Bonnybrook) Digested	12,800	371
Calgary (Fish Creek) Digested	19,500	218
Edmonton (Goldbar) Digested	22,000	285
Regina Digested	18,900	420
Saskatoon Digested	9,900	352
Saskatoon Digested	19,400	597
Burlington Digested	7,480	451
Galt Digested	28,200	421
Guelph Digested	16,200	727
Hamilton Digested	11,500	1,190
Ingersoll Digested	16,100	640
Kitchener Digested	18,600	254
Ottawa Digested	11,700	693
Waterloo Digested	8,840	311
Windsor Digested	20,300	548
Toronto (Ashbridges Bay) Digested	16,600	328
Toronto (Humber) Digested	5,400	572
Toronto (North) Digested	900	22.6
Granby Digested	1,920	68.7
Moncton Digested	7,530	701
Truro Digested	8,410	477
median digested	14,450	421

The median values of triclosan in raw sludge and digested biosolids were 10,600 and 14,450 ng/g TS, respectively, suggesting that there is no reduction of triclosan as a result of digestion. Similar results were observed for hexachlorophene, with median values in raw and digested sludge samples of 208 and 421 ng/g TS, respectively. The highest concentrations of triclosan in raw sludge and digested biosolids were found in samples from Ottawa and Galt (ON) at 17,900 and 28,200 ng/g TS, respectively. Digested sludge from the Toronto North facility had the lowest concentration of triclosan and hexachlorophene. The highest concentration of hexachlorophene in raw sludge in this survey was in a sample from Burlington, ON, while the highest concentration in digested biosolids was observed in a sample from Hamilton, ON.

Concentrations of triclosan in other sludge samples are provided in Table 72. A recent survey of Canadian sludges by XCG Consultants (2007) reported concentrations of triclosan in a range of 900 – 28,000 ng/g TS, with a median value of 13,000 ng/g TS. In four Ontario treatment plants, concentrations of Triclosan ranged between 680 and 11,550 ng/g TS. Concentrations reported in other publications were of a similar magnitude, between 3,200 and 42,000 ng/g TS.

Table 72. Concentration of Triclosan in Other Sludge and Biosolids Samples

Sludge Source	Concentration (ng/g TS)		Reference
	Range	mean (median)	
Canadian sludge (1995-1998)	900 - 28,000	13,000	XCG (2007)
Treated Biosolids (4 Ontario plants)	680 – 11,550		Chu and Metcalfe (2007)
Mid-Atlantic U.S. plant	20,000 - 55,000	30,000 ± 11,000[a]	Heidler and Halden (2007) (n=3)
Not specified (literature review)	nd – 15,600		Harrison *et al*. (2006)
dewatered anaerobically digested or dewatered secondary sludge (Greece)	190 – 9,850	3,210 (2,710)	Stasinakis *et al*. (2008) (n=27)
Not specified (France)		41,900 ± 37,000	Ruel *et al*. (2008) (from literature database; number not specified)
Not specified (U.S. survey)		16,100 (3,860)	U.S. EPA (2009) (n=78)

nd = not detected [a] mean ± standard deviation

Biosolids treatment processes had no real discernible effect on reducing concentrations of triclosan, as indicated in Table 73.

Table 73. Concentration of Triclosan following Biosolids Treatment Processes

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

[a] mean ± standard deviation

3.6.3 Fragrance Compounds

Two main classes of fragrance compounds are used in consumer and commercial products, namely the nitro musks and the polycyclic musks. Nitro musks were first used as synthetic replacements for the natural musk obtained from glands of the male musk deer (Lee *et al.*, 2003). Polycyclic musks have now become the most commonly used synthetic musk due to health concerns and concerns over persistence of the nitro musks in the environment. Both classes of musks are used not only for their own unique smell that influences the odour characteristic, but also for enhancing the quality of a fragrance (OSPAR, 2000). The musk compounds are used in fragrances for detergents, fabric softeners, fabric conditioners, cleaning agents, air fresheners, and cosmetics such as soaps, shampoos and perfumes (OSPAR, 2000). Common fragrance compounds in use are found in Table 74.

Table 74. 74Identification and Formulations of Common Synthetic Fragrance Compounds

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

Polycyclic musks have now become the most commonly used synthetic musk due to concerns over environmental persistence and health issues related to the nitro musks. Peck and Hornbuckle (2004) identified a number of health concerns related to nitro musks, including estrogenic activity and accumulation in human adipose tissue and breast milk.

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

Concentrations of polycyclic and nitro musk fragrances from a survey of Canadian biosolids samples are presented in Table 75 (Lee *et al.*, 2003). Galaxolide (HHCB) and Tonalide (AHTN) were the two predominant polycyclic musks, with median concentrations in raw sludge samples of 11,850 and 8,005 ng/g TS, respectively. Traesolide (ATII) was observed with a median value of 1,345 ng/g TS, approximately an order of magnitude lower than the HHCB or AHTN. The remaining two polycyclic musks investigated, Celestolide (ADBI) and Phantolide (AHDI or AHMI) were substantially lower at 175 and 110 ng/g TS, respectively. The highest concentration of HHCB was in a digested biosolids sample from the Toronto Humber Wastewater Treatment Plant, at 26,700 ng/g TS, while the highest for AHTN was 20,600 from the Calgary Bonnybrook facility. With respect to the nitro musks analyzed, musk xylene was found at the highest concentration, 422 ng/g TS, in a sample of raw sludge from Montreal, while musk ketone was consistently found at higher concentrations than musk xylene, particularly in the raw sludge samples (median value of 144.5 ng/g TS).

Concentrations of the polycyclic musks increased from raw sludge to anaerobically digested biosolids, suggesting that no reduction was occurring to due anaerobic biodegradation. Anaerobic digestion had an apparent beneficial reduction of the nitro musk compounds with Musk ketone and Musk xylene having median concentrations of 4.5 and 3.3 ng/g TS, respectively in the digested biosolids samples (Lee *et al*., 2003).

Additional concentration data are provided in Table 76 for polycyclic musks and Table 77 for nitro musk compounds. Data provided by Smyth *et al*. (2007) are from a survey of five wastewater treatment plants in the Grand River watershed of Ontario, while data provided by Yang and Metcalfe (2005) are from the Peterborough, ON facility. Data compiled by Webber and Sidwha (2005) are a summary of the data of Lee *et al*. (2003) presented above in Table 75. The concentration profiles in Tables 76 and 77 follow those in Table 75. Of the polycyclic musks, HHCB and AHTN were present at the highest concentrations, followed by ATII. Concentrations of ADBI and AHMI were of similar magnitude but much lower than the other polycyclic musks identified. The musk DPMI was not detected in the five Ontario plants tested by Smyth *et al*. (2007). Concentrations of the polycyclic musks from the Peterborough facility (Yang and Metcalfe, 2005) were substantially lower than those identified by Smyth *et al*. (2007) and Lee at al. (2003). It is not clear whether the differences in magnitude were due to differences in site-specific inputs, differences in analytical procedures, or other unidentifiable factors.

Table 75. Fragrance Concentrations in Canadian Municipal Sludges (Lee et al., 2003)

Biosolids Source	Fragrance Concentration (ng/g TS)						
	Galaxolide (HHCB)	Tonalide (AHTN)	Celestolide (ADBI)	Phantolide (AHDI or HMI)	Traesolide (ATII)	Musk Xylene (MX)	Musk Ketone (MK)
Raw sludge (Adelaide)	4850	6150	170	<30	1270	33.2	142
Raw sludge (Toronto (North))	21200	8710	220	730	2070	12.8	24.3
Raw sludge (Burlington)	15200	8650	230	120	1650	14.4	17.2
Raw sludge (Edmonton (Goldbar))	6390	8060	130	110	1260	7.2	158
Raw sludge (Montreal (MUC-PSI))	1340	5360	90	80	1000	422	191
Raw sludge (Ottawa)	13200	8650	180	90	1130	46.1	245
Raw sludge (Quebec City)	10500	7300	160	<30	1470	341	364
Raw sludge (Regina)	9070	7260	170	80	1190	144	347
Raw sludge (Saskatoon)	7480	7950	140	130	1360	4.2	94.6
Raw sludge (Toronto (Ashbridges Bay))	21800	11000	230	110	2200	12.6	106
Raw sludge (Toronto (Humber))	17400	7020	200	70	1330	20.3	147
Raw sludge (Toronto (Highland Creek))	20900	10000	390	340	2100	17.6	36.7
Anaerobic digested (Burlington)	12000	8010	190	80	1360	3.3	3.7
Anaerobic digested (Calgary (Bonnybrook))	20800	20600	570	130	4150	5.1	7.3
Anaerobic digested (Calgary (Fish Creek))	18100	18500	480	180	3250	3.9	4.1
Anaerobic digested (Edmonton (Goldbar))	17800	18600	350	150	3680	2.9	6.4
Anaerobic digested (Guelph)	14500	14900	350	130	2180	1.8	2.4
Anaerobic digested (Ingersoll)	4460	6270	160	60	1200	2.3	2.8
Anaerobic digested (Ottawa)	18800	16700	370	130	3080	2.7	4.9
Anaerobic digested (Regina)	12600	12000	320	120	1870	2	4.1
Anaerobic digested (Saskatoon)	8890	9440	180	110	1650	3.3	4.8
Anaerobic digested (Toronto (Ashbridges Bay))	24300	12400	300	120	2290	13	8.3
Anaerobic digested (Toronto (Humber))	26700	12300	310	110	1610	6.9	4.5
Digested sludge (Toronto (North))	24500	12100	220	90	2330	3.8	7.2
Anaerobic digested (Vancouver)	9580	9050	260	60	1240	1.4	1.4
Anaerobic digested (Waterloo)	7340	12700	490	90	1810	2.9	2.2
Anaerobic digested (Windsor)	7810	9510	370	150	1380	3.4	36.7
Median concentration raw sludge	11850	8005	175	110	1345	18.95	144.5
Median concentration anaerobic digested biosolids	14500	12300	320	120	1870	3.3	4.5

Table 76. Polycyclic Musk Compounds in Canadian Sludge and Biosolids Samples

Sludge Source	Fragrance Concentration (ng/g TS)						Reference
	Galaxolide (HHCB)	Tonalide (AHTN)	Celestolide (ADBI)	Phantolide (AHDI or AHMI)	Traesolide (ATII)	Cashmeran (DPMI)	
Raw sludge #1	12000	3550	100	79.6	681	nd	Smyth *et al*. (2007)
Aerobic digested biosolids #1	9430	2110	67.3	57.4	465	nd	
Raw sludge #2	33700	5860	207	114	1420	nd	
Aerobic digested biosolids #2	40300	8490	255	162	1890	nd	
Raw sludge #3	28400	8020	209	182	1400	nd	
Anaerobic digested biosolids #3	42000	10400	280	201	1910	nd	
Raw sludge #4	30200	8210	208	209	1500	nd	
Anaerobic digested biosolids #4	55500	13800	424	432	2880	nd	
Raw sludge #5	42600	11500	456	191	1630	nd	
Anaerobic digested biosolids #5	46300	10500	510	441	1720	nd	
Raw sludge (Canadian survey)	1300 – 22000 (9800) [a]	5400 – 11000 (7600)	130 – 390 (190)	70 – 340 (110)	1000 – 2100 (1300)	na	Webber and Sidwha (2005)
Digested biosolids (Canadian survey)	4500 - 25000 (15000)	6300 - 21000 (12000)	160 – 570 (320)	60 - 180 (120)	1200 – 4200 (1900)	na	
Raw sludge	3303	720	23.6	20.1	198.5	31.4	Yang and Metcalfe (2005)
Return activated sludge	3310	776	29.7	27.1	264	46.9	
Digested biosolids	6788	1349	51.2	33.8	413	57.3	
median raw sludge (n=7)	29300	6940	208	148	1410		
median aerobic biosolids (n=2)	24870	5300	161	110	1178		
median anaerobic biosolids (n=4)	44150	10450	352	317	1815		

na = not analysed; nd = not detected

[a] median value in parentheses

Table 77. Nitro Musk Compounds in Canadian Sludge and Biosolids Samples

Sludge Source	Fragrance Concentration (ng/g TS)					Reference
	Musk Xylene (MX)	Musk Ketone (MK)	Musk Ambrette (MA)	Musk Moskene (MM)	Musk Tibetene (MT)	
Raw sludge #1	64.6	115	44	nd	nd	Smyth *et al.* (2007)
Aerobic digested biosolids #1	18.9	45.3	31.3	nd	nd	
Raw sludge #2	96.9	290	nd	151	19.5	
Aerobic digested biosolids #2	25.1	242	nd	6	67.2	
Raw sludge #3	78.2	116	nd	nd	nd	
Anaerobic digested biosolids #3	61	8.16	nd	nd	nd	
Raw sludge #4	59.8	148	11.5	nd	nd	
Anaerobic digested biosolids #4	81.5	11.2	7.6	nd	nd	
Raw sludge #5	25	226	93.2	nd	nd	
Anaerobic digested biosolids #5	3.4	27.6	nd	nd	nd	
Raw sludge (Canadian survey)	4 – 422 (16)[a]	17 – 364 (124)				Webber and Sidwha (2005)
Digested biosolids (Canadian survey)	1 – 7 (3)	1 – 37 (5)				
Raw sludge	76.6	39.8	nd	nd	nd	Yang and Metcalfe (2005)
Return activated sludge	115	73.1	nd	nd	nd	
Digested biosolids	95.1	53	nd	nd	nd	
median raw sludge (n=7)	70.6	132				
median aerobic biosolids (n=2)	22	143.7				
median anaerobic biosolids (n=4)	71.25	19.4				

nd = not detected
[a] median value in parentheses

As observed with the data of Lee *et al*. (2003), aerobic digestion resulted in a decrease in the concentrations of the polycyclic musks in Table 76, whereas increased concentrations of the polycyclic musks were observed following anaerobic digestion.

With respect to nitro musks, the data in Table 77 indicate that Musk ketone and Musk xylene were the dominant compounds, with the Musk ketone present at the highest concentrations. Musk ambrette, Musk moskene and Musk tibetene were detected sporadically in the survey by Smyth *et al*. (2007), and were not detected in the Peterborough sludge samples by Yang and Metcalf (2005). Data in Table 77 used to estimate median concentrations present a confusing picture, likely due to the limited sample sizes used for assessment. The evaluation indicated that Musk xylene concentrations in raw sludge would be reduced by aerobic digestion, but were essentially unchanged by anaerobic digestion. Conversely, it appeared that Musk ketone would be reduced in concentration by anaerobic digestion of the raw sludge (in agreement with the data from Lee *et al*. (2003)), whereas aerobic treatment would result in a slight increase in concentration.

Additional polycyclic musk concentration data from other biosolids samples are provided in Table 78. HHCB an AHTN are the most commonly characterized polycyclic musks in these samples. When other polycyclic musk data are presented, the concentrations are much lower than those reported for HHCB and AHTN.

In addition to the polycyclic and nitro musks identified above, a number of other fragrance compounds have been identified. These are summarized in Table 79. Most of the additional compounds were identified in the literature survey of biosolids completed by Harrison *et al*. (2006).

Kinney *et al*. (2006) reported high levels of indole (maximum value of 7,000 ng/g OC) and d-limonene (maximum value of 744 ng/g OC) in samples of return activated sludge and dewatered sludge. Otherwise, with the exception of musk ketone, and its derivative, amino musk ketone, the maximum concentrations of the alternate fragrance compounds were less than 100 ng/g TS.

Table 78. Concentrations of Polycyclic Musk Compounds in Biosolids from Other Studies

Biosolids Source	Concentration (ng/g TS)						Reference
	Galaxolide (HHCB)	Tonalide (AHTN)	Celestolide (ADBI)	Phantolide (AHDI or AHMI)	Traesolide (ATII)	Cashmeran (DPMI)	
Digested	26,000	4,000					Jones-Lepp and Stevens (2007)
Biosolids Class A	5,000-18,000	2,000-4,000					
Biosolids Class B	10,000	3,000					
Biosolids class A	13-177,000	78-427,000					
Waste activated sludge	3,210 ng/g OC	15,900 ng/g OC					Kinney *et al*. (2006)
Dewatered sludge	3,150 ng/g OC	16,700 ng/g OC					
Digested sludge	3,068 - 6,788	1,525-1,349					Heidler and Halden (2008)
Not specified	ND – 8,100	ND – 5,100	10–1,100	32–1,800	44–1,100	ND – 332	Harrison *et al*. (2006)
Unknown sludge (Germany)	4,300 – 13,000 (8,900)	4,000 – 13,000 (8300)	120 – 290 (200)				Webber and Sidwha (2005)

Table 79. Concentrations of Other Fragrance Compounds in Biosolids

Fragrance Compound	Concentration (ng/g TS)		Concentration (ng/g OC)	
	Not specified	Unknown sludge (Germany)	Waste Activated	Dewatered
Musk Xylene (MX)	ND – 32.5	<5		
Musk Ketone (MK)	ND – 1300	<10 – 60		
Acetyl Cedrene	9.0 – 31.1			
Amino Musk Ketone	ND – 362			
Amino Musk Xylene (AMX)	ND –31.5			
Diphenyl Ether	ND – 99.6			
Galaxolide lactone	0.6 – 3.5			
Hexyl salicylate	Trace – 1.5 [52			
Hexylcinnamic Aldehyde (Alpha)	4.1			
Methyl ionone (gamma)	1.1 – 3.8			
OTNE	7.3 – 30.7			
D-Limonene			744	630
Indole			4,290	7,000
Reference	Harrison *et al*. (2006)	Webber and Sidwha (2005)	Kinney *et al*. (2006)	

Concentration data for fragrance compounds in four biosolids treatment processes, including composting, lime treatment, heat drying, and anaerobic digestion are provided in Table 80 (LaGuardia *et al*., 2004; Kinney *et al*., 2006).

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

There are few data available on calculated removal efficiencies of fragrances during biosolids treatment. Studies by Carballa *et al*. (2007a, 2007b) focusing on treatment using anaerobic digestion are summarised in Table 81.

Table 80. Comparison of Fragrance Compound Concentrations in Biosolids Treatment Processes

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

Table 81. Removal Efficiencies of Two Polycyclic Musks by Anaerobic Digestion (Carballa et al., 2007a)

Anaerobic Sludge Type	Solids Retention Time (d)	Removal Efficiency	
		Galaxolide (HHCB)	Tonalide (AHTN)
mesophilic	30	60%	50%
	20	65%	60%
	10	70%	62%
thermophilic	20	70%	75%
	10	75%	85%
	6	80%	80%
Average		(69 ± 9)%	(63 ± 14)%

[a] mean ± standard deviation

The data presented in Table 81 are not intuitive, as they seem to indicate that the removal efficiencies decline as the solids retention time (SRT) in the digester increases. Typically longer SRT values provide greater time for acclimation and biodegradation to occur in a reactor. In general, the data indicate that removal efficiencies of the two polycyclic fragrances are similar, with HHCB being slightly more degradable than AHTN under mesophilic conditions. Removal efficiencies were nearly identical under thermophilic treatment.

Table 82 summarizes the effect of pre-ozonating sludge prior to anaerobic digestion under mesophilic and thermophilic conditions (Carballa *et al*., 2007b). Under mesophilic conditions, pre-ozonation of the feed sludge had a positive influence on the removal efficiency of the two musk compounds, with improvement of approximately 20 percentage points. In thermophilic treatment, the data appear to indicate that pre-ozonation resulted in lower removal efficiencies for the two musks. The cause of lower removal following pre-ozonation is unclear.

Table 82. Effect of Pre-Ozonation on Anaerobic Digestion of Two Polycyclic Musks (Carballa et al., 2007b)

Sludge Type	Operating condition and SRT	Removal Efficiency	
		Galaxolide (HHCB)	Tonalide (AHTN)
anaerobic digestion - mesophilic	Non-ozonated 20 d	(65 ±5) [a] %	(60 ± 5)%
anaerobic digestion - mesophilic	Ozonated 20 d	(85±0)%	(82±2)%
anaerobic digestion - thermophilic	Non-ozonated 10 d	(78 ± 10)%	(82 ± 1)%
anaerobic digestion - thermophilic	Ozonated 10 d	(69±2)%	(30±3)%

[a] mean ± standard deviation (n=2 or 3)

Studies conducted by Carballa *et al*. (2007a, 2007b) with spiked laboratory anaerobic reactors indicate digestion results in reduced concentrations of the HHCB and AHTN. The laboratory results disagree with the field data compiled by Lee and Peart (2002), Smyth *et al*, (2007, and Webber and Sidwha (2005) and Yang and Metcalfe (2005).

3.6.4 Fluorescent Whitening Agents

Fluorescent whitening agents (FWAs) are chemicals used with textiles and papers to increase the appearance of whiteness by absorbing invisible ultraviolet light and re-emitting it in the blue region of the visible spectrum. Concentrations of FWAs in sludge samples were reported in the survey of Harrison *et al*. (2006). The compound DAS 1 was observed to have the highest levels in this class of compounds, with a maximum value of 112,000 ng/g TS (Table 83). The agent DSBP was present at approximately half the concentration of DAS 1, while the compound BLS was an approximate order of magnitude lower than the DSBP levels.

Table 83. Concentration of Fluorescent Whitening Agents in Biosolids (Harrison et al., 2006)

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

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

3.6.5 Quaternary Ammonium Compounds

Quaternary ammonium compounds represent an important class of cationic surface-active agents which are used in a variety of commercial products. They are associated with an anion, which may include either a halide salt (chloride, bromide, etc.), sulfate, carbonate, acetate, or nitrate. Quaternary ammonium compounds are generally classified as monoalkyltrimethyl ammonium salts, monoalkyldimethylbenzyl ammonium salts, and dialkyldimethyl ammonium salts (Petrille and Werner, 1996).

Quaternary ammonium compounds have an extremely strong affinity for negatively charged substrates. Their highly adsorptive properties make them suitable for a wide variety of commercial applications. They are used as agents in personal care products such as fabric softeners, laundry detergents, anti-static sprays. In heavy industrial applications, they are used to enhance flotation properties in the mining industry, in asphalt and petroleum additives, and in the manufacturing of drilling muds. Other major uses include corrosion inhibitors, germicides/deodorizers, and biocides. Because of their germicidal and biocidal properties, quaternary ammonium compounds may be acutely toxic to specific aquatic organisms at concentrations as low as 10 μg/L (Petrille and Werner, 1996). In Europe, the detergent industry began a voluntary phase-out of the QAC ditallowdimethylammonium chloride in the 1990s.

Concentrations of the QAC ditallowdimethylammonium cation (DDAC-C18) in the anaerobically digested biosolids of six Swiss wastewater treatment plants were documented by Fernández *et al* (1996). Concentrations were high compared to other ESOCs, in the mg/g dry weight range corresponding to concentrations in the parts per thousand range. The intent of the study was to monitor the decline of the QAC following its substitution in laundry products in 1991. In the base year of 1991, prior to the phase-out of the compound, the mean concentrations in digested sludges from the six treatment plants ranged from 2.57 to 5.87 mg/g DS (**Table 84**). Over the span of three years, the mean concentration of the DDAC-C18 declined by approximately 90% from 1991 levels. Because no concentration data were reported for the digester feed sludge, it is not possible to determine the removal of this compound by anaerobic digestion.

Table 84. Concentrations of the QAC Ditallowdimethylammonium Cation in Anaerobically Digested Biosolids from 6 Swiss Wastewater Treatment Plants (Fernández et al., 1996).

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

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

More recently, Martinez-Carballo *et al*. (2007) reported concentrations of several QACs in sludges (type not revealed) from three Austrian wastewater treatment plants, collected during two sampling campaigns in 2004. Total concentrations of all QACs ranged from 22 to 103 mg/kg (ppm), which is similar in magnitude to the concentrations reported by Fernández *et al* (1996) in 1993 and 1994 (Table 84). The compound C18-chain DDAC (ditallowdimethylammonium cation), which was replaced in fabric softeners by the detergent industry in the 1990s, continued to be the predominant species present, with a median concentration (n=6) of approximately 10 mg/kg DS. Other QACs at elevated concentrations included C12-chain benzalkonium chloride (BAC-C12), C14-chain benzalkonium chloride (BAC-C14), and C10-chain DDAC (didecyldimethylammonium cation). The C16-chain trialkylammonium chloride was also detected at elevated concentrations, ranging from 0.16-8.4 mg/kg DS (Martinez-Carballo *et al*., 2007).

No other removal efficiency publications for QAC concentrations in biosolids and sludges were identified.

3.6.6 Siloxanes

Siloxanes are organic silicon polymers manufactured as additives that improve the properties of personal care products such as cosmetics, shampoos and deodorants. Industrial applications include paper coatings and textile manufacturing. Their use is widespread due to beneficial properties of low surface tension and water-repelling activity. Octamethylcyclotetrasiloxane (D4) and decamethylcyclopentasiloxane (D5) are the most common cyclical siloxanes found.

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

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

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

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

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

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

Removal of the predominant siloxanes octamethylcyclotetrasiloxane (D4) and decamethylcyclopentasiloxane (D5) by chemical oxidants in spiked laboratory-scale waste activated sludge tests was examined by Appels *et al*. (2008). The oxidants examined included Fenton's reagent (hydrogen peroxide in the presence of iron salts), peroxymonosulphate (POMS) and dimethyldioxirane (DMDO). Results are presented in Table 85.

Table 85. Removal of Siloxanes D4 and D5 by Chemical Oxidation (Appels et al., 2008)

Chemical Oxidant	Dosage Rate	Percent Reduction by Dosage (%)	
		octamethylcyclotetrasiloxane (D4)	decamethylcyclopentasiloxane (D5)
Fenton's Reagent H_2O_2 dosage (g/kg DS)	15	20%	26%
	25	29%	37%
	35	38%	40%
	50	48%	43%
Peroxymonosulphate (POMS) dosage (g/kg DS)	5	20%	25%
	15	36%	29%
	30	36%	38%
	60	38%	42%
Dimethyldioxirane (DMDO) dosage (mL/kg DS)	55	17%	43%
	165	48%	45%
	330	72%	47%
	660	85%	48%

Removal efficiencies of D4 and D5 were typically in the 40% to 50% range for the oxidants at the highest dose rates applied, although the DMDO appeared to result in a substantially better reduction of D4 at the two highest doses, reaching an 85% reduction efficiency at a dose rate of 660 mL of DMDO per kg DS.

No other removal efficiency publications for siloxane concentrations in biosolids and sludges were identified.

3.6.7 Section Summary

Important points regarding personal care products in sludges are as follows.

1. Triclosan is found in sludge and biosolids samples at a concentration approximately an order of magnitude higher than is hexachlorophene.
2. Concentration data for triclocarban in sludges and biosolids are extremely sparse.
3. There is no apparent reduction of triclosan by anaerobic digestion or other biosolids treatment processes such as composting, lime addition or heat treatment.
4. Polycyclic musks are present at higher concentrations than nitro musks.
5. HHCB and AHTN are the predominant polycyclic musks, followed by ATII.
6. The two main nitro musks identified in sludge samples were Musk ketone and Musk xylene.
7. Full-scale anaerobic digestion does not appear to reduce concentrations of polycyclic musks in sludges, with concentrations in the digested biosolids higher than in the raw sludge. Laboratory spiked studies indicate reduction in AHTN and HHCB concentrations are possible.
8. Aerobic treatment conversely, appears to cause a reduction in concentrations of polycyclic musks.
9. Documentation of the occurrence of the quaternary ammonium compounds in sludges and biosolids is limited, but reported concentrations of the compounds are significantly higher than for many of the other types of ESOCs.
10. Occurrence and concentrations of siloxanes in sludges and biosolids are poorly documented.
11. There are insufficient data reported in the literature to determine the effectiveness of the different biosolids treatment processes for reductions of the personal care products.

3.7 METALS AND METALLOIDS

3.7.1 Introduction

Concentrations of metals in sludges and biosolids have been of concern for decades because of the use of biosolids as a soil amendment in agriculture and silviculture, as well as in recreational uses in parks and golf courses. Concentrations of metals have been reported and have been well documented in other surveys dating back to the early 1970s (e.g., Leeper, 1972; Page 1974) and later in the 1980s and 1990s (e.g., Monteith, 1987, Canviro Consultants Ltd. 1988; Webber and Nichols, 1995) and more recently (XCG, 2007). Reported concentrations of the most common metals and elements are typically in the mg/kg (ppm) range. The intent of this review is not to duplicate these earlier efforts given the project schedule, but to retrieve and expand the body of literature in a limited review of more recent data.

The substances included in this review include a number of elements that include both metals and metalloids, such as arsenic and selenium, which will be referred to as “metals” for simplicity. Metals accumulate in sludges at wastewater treatment when they are discharged by domestic and industrial sources. Aluminum and selenium are present in personal care products. Copper, lead and zinc can enter wastewater from plumbing. Concerns with the metals in biosolids are related to their potential uptake by agricultural crops or foraging animals. Because of the diversity of the metals in this class of contaminants, concerns with respect to human health can be varied. Mercury, cadmium and lead are neurotoxins for example, while cadmium has also been linked to kidney disease.

3.7.2 Occurrence Data

A comprehensive survey of concentrations of metals in the U.S. was recently released by the EPA (2009) in the Targeted National Sewage Sludge Survey (TNSSS) report. Concentrations from this and other recent surveys are presented in Table 86. The EPA survey provides a list of both commonly reported metals and those that are less well documented. The data provided in Table 86for the rows of metals below selenium are not as reported in the source table from the EPA (2009) report (Table B-7). In comparison with that report’s Table B-6, the values of Table B-7 have been shifted by one row (Stevens, 2009). The effect is that in Table B-7, the reported concentration for thallium is almost two orders of magnitude higher than that for sodium, and the concentration of zinc is less than those for the uncommon elements vanadium and yttrium. As a result, the values from Table B-7 following selenium by row have been shifted upwards by one row for compiling in Table 86 and the value for zinc, which is then missing, was taken as the value reported as “Aggregated Data” in Table B-6 of the EPA (2009) report.

Concentrations of metals common to the three surveys provided in Table 86 are relatively consistent, on an order of magnitude basis, between the three studies. In the TNSSS, (U.S. EPA, 2009), aluminum and iron are present at the highest concentrations because they are metals frequently used as flocculants and precipitants for phosphorus in wastewater treatment. Zinc and copper are among the next highest concentrations, at median concentrations of 764 and 446 mg/kg respectively. Data provided by Perron and Hébert (2007) for sludges from 14 mechanical treatment facilities in Québec and by Ruel *et al*. (2008) for a chemically-assisted primary sludge are in agreement with zinc and copper present at the highest concentrations of the metals analysed. Zinc and copper were not among the metals in sludges reported by XCG (2007), in which the metals with the highest concentrations were chromium and lead. In the EPA (2009) report, the median concentration of mercury (0.83 mg/kg TS) is higher than for the less frequently reported beryllium and thallium 0.27 and 0.13 mg/kg TS, respectively.) The concentration data from the 14 Quebec treatment plants (Perron and Hébert, 2007) are substantially lower than concentrations for the same metals reported by the EPA (2009).

3.7.3 Organotin Compounds

Concentrations of organotin compounds in sludges have received some attention because of their toxic properties to aquatic organisms. Table 87 provides concentration data for organotin

Table 86. Concentrations of Metals in Sewage Sludges and Biosolids.

Metal/Metalloid	Concentration (mg/kg TS)			
	sewage sludge survey	Mean of 14 Quebec mechanical plants (2002-2006)	17 Canadian sludges (1995-1998)	anaerobic digestion, limed, drying
Aluminum (Al)	13,480 (11,200)[a]			
Antimony (Sb)	2.26 (1.42)			
Arsenic (As)	6.76 (4.95)	4.3	0.6 - 4 (2)[b]	not reported
Barium (Ba)	572 (452)			
Beryllium (Be)	0.38 (0.27)			
Cadmium (Cd)	2.48 (1.72)	1.2	0.2 – 13 (5)	3.5 ± 21[c]
Chromium (Cr)	78.2 (30.6)	33	15 – 1,800 (82)	43.2 ± 38
Cobalt (Co)	11.0 (4.44)	7.9		
Copper (Cu)	559 (449)	521		335 ± 338
Iron (Fe)	24,740 (13,250)			
Lead (Pb)	74.0 (44.4)	29	4.6 – 186 (75)	71 ± 70
Mercury (Hg)	1.27 (0.83)	0.9	0.5 - 5 (2.6)	3 ± 2.3
Molybdenum (Mo)	15 (11)	6.9		
Nickel (Ni)	47.4 (22.8)	34	8 – 68 (36)	28.6 ± 38
Selenium (Se)	7.1 (6.2)	2		
Silver (Ag)	31 (22)			
Thallium (Th)	*0.17 (0.13)*			
Tin (Sn)	*43.5 (36.2)*			
Titanium (Ti)	*221 (80.9)*			
Vanadium (V)	*33.9 (11.6)*			
Yttrium (Y)	*4.55 (3.54)*			
Zinc (Zn)	*970 (764)*	392		875 ± 1005
Reference	EPA (2009)	Perron and Hébert (2007)	Webber and Nichols (1995)	Ruel *et al.* (2008)

[a] mean (median) (n=74) [b] range (median)

[c] mean ± standard deviation (literature survey, number not specified)

for cells in *grey shading* see text above for explanatory note

Table 87. Concentrations of Organotin Compounds in Sludges

Organotin compound	Concentration (mg/kg TS)			
	Survey 25 Swiss plants	Literature	Raw sludge (16 results)	Digested sludge (18 results)
Triphenyltin	0.50	0.04 - 3.4	not reported	not reported
Tributyltin	1.1	0.1 - 3.4	0.014 – 0.176 (0.095)[a]	0.072 – 0.502 (0.111)
Dibutyltin	1.5	0.04 - 4.8	0.076 – 0.336 (0.146)	0.098 – 0.424 (0.264)
Monobutyltin	0.5	0.02 - 6.9	0.113 – 0.205 (0.144)	0.211 – 0.357 (0.254)
Total butyltin	not reported	not reported	0.240 – 0.524 (0.388)	0.424 – 1.080 (0.616)
Reference	Fent (1996)		Webber and Sidwha (2005)	

[a] range (median)

compounds from two publications. Concentrations of the organtins in the earlier literature provided by Fent (1996) are higher than those reported in Webber and Sidwha (2005) for data from the North Toronto plant. In the Toronto data, the monobutyltin and dibutyltin appear to be present at a slightly higher concentration than tributyltin. The data of Fent (1996) include the compound triphenyltin, present at concentrations similar to the butyltin compounds. The survey of sludges by Ruel *et al*. (2008) listed a concentration of tribute tin as 0.09 ± 0.05 mg/kg TS, which is similar to the values presented by Webber and Sidwha (2005), but lower than those of Fent (1996).

The data of Webber and Sidwha (2005) comparing the butyltins in raw and digested sludges form the North Toronto plant indicate that the compounds are not reduced by anaerobic degradation. Conversely, Fent (1996) identified that some biodegradation of tributyltin was possible (up to a maximum of 30%) based on laboratory studies of aerobic and anaerobic digestion under both mesophilic and thermophilic conditions.

3.7.4 Section Summary

The main points of interest from this survey follow.

1. The concentration database for metals and metalloids is limited because this review was focused on data from the year 2000 on, and much of the documented research on metals occurred previously.
2. After iron and aluminum, the metals of highest concentration are zinc and copper, two metals commonly used in household plumbing.
3. There are few data characterizing concentrations of elements such as beryllium, thallium, antimony, titanium, and vanadium in biosolids.
4. Organotin compounds are present in sludges at low concentrations of less than 1 mg/kg TS (less than 1,000 ng/g TS).
5. Limited data suggest the organotin compounds are not reduced in concentration by anaerobic digestion.

3.8 OTHER SUBSTANCES

3.8.1 Introduction

This section brings together compounds which were not readily included in the previous sections. The major groupings include polyaromatic hydrocarbons (PAHs) and polychlorinated polyaromatic compounds (biphenyls (PCBs); dibenzofurans (PCDFs); and dibenzo-p-dioxins (PCDDs).

PAHs are a product of carbon combustion, and enter the environment from volcanoes, forest fires, residential wood burning, and exhaust from automobiles and trucks (NRCC, 1983). Atmospheric deposition, and road oils and exhaust particulates are thus major routes to wastewater treatment via combined sewers. Food cooked at high temperatures (e.g., grilling of barbecuing) may also produce PAHs, which may then be discharged with dishwater. PCBs were once widely used in a variety of products such as electrical transformer fluids, but their manufacture and use have been phased out. PCDDs and PCDFs result from combustion of products consisting of chlorinated organics (e.g. polyvinyl chloride plastics) and as a by-product of pentachlorophenol production. Atmospheric deposition of these chlorinated substances is likely a major contributor in wastewater treatment. Health concerns related to the PAH and polychlorinated polyaromatic classes of compounds are as potential human carcinogens.

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

3.8.2 Polyaromatic Hydrocarbons

Concentrations of the PAHs in sludges are provided in Table 88. Based on the survey of Canadian sludges (XCG, 2007), these compounds have median concentrations typically lying in the range of 100 to 1500 ng/g TS. The simplest PAHs, naphthalene and phenanthrene, consisting of two and three fused benzene rings, respectively, have the highest median concentrations of the PAHs in the Canadian survey (XCG, 2007) at 2,700 (phenanthrene) and 1,500 (naphthalene) ng/g TS. The literature review of Harrison *et al*. (2006) demonstrated that the maximum concentrations of the PAHs could be higher than those summarized by XCG (2007), with the upper range of naphthalene, methylnaphthalene isomers and benzo(a)anthracene at or above 100,000 ng/g TS. The U.S. EPA's TNSSS (EPA, 2009) included only two PAHs on its list of target analytes. Median concentrations of benzo(a)pyrene and 2-methylnaphthlene were 302 and 200 ng/g TS, respectively. Concentrations of four PAHs reported by Kinney *et al*. (2006) in waste activated sludge and dewatered sludge were less than 200 ng/g organic carbon.

Concentrations of PAHs following biosolids treatment processes were provided by Kinney *et al*. (2006) and appear in Table 89. For the lower molecular weight PAHs anthracene and phenanthrene, composted and air dried biosolids have apparent lower concentrations than biosolids produced by heat drying or after anaerobic digestion. This trend did not follow through in the two higher molecular weight PAHs fluoranthene and pyrene, for which there was no discernible difference between composting air drying and heat drying. The anaerobic digested sludge had the highest concentrations of the four PAHs examined. There are too few data to determine whether anaerobic digestion is the least effective biosolids treatment for reduction of PAHs.

3.8.3 Polychlorinated Polyaromatics

Concentrations of PCBs, PCDDs and PCDFs in sludges are summarized in Table 90 in two different units of expression. Some reports list the PCDDs and PCDFs in terms of toxic equivalents of the 2,3,7,8-tetrachlorodibenzo-p-dioxin, the most toxic congener of this class of compounds. For the literature surveyed, the range and means reported from different countries appear to be very similar, with mean values in the range of 0.020 ng TEQ/g TS. More recent data from Québec and Ontario (unpublished) indicate a median of 0.008 ng TEQ/g TS for land applied biosolids. Concentrations of the PCDDs and PCDFs as total congener concentrations were documented by XCG (2007), with mean values of the total congeners at least an order of magnitude higher than the TEQ-based concentrations.

Table 88. Concentrations of Polyaromatic Hydrocarbons in Sludges

Compound	Concentration (ng/g TS)				
	19 Canadian sludges	Sludge survey	Literature review	WAS[c]	Dewatered sludge[c]
Acenaphthene	nd - 3,000 (400)[a]		nd - 6,600		
Acenaphthylene	nd – 3,400 (100)		3.6 - 300		
Anthracene	3 – 3,300 (200)		nd - 44,000	92	74
Phenanthrene	900 - 14,000 (2,700)		<10 - 44,000	159	166
Benzo(a)anthracene			nd - 99,000		
Chrysene			nd - 32,400		
Benzo(a)anthracene + Chrysene	170 – 36,000 (1,100)				
Benzo(b)fluoranthene + Benzo(k)fluoranthene	130 – 39,000 (700)		6 - 34,200		
Benzofluorene congeners			nd - 8,100		
Benzo(g,h.i)perylene	30 - 15,000 (300)		nd - 12,900		
Benzo(a)pyrene	50 - 25,000 (300)	661 (320)[b]			
Benzopyrene congeners			nd - 24,700		
Dibenzo(ah)anthracene	nd - 5,100 (20)				
Dibenzoanthracene congeners			nd - 13,000		
Fluoranthene	250 - 27,000 (1,000)		nd - 60,000	166	166
Fluorene	nd - 3,300 (800)		<10 - 8,100		
Indene(1,2,3-cd)pyrene	nd - 15,000 (200)		nd - 9,500		
Naphthalene	80 - 13,000 (1,500)		nd - 6,610,000		
Perylene			nd - 69,300		
Pyrene	260 - 24,000 (1,300)		10 - 37,100	186	169
2-methylnaphthylene		449 (200)			
Methylnaphthalene isomers			nd - 136,000		
Methylphenanthrene isomers			nd - 37,400		
Reference	XCG (2007)	EPA (2009)	Harrison *et al.* (2006)	Kinney *et al.* (2006)	

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

Table 89. Concentrations of Polyaromatic Hydrocarbons following Biosolids Treatment Processes (Kinney et al., 2006)

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

No removal efficiency data for PAHs were identified in the literature review.

Table 90. Concentrations of Polychlorinated Polyaromatics in Sludges

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

^{a} range (mean)   nd = not detected

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

3.8.4 Section Summary

The main points of interest from this section follow.

1. The upper range of naphthalene, methylnaphthalene isomers and benzo(a)anthracene were at or above 100,000 ng/g TS in the literature review of Harrison *et al*. (2006), although a survey of Canadian sludges resulted in median concentrations typically lying in the range of 100 to 1,500 ng/g TS.
2. The simplest PAHs, naphthalene and phenanthrene, consisting of two and three fused benzene rings, respectively, have the highest median concentrations of the PAHs in the Canadian survey.
3. Data on the effect of biosolids treatment processes on reducing concentrations of PAHs are very limited. For the lower molecular weight PAHs anthracene and phenanthrene, composted and air dried biosolids have apparent lower concentrations than biosolids produced by heat drying or after anaerobic digestion. The anaerobic digested sludge had the highest concentrations of the four PAHs examined.
4. For the literature surveyed, the range and means of the PCDDs and PCDFs reported from different countries appear to be very similar, with mean values in the range of 0.020 ng TEQ/g TS.
5. Concentrations of total PCBs listed in Canadian sludge samples appeared to be higher than corresponding sludge samples from Europe.

4. CONTAMINANTS IN SEPTAGE

The electronic databases were also searched for publications reporting on the occurrence and fate of emerging substances of concern (ESOCs) in septage or septage applied to land. The search revealed an almost complete lack of information on these topics. A considerably larger body of literature can be found with respect to transport and fate of contaminants in septic tank effluent, however this was deemed outside of the scope of the report, concerning biosolids or septage, as the residual solids, which might be used in beneficial applications.

The two studies of occurrence of ESOCs in septage that were identified in the literature search related to investigation near Cape Cod, MA. The data on occurrence and concentrations in the two studies are provided in Table 91. Within the data are recognizable classes of ESOCs including alkylphenol and their ethoxylates, the plasticizer Bisphenol A, estrogenic hormones (E2 and E1), fluorescent whitening agents (DAS and DBSP), the anti-oxidant BHA used in food packaging and several chlorophenols. Caffeine and its metabolite paraxanthine were also identified in one of the studies.

The data provided in Table 91 provide only a limited overview of the occurrence and concentrations of certain target analytes. There is no identification or potential removal of the contaminants through the septic tank (i.e. anaerobic treatment).

Because there are many types of ESOCs, few surveys can afford to test for all the different potential classes. For example, no data were found regarding occurrence, concentrations or removal efficiencies of pharmaceuticals, flame retardants, perfluorinated substances, and other personal care products such as anti-microbials.

Table 91. Occurrence and Concentrations of ESOCs in Septage

Contaminant	No. Detects/ No. Analyzed	Conc'n (µg/L)		Conc'n (µg/L)
		Range	Mean of Detects	2 samples reported
Nonylphenol	2/2	1000-1500	1200	16, 10
Octylphenol	2/2	35-42	39	
Octylphenol monoethoxylate	2/2	8.0-9.8	8.9	
Octylphenol diethoxylate	0/2	n.d.	n.d.	
Nonylphenol monoethoxylate	2/2	440-580	510	
Nonylphenol diethoxylate	2/2	79-100	90	
Sum nonylphenol mono-, di- and triethoxylates				3.9, 4.8
Nonylphenol monoethoxycarboxylate	2/2	37-57	47	7.8, 8.2
Nonylphenol diethoxycarboxylate				1.6, 2.3
Bisphenol A	4/5	0.11-1.7	0.82	
4,4'-dihydroxybiphenyl (4,4'-biphenyldiol)	5/5	0.04-1.4	0.77	
4-tert-butylphenol	5/5	0.16-3.2	0.85	
Phenylphenol (total)	5/5	0.16-3.9	1.7	
4-tert-pentylphenol	2/5	0.03-0.03	0.03	
Butylated hydroxyanisole (BHA)	5/5	0.13-0.53	0.3	
2-sec-butylphenol	2/5	0.03-0.08	0.055	
4-nitrophenol	1/5	1 detect	0.16	
6-bromo-2-naphthol	1/5	1 detect	0.05	
2,4-dichlorophenol	2/5	0.07-0.10	0.085	
3,4-dichlorophenol	1/5	1 detect	0.02	
3,5,6-trichloro-2-pyridinol	2/5	0.16-0.19	0.18	
Pentachlorophenol	2/5	0.04-0.05	0.045	
DAS [4,4-bis[(4-anilino-6-morpholino-1,3,5- triazin-2-yl)amino]stilbene-2,2-disulfonate]				2.04, 1.67
DSBP [4,4-bis(2-sulfostyryl)biphenyl]				0.0065, 0.0028
Caffeine				22.9, 17.3
Paraxanthine (caffeine metabolite)				65.1, 54.9
E2 (17-β-estradiol)				0.019, 0.016
E1 (Estrone)				0.074, 0.049
Boron				216±8
Reference	Rudel *et al*. (1998)			Swartz *et al*. (2006)

5. ANALYSIS OF LITERATURE REVIEW FINDINGS

The interpretation of the published results on occurrence, concentrations and removal efficiencies of contaminants in sludges and biosolids is complex. Terminology of residual wastewater solids, as used by the different authors in the publications, is not consistent. Based on definitions provided in Section 1, the references to “sludge” in the publications reviewed are construed to mean “sewage sludge”. Often, however, the word sludge may be used when in fact the more appropriate term may be “biosolids”, as the residual solids have been subjected to a stabilization process. In much of the data reviewed, including other literature reviews, the sludges or biosolids are not specified by type (raw or treated, primary or secondary, etc) which makes the effort of determining if some processes are more beneficial than others in minimizing the concentrations of these substances. Some reviews, which summarize concentration data, group different types of sludges together without regard to the nature of the sludges.

There is a great disparity in published literature in the attention devoted to the occurrence of different ESOCs in sludges and biosolids. Some compounds have been examined comprehensively, and there is a substantial database on occurrence of these substances. Examples of the well-documented substances include the plasticizer bis(2-ethylhexyl)phthalate, the surfactant nonylphenol and some of its ethoxylates, the synthetic musk fragrances HHCB and AHTN, the flame retardants polybrominated diphenyl ethers, and the bacteriostat triclosan. In other cases however, there is a significant lack of information on concentrations of other ESOCs in sludges and biosolids, including many antibiotics and other pharmaceuticals. CCME’s report on the State of Knowledge of Municipal Effluent Science and Research identified many classes of personal care products in treated effluents, including parabens (anti-microbial preservatives), sunscreen agents and insect repellents, for which no occurrence data in sludges or biosolids were identified. Lack of adequate analytical protocols may hinder this effort.

There appeared in the review to be evidence that sludges from some countries have lower concentrations than others, which may be reflective of manufacturing, consumption or use restrictions. Such products include brominated flame retardants and pharmaceuticals.

The concentrations of different ESOCs reviewed in this report can vary widely in sludges and biosolids, from the low part per billion (ng/g TS) (e.g. estrogens and androgens to the part per thousand level, for plant and animal sterols, and from literature in the 1990s, linear alkylbenzene surfactants. LAS concentrations may now be lower, but there is a scarcity of recent data for these compounds. Table 92 provides a depiction of the concentration ranges observed in sludges and biosolids in this review.

High concentrations (e.g., mg/g TS range) of substances identified in the sludges and biosolids are not necessarily a cause for concern. The plant and animal sterols for example are natural products that may serve as an anthropogenic indicator or marker. Conversely, very low concentrations (e.g., ng/g TS range) of substances such as hormones, polybrominated diphenyl ethers and perfluorinated organic compounds that may be found in biosolids destined for land application are likely to be of greater concern due to their potential for endocrine disruption or persistence, bioaccumulation or toxicity.

Table 92. Approximate Range of Concentrations of ESOCs in Sludges and Biosolids

Contaminant or Class of Contaminants	Concentration Range		
	parts per billion (ng/g TS)	parts per million (µg/g TS)	parts per thousand (mg/g TS)
Bisphenol A	■	■	
Phthalates	■	■	
PFOCs	■		
LAS		■	■
Chlorophenolics	■	■	
Pesticides	■	■	
Solvents	■		
Alkylphenols		■	
PBDEs	■		
Pharmaceuticals	■	■	
Estrogens and androgens	■		
Plant Sterols		■	■
Animal Sterols		■	■
Triclosan		■	
Musk Fragrances	■	■	
Quaternary Ammonium Compounds		■	
Siloxanes		■	
Polycyclic Aromatic Hydrocarbons	■	■	
Polychlorinated polyaromatics	■		

With respect to different biosolids treatment processes, in most publications only the final treated biosolids concentrations are typically documented. Without the accompanying raw sludge concentrations, an evaluation of the effectiveness of the processes becomes more tenuous. In the data provided by Kinney *et al*. (2006), there appears to be evidence of some reduction in ESOC concentrations resulting from certain biosolids treatment processes such as composting or drying, based only on differences in concentrations between the treated biosolids. Without raw sludge data, however, no firm conclusions can be drawn.

The potential of different biosolids treatment processes to reduce concentrations of contaminants in the feed sewage sludge, based on the literature data, is summarized in Table 93. Where a table entry is indicated as having some removal efficiency, the magnitudes of removal efficiency have not been differentiated.

The treatment process most characterized for ability to reduce contaminant concentrations is the anaerobic digestion process. For example in the studies by Carballa *et al*. (2006, 2007a, 2007b), concentrations of a variety of contaminants are provided for both raw sludge and sludges digested under different temperature regimes and retention times. From this review it appears that certain ESOCs can be reduced by anaerobic digestion, while others are recalcitrant (e.g., Bisphenol A, musk fragrances, triclosan), or perhaps even increased in concentration (e.g., 4-nonylphenol) by anaerobic biotransformation processes.

Table 93. Potential of Biosolids Treatment Processes for Reduction of ESOCs in Sewage Sludge

Compound or Class of Compounds	Aerobic digestion	Anaerobic digestion	Composting	Alkaline stabilis’n	Heat drying	Other drying (e.g. air or solar drying)
Industrial chemicals						
Bis(2-ethylhexyl) phthalate	NA	R	R	NA	R	NA
Alkylphenols and their ethoxylates	R	X	R	R?	R?	NA
Bisphenol A	NA	X	NA	NA	NA	NA
Linear alkylbenzene surfactants	R	N	NA	NA	NA	NA
Perfluorinated organic compounds	NA	NA	NA	NA	NA	NA
Brominated flame retardants	NA	R	NA	NA	NA	NA
Personal Care Products						
Anti-microbials	NA	X	NA	NA	NA	NA
Nitro musk fragrances	R	R	NA	NA	NA	NA
Polycyclic musk fragrances	X	X	NA	NA	NA	NA
Quaternary ammonium compounds	NA	NA	NA	NA	NA	NA
Siloxanes	NA	NA	NA	NA	NA	NA
Metals						
Organotins	NA	X	NA	NA	NA	NA
Other						
Polyaromatic hydrocarbons	NA	NA	NA	NA	NA	NA
Polychlorinated dioxins and furans	NA	NA	NA	NA	NA	NA

R = some reduction indicated
X = no reduction indicated
NA = no data available
R? = mixed results

It is evident from Table 93 that published knowledge of the potential for reduction of ESOCs in wastewater sludges by composting, alkaline stabilization or drying processes is incomplete.

There is a major lack of published data regarding ESOC occurrence, concentration and removal in septage. Only one study published after the year 2000 was identified, making difficult a comparison of concentrations in septage relative to other wastewater sludges or biosolids. No studies on the effectiveness of treatment of septage for reduction of ESOC concentrations were identified.

Because many of the ESOCs examined in this review are hydrophobic, they concentrate in the residual wastewater solids (sludges). The understanding of the fate of these compounds by different biosolids processes is largely unknown. Because land application of biosolids is an important management technique in Canada, it is desirable to minimize any potential adverse effects to the terrestrial environment due to amendment of soils with biosolids. Consequently, there is a need to understand whether certain biosolids treatment processes are better than others at reducing concentrations of ESOCs in wastewater sludges. With respect to non-persistent ESOCs in biosolids applied to land, a mitigating approach may be to prescribe an interim period between the time of land application and the beginning of seeding or grazing to allow soil microbes time to degrade the compounds.Should it be determined from literature studies or actual testing that certain types of ESOCs remain unaffected by biosolids treatment processes, then other means of limiting the concentrations of these recalcitrant compounds in biosolids should be explored, such as by source control, pretreatment and sewer use limits, or more extreme measures such as product re-formulations or outright bans on manufacture or use.

Reductions of metal concentrations such as nickel, chromium and cadmium were effectively accomplished in the 1980s and 1990s by source control, pretreatment and sewer use limits. In Switzerland, there was a clear reduction in LAS concentrations in biosolids after restrictions on the use of the compounds was implemented in the early 1990s. More recently, bans on use of certain PBDEs in European countries and North America are resulting in reduced concentrations of these compounds in biosolids.

6. RECOMMENDATIONS

Based on the literature review and above assessment, the following recommendations are offered:

1. There is a need to define criteria for what is an adequate database for characterization of contaminants in sludges and biosolids, then to apply the criteria to the compiled data. An example of the review criteria might consist of a minimum number of qualified references (e.g., n=6), and specified relative standard deviation about a mean concentration (e.g. RSD = 25%).
2. Where there are insufficient data, the availability of adequate analytical protocols for the ESOCs of interest needs to be determined by qualified analytical personnel. If adequate analytical procedures are not available, then method development should be set as a priority.
3. If acceptable analytical protocols are available, the sampling survey proposed as part of this study to investigate the ability of biosolids treatment processes to reduce concentrations of ESOCs in sewage sludge and biosolids should be .initiated. Assessment of biosolids treatment effectiveness requires both raw and treated biosolids samples, as well as any potential process sidestreams to aid in mass balance closures.
4. As part of the biosolids treatment survey, sites with septage treatment should be included so that a database of ESOCs in septage can be expanded.
5. In the proposed survey of biosolids treatment processes, within budgetary limits, different types of pharmaceuticals, synthetic musk fragrances and alkylphenols (including Bisphenol A) should be included as primary target analytes. Secondarily, as budgetary limitations permit, classes of ESOCs such as human hormones, brominated flame retardants, perfluorinated organic compounds, quaternary ammonium compounds, and siloxanes should be analysed.
6. Should it be determined from literature studies or actual testing that certain types of ESOCs remain unaffected by biosolids treatment processes, then other means of limiting the concentrations of these recalcitrant compounds in biosolids should be explored, such as by source control, pretreatment and sewer use limits, or more extreme measures such as product re-formulations or outright bans on manufacture or use. Such actions should be consistent across Canada.
7. Lastly, data produced by this and similar reviews, and by the forth-coming field investigation, need to be transferred out to appropriate agencies and researchers.

REFERENCES

Ahel, M., Molnar, E., Ibric, S. and Giger, W. 2000. Estrogenic metabolites of alkylphenol polyethoxylates in secondary sewage effluents and rivers. *Wat. Sci. Technol.* **42(7-8)**, 15-22.

Andersen, H., Siegrist, H., Halling-Sorensen, B., and Ternes, T.A., 2003. Fate of Estrogens in a Municipal Sewage Treatment Plant. *Environ. Sci. Technol*. **37(18)**, 4021-4026.

Angelidaki, I., Toräng, L., Waul, C.M., and Schmidt, J.E. 2004. Anaerobic bioprocessing of sewage sludge, focusing on degradation of linear alkylbenzene sulfonates (LAS). *Wat. Sci. and Technol.* **49(10)**, 115–122.

Appels, L., Baeyens, J. and Dewil, R., 2008. Siloxane removal from biosolids by peroxidation. *Energy Conversion and Management*, **49**, 2859–2864.

Barnabé, S., Beauchesne, I., Cooper, D.G., Nicell, J.A. 2008. Plasticizers and their degradation products in the process streams of a large urban physicochemical sewage treatment plant. *Wat. Res*., **42**, 153 – 162.

Bossi, R., Strand, J., Sortkjær, O., and Larsen, M.M., 2008. Perfluoroalkyl compounds in Danish wastewater treatment plants and aquatic environments. *Environment International* **34,** 443–450.

Brown, S., Clarke, D., Doubrava, M., O'Connor, G., 2008. Fate of 4-nonylphenol in a biosolids amended soil. *Chemosphere* **(2008),** in press.

CCREM (Canadian Council of Resource and Environment Ministers). 1987. Canadian Water Quality Guidelines.

Canada Gazette, 2008. Polybrominated Diphenyl Ethers Regulations under the Canadian Environmental Protection Act, 1999. Accessed February 24, 2009 at http://canadagazette.gc.ca/partII/2008/20080709/html/sor218-e.html.

Canviro Consultants Ltd. 1988. Thirty-seven municipal water pollution control plants: Pilot monitoring study Volume 1. Interim report. Report submitted to Ontario Ministry of the Environment. Toronto. December.

Carballa, M., Omil, F., Alder, A.C., Lema, J.M. 2006. Comparison between the conventional anaerobic digestion of sewage sludge and its combination with a chemical or thermal pre-treatment concerning the removal of pharmaceuticals and personal care products. Wat. Sci. & Technol., 53(8), 109–117.

Carballa, M., Omil, F., Ternes, T., Lema, J.M. 2007a. Fate of pharmaceutical and personal care products (PPCPs) during anaerobic digestion of sewage sludge. *Water Research*, **41**, 2139-2150.

Carballa, M., Manterola, G., Larrea, L., Ternes. T., Omil, F., Lema, J.M. 2007b. Influence of ozone pre-treatment on sludge anaerobic digestion: Removal of pharmaceutical and personal care products. *Chemosphere*, **67**, 1444-1452.

Carex Canada. 2009. Pentachlorophenol. http://www.carexcanada.ca/research/carcinogens/en/pentachlorophenol.pdf. Accessed June 24, 2009.

Cavalli, L. 2004. Surfactants in the Environment: fate and effect of linear alkylbenzene sulfonates (LAS) and alcohol-based surfactants. In: Handbook of Detergents. Part B. Environmental Impacts. Edited by U. Zoller., pp.373-348.

Chu, S. and Metcalfe, C.D. 2007. Simultaneous determination of triclocarban and triclosan in municipal biosolids by liquid chromatography tandem mass spectrometry. *Journal of Chromatography A*, **1164**, 212–218.

Clarke, B., Porter, N., Symons, R., Marriott, P., Ades, P., Stevenson, G. and Blackbeard, J. 2008. Polybrominated diphenyl ethers (PBDEs) and polybrominated biphenyls (PBBs) in Australian sewage sludge. *Chemosphere*, doi:10.1016/j.chemosphere.2008.06.034.

Das, K., and Xia, K., 2008. Transformation of 4-nonylphenol isomers during biosolids composting. *Chemosphere*, **70**, 761–768.

Daughton, C.G. and Ternes, T.A. 1999. Pharmaceuticals and Personal Care Products in the Environment: Agents of Subtle Change? *Environ. Health Perspectives*, **107(Supp. 6)** 907-938.

Dewil, R., Appels, L., Baeyens, J., Buczynska, A., and Vaeck, L. V., 2007. The analysis of volatile siloxanes in waste activated sludge. *Talanta*, **74**, 14–19.

Eljarrat, E., Marsh G., Labandeira, A., and Barcelo, D. 2006. Effect of Sewage Sludges Contaminated with Polybrominated Diphenylethers on Agricultural Soils. *Chemosphere*, **71**, 1079-1086.

Environment Canada, 2006. Ecological Screening Assessment Report on Polybrominated Diphenyl Ethers (PBDEs). Canadian Environmental Protection Act Environmental Registry. Accessed February 24, 2009 at http://www.ec.gc.ca/CEPARegistry/documents/subs_list/PBDE_SAR/PBDEs_SAR_EC_June_2006_(en).pdf.

Environment Canada 2009a. Contaminants in herring gull eggs from Great Lakes: 25 years of monitoring levels and effects. http://www.on.ec.gc.ca/wildlife/factsheets/fs_herring_gulls-e.html. Accessed June 24, 2009.

Environment Canada 2009b. Backgrounder: nonylphenol ethoxylates (NPEs). http://www.ec.gc.ca/CEPARegistry/subs_list/NPE_BG.cfm. Accessed June 24, 2009.

Environment Canada 2009c. Backgrounder – Siloxanes D4, D5 and D6. http://www.ec.gc.ca/default.asp?lang=En&n=714D9AAE-1&news=546F7166-9C61-4CA5-BB67-804EC3F2A0ED. Accessed June 26, 2009.

Fent, K., 1996., Organotin compounds in municipal wastewater and sewage sludge: contamination, fate in treatment process and ecotoxicological consequences. Sci. Tot. Environ. 185(1-3), 151-159.

Fernández, P., Alder, A.C., Suter, M., and Giger, W. 1996. Determination of the quaternary ammonium surfactant ditallowdimethylammonium in digested sludges and marine sediments by supercritical fluid extraction and liquid chromatography with post-column ion-pair formation. *Anal. Chem*., **68**, 921-929.

Gerecke, A., Giger, W., Hartmann, P., Heeb, N.V., Kohler, H.E., Schmid, P., Zennegg, M. and Kohler, M. 2006. Anaerobic degradation of brominated flame retardants in sewage sludge. *Chemosphere*, **64**, 311-317.

Gevao, B., Muzaini, S., Helaleh, M. 2008. Occurrence and concentrations of polybrominated diphenyl ethers in sewage sludge from three wastewater treatment plants in Kuwait. *Chemosphere*, **71**, 242–247.

Ghanem, A., Bados, P., and Estaun, A.R., Alencastro, L.F., Taibi, S., Einhorn, J., and Mougin, C., 2007. Concentrations and specific loads of glyphosate, diuron, atrazine, nonylphenol and metabolites thereof in French urban sewage sludge. *Chemosphere* **69,** 1368–1373.

Gibson, R.W., Wang, M., Padgett, E., Lopez-Real, J.M., and Beck, A.J., 2007. Impact of drying and composting procedures on the concentrations of 4-nonylphenols, di-(2-ethylhexyl) phthalate and polychlorinated biphenyls in anaerobically digested sewage sludge. *Chemosphere,* **68**, 1352–1358.

Gielen GHJP 2007. The fate and effects of sewage-derived pharmaceuticals in soil. Doctoral thesis, University of Canterbury (NZ).

Giger, W., Brunner, P.H. and Schaffner, C. 1984. 4-nonylphenol in sewage sludge: accumulation of toxic metabolites form non-ionic surfactants. *Science*, **225**, 623-625.

Göbel, A., Thomsen, A., McArdell, C. Joss, A. and Giger, W. 2005. Occurrence and Sorption Behavior of Sulfonamides, Macrolides, and Trimethoprim in Activated Sludge Treatment. Environ. Sci. Technol., **39**, 3243-3249.

Golet, E.M., Strehler, A., Alder, A.C. and Giger, W. 2002. Determination of Fluoroquinolone Antibacterial Agents in Sewage Sludge and Sludge-Treated Soil Using Accelerated Solvent Extraction Followed by Solid-Phase Extraction. *Anal. Chem.***,** **74**, 5455-5462.

Golet E.M., Xifra, I., Siegrist, H., Alder, A. and Giger, W. 2003). Environmental Exposure Assessment of Fluoroquinolone Antibacterial Agents from Sewage to Soil. Environ. Sci. Technol., **37(15)**, 3981-3989.

Green Ontario, 2009. Ontario's pollution strategy. http://www.greenontario.org/strategy/toxics_Ontario.html. Accessed June 24, 2009.

Halden, R.U. 2007. PPCP Perspectives: Emerging Knowledge on Emerging Contaminants. Presentation at Northeast Water Science Forum, Pharmaceuticals and Personal Care Products: State of the Science. Portland, ME. August 8.

Hale, R.C., and La Guardia, M.J., 2002. Have Risks Associated With The Presence Of Synthetic Organic Contaminants In Land-Applied Sewage Sludges Been Adequately Assessed? *New Solutions*, **12(4)**, 371-386.

Harrison, E.Z., Oakes, S.R., Hysell, M., and Hay, A., 2006. Review - organic chemicals in sewage sludges. *Sci. of the Total Environ.* **367**, 481–497.

Health Canada 2009a. Perfluorooctane sulfonate (PFOS) and Health. http://www.hc-sc.gc.ca/ewh-semt/pubs/contaminants/perflurooctane_sulfonate-eng.php. Accessed June 23, 2009.

Health Canada 2009b. Perfluorinated Carboxylic Acids and Their Precursors (including Fluorotelomers). http://www.chemicalsubstanceschimiques.gc.ca/interest-interet/pfca-acp_e.html. Accessed June 23, 2009.

Health Canada, 2009c. Chlorophenols http://www.hc-sc.gc.ca/ewh-semt/pubs/water-eau/chlorophenols/index-eng.php. Accessed June 24, 2009.

Heidler, J. and Halden, R.U. 2007. Mass balance assessment of triclosan removal during conventional sewage treatment. *Chemosphere*, **66**, 362–369.

Heidler, J., and Halden, R.U. 2008. Meta-Analysis of Mass Balances Examining Chemical Fate during Wastewater Treatment. *Environ. Sci. Technol.* **42(17)**, 6324-6332.

Hydromantis, Inc., Minnow Environmental and University of Waterloo. 2005. Review of the State of Knowledge of Municipal Effluent Science and Research: Review of Effluent Substances. Report to the Canadian Council of Ministers of the Environment, Winnipeg, MB. Available at: http://www.ccme.ca/assets/pdf/csr_rev_effluent_substances.pdf.

IPCS, 2009. Hexachlorophene, International Programme for Chemical Safety. http://www.inchem.org/documents/icsc/icsc/eics0161.htm. Accessed June 25, 2009.

Jacobsen, A.M., Mortensen, G.K., and Bruun Hansen, H.C. 2004. Organic compounds in the environment. *J. Environ. Qual.* **33**, 232–240.

Jaganyi, D., 2007. Methodology and survey of organic pollutants in South African sewage sludges, volume 1. Report to the Water Research Commission on the project "Survey and Methodology for Analysing Organic Pollutants in South African Sewage Sludges".

Jones-Lepp, T. L., and Stevens, R., 2007. Pharmaceuticals and personal care products in biosolids/sewage sludge: the interface between analytical chemistry and regulation. *Anal Bioanal Chem*. **387**, 1173–1183.

Kinney, C., Furlong, E., Zaugg, S., Burkhardt, M.R., Werner, S., Cahill, J.D., and Jorgensen, G.R., 2006. Survey of organic wastewater contaminants in biosolids destined for land application. *Environ. Sci. & Technol.* **40 (23)**, 7207–7215.

LaGuardia, M., Hale, R.C., Harvey, E., Bush, E., Mainor, T.M., and Gaylor, M.O., 2004. Organic contaminants of emerging concern in land-applied sewage sludge (biosolids). *J. of Residual Sci. Technol***. 1**, 111-122.

Langenkamp, H., Part, P., Erhardt, W. and Pruess, A. 2001. Organic Contaminants in Sewage Sludge for Agricultural Use. European Commission, Joint Research Centre, Institute for Environment and Sustainability, Soil and Waste Unit.

Lee, H., and Peart, T. 2002. Organic Contaminants in Canadian Municipal Sewage Sludge. Part I. Toxic or Endocrine-Disrupting Phenolic Compound. *Water Qual. Res. J. Canada*, **37(4)**, 81–696.

Lee H., Peart, T. E., and Sarafin, K., 2003. Occurrence of polycyclic and nitro musk compounds in Canadian sludge and wastewater samples. *Water Qual. Res. J. Canada,* **38(4)**, 683-702.

Leeper, G.W. 1972. Reactions of heavy metals with soils with special regard to their application in sewage wastes. Report prepared for U.S. Army Corps of Engineers under contract No. DACW73 – 73-C- 0026.

Lindberg, R.H., Senneberg, P., Johansson, M.I., Tysklind, M. and Andersson, B.A.V. 2005. Screening of Human Antibiotic Substances and Determination of Weekly Mass Flows in Five Sewage Treatment Plants in Sweden. Environ. Sci. Technol., **39(10)**, 3421-3429.

Lindberg, R.H., Olofsson, U., Rendahl, P., Johansson, M.I., Tysklind, M. and Andersson, B.A.V. 2006. Behavior of Fluoroquinolones and Trimethoprim during Mechanical, Chemical, and Active Sludge Treatment of Sewage Water and Digestion of Sludge. *Environ. Sci. Technol.*, **40(3)**, 1042-1048.

Loganathan, B.G., Sajwan, K.S., Sinclair, E., Kumar, K., S., and Kannan, K., 2007. Perfluoroalkyl sulfonates and perfluorocarboxylates in two wastewater treatment facilities in Kentucky and Georgia. *Wat. Res.* **41**, 4611–4620.

Martínez-Carballo, E., González-Barreiro, C., Sitka, A., Kreuzinger, N., Scharf S. and Gans, O. 2007. Determination of selected quaternary ammonium compounds by liquid chromatography with mass spectrometry. Part II. Application to sediment and sludge samples in Austria. *Environ. Poll.* **146(2)** 543-547.

Melcer, H., Klecka, G., Monteith, H. and Staples, C. 2007. Wastewater Treatment of Alkylphenols and Their Ethoxylates. Water Environment Federation, Alexandria, VA. January.

Metcalf & Eddy. 1991.Wastewater Engineering: Treatment, Disposal, Reuse (3rd ed.). edited by G. Tchobanoglous and F.L. Burton. McGraw-Hill. Toronto.

Miao, X., Yang, J. and Metcalfe, C.D. 2005. Carbamazepine and its metabolites in wastewater and in biosolids in a municipal wastewater treatment plant. *Environ. Sci. Technol.*, **39**, 7469-7475.

Mittelstaedt, M. 2009. Canada to pull plug on “rubber-duck” chemicals. Toronto Globe and Mail online version. June 20, 2009.

Monteith, H.D. 1987. Fluctuations of Trace Contaminants in Sewage Treatment Plants. Monograph No. 1., Canadian Association on Water Pollution Research and Control, Burlington, ON.

Mueller, J. A. Di Toro, D.M. and Maiello, J.A. 1995. Fate of octamethylcyclotetrasiloxane (OMCTS) in the atmosphere and in sewage treatment plants as an estimate of aquatic exposure. *Environ. Toxicol. Chem*. **14(10)**, 1657-1666.

NRCC (National Research Council of Canada) 1983. Polycyclic Aromatic Hydrocarbons in the Aquatic Environment: Formation, Sources, Fate and Effects on aquatic Biota. Associate Committee on Scientific Criteria for Environmental Quality. NRCC No. 18981, Ottawa. 209 pp.

Nieto, A., Borrull, F., Pocurull, E. and Marcé, R.M. 2007. Pressurized liquid extraction of pharmaceuticals from sewage-sludge. *J. Sep. Sci.* **30**, 979 – 984.

OSPAR, 2000. *OSPAR Commission Background Document on Musk Xylene and Other Musks*.

Our Stolen Future. 2009. About phthalates. http://www.ourstolenfuture.org/NEWSCIENCE/oncompounds/phthalates/phthalates.htm. Accessed June 22.

Page, A.L. 1974. Fate and effects of trace elements in sewage sludge when applied to agricultural lands. A literature review study. U.S. EPA Report No. EPA-670/8-74-005. Office of Research and Development, Cincinnati, OH.

Peck, A.M. and Hornbuckle, K.C. 2004. Synthetic Musk Fragrances in Lake Michigan. *Environ. Sci. Technol.*, **38**, 367-372.

Perron , V. and Hébert, M. 2007. Caractérization des Boues d'Épuration Municipales. Partie II: Élément Traces Métalliques. Vecteur Environnement (Québec). November, pp.42-46.

Petrille, J.C. and Werner, M.W. 1996. Methods of detoxifying quaternary ammonium compounds toward aquatic organisms. http://www.freepatentsonline.com/5518636.html. Accessed June 29, 2009.

Pryor, S.W., Hay, A.G., and Walker, L.P., 2002. Nonylphenol in anaerobically digested sewage sludge from New York State. *Environ. Sci. Technol*. **36**, 3678-3682.

Radjenović, J., Petrović, M. and Barceló, D. 2009. Fate and distribution of pharmaceuticals in wastewater and sewage sludge of the conventional activated sludge (CAS) and advanced membrane bioreactor (MBR) treatment. *Wat. Res.*, **43**, 831 – 841.

Rayne, S. and Ikonomou, M. 2005. Polybrominated diphenyl ethers in an advanced wastewater treatment plant. Part 1: Concentrations, patterns and influence of treatment processes. *J. Environ. Eng. Sci.* **4**, 353-367 (supplementary data tables).

Rogers, H.R., 1996. Sources, behaviour and fate of organic contaminants during sewage treatment and in sewage sludges. *The Science of the Total Environment* **185**, 3-26.

Rudel, R.A., Mely, S.J., Geno, P.W., Sun, G., and Brody, J.G. 1998. Identification of Alkylphenols and Other Estrogenic Phenolic Compounds in Wastewater, Septage, and Groundwater on Cape Cod, Massachusetts. *Environ. Sci. Technol*. **32**, 861-869.

Ruel, S.M., Choubert, J.M., Ginestet, P., and Coquery, M., 2008. Semi-quantitative analysis of a specific database on priority and emerging substances in wastewater and sludge. *Wat. Sci. & Technol* **57(12)**, 1935-1944.

Schultz, M.M., Higgins, C.P., Huset, C.A., Luthy, R.G., Barofsky, D.F. and Field, J.A. 2006. Fluorochemical Mass Flows in a Municipal Wastewater Treatment Facility. *Environ. Sci. & Technol.* **40(23)**, 7350-7357.

Shin, M., Lee, D-Y., Falletta, P. and Seto, P. 2006. Anaerobic Microbial Dehalogenation of Polybrominated Diphenylethers (PBDEs) in Batch Culture system. Presentation at 27th Annual SETAC North America Meeting, Montreal, QC. November 5-9.

Sinclair, E. and Kannan, K. 2006. Mass Loading and Fate of Perfluoroalkyl Surfactants in Wastewater Treatment Plants. *Environ. Sci. & Technol.* **40(5)**, 1408-1414.

Smyth, S.A., Lishman, L.A., McBean, E.A., Kleywegt, S., Yang, J., Svoboda, M.L., Lee, H-B., and Seto, P., 2007. Fate of Polycyclic and Nitro Musks during Aerobic and Anaerobic Sludge Digestion. Proceedings, International Water Association Specialist Conference on Moving Forward Biosolids Sustainability, Moncton NB, June 2007.

Soares, A., Guieysse, B., Jefferson, B., Cartmell, E., and Lester, J.N., 2008. Nonylphenol in environment: A critical review on occurrence, fate, toxicity and treatment in wastewaters. *Environment International* **34**, 1033–1049.

Song, M., Chu, S., Letcher, R.J. and Seth, R. 2006. Fate, partitioning and mass loading of polybrominated diphenyl ethers (PBDEs) during the treatment processing of municipal sewage. *Environ. Sci. Technol.* **40**, 6241-6246.

Spongberg A.L. and Witter, J.D. 2008. Pharmaceutical compounds in the wastewater process stream in Northwest Ohio. *Sci. of the Tot. Environ.* **397**, 148 – 157.

Stasinakis, A.S., Gatidou, and G., Mamais, D., 2008. Occurrence and fate of endocrine disrupters in Greek sewage treatment plants. *Water Res.* **42**, 1796 – 1804.

Stevens, R. 2009. U.S. Environmental Protection Agency, Washington, D.C. Personal Communication to H. Monteith, Hydromantis Inc., March 17, 2009.

Swackhamer, D.L., Paerl, H.W., Eisenreich, S.J. Hurley, J. Hornbuckle, K.C., McLachlan, M., Mount, D. Muir, D. and Schindler, D. 2004. Impacts of Atmospheric Pollutants on Aquatic Ecosystems. Issues in Ecology, **12**, Summer. Accessed at http://www.epa.gov/owow/airdeposition/ESA_Air_Dep_Ecosystems.pdf. March13,2009.

Swartz, C.H., Reddy, S., Benotti, M.J., Yin, H., Barber, L.B., Brownawell, B.J., and Rudel, R.A. 2006. Steroid Estrogens, Nonylphenol Ethoxylate Metabolites, and Other Wastewater Contaminants in Groundwater Affected by a Residential Septic System on Cape Cod, MA. *Environ. Sci. Technol*. **40**, 4894-4902.

Tan, Gevao, B., Muzaini, S., Helaleh, M. 2007. Comprehensive study of endocrine disrupting compounds using grab and passive sampling at selected wastewater treatment plants in South East Queensland, Australia. *Environment International,* **33**, 654–669.

Ternes T., Joss, A., Kreuzinger, N., Miksch, K., Lema, J.M., von Gunten, U., McArdell, C.S., and Siegrist, H., 2005. Removal of pharmaceuticals and personal care products: results of the Poseidon project. Proceedings of WEFTEC05 on CD-ROM, Water Environment Federation Annual Conference and Technical Exposition, Washington, D.C.

UNEP 2009. O-Cresol. United Nations Environment Program Screening Information Data Sheets (SIDS). http://www.chem.unep.ch/irptc/sids/oecdsids/95487.pdf. Accessed June 24, 2009.

U.S. DHHS 2004. Toxicological profile for polybrominated biphenyls and polybrominated diphenyl ethers. U.S. Dept. of Health and Human Services, Public Health Service, Agency for Toxic Substances and Disease Registry. September.

U.S. EPA. 2008. Registration eligibility decision and risk assessment for the pesticidal uses of triclosan. http://www.epa.gov/oppsrrd1/REDs/factsheets/triclosan_fs.htm. Accessed June 25, 2009.

U.S. EPA. 2009. Target National Sewage Sludge Survey. Report No. EPA-822-R-08-014.

USGS 2004. Brominated Flame Retardants in the Environment. Columbia Environmental Research Center. November.

U.S. National Institutes of Health. 2009. Since You Asked - Bisphenol A: Questions and Answers about the National Toxicology Program's Evaluation of Bisphenol A. Accessed at http://www.niehs.nih.gov/news/media/questions/sya-bpa.cfm. March 13.

Watts, R.J., Kong, S., Haling, C.S., Gearhart, L., Frye, C.L., and Vigon B.W., 1995. Fate and effects of polydimethylsiloxanes on pilot and bench-top activated sludge reactors and anaerobic/aerobic digesters. *Wat. Res*. **29(10)**, 2405-2411.

Webber, M. D. and Nichols, J.A. 1995. Organic and Metal Contaminants in Canadian Municipal Sludges and a Sludge Compost. Wastewater Technology Centre Report, Burlington, ON, February.

Webber, M.D. and Sidhwa, P., 2005. Pharmaceuticals and Personal Care Products (PPCPs) in Canadian Wastewaters and Municipal Sludges – A Review. Proceedings of the 3rd Canadian organic residuals recycling conference, Calgary, AB, June 1-4, 2005.

WHO, 2003. Concise International Chemical Assessment Document #48. 4-Chloroaniline. World Health Organization. http://www.inchem.org/documents/cicads/cicads/cicad48.htm. Accessed June 24, 2009.

Williams, T.O. 2007. Occurrence of Microconstituents in Biosolids. Proceedings of WEFTEC07 on CD-ROM, Water Environment Federation Annual Conference and Technical Exposition, San Diego, CA.

Wu, C., Spongberg, A.L. and Witter, J.D. 2008. Determination of the persistence of pharmaceuticals in biosolids using liquid-chromatography tandem mass spectrometry. *Chemosphere*, **doi:10.1016/j.chemosphere.2008.06.026**.

XCG Consultants Ltd. 2007. Fate and Significance of Contaminants in Wastewater Sludge Generated At Municipal and Other Publicly-Owned Wastewater Treatment Facilities. Report to Environmental Canada, Ottawa, ON

Xia, K., Bhandari, A., Das, K., and Pillar, G. 2005. Occurrence and fate of pharmaceuticals and personal care products (ppcps) in biosolids. *J. Environ. Qual.* **34**, 91–104.

Xu, W., Zhang, G., Li, X., Zou, S., Li, P., Hu, Z. and Li, J. 2007. Occurrence and elimination of antibiotics at four sewage treatment plants in the Pearl River Delta (PRD), South China. *Wat. Res*., **41**, 4526 – 4534.

Yang, J.-J., Metcalfe, C.D. 2005. Fate of synthetic musks in a domestic wastewater treatment plant and in an agricultural field amended with biosolids. *Sci. of the Total Environ.* **363(1-3)**, 149-165.