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

Final Report – Literature Review
CCME Project # 447-2009

EXECUTIVE SUMMARY

Submitted to:

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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 term 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 from 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, methyl naphthalene 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 reformulations 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 be 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.