IMPACTS OF ALKALINE STABILIZED BIOSOLIDS APPLICATION ON THE FATE AND TRANSPORT OF EMERGING SUBSTANCES OF CONCERN IN AGRICULTURAL SOILS, PLANT BIOMASS, AND GROUNDWATER

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Research conducted 2013-2015

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WHY DID WE DO THIS RESEARCH?

Over the past 15 years, emerging substances of concern (ESOC) from pharmaceuticals and personal care products have been detected more frequently and in greater quantities in our environment. There is growing awareness of the potential for these compounds to impact ecosystem health. Across Canada, increasing urbanization means that rising quantities of ESOC are being released into the environment during treatment of wastewaters, particularly aquatic environments via treated effluent and terrestrial environments through the land application of municipal biosolids.

Biosolids disposal is a key issue for municipalities, who face high cost of management and legislative restrictions on how to adequately treat wastewaters and sewage solids. Across North America and Europe, up to one-third of the biosolids produced by municipalities are applied to agricultural soils.[1] The remainder are generally incinerated, landfilled or anaerobically digested. Incineration is a costly, energy intensive option that may not be available to smaller municipalities. In addition, landfilling and anaerobic digestion disposal have the potential to release ESOC into the environment.

Sewage solids collected during wastewater treatment are routinely consolidated and undergo a range of possible treatments to reduce their potential environmental impact. Some of the solids treatment options include composting, anaerobic digestion, and alkaline stabilization. The established treatment technologies convert raw sewage solids into a biosolid which becomes a rich source of nutrients for soils, reduces pathogens and heavy metal content to regulated standards. Alkaline stabilization requires adding material which raises pH of the solids to 12, which effectively sterilizes the material, and can subsequently be used as an agricultural liming agent and fertility source. Recent surveys of biosolid treatment approaches has shown alkaline stabilization to be effective at reducing the concentrations of ESOC.

Our capacity to detect the presence of ESOC currently outstrips our understanding of their impact on terrestrial ecosystems. A significant body of evidence demonstrates that ESOC — even at very low concentrations — have significant impacts on aquatic environments.[2,3] However, the impact of ESOC on terrestrial environments and mitigating risk through land use management has yet to be determined in any definitive way.

WHAT DID WE DO?

This 2013-2015 project studied how agricultural soils responded to short- and long-term applications of alkaline-stabilized biosolids (ASB), including:

- The impact of alkaline stabilization on ESOC transport in soils and water;
- How ESOC impacted biological end-point health indicators;
- Optimal rate and frequency of ASB land applications.

The ESOC measured were all commonly-used Suite I and Suite II pharmaceuticals, including Gemfibrozil, Diclofenac, Warfarin, Caffeine, Dimethylxanthine, Carbamazepine, Norfloxacin and Metformin, Acetaminophen, Cotinine, Paraxanthine, Caffeine, Naproxen, Salbutamol, Metoprolol, Venlafaxine, Warfarin, Lorazepam, Quetiapine, Ramipril, Atorvastatin, and phthalates (Dimethyl phthalate, Diethyl phthalate, Di-n-butyl phthalate, Di pentyl phthalate, Benzyl butyl phthalate, Di ethyl hexyl phthlate, Di-n-octyl phthalate).

The baseline location was an agricultural field where ASB had been applied annually, since 2009 over different amendment rates. Field studies were conducted at four sites, with varying frequencies and rates, to assess various environmental aspects of ASB application. ESOC concentrations were measured in agricultural tile-drained water and groundwater, in differently textured agricultural soils, plant biomass, and the impacts of ESOC on several biological end-point indicators were also evaluated. The fate and transport of ESOC were then modelled using both Hydrus 1-D and the Root Zone Water Quality Models (RZWQ).

WHAT DID WE FIND?

ESOC FATE, TRANSPORT AND IMPACT ON AGRICULTURAL ECOSYSTEMS

Suite I ESOC were monitored at an agricultural field site with plots where ASB had been applied annually from 2009 to 2014, as well as plots where ASB were applied only in 2009. Biosolids were applied the following rates: 0 Mg ha^{-1} (control), 14 Mg ha^{-1} (recommended agronomic rate), 28 Mg ha^{-1} (2x recommended rate), and 42 Mg ha^{-1} (3x recommended rate).

ESOC accumulated in soil with each subsequent annual application of ASB both one month post-application (Figure 1) and at post-harvest. Residual concentrations increased after two years with higher rates of application as a result of continued decomposition in soil over time. Between 2009 and 2014, the plots which received annual applications experienced changes in soil characteristics, such as cation exchange capacity, pH, and organic matter content, which influenced retention of ESOC. ESOC concentrations increased rapidly after ASB applications and were reduced at post-harvest by 40 to 60%.

Phthalate concentrations in two biosolids samples were lower than concentrations in untreated sewage (Figure 2). After multiple years of application, phthalate concentrations in soil, water, and plant tissue were considerably reduced relative to what was added. Plant uptake of phthalates was negligible. Modeling suggested that a primary pathway of phthalate transport was into drainage water.

Ecological and biological health end-point indicators were measured over two field seasons. A diverse population of nematodes, used as sensitive soil ecosystem indicators, preferentially inhabited areas where ASB was applied. Plant feeding nematodes were found infrequently in the lime and untreated control conditions, and higher numbers were observed in all plots where ASB had been applied. This population response is commonly observed when food conditions are sufficient to meet the diverse needs of different species of organisms.

Phospholipid fatty acid profiles — a measure of fatty acid signatures of soil microbial populations, is a sensitive bioindicator of soil disturbance.[4] Significant positive responses to ASB application were measured in most microbial bioindicators, with the exception of eukaryotes and anaerobic bacteria. At the long-term ASB application field site, significant differences in both the gram negative and gram positive bacteria were found between plots receiving annual ASB applications and plots only receiving a one-time dose of each rate in 2009.

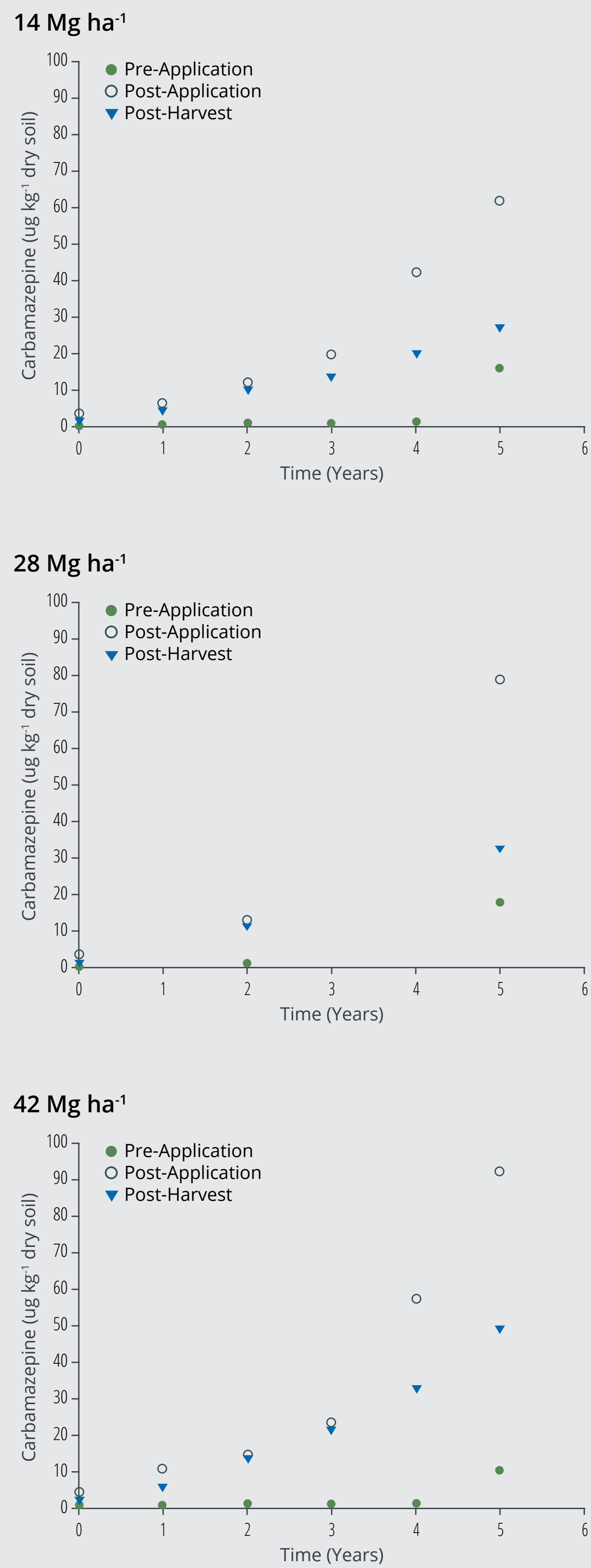

Figure 1. Carbamazepine (as a representative ESOC) concentrations in an agricultural soil one month post-ASB application from 2009 (Year 0) to 2014 (Year 5) in Nova Scotia, Canada.

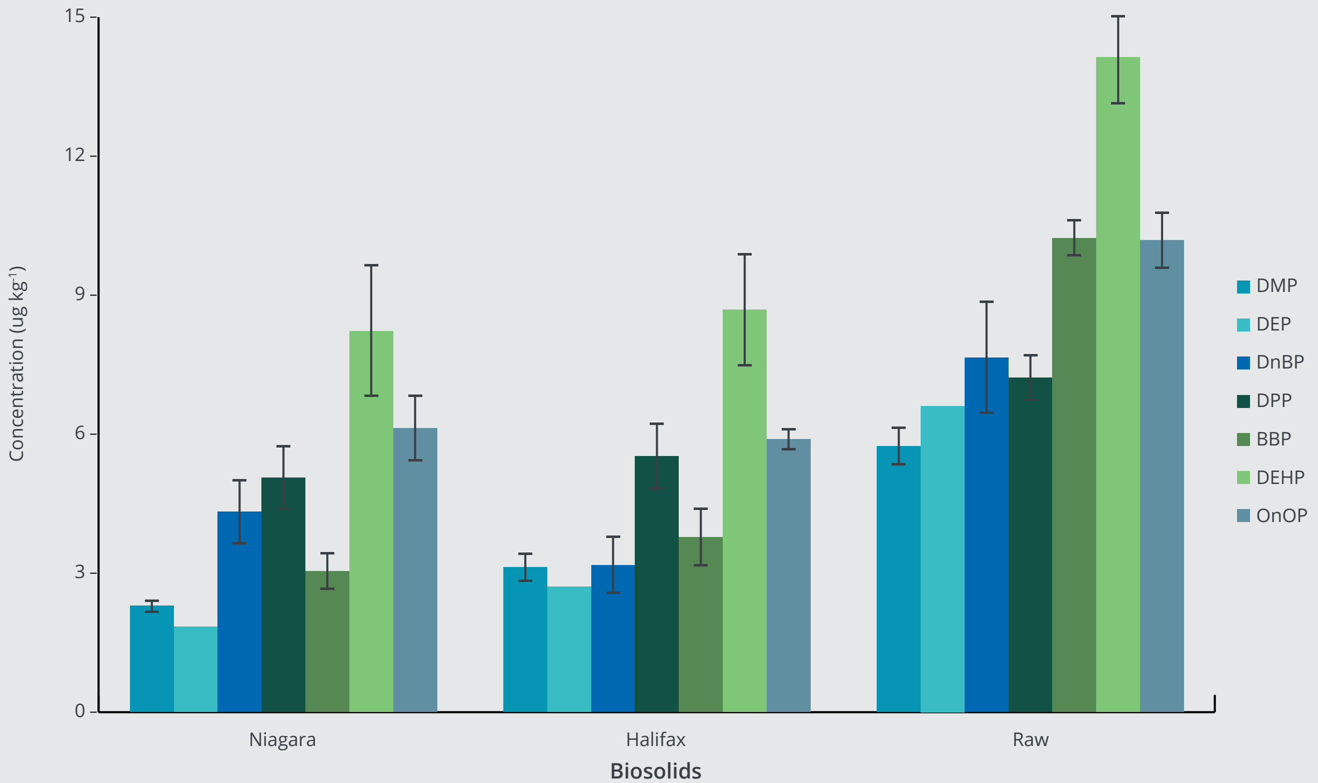

Figure 2. Concentrations of seven commonly used plasticizers (phthalates) in two alkaline stabilized biosolids from N-Viro Systems Canada in Niagara, Ontario and Halifax, Nova Scotia and a raw sewage solid from Halifax, Nova Scotia.

ESOC INTERACTIONS WITH SOIL AND ECO-TOXICOLOGICAL EFFECTS

Assessing how ESOC react in soils poses analytical challenges given differences in soil texture, pH, organic matter content, and microbiological activity. In this project, residual concentration of phthalates after harvest were determined in a neutral pH loam soil (Mt. Hope, Ontario), a slightly alkaline silt loam (Lindsay River, Ontario), and an acidic sandy loam (Truro, Nova Scotia). The soils were amended with fertilizer, ASB at our three established rates, and a raw sewage solid from Halifax.

The results suggest that soil texture and chemical characteristics play a significant role in the presence and concentration of certain phthalates. The acidic Nova Scotia soil had the highest overall concentrations of multiple phthalates, while the slightly neutral Mt. Hope soil had the lowest concentrations. ESOC mobility is strongly affected by sorption (i.e., absorption and adsorption) onto the soil and organic matter surfaces. Thus, it is important to assess their dynamics alone, as well as their interaction with these surfaces when in a mixture of ESOC. In this study, the competitive interaction of four non-steroidal anti-inflammatory drugs (naproxen, ketoprofen, ibuprofen, and diclofenac) was examined in the presence of a slightly neutral loam soil (Mt. Hope, Ontario). Diclofenac and ibuprofen bound more strongly to the soil surface when present in a mixture than as an individual compound. When the NSAIDS were present in a mixture, they desorbed into the soil solution more slowly than when present as an individual compound.

Ecotoxicological assessment of selected ESOC on earthworms (*Eisenia fetida*) was conducted to examine the metabolic response to compounds using an acute exposure (48-hour) toxicity testing. Further testing was conducted in a 14-day artificial soil to examine individual ESOC at five concentrations (plus a control) after 0, 2, 7, and 14 days to document the metabolic response over time. Metabolic responses to the different ESOC were measured to determine whether biochemical markers of toxicity — either general or specific, might emerge. In an acute exposure experiment to triclosan, earthworm physiological responses were highly variable, but a clear demarcation of mortality was observed at the 0.1 and 1 mg cm-2 concentrations. Significant changes in serine, leucine and spermidine were observed at these thresholds relative to the lower concentrations.

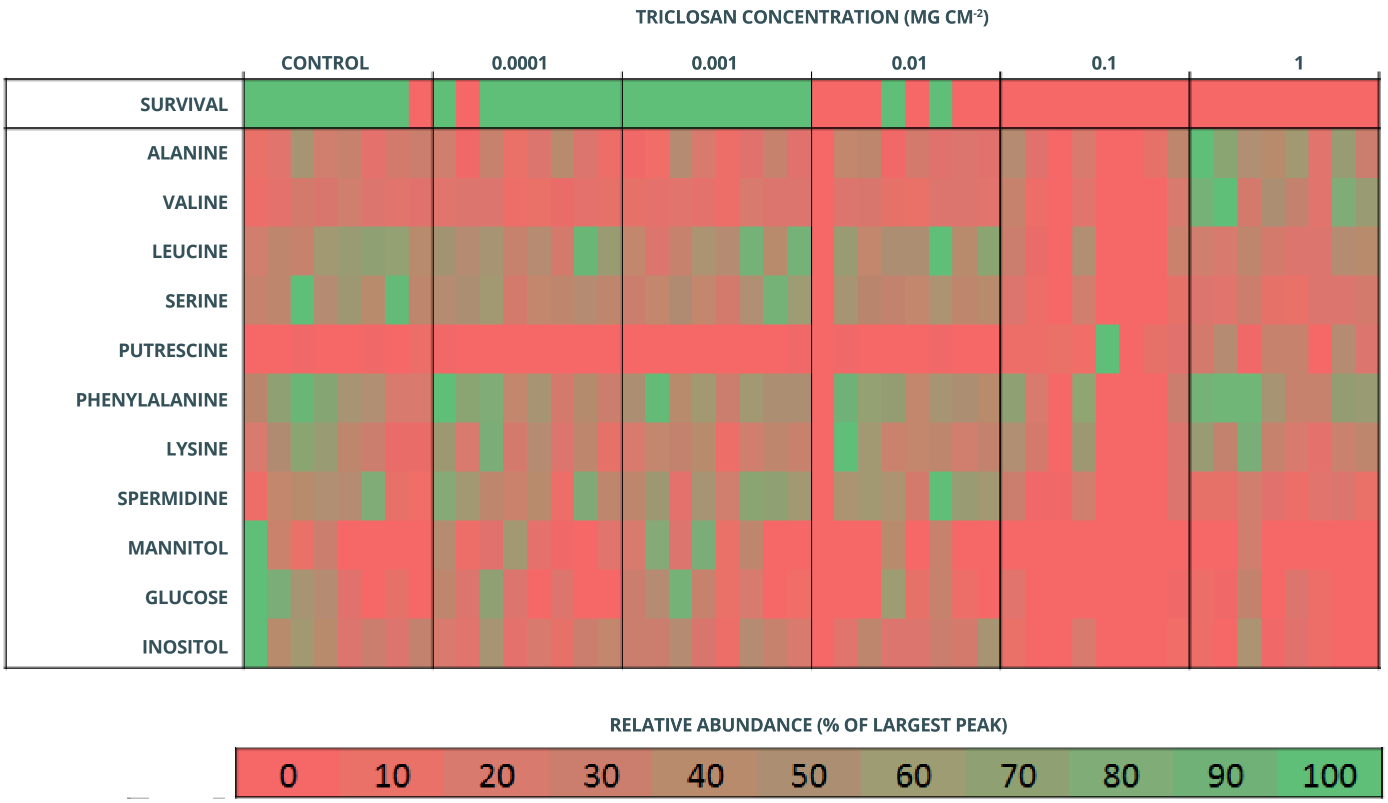

Figure 3. Heat map visualization of earthworm metabolite response to increasing exposure concentrations to triclosan in a 48 h toxicity test. Under Survival, increased red colour is equivalent to high mortality.

The metabolome of earthworms was markedly changed as exposure to more lethal concentrations increased. In particular, alanine, valine, and putrescine relative abundances were much greater than all other amino acids and metabolic compounds.

Subsequent work examining earthworm exposure to ESOC in a 14-day study using a spiked artificial soil, at the same concentration range as the acute 48-hour test, resulted in no earthworm mortality. This suggests that soil systems act as a buffer to chemical exposure for some organisms, although this may result in long-term chronic exposure at sub-lethal concentrations.

WHAT DOES THIS MEAN FOR STAKEHOLDERS AND DECISION MAKERS?

Outcomes from this project highlight the importance of systems-based approaches to determining potential risks from the use of biosolids. Detecting the presence of ESOC in soil is an inadequate single metric of concern. In some of our studies, very high rates of application were used, and at frequencies much greater than would normally be used. Despite observing accumulation of ESOC and high retention seasonally in some agricultural soils, there were no significant negative effects in the biological end-point health indicators measured in our studies. In the laboratory, ESOC were often detected but plant growth was not inhibited. In the field, crop yields showed positive responses to annual ASB applications as a result of nutrient additions and amelioration of soil pH (especially in acidic soils).

Linking the presence of ESOC to broader population level dynamics requires rigorous monitoring over time, and must be balanced by understanding the degradation kinetics and transport of these compounds. Current results from groundwater monitoring suggest limited to no movement of ESOC one year after ASB application.

Ultimately, the primary solution for removing ESOC from the environment is through source controls, but appropriate treatment and management of biosolids within agricultural ecosystems can mitigate many of the potential risks. Municipalities should partner with farming federations and regulatory agencies to ensure that best management practices of biosolids land application are occurring.

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