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Detection and degradation of organic contaminants in an agricultural soil amended with alkaline treated biosolids

1 CEU IN SOIL AND WATER MANAGEMENT

EDITOR'S NOTE

Phenanthrene is a three-ringed polycyclic aromatic hydrocarbon (PAH) that is frequently found as a result of petroleum hydrocarbon contamination (CCME 2008). Phenanthrene solubility in water is low (1.15 µg L^{-1}), and it has a log K_{OC} of 4.3, both suggesting a high degree of sorption to organic matter and accumulation in the solid fraction during wastewater treatment (Sverdrup et al. 2002).). Although not a suspected carcinogenic PAH in humans (CCME 2010), phenanthrene has been shown to exhibit toxic effects on soil nitrogen mineralization, and reduces both the total number of protozoans and the number of heterotrophic flagellates in soil (Sverdrup et al. 2002). The CCME has set a soil quality guideline for the protection of environmental and human health of 43 µg g^{-1} (ppm) in agricultural and residential soils for the ingestion of soil and food, and a guideline of 46 ng g^{-1} (ppb) for the protection of freshwater life.

Biosolids produced from municipal wastewater treatment processes are often used as soil amendments across North America. Over the past few decades, detection and quantification of priority pollutants and emerging contaminants, such as pharmaceuticals and personal care products (PPCPs), in biosolid amended soils (Bright and Healey, 2003; Kinney et al. 2006; Pham and Proulx, 1997; Webber and Lesage, 1989), as well as surface and subsurface drainage water (Lapen et al. 2008; Topp et al. 2008), has led to increased attention and regulation of these materials (NSE, 2010). The Canadian Council of Ministers of the Environment (CCME) recently conducted a survey of emerging contaminants in biosolids produced at eleven Wastewater Treatment Plants (WWTPs) across Canada and identified a multiplicity of emerging contaminants in biosolids from each WWTP examined (Monteith, 2010). Eight compounds out of 57 tested, including triclosan, triclocarban, and carbamazepine, were detected in >95% of all samples (Monteith, 2010). Similarly, the Targeted National Sewage Sludge Survey conducted by the U.S. Environmental Protection Agency (USEPA) reported 12 out of the 72 pharmaceuticals tested in more than 95% of samples analyzed (USEPA, 2009).

The potential presence of organic contaminants in biosolids has raised concerns related to their use in agriculture. Depending on the chemical properties of the compounds, there is a risk of contaminants leaching to groundwater following irrigation or rainfall events (Chefetz et al. 2008). There is also evidence at the field-scale that PPCPs in soil

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can accumulate in soil organic matter and in terrestrial organisms such as earthworms (Kinney et al. 2008). A few studies have documented PPCP uptake into plants. Wu et al. (2010) showed compound-specific uptake of several PPCPs into the roots, shoots, and leaves of soybeans from both biosolid-amended and wastewater-irrigated soil in a greenhouse trial. In a study using spiked soil, Karnjanapiboonwong et al. (2011) found that pinto beans accumulated PPCPs into their roots, with higher concentrations in sand compared to a sandy loam soil. Addressing the problem at the treatment facility is proving a challenge worldwide, as many compounds of emerging concern enter the wastewater stream in products used every day. For example, a widely distributed antimicrobial compound called triclosan, used in soaps, toothpastes, bodywash, and other personal care products, is often detected in the influent water entering WWTPs globally (Ricart et al. 2010; Waltman et al. 2006; Ying and Kookana 2007). Heidler and Halden (2007) performed a mass balance study on triclosan fate in a WWTP and found that while there was a 98% reduction between influent and effluent, almost half of the triclosan entering the facility was unaccounted for and only assumed to be degraded. Lozano et al. (2010) reviewed studies on the fate of triclosan in wastewater treatment processes, finding high removal rates (generally >90%) although it was not clear whether the mechanism was through degradation or sorption. The physico-chemical properties of triclosan (aqueous solubility =12 mg L^{-1}, $\log k_{ow}$=4.8, $\log k_{oc}$=3.8 to 4.0) suggest sorption to organic matter in biosolids, as a significant removal mechanism in the wastewater treatment facility (Lozano et al. 2010).

Application of biosolids to agricultural soil is a practice that will continue to increase under the current policy framework in many countries and as world population grows. The objective of this study was to detect and monitor organic contaminant concentrations in an agricultural soil receiving increasing rates of alkaline treated biosolid (ATB) applications under laboratory and field conditions.

MATERIALS AND METHODS

MATERIALS AND EXPERIMENTAL DESIGN

Soil was obtained for both studies from an on-going field study using an alkaline treated biosolid (ATB) as a soil amendment at the Bio-Environmental Engineering Center (BEEC) in Bible Hill, Nova Scotia, Canada (45°23' N, 63°14' W). The soil is described as a gleyed humic ferric podzol in the Tormentine (Truro Series) with a sandy loam textural classification. The ATB was produced from sewage sludge originating from Advanced Primary treatment followed by the N-Viro Soil™ process in the Halifax Regional Municipality, Nova Scotia, Canada. The N-Viro process introduces a combination of cement kiln dust and quicklime with the raw solids producing an exothermic reaction, increasing the pH to 12 which is deemed sufficient to kill pathogenic microorganisms (N-Viro Systems Canada). The N-Viro product was used as received in the field trials but was homogenized by passing through a 2 mm sieve for the incubation study.

A four month laboratory soil incubation with biosolids was conducted to measure contaminant dynamics under controlled environmental conditions. The study was established in a completely randomized design repeated over time with treatment vessels randomly distributed throughout the incubation chamber. A large soil composite was obtained from around the perimeter of the field study plots from a depth of 0 to 30 cm. The soil was air-dried and homogenized by passing through a 2 mm sieve. An unamended control plus four rates (2.08, 4.16, 8.32, 12.48 mg ATB d.w. g^{-1} soil), equivalent to the field study rates of 0, 7, 14, 28, and 42 Mg ATB w.w. ha^{-1}, were incubated for 121 days at 20°C. Each treatment was replicated four times and samples were taken at eleven different time intervals throughout the study and frozen until ready for extraction and analysis by *Gas Chromatography-Mass Spectrometry* (GC-MS). The homogenized soil and ATB were mixed, and then received high purity water to achieve a gravimetric moisture content of 18%. Additional incubation study details are provided in Gillis and Price (2011).

A plot-scale field study was also established to compare different rates of ATB application relative to the recommended agronomic rate in use of the commercial product (14 Mg ATB w.w. ha^{-1}). Plots were 5 m × 12 m and received annual applications at the rates described above. The field was previously planted to soybeans but after the initial ATB application was sown to corn. The initial ATB treatment applications were split equally between Fall and Spring but in subsequent years were applied in full prior to planting in the spring. The ATB was broadcast manually across plots, hand raked to distribute evenly, and incorporated by a tractor-mounted rototiller. An aggregate sample of six Oakfield soil cores was taken from the 0 to 15 cm depth in each plot, and immediately stored in a cooler with ice packs after sampling in the field. Samples were brought to the laboratory and frozen until required for analysis.

RESULTS

CONTAMINANT CONCENTRATIONS IN ATB

There were no significant differences in the concentration of triclosan or phenanthrene between batches of the ATB samples used in our studies (data not shown) as measured by an independent accredited environmental laboratory (RPC Analytical, Moncton, NB) and in comparison to values reported by the CCME (data not shown). Triclosan was detected in all three batches, while phenanthrene was not included in the CCME analysis. Analyte concentrations in ATB were used to generate predicted triclosan and phenanthrene concentrations in amended soils.

SOIL INCUBATION STUDY

Soil samples from days 0 and 121 from the incubation study were also analyzed by an independent accredited environmental laboratory (RPC Analytical, Moncton, NB). Triclosan was the only analyte detected (reporting limit (RL) of 50 ng g^{-1}), in two of three samples from day 0, but none from day 121 (data not shown). In comparison, during our analysis triclosan was detected in biosolid-amended incubation soils at concentrations that were greater

than our RL and within the linear range of the calibration curve (Figures 1 and 2). Phenanthrene was also detected at concentrations that were within the linear calibration range and had signal to noise ratios >10, but were below the RL and were therefore considered to be approximations. The average concentration of triclosan measured over the soil incubation study period ranged from 92 ng g^{-1} on day 3, to 20 ng g^{-1} by the end of the incubation on day 121. The 20 ng g^{-1} value was below the 21 ng g^{-1} RL, but close to the concentration of the spiked samples from the incubation study (20 ng g^{-1}) and higher than the spiked concentration in the field samples (18 ng g^{-1}). These values were considered reliable since a strong signal to noise ratio (>10) was consistently obtained. There was an increase in the average concentration between day 0 and 3 that was not significant, but the average concentration decreased after day 3 (Figure 1). There was a 78% reduction in triclosan concentrations between the highest average concentration measured on day 3 and the lowest on day 121. Phenanthrene dynamics in soil were similar to triclosan, although there was a slower decrease in concentrations that began after day 6 of the incubation (Figure 2). Concentrations ranged from 13 ng g^{-1} on day 3, to 3 ng g^{-1} on day 121 representing a 77% reduction, although concentrations were generally below the spiked concentrations and fell on the lower end of the calibration curve by day 121.

ALKALINE TREATED BIOSOLID AMENDMENT FIELD STUDY

Only triclosan was detected in the field-based soil samples but at lower concentrations than what was measured in the soil incubation samples (Figure 3). Incubation ATB amendment rates were matched to the field study, assuming incorporation into the top 15 cm of soil and a bulk density of 1600 kg m^{-3}, although the initial ATB field application was split 50:50 between Fall and Spring. Using the average range of triclosan concentrations in the ATB (data not shown), we predicted field soil triclosan concentrations to be between 10 to 40 ng g^{-1} after the first application, and 20 to 80 ng g^{-1} after the second application. Measured triclosan concentrations after the first application in Fall 2008 were similar to the predicted (Nov. 08, Figure 3), while the concentrations measured after the Spring application (July 09, Figure 3) did not increase as expected. By the Oct. 09 sampling, concentrations decreased to levels significantly lower than the Nov. 08 sampling.

DISCUSSION

The predicted concentration range of triclosan in the soil incubation study following application of the ATB was estimated to be between 20 to 80 ng triclosan g^{-1} soil, based on the 12.48 mg ATB g^{-1} dry soil amendment rate and a low to high triclosan concentration range of 1500 to 6500 ng g^{-1} (data not shown). The highest concentrations measured in ATB amended incubation soils on day 3 were higher than predicted, although within an order of magnitude, but triclosan concentrations generally fell within the predicted range. After the third day of the incubation, triclosan concentrations decreased significantly coinciding with rapid carbon decomposition (Figure 1), as measured through respirometry during the incubation study (Gillis and Price 2011). Phenanthrene dynamics in soil were similar to triclosan, although there was a slower decrease in average concentration that began after day 6 of the incubation (Figure 2). Average concentrations ranged from 13 ng g^{-1} on day 3, to 3 ng g^{-1} on day 121 representing a 77% reduction.

No triclosan was detected in field samples prior to the Fall 2008 ATB application. Following the Fall 2008 field application of biosolids, a sharp increase in soil triclosan concentration was observed in November 2008 which remained elevated over the winter period. In contrast, average field soil triclosan concentrations measured in the months following the Spring 2009 application did not increase, and concentrations measured

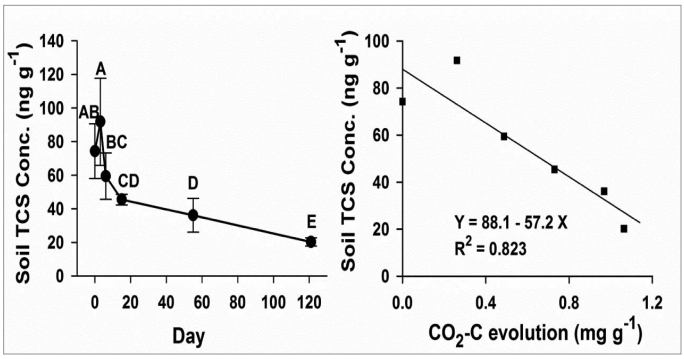

FIG. 1

Left: Triclosan concentration over time from incubation soil amended with the equivalent of 42 t ATB ha^{-1}. Error bars represent 95% Confidence Interval, and days with the same letter are not significantly different (α=0.05). Right: Relationship between triclosan concentration and the cumulative evolved CO_2-C from biosolid-amended soil. This supports the idea of aerobic microbial degradation as a likely removal pathway for triclosan.

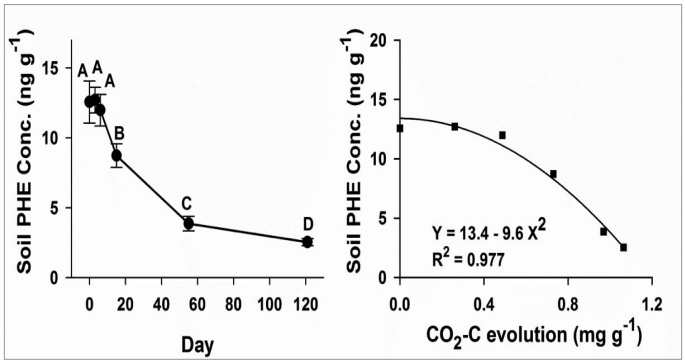

FIG. 2.

Left: Phenanthrene concentration in amended incubation soil. Values are below reporting limit but within the linear range of the calibration curve and are considered approximate. Error bars show 95% CI, and days with the same letter are not significantly different (α=0.05). Right: Relationship between phenanthrene concentration and the cumulative evolved CO_2-C from biosolid-amended soil. In contrast to triclosan, concentrations of phenanthrene do not decrease until about half of the CO2 has been evolved.

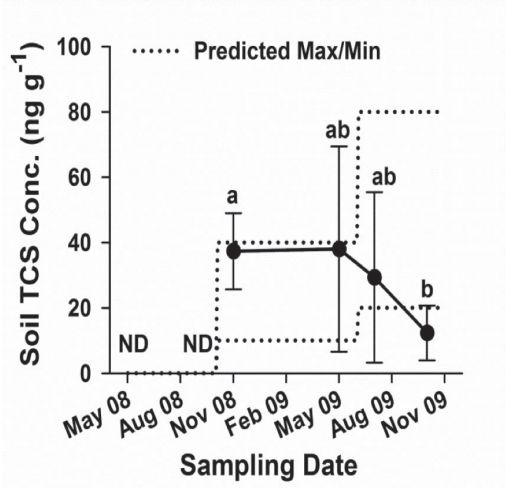

FIG. 3.

Measured and predicted soil triclosan concentrations in the top 15 cm of field plots receiving annual biosolid applications. Application rate was 21 t ha^{-1} in Oct. 2008 and again in June 2009. No triclosan was detected in the May 08 and Sept. 08 soil samplings. Predicted concentrations are based on the range of triclosan concentrations measured in ATB (data not shown). Error bars show 95% C.I. (d.f.=8). ND means not detected (concentrations below linear calibration range).

in October 2009 were significantly lower than those measured in November 2008. This may be a consequence of the high microbial activity during the spring period leading to rapid triclosan removal, as seen early on in the incubation study. Higher soil triclosan concentrations over winter, following the Fall 2008 application, suggests a possible role for microorganisms in the removal of triclosan from agricultural soils.

The soil triclosan concentrations decreased significantly by the end of the 2009 season, one year after the first application, and only four months after the second biosolids application. Our study provides some evidence that triclosan may have the potential to persist over colder climatic periods. Cha and Cupples (2010) suggest that triclosan has a low leaching potential based on modelling of their sorption and biodegradation data, and results from Xia et al. (2010) show that triclosan concentrations were up to five times higher in the top 0 to 15 cm of soil compared to 15 to 30 cm depth after 33 years of annual biosolids applications. Based on the highest predicted soil triclosan concentrations of 40 ng g^{-1} and 80 ng g^{-1}, after one and two ATB applications in the top 15 cm of the field soil, the over winter removal rate in our field study was small (between November 2008 and May 2009). However, during the one month interval in the spring period after ATB was applied, a 63% removal rate of triclosan from the field soil samples was observed compared to the predicted values. Using the average concentration from the Oct. 2009 sampling and the highest predicted concentration in June 2009, up to 85% of the triclosan was removed after four months, while there was a 68% decrease in measured triclosan concentration between the May 2009 and Oct. 2009 samplings (Figure 3). One study reported up to 78% of triclosan was removed from biosolid-amended soils under field conditions after 7 to 9 months, and up to 96% removed after 16 to 21 months (Lozano et al. 2010). These results correspond to the removal rate observed in our incubation study, which was also 78% after 4 months under idealized conditions.

CONCLUSION

The goal of this study was to monitor the presence of organic contaminant concentrations in an alkaline treated biosolid-amended agricultural soil under laboratory and agricultural field conditions. We were able to detect and quantify two contaminants in the ATB amended-soil. The compound most reliably quantified in this study was triclosan which is a widely used anti-microbial agent and is being consistently found in environmental samples. Triclosan was detected at levels greater than the reporting limit in agricultural soils receiving an alkaline treated biosolid. Average triclosan concentrations in a soil incubation with biosolids ranged from 92 ng g^{-1} post-application to 20 ng g^{-1} at the end of the study, representing a 78% decrease over 4 months under idealized conditions. Future studies on triclosan dynamics after biosolids applications in the field need to consider a more frequent sampling regime after application to capture the most active part of the process. Phenanthrene was detected in incubation soils at concentrations that were below the Reporting Limit spiking concentration, but were captured on the lower end of the calibration curve and were considered approximate. In the field study, triclosan was the only analyte detected in soil samples. Concentrations in Nov. 2008 following a Fall 2008 biosolids application increased to detectable levels in all three plots measured post-application, and concentrations did not change significantly over the winter period when sampled in Spring. Following the Spring 2009 application, triclosan concentrations did not increase as predicted and eventually decreased to levels on the Oct. 2009 sampling that were significantly lower than Nov. 2008. The results indicate that triclosan in Fall-applied biosolids may persist overwinter, but removal of triclosan became apparent following the warmer summer months.