

DIVISION OF ENVIRONMENTAL CHEMISTRY

238th ACS National Meeting

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August 16-20, 2009

WEDNESDAY EVENING

Emerging Contaminants, Pharmaceuticals and Personal Care Products, and Organohalogenes in Wastewater and Municipal Biosolids

Posters

A. Sapkota, *Organizer*

R. U. Halden, *Organizer, Presiding*

6:00 - 8:00

200. Analysis of perfluorinated chemicals and their fluorinated precursors in sludge: Method development and initial results. **H. Yoo**, J. J. Ellington, J. W. Washington, T. M. Jenkins, L. E. Libelo

201. Fate of pharmaceuticals and personal care products in agricultural soils amended with biosolids. **E. Walters**, K. McClellan, R. U. Halden

202. Development of a model to estimate prescription pharmaceutical influent concentrations and loadings to wastewater treatment plants in Virginia. **K. J. Ottmar**, E. S. Houle, E. C. Kurland, D. E. Sanchez, S. B. Schlesinger, L. M. Colosi, J. A. Smith

203. Empirical model for predicting concentrations of refractory hydrophobic organic compounds in digested sludges from municipal wastewater treatment plants. **R. P. Deo**, R. U. Halden

204. *In silico* screening for unmonitored high production volume (HPV) chemicals prone to accumulate in biosolids. **R. P. Deo**, R. U. Halden

205. Refined predicted no-effect-concentration (PNEC) for triclocarban in freshwater environment. **F. Ayala-Fierro**, L. Jeram, O. Kretschik

206. Applicability of passive sampling modules for the determination of contaminants of emerging interest in digested municipal sewage sludge (biosolids). **A. D. Fox**, R. U. Halden

ABSTRACTS

ENVR 200

Analysis of perfluorinated chemicals and their fluorinated precursors in sludge: Method development and initial results

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A rigorous method was developed to maximize the extraction efficacy for perfluorocarboxylic acids (PFCAs), perfluorosulfonates (PFSAs), fluorotelomer alcohols (FTOHs), fluorotelomer acrylates (FTAc), perfluorosulfonamides (FOSAs), and perfluorosulfonamidoethanols (FOSEs) from wastewater-treatment sludge. PFCAs and PFSAs in test sludge were analyzed by LC/MS/MS. Of five solvents tested for their PFCAs/PFSAs extraction effectiveness, 50%/50% (v/v) ACN/MeOH extraction yielded the highest concentrations. Pretreatment of sludge with NaOH and HCl, prior to extraction, recovered additional PFCAs/PFSAs (e.g., PFOA and PFOS), but KOH and K₂S₂O₈ digestion were less effective than no pretreatment. Semi-volatile fluorochemicals in sludge were extracted with methyl tert-butyl ether (MTBE) using GC-MS. NaOH-treated sludge resulted in recovery of more FTOHs, especially 8:2 FTOH. Presently we are investigating if this observation comes from the OH--facilitated hydrolysis of FTAc. With these efforts, we have been able to measure at least ten semi-volatile fluorochemicals from test sludge at the concentrations of sub-ng to tens ng/g (ww). The identification of a few suspected volatile fluorochemicals, for which no standards exist, was evaluated with a derivitization technique.

ENVR 201

Fate of pharmaceuticals and personal care products in agricultural soils amended with biosolids

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With the publication of the Targeted National Sewage Sludge Survey by the U.S. EPA earlier this year, comprehensive data regarding pharmaceuticals and personal care product (PPCP) contamination of biosolids in the U.S was provided. However, many uncertainties still remain concerning the fate of PPCPs in agricultural soils following land application of digested sewage sludge. We have therefore conducted a study on the weathering of biosolids in agricultural soils over the course of three years. Between years 2005 and 2008, 12 different soil samples were collected and analyzed for 72 PPCPs using liquid chromatography tandem mass spectrometry (EPA Method 1694). More than fifteen of the 72 analytes were detected in at least one sample at concentrations ranging from >1 to about 4,900 µg/kg dry weight. The antimicrobials triclocarban and triclosan were found to be present at the highest concentrations both prior and after long-term weathering. Concentrations of the majority of PPCPs decreased notably over time, but the active ingredients of antimicrobial consumer products remained detectable at parts-per-million levels even after three years of weathering under the ambient conditions prevailing in Maryland.

ENVR 202

Development of a model to estimate prescription pharmaceutical influent concentrations and loadings to wastewater treatment plants in Virginia

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A model to predict the influent concentrations and loadings of prescription pharmaceuticals to wastewater treatment plants has been developed and validated with existing published data. Prescription numbers exceeded three billion in 2007 and have been steadily climbing for several years, resulting in large quantities of pharmaceuticals being consumed and then excreted with human wastes. With little known about the fate and transport of many of these compounds, this research addresses the knowledge gap at the first occurring process, the wastewater treatment plant. The model accounts for annual prescription numbers, average daily dose taken, *in vivo* metabolic conversion, wastewater treatment plant servicing population, wastewater treatment plant average daily treatment volume, and the prescription-per-person conversion. Using available data, influent concentrations have been estimated to within one order of magnitude and as such, provide a valuable first projection that can be used to estimate loadings to receiving waters.

ENVR 203

Empirical model for predicting concentrations of refractory hydrophobic organic compounds in digested sludges from municipal wastewater treatment plants

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An empirical model is presented allowing for the prediction of concentrations of hydrophobic organic compounds (HOCs) prone to accumulate and persist in digested sludge (biosolids) during conventional municipal wastewater treatment. The sole input requirements of the model are the concentration of the individual HOCs entering the wastewater treatment plant in raw sewage, the compound's respective octanol-water partitioning coefficient (K_{OW}), and a fitting parameter (pfit) established from literature values. The accuracy of the model was successfully confirmed at the 99% confidence level in a paired test that compared predicted concentrations in biosolids to empirical measurements reported in the literature. After successful validation, the resultant model was applied to predict levels of various HOCs for which occurrence data in biosolids thus far were lacking. The empirical model has minimal input requirements and can serve as a screening tool to predict potentially problematic concentrations of hydrophobic pollutants in biosolids.

ENVR 204

***In silico* screening for unmonitored high production volume (HPV) chemicals prone to accumulate in biosolids**

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Tens of thousands of chemicals are produced and used in the U.S. in quantities exceeding 450,000 kg (1 million pounds) per year, while limited information is available on their various fates during municipal wastewater treatment. This study employed a quantitative empirical model to predict the fraction of the mass of high production volume (HPV) chemicals that is expected to persist in digested sludge following treatment of municipal wastewater and the generated sludges. The model uses as input a given compound's octanol-water partition coefficient (K_{OW}) and a fitting parameter (pfit) that was established from literature information. The 207 HPV chemicals included in this study were hydrophobic in nature ($\log K_{OW}$ of ≥ 4.0) and had no prior record of measurement in digested municipal sludge. Application of the empirical model led to the identification of over a dozen HPV chemicals that are of potential concern, as indicated by significant persistence ($>50\%$ accumulation in sludge after treatment) and toxicity (LD_{50} values <500 mg/kg). Model output can inform and guide the targeted analysis of presently unmonitored chemicals in digested sludge.

ENVR 205

Refined predicted no-effect-concentration (PNEC) for triclocarban in freshwater environment

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Old monitoring studies resulted in triclocarban predicted in-stream concentration of 0.05 g/L in surface waters. Recently the High Production Volume robust summaries reported 0.2 µg/L in Delaware River, which was not considered typical. The old sample-collection sites did not have advanced wastewater treatment. Since then the number of trickling filter plants has declined whereas highly efficient activated sludge systems have increased while triclocarban usage has declined. Improved systems would likely improve triclocarban removal resulting in decreased levels in wastewater treatment plant effluents. Recently the triclocarban environmental exposure and toxicity have been the subject of discussion. The species sensitivity distribution (SSD) approach was used to better understand aquatic risks. It is believed that SSD represents more realistic threshold of effect than PNEC. Refined PNEC would be helpful to answer many of the questions raised lately. Results from this work will be presented.

ENVR 206

Applicability of passive sampling modules for the determination of contaminants of emerging interest in digested municipal sewage sludge (biosolids)

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Contaminants of emerging interest such as pharmaceuticals and personal care products (PPCPs), polybrominated diphenyl ethers (PBDEs), polycyclic aromatic hydrocarbons (PAHs), steroids and hormones have been found in surface waters and in some drinking water distribution systems. Sources of contamination in the water supply may include effluent from wastewater treatment plants (WWTPs) and digested municipal sewage sludge that is used as a fertilizer and soil conditioner in residential and agricultural settings. WWTPs are not specifically equipped to remove these types of contaminants and routine sampling for these compounds is not being performed. The current method used to sample sludge from WWTPs is time consuming and expensive. Laboratory analyses often are complicated by severe matrix interferences. We explored

the applicability of passive sampling modules for the rapid and inexpensive qualitative and quantitative determination of pollutants in digested municipal sewage sludge. The approach involves the contacting of passive samplers with liquid municipal sludge followed by analysis by GC-MS/MS. This approach holds promise, as it is less expensive and may be more reliable than traditional methods that are susceptible to adverse impact by chemical interferences. Trace analysis of emerging contaminants by passive sampling was found to be applicable for a number of established and emerging contaminants. The approach deserves further study as it potentially provides a practical and inexpensive means for routine monitoring of contaminants in sludge destined for land application.