

## DIVISION OF ENVIRONMENTAL CHEMISTRY

238th ACS National Meeting

Washington, DC

August 16-20, 2009

### WEDNESDAY MORNING

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

A. Sapkota, *Organizer*

R. U. Halden, *Organizer, Presiding*

**8:30** — Introductory Remarks.

**8:35** —**77.** Occurrence and fate of pharmaceuticals and EDCs in U.S. drinking water. **S. A. Snyder**, M. J. Benotti, B. Vanderford

**9:10** —**78.** Occurrence of emerging contaminants in sewage sludge. **R. Stevens**

**9:45** —**79.** Analysis of PPCPs in biosolids originating from the 2001 EPA National Sewage Sludge Survey. **K. McClellan**, R. U. Halden

**10:15** — Intermission.

**10:30** —**80.** Quaternary ammonium compounds in biosolids: High level persistent contaminants in need of much greater attention. **B. J. Brownawell**, X. Li, D. McHugh, J. Ruggieri, P. A. Lara-Martin, D. W. Bemis, C. Kinney

**11:00** —**81.** Characterizing poorly understood sources of organic wastewater compounds. **P. J. Phillips**, D. W. Kolpin

**11:30** —**82.** Biosolids and earthworms: Bioaccumulation, toxicity, and removal of anthropogenic organic contaminants. **C. Kinney**, E. T. Furlong, D. W. Kolpin, D. W. Bemis, C. Kelly, A. Hay, S. D. Zaugg

**12:00** —**83.** Occurrence and bioavailability of brominated flame retardants (BFRs) in land applied municipal biosolids. **R. C. Hale**, M. J. La Guardia, L. Hundal

## ABSTRACTS

### ENVR 77

#### Occurrence and fate of pharmaceuticals and EDCs in U.S. drinking water

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The drinking water for more than 28 million people was screened for a diverse group of pharmaceuticals, potential endocrine disrupting compounds (EDCs), and other unregulated organic contaminants. Source water, finished drinking water, and distribution system (tap) water from 19 U.S. water utilities was analyzed for 51 compounds between 2006 and 2007. The 11 most frequently detected compounds were atenolol, atrazine, carbamazepine, estrone, gemfibrozil, meprobamate, naproxen, phenytoin, sulfamethoxazole, TCEP, and trimethoprim. Median concentrations of these compounds were less than 10 ng/L, except for sulfamethoxazole in source water (12 ng/L), TCEP in source water (120 ng/L), and atrazine in source, finished, and distribution system water (32, 49, and 49 ng/L). Atrazine was detected in areas far removed from application where wastewater was the only known source of organic contaminants. The occurrence of compounds in finished drinking water was controlled by the type of chemical oxidation (ozone or chlorine) used at each plant. At one drinking water treatment plant, summed monthly concentrations of the detected analytes in source and finished water are reported. Atenolol, atrazine, DEET, estrone, meprobamate, and trimethoprim can serve as indicator compounds representing the potential contamination from other pharmaceuticals and EDCs and monitoring the efficacy of different treatment processes.

### ENVR 78

#### Occurrence of emerging contaminants in sewage sludge

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Results from the Targeted National Sewage Sludge Survey (TNSSS) show land application of sewage sludge continues to be practiced in the United States. The U.S. Environmental Protection Agency (EPA) is required to regulate contaminants in sewage sludge that may be present at levels of concern to public health and the environment. In an effort to investigate new and emerging contaminants, EPA recently conducted the

TNSSS. The objective of the survey was to determine which analytes were present in sewage sludge and obtain national estimates of their concentrations. This information will help EPA assess if those compounds are occurring and whether the concentrations in sewage sludge are of concern. The sampling effort collected sewage sludge from 74 randomly selected publicly owned treatment works (POTWs) in 35 states. The sampling design was stratified to assure a distribution in sewage sludge production and location of the sampled POTWs was representative of those in the contiguous United States employing secondary treatment or better and generating at least one million gallons of flow per day. Samples were collected in 2006 and 2007. The TNSSS contains results for 145 analytes, including four anions (nitrite/nitrate, fluoride, water-extractable phosphorus), 28 metals, four polycyclic aromatic hydrocarbons, two semi-volatiles, 11 flame retardants, 72 pharmaceuticals, and 25 steroids and hormones. Some analytes were found in all 84 samples, while others were found in none or only a few of the sewage sludge samples.

## ENVR 79

### **Analysis of PPCPs in biosolids originating from the 2001 EPA National Sewage Sludge Survey**

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In response to the U.S. National Academies' call for a better assessment of chemical pollutants contained in municipal sludge, we determined the mean concentration of 72 pharmaceuticals and personal care products (PPCP) in 110 biosolids samples collected in 2001, and compared the results to data from the 2006/2007 Targeted National Sewage Sludge Survey (TNSSS) that was recently released by the U.S. Environmental Protection Agency (EPA). Composite samples of archived sewage sludges, collected at 94 U.S. wastewater treatment plants from 32 states and the District of Columbia, were analyzed by liquid chromatography tandem mass spectrometry using EPA Method 1694. Thirty-eight (54%) of the 72 analytes were detected in at least one composite sample at concentrations ranging from 2 to 48,000  $\mu\text{g kg}^{-1}$  dry weight. Triclocarbon and triclosan were the most abundant, accounting for 65% of the total PPCP mass found. A comparison with data from the 2006/2007 TNSSS demonstrated PPCP deposition on land to be a long-standing and significant phenomenon. The loading to U.S. soils from nationwide sewage sludge recycling was estimated at 210-250 metric tons per year for the sum of the 72 PPCPs investigated. Predicted concentrations in amended soil and pore water were calculated and interpreted in the context of toxic threshold concentrations of susceptible biota.

## ENVR 80

### Quaternary ammonium compounds in biosolids: High level persistent contaminants in need of much greater attention

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Quaternary ammonium compounds (QACs) are an important class of cationic surfactants that find important uses in fabric softeners and personal care products, and many are used as antimicrobials. An initial assessment of the distribution of 19 QACs in nine biosolid samples is reported. Concentrations of total QACs in both Class A and B biosolids, varied between 190 and 760 µg/g. The compositions of QACs in most samples were consistent with those found in sewage sludge and in estuarine sediments impacted by untreated municipal waste waters. Approximately half of the total QAC concentrations are accounted for by C<sub>16</sub>:C<sub>16</sub>, C<sub>16</sub>:C<sub>18</sub>, and C<sub>18</sub>:C<sub>18</sub> dialkyldimethylammonium compounds which likely continue to find use in fabric softeners. Other QACs determined at >10 µg/g include C<sub>14</sub>-C<sub>18</sub> homologs of benzylalkyldimethylammonium, and the disinfectant C<sub>10</sub>:C<sub>10</sub> dialkyldimethylammonium. Of great significance is the discovery of extremely high levels of a C<sub>22</sub> alkyltrimethylammonium, a previously unreported persistent environmental contaminant. An ingredient in many hair care products, its use has grown exponentially in recent decades. Concentrations of C<sub>22</sub> alkyltrimethylammonium in seven samples collected in 2003 ranged between 22 and 53 µg/g, and as high as 290 µg/g in one of two samples collected in 2009. QACs are strongly sorbed to solid matrices, providing a mechanism for their recalcitrance during the production of biosolids. Vermicomposting and control treatment of a Class A biosolid over 12 weeks resulted in no easily detected changes in QAC compositions or concentrations, further highlighting the persistence of QACs in biosolid matrices.

## ENVR 81

### Characterizing poorly understood sources of organic wastewater compounds

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Poorly characterized sources of organic wastewater compounds (OWCs) such as wet-weather discharges from combined-sewer-overflow (CSO) and discharges from

pharmaceutical manufacturing facilities (PMFs) can have high concentrations of select compounds. Samples of wastewater treatment plant (WWTP) effluent and CSO effluent at a WWTP in Vermont showed that concentrations of OWCs that are effectively decreased during normal wastewater treatment were generally similar to or higher in CSO effluent than in WWTP effluent. Conversely, concentrations of OWCs that are ineffectively decreased during treatment are generally higher in WWTP effluent than in CSO effluent. Concentrations of multiple pharmaceuticals in 30 samples from two WWTPs containing input from PMFs were as much as 1,000 times higher than concentrations in samples from WWTP without PMF inputs, suggesting that PMFs can be a significant source of pharmaceuticals to receiving WWTPs.

## ENVR 82

### **Biosolids and earthworms: Bioaccumulation, toxicity, and removal of anthropogenic organic contaminants**

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Municipal sewage sludge, if it meets regulatory requirements, can be classified as biosolids and land applied as an organic rich source of plant nutrients. Biosolids are known to contain a complex mixture of anthropogenic organic contaminants including pharmaceuticals, disinfectants, and detergent metabolites. Once land applied, the organic contaminants in biosolids including disinfectants, synthetic fragrances, and detergent metabolites, have been measured to rapidly transfer and accumulate in earthworm tissue. While concentrations of some organic contaminants were below detection levels in soil samples, their detection in earthworm tissue suggests bioaccumulation is taking place, and that earthworms may serve as a valuable tool for identifying terrestrial contamination. Subsequent controlled laboratory experiments suggest that some sewage sludge may be toxic to earthworms (*Eisenia fetida*) as measured by decreased reproduction and mortality. Other laboratory results suggest that vermicomposting may accelerate the removal of some organic contaminants present in biosolids such as triclosan, 4-tert-octylphenol, and indole.

**Occurrence and bioavailability of brominated flame retardants (BFRs) in land applied municipal biosolids**

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A succession of halogenated compounds has been used as polymer and textile flame retardants. Some hydrophobic and persistent representatives concentrate in wastewater solids. Hence, burdens of PBBs, PCBs and polybrominated diphenyl ethers (PBDEs) in historical sewage sludges may be employed to track the evolution of their usage. While PBDEs were long assumed to be retained within polymer products, mg/kg burdens in contemporary house dust and sewage sludge portend noteworthy emissions. Repeated application of biosolids containing such persistent compounds can lead to soil accumulation. PBDEs were determined in biosolids and receiving soils contained within test plots. Soil levels varied as a function of application rate and frequency. BDE-209 was the dominant congener detected. Based on congener profiles, PBDEs exhibited minimal *in situ* degradation. Concentrations were generally below quantitation limits in roots, stover and grain of corn grown on the treated plots. This indicates that bioaccumulation in such vegetative crops is limited.