

Anthropogenic Organic Chemicals in Biosolids from Selected Wastewater Treatment Plants in Georgia and South Carolina

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Abstract. The levels of anthropogenic organic chemicals were investigated in biosolids collected from 12 wastewater treatment plants, serving rural, industrial, and urban communities, in Georgia and South Carolina. A variety of anthropogenic organic chemicals were identified and detected in the biosolids at concentrations from $\mu\text{g kg}^{-1}$ to mg kg^{-1} . 4-nonylphenol (4-NP), a non-naturally occurring endocrine disruptor, is one of the most detected organic chemicals. Its level was detected at as high as 1400 mg kg^{-1} in several biosolids from urban and industrial areas. If biosolids is disposed of to the environment, there is a potential for biosolids-associated organic contaminants to enter into the water environment through leaching and runoff.

INTRODUCTION

The continued exponential growth in human population has created a corresponding increase in generation of biosolids, end product of wastewater treatment plants (WWTPs). The annual production of biosolids in the United States is projected to increase sharply to 47 million tons within the next decade (EPA, 1999). For example, in year 2000 the total annual biosolids production in Georgia is close to 1 million tons, almost 60% of which is produced by the 55 WWTPs within the 10 county regions around metro Atlanta (Goveron, 2000).

Land application is becoming a major means for biosolids disposal because of its beneficial effects on agricultural productivity of soils. In addition, landfilling is also commonly used for biosolids disposal (EPA, 1999). Due to its close association with human activities, biosolids often serve as a sink for anthropogenic organic chemicals and their partial metabolites that cannot be completely degraded during the wastewater treatment processes (La Guardia, 2001; Bhandari and Xia, 2003; Keller et al., 2003). A recent report by the National Academy of Sciences (2002) stated that the U.S. EPA's standards that govern using

biosolids on soil are based on outdated science. EPA currently has no regulations on the levels of organic chemicals in biosolids although land application and landfill of biosolids could have a high potential of continuously introducing organic contaminants into the water resource due to surface runoff and leaching.

To protect the environment especially our water resources, there is an urgent need for better understanding the behavior, fate, and transport of anthropogenic organic chemicals in biosolids. Information generated from this investigation will help governmental decision-makers, WWTP managers, and the general public better assess the environmental risks of land disposal of biosolids.

METHODS AND MATERIALS

Sample Collection and Extraction. Biosolids and compost samples were collected from 12 WWTPs in Georgia and South Carolina (Table 1), immediately packed with ice for transportation, and stored in a -20°C freezer until extraction. Before the extraction, a subsample of each biosolids or compost was freeze-dried. 5 gram of freeze-dried sample was extracted using 20 mL hexane/acetone (1:1 volume) on an accelerated extraction system (ASE 100, Dionex). The extractions were as follows: one extraction cycle, pressure at 1500 psi, temperature at 100°C , static 20 min, 60% flush, purge 100 s. 1 mL of the extract is transferred to a GC vial and analyzed on a gas chromatography with mass spectrometer detector (GC/MS) (Thermo Finnigan Polaris Q).

GC/MS Analytical Conditions. The GC conditions were as follows: initial column T = 60°C , held for 0.5 min, increase to 150°C at $10^{\circ}\text{C}/\text{min}$ ramp rate, held for 1 min, increase to 300°C at $3^{\circ}\text{C}/\text{min}$ ramp rate, held for 3 min, inlet temperature = 200°C , transfer line temperature = 250°C , ion source temperature = 200°C , splitless mode at He gas flow rate = 1.2 mL/min. The injection volume is 1 μL . The mass

Table 1. Characteristics of the Georgia WWTPs investigated

WWTP Name Code	Location	Population served	Community served	Wastewater treatment method
MT	East, GA	33,000	Mostly residential	Aerobic digestion
CL1	Middle, SC	125,000	Textiles and refractory industry	Anaerobic digestion
CL2	Middle, SC	30,000	Mostly residential	Aerobic digestion
FL	Southwest, GA	60,000	Mostly residential	Aerobic digestion
MB	East, SC	50,000	Mostly residential	Aerobic digestion
HHI	Southeast, GA	25,000	Mostly residential	Aerobic digestion
AS	North, GA	40,000	College town with medium size industry	Anaerobic digestion
MR	Northwest, GA	70,000	Urban residential area	Aerobic digestion
MC	West, GA	30,000	Mostly residential	Anaerobic digestion
BS	Southeast, GA	29,000	Residential and industry	Aerobic digestion
AT	Northwest, GA	600,000	Urban area and industry	Anaerobic digestion
AG	East, GA	175,000	Residential, industry (paper, chemical, food processing, and detergent), and four large regional hospitals	Anaerobic digestion

spectra were determined by electron impact at 70 eV at a MS range of 40 - 500 u. The analytical column is Agilent DB-5MS (30 m x 0.25 mm x 0.25 μm). 4-NP was qualified and quantified based on GC/MS analysis of 4-NP model compound. The NIST/EPA/NIH Mass Spectral Database Library (NIST 02) was used to qualify significant peaks on the GC/MS spectra for other organic chemicals in the extracts.

RESULTS & DISCUSSION

Levels of 4-NP. Figure 1 shows the level of 4-NP in the biosolids and composts from the selected WWTPs. Up to 1400 mg kg⁻¹ 4-NP was detected in the biosolids from treatment plant CL1. This level is more than 100 times higher than the current limit for 4-NP in biosolids set by the European Union. This treatment plant receives influent mainly from many local textile and refractory industry. The biosolids generated from this plant is disposed of through landfill.

In the same region of CL1, the residential wastewater is treated in a different plant (CL2). The concentration of 4-NP in the biosolids from this plant is 179 mg kg⁻¹, a much lower level than that in the biosolids from plant CL1. Plants MT, FL, MB, HHI, MR, and MC treat wastewater mostly from residential areas. The level of 4-NP in the biosolids from these plants ranges from not-detectable level to about 240 mg kg⁻¹. Much higher levels of 4-NP were detected in biosolids from WWTPs (plants AS, AT, AG) treating wastewater mainly from industry. This suggests that industry is likely the major source of 4-NP in biosolids. Plant BS is the only exception. Although it receives

industrial wastewater, 4-NP in its biosolids was not detectable because it is not used in the local industry.

The biosolids from plant CL2, FL, AS, and MC is composted before disposal. The composting process decreases the 4-NP content significantly, from 65% to 100%. Composting is most likely a cost effective means for reducing organic chemicals in biosolids.

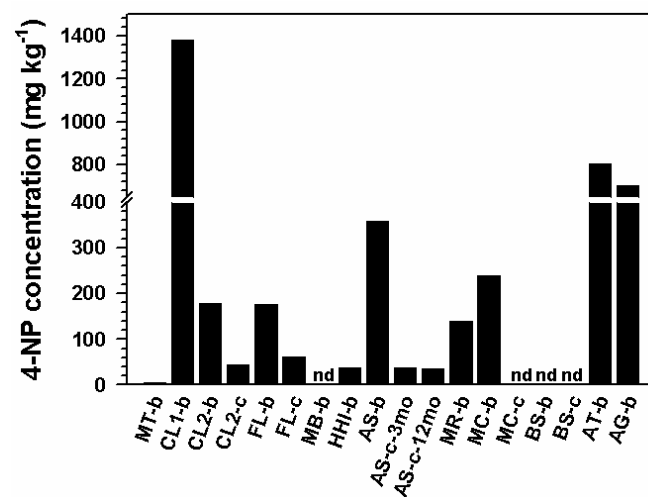


Figure 1. Concentrations of 4-NP in biosolids and composts from selected WWTPs in Georgia and South Carolina. The capital letters indicate the name of the WWTP. b, biosolids; c, compost; c-3mo, biosolids composted for 3 months; c-12mo, biosolids composted for 12 months; nd, not-detectable.

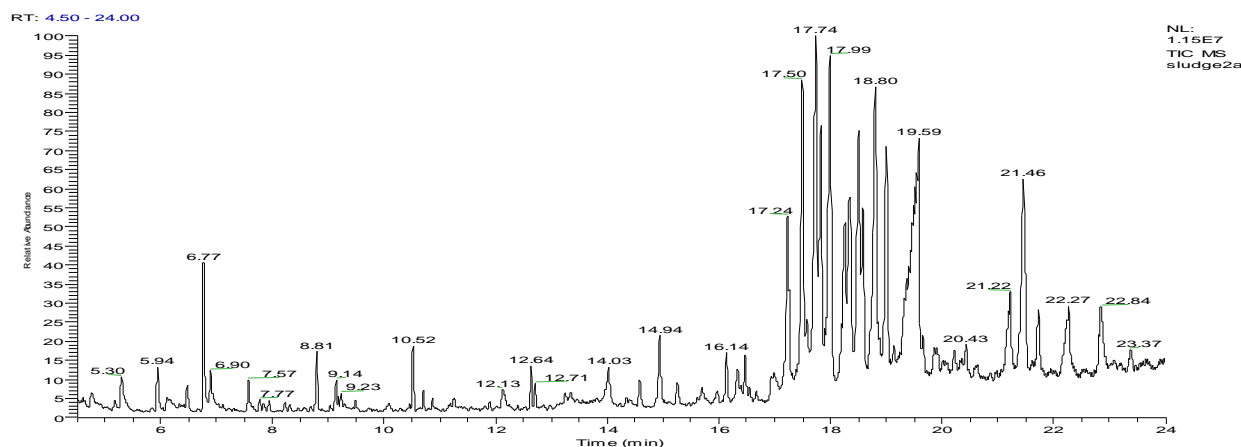


Figure 2. GC chromatogram of a hexane/acetone (1:1 volume) extract of biosolids from plant CL1.

Table 2. Selected organic chemicals in biosolids from plant CL1. GC chromatogram shown in figure 2 was used for the identification.				
Retention time (min)	Compound name	CAS #	use	Toxicity
4.77	3,5-Dimethylaniline	108-69-0	Intermediate used in manufacture of azo dyes	LC ₅₀ (48h)=17 mg L ⁻¹ for medaka fish (Tonogai et al., 1982)
5.30	2-Isopropyltoluene	527-84-4	Solvents, synthetic-resin manufacture, metal polishes, organic synthesis	Possibly cause Chromosome damage (NIH)
5.94	4-methyl-phenol (p-Cresol)	106-44-5	solvent, disinfectant and chemical intermediate in the production of synthetic resins	possible human carcinogen (USEPA, 1990), LC ₅₀ (24h)=21 mg L ⁻¹ for Crucian Carp (Verschueren, 1983)
10.52	3-Methylindole	83-34-1	Perfume and Food flavoring additive	Toxic to lung tissues (Regal et al., 2001) Ecotoxicity is unknown
11.26	2,3-dichloroaniline	608-27-5	Dye and pharmaceutical ingredient, pesticides	LC ₅₀ (96h)=2.3 mg L ⁻¹ for amphipod (U.S. EPA, 1988)
14.03	1-(1-chloroethenyl)-2-methyl-benzimidazole	78708-24-4	fungicides	Ecotoxicity is unknown
17.24-18.80	4-nonylphenol isomers	104-40-5	Metabolite of surfactant, plastic and rubber stabilizer, demulsifier,	Endocrine disruptor
21.22 & 21.46 & 21.73	Benz[a]anthracene	56-55-3	products of incomplete combustion of wood	probable human carcinogen; LC ₅₀ (96h)=5 µg L ⁻¹ for Daphnia pulex (Trucco et al., 1983)

Other organic chemicals identified. Table 2 lists the selected organic chemicals in biosolids from plant CL1, which receives industrial wastewater. The identified compounds are commonly used in textile and refractory industry, the major industry in the area. Although 4-NP was not detected in plant BS, many other organic chemicals were identified in its biosolids. For example, significant amount of aziridine commonly used as flocculation aids in paper industry and adhesives and binders in textile industry was identified. Plant BS receives wastewater from local paper and textile factories. In biosolids from WWTPs (AT and MR) severing large urban area, organic chemicals such as polycyclic musk, 4-nonylphenol, steroid, 2-methyl-1-chloro-anthraquinone, and 4-fluoro-3'-methoxybiphenyl were found. Those chemicals are closely related to urban use. Polycyclic musk is used as fragrance in fabric softener. 4-nonylphenol is the metabolite of surfactants added in household cleaning products. Steroid is the major ingredient in contraceptive pills. 2-methyl-1-chloro-anthraquinone is used in geese repellent around airport. 4-fluoro-3'-methoxybiphenyl is a pesticide for protecting conifers from southern pine beetle. Research has shown ecotoxicity for some of the identified compounds (Table 2).

The results from in this study indicate that conventional treatment processes used at these WWTPs are not completely effective in degradation of organic contaminants. A large portion of organic contaminants appeared to adsorb to the biosolids, a phenomenon that likely prevented their degradation in the bioreactors in WWTPs. Composting of biosolids appeared to be effective in degrading organic chemicals. Future research on the transport and transformation of those compounds in biosolids disposed of to the environment and their impact on surface and ground water quality are needed.

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