ANTHROPOGENIC ORGANIC CHEMICALS IN BIOSOLIDS FROM SELECTED WASTEWATER TREATMENT PLANTS IN GEORGIA AND SOUTH CAROLINA

Kang Xia and Greg Pillar

AUTHORS: Department of Crop and Soil Sciences, University of Georgia, Athens, GA 30602, (kxia@uga.edu, phone: 706-542-0899).
REFERENCE: Proceedings of the 2003 Georgia Water Resources Conference, held April 23-24, 2003, at the University of Georgia. Kathryn J. Hatcher, editor, Institute of Ecology, The University of Georgia, Athens, Georgia.

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 μg 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. Disposal of biosolids to the environment will create a high 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Academy of Sciences (2002) stated that the U.S. EPA's standards that govern using biosolids on soil are based on outdated science.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 of 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^{o}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^{o}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^{o}C, held for 0.5 min, increase to 150^{o}C at 10^{o}C/min ramp rate, held for 1 min, increase to 300^{o}C at 3^{o}C/min ramp rate, held for 3 min, inlet temperature = 200^{o}C, transfer line temperature = 250^{o}C, ion source temperature = 200^{o}C, splitless mode at He gas flow rate

Table 1. Characteristics of the Georgia WWTPs investigated

WWTP Name Code	Location	Population served	Community served	Wastewater treatment method
1	Georgia	33,000	Mostly residential	Aerobic digestion
2	South Carolina	125,000	Textiles and refractory industry	Anaerobic digestion
3	South Carolina	30,000	Mostly residential	Aerobic digestion
4	Georgia	60,000	Mostly residential	Aerobic digestion
5	South Carolina	50,000	Mostly residential	Aerobic digestion
6	Georgia	25,000	Mostly residential	Aerobic digestion
7	Georgia	40,000	Mostly industry	Anaerobic digestion
8	Georgia	70,000	Urban residential area	Aerobic digestion
9	Georgia	30,000	Mostly residential	Anaerobic digestion
10	Georgia	29,000	Residential and industry	Aerobic digestion
11	Georgia	600,000	Urban area and industry	Anaerobic digestion
12	Georgia	175,000	Residential, industry (paper, chemical, food processing, and detergent), and regional hospitals	Anaerobic digestion

= 1.2 mL/min. The injection volume is 1 μL. The mass 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 2. 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 treatment plant 2 the residential wastewater is treated in a different treatment plant (#3). 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 treatment plant 2. Treatment plants #1, #4, #5, #6, #8, and #9 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 #7, #11, #12) treating wastewater mainly from industry. This suggests that industry is likely the major source of 4-NP in biosolids. Treatment plant #10 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 treatment plants #2, #4, #7, and #9 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.

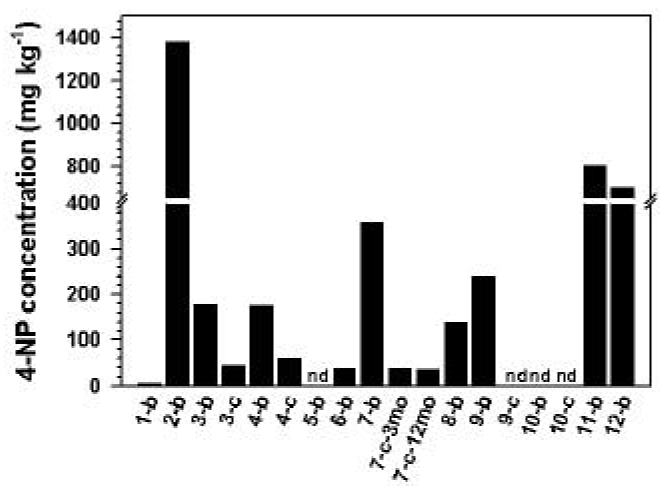

Figure 1. Concentrations of 4-NP in biosolids and composts from selected WWTPs in Georgia and South Carolina. The capital letters indicate the name of the WWTP. b, biosolids; c, compost; c-3mo, biosolids composted for 3 months; c-12mo, biosolids composted for 12 months; nd, not-detectable.

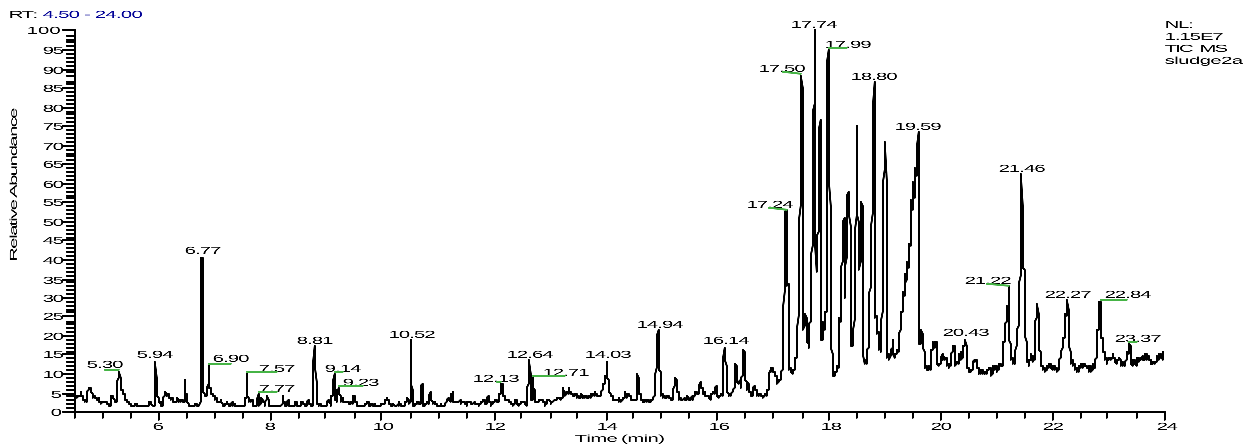

Figure 2. GC chromatogram of a hexane/acetone (1:1 volume) extract of biosolids from treatment plant #2.

Table 2. Selected organic chemicals in biosolids from treatment plant #2.
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 treatment plant #2, 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 treatment plant #10, 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. Treatment plant #10 receives wastewater from local paper and textile factories. In biosolids from WWTPs (#11 and #8) 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 softner. 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 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.

ACKNOWLEDGMENTS

The authors wish to thank Mr. Gene Weeks of the Department of Crop and Soil Sciences at UGA for sample collection.

LITERATURE CITED

Bhandari, A., and K. Xia. 2003. Hazardous Organic Chemicals in Biosolids Recycled as Soil Amendments. In *The Handbook of Environmental Chemistry Vol. 5. Water Pollution: Environmental Impact Assessment of Recycled Hazardous Waste Materials on Surface and Ground Waters*. (In print).

EPA. 1999. Biosolids Generation, Use and Disposal in the United States. U.S. Environmental Protection Agency, Office of Solid Waste, Report No. EPA530-R99-009.

Goveron, J. D. 2000. Characterization and quantification of Georgia's municipal biosolids production and disposal. Report prepared by Engineering Outreach Services for the Pollution Prevention Assistance Division, GA DNR.

Keller, H., K. Xia, and A. Bhandari. 2003. Occurrence and transformation of estrogenic nonylphenol polyethoxylates and their metabolites in three northeast Kansas wastewater treatment plants. *Periodical of Hazardous, Toxic, and Radioactive Waste Management*. (In print).

La Guardia, M. J., R. C. Hale, E. Harvey, T. M. Mainor. 2001. Alkylphenol Ethoxylate Degradation Products in Land-Applied Sewage Sludge (Biosolids). *Environ Sci Technol.* 35:4798-4804.

National Academy of Sciences. 2002. Biosolids applied to land: advancing standards and practices. July 2, 2002, National Academy Press, Washington DC.

Regal, K. A., G.M. Laws, C. Yuan, G.S. Yost, and G.L. Skiles. 2001. Detection and Characterization of 3-Methylindole-DNA Adducts in vitro Systems, Chem. Res. Toxicol. 14: 1014-1024.

Tonogai, Y., S. Ogawa, Y. Ito, and M. Twaida. 1982. Actual survey on TLm (median tolerance limit) values of environmental pollutants, especially on amines, nitriles, aromatic nitogen compounds and artificial dyes. J. Toxicol. Sci. 7: 193-203.

U.S. EPA. 1990. Health and Environmental Effects Document for 4-Methylphenol. Prepared by the Office of Health and Environmental ASssessment, Environmental Criteria and Assessment Office, Cincinnati, Ohio for the Office of Solid Waste and Emergency Response.

U.S.EPA.1988. http://www.epa.gov/opptintr/chemtest/aniline2.pdf

Verschueren, K. 1983. Handbook of Environmental Data of Organic Chemicals. 2nd ed. New York, NY