

Project Proposal

1. Title of Proposal: Occurrence of Pharmaceuticals and Personal Care Products (PPCPs) at an effluent-dominated wastewater application site: Estrogens, Triclosan, and Caffeine.

2. Focus Category: Groundwater, Solute transport, Water quality

3. Keywords: Micropollutants, Endocrine disruptor, Pharmaceuticals and Personal Care Products, Sorption,

4. Duration: March 1, 2009 through February 28, 2010

5. Federal Funds Requested: \$4,967

6. Non-Federal (matching) Funds Pledged: \$10,025

7. Principal Investigator (graduate student):

Adcharee Karnjanapiboonwong, Graduate Research Assistant,
Department of Environmental Toxicology, Texas Tech University, Box 41163, Lubbock,
TX 79409-1163 Email: adcharee.kwong@tiehh.ttu.edu Phone: (806)252-2039

8. Co-Principal Investigator (faculty advisor):

Dr. Todd A. Anderson, Professor, Department of Environmental Toxicology,
Texas Tech University, Box 41163, Lubbock, TX 79409-1163
Email: todd.anderson@ttu.edu Phone: (806)885-0231

9. Congressional District(s) where project will occur: 19th Texas

10. Abstract

Pharmaceuticals and personal care products (PPCPs) have recently been identified in the environment and are considered potent endocrine disruptors, drivers for the development of antibiotic resistance, and considered as persistent chemicals. These contaminants can reach the soil and aquatic environment through land application of wastewater and agricultural runoff. Several studies have determined that these compounds are not completely removed during the wastewater treatment process, and can be detected in stream surveys in the United States.

The overall goal of this research is to study the fate of pharmaceuticals at field scale. The unique study site is a wastewater land application site used for nutrient removal and non-edible crop production. The Lubbock Land Application Site (LLAS) has received wastewater effluent for over 70 years, and is an ideal site to determine the long-term fate of PPCPs in the environment above drinking water sources. Factors affecting the fate of target PPCPs will be investigated.

11. Statement of Critical Regional Water Problems

Although pharmaceuticals and personal care products (PPCPs) may exist in minute quantities, long-term release of them may result in significant environmental concentrations. PPCPs enter the Lubbock Water Reclamation Plant (LWRP), a major full-scale wastewater treatment plant in Lubbock, TX, via the disposal of residential wastewater which is the main source (85%) of influent to the plant. Previous work was conducted at the LWRP to investigate the levels of a common antibiotic, amoxicillin. Wastewater samples were analyzed for amoxicillin as well as antibiotic resistance. The results indicated that amoxicillin can be detected in the influent of the plant. Since target PPCPs: estrone, 17 β -estradiol, 17 α -ethynylestradiol, estriol, caffeine, and triclosan may not be completely removed during the wastewater treatment process, these compounds may be discharged into streams and land application sites, and eventually contaminate aquatic environment or persist in surface water, groundwater, and soil. If these compounds persist in the effluent, the choice of wastewater treatment and water reuse

alternatives needs to be considered carefully to minimize exposure to humans, or treatment processes must be improved to protect humans and the environment. In addition, as the City of Lubbock prepares to change their water reuse practices from irrigation of farmland to stream discharge into a reservoir system, the fate of PPCPs should be evaluated. Therefore, this study should be completed to determine if PPCPs represent a future problem.

12. Nature, Scope, and Objectives of the Research.

The proposed research outlined here is part of a larger project (funded by the U.S. EPA) on the long-term fate (occurrence, sorption, biodegradation, plant uptake) of pharmaceuticals and law and policy questions related to water re-use. The proposed research will only focus on a portion of those objectives consistent with the amount of funds requested.

During the last few years, PPCPs have been identified in the environment and studies have focused on their ecotoxicity [1]. Some natural estrogens, such as estriol, estradiol and estrone are considered to be potent endocrine disruptors [2,3]. However, the fate and the persistence of these compounds is still unclear [1,2,4,5]. Other antimicrobial compounds, such as triclosan which is used in many personal care products are believed to lead to the development of antibiotic resistance and are considered as persistent chemicals in the environment [6]. These PPCPs transport to municipal wastewater treatment plants and eventually are discharged into the aquatic environment or persist in surface water, ground water, and soil [7,8]. Several studies determined that these compounds are not completely removed during the wastewater treatment process, and can be detected in stream surveys in the United States [2,9,10].

Objectives

The goal of the proposed research is to investigate the fate of PPCPs at field scale. Specific objectives include:

1. Developing analytical methods to measure PPCPs in water, wastewater and soil.
2. Extending developed methods to analyze target PPCPs in wastewater, groundwater and soil collected from study site (Lubbock Land Application Site).

Experimental Approach

The research is divided into two phase. In Phase I, information regarding the presence and absence of PPCPs in the effluent of the Lubbock Water Reclamation Plant and the groundwater at the Lubbock Land Application Site will be collected. Phase II will identify the presence and concentration of the target PPCPs in soil samples collected from the Lubbock Land Application Site.

Phase I: Evaluate the presence of target PPCPs in groundwater recharged through wastewater reclamation at a Lubbock Land Application Site (LLAS).

Water samples will be collected to gather data regarding the presence and absence of PPCPs at the LLAS and their persistence in the groundwater recharged by surface irrigation. Water samples will be collected at the Lubbock Water Reclamation Plant (LWRP) to evaluate the presence and absence of PPCPs in the wastewater discharged as well as determine the impact of the current treatment technologies employed at the treatment plant. The target PPCPs to be evaluated in this study are: *estrone*, *17 β -estradiol*, *estriol*, *17 β -ethynylestradiol*, *caffeine*, and *triclosan*. Water and sludge samples from the treatment plant will be collected from the

following locations: *Plant influent, aeration basin, plant effluent, digested sludge, and digested sludge supernatant*. The groundwater samples will be collected from a tap near the wells.

The solid phase extraction, and conventional (HPLC) and hyphenated (HPLC-MS) analytical techniques exist will be used to for the analysis of PPCPs in samples. The methods relevant to the proposed work [4,7] will serve as a starting point and will then be developed based on the target PPCPs and equipment available. Confirmatory analyses on a portion of the samples (10-20%) will utilize HPLC-MS.

Phase II: Ascertain the quantity of PPCPs in the soil at the wastewater application site.

At the LLAS, PPCPs may accumulate in the soil, but at different concentrations from those that may be predicted by the soil-water partition coefficient for the contaminant. Therefore, soil samples will be collected at soil surface and analyzed for the targeted PPCPs. Soil sample collection will coincide with water sample collection (Phase I) at the LLAS.

Methods for the extraction of PPCPs from sewage sludges, sludge-treated soils, and surface soils are available [11-14]. These methods will serve as a starting point and will then be developed based on the target PPCPs. The analytical methods to measure PPCPs in water, wastewater, sludge and soil will be developed with the equipment available. Conventional HPLC (UV, Fluorescence) will be the primary mode of analysis. Confirmatory analyses on a portion of the samples (10-20%) will utilize HPLC-MS.

13. Results Expected from this Project

The outcomes of this work include identifying the fate and transport of PPCPs in natural system, and determining PPCPs in water, wastewater, and soil. Factors affecting transport and persistence of PPCPs in the environment may be obtained from data collected during the study. The information collected from this research such as the amount of PPCPs in influent and effluent may be useful for wastewater treatment system to be upgraded to minimize these compounds. The study may provide long-term attainment in case that the water reuse practices are changed from irrigation of farmland to stream discharge into a reservoir system. Accordingly, the fate of PPCPs should be evaluated if they are persist in wastewater treatment systems which means that target pollutants have possibility to accumulate in an aquatic system such as the future reservoir system.

References

1. Daughton, C.G. and Ternes, T.A. (1999). Pharmaceuticals and personal care products in the environment: Agent of subtle change? *Environmental Health Perspectives* 107(S6): 907-938.
2. Gross, B., Montgomery-Brown, J., Naumann, A. and Reinhard, M. (2004). Occurrence and fate of pharmaceuticals and alkylphenol ethoxylate metabolites in an effluent-dominated river and wetland. *Environmental Toxicology and Chemistry* 23(9): 2074-2083.
3. Ying, G.G., Kookana, R. and Waite, T.D. (2004). Endocrine disrupting chemicals (EDCs) and pharmaceuticals and personal care products (PPCPs) in reclaimed water in Australia. Australian water conservation and reuse research program. ISBN 0643091807.
4. Kolpin, D.W., Furlong, E.T., Meyer, M.T., Thurman, E.M., Zaugg, S.D., Barber, L.B. and Buxton, H.T. (2002). Pharmaceuticals, hormones, and other organic wastewater

- contaminants in U.S. streams, 1999-2000: A national reconnaissance. *Environmental Science & Technology* 36(6): 1202-1211.
5. Ankley, G.T., Brooks, B.W., Huggett, D.B. and Sumpter, J.P. (2007). Repeating history: pharmaceuticals in the environment. *Environmental Science & Technology* 41(24): 8211-8217.
 6. Ying, G.G. and Kookana, R.S. (2006). Triclosan in wastewaters and biosolids from Australian wastewater treatment plants. *Environment International* 33(2): 109-205.
 7. Chu, S. and Metcalfe, C.D. (2007). Simultaneous determination of triclocarban and triclosan in municipal biosolids by liquid chromatography tandem mass spectrometry. *Journal of Chromatography A* 1164: 212-218.
 8. Allaire, S.E., Castillo, J.D. and Juneau, V. (2006). Sorption kinetics of chlortetracycline and tylosin on sandy loam and heavy clay soils. *Journal of Environmental Quality* 35: 969-972.
 9. Haggard, B.E., Galloway, J.M., Green, W.R. and Meyer, M.T. (2006). Pharmaceuticals and other organic chemicals in selected north-central and northwestern Arkansas streams. *Journal of Environmental quality* 35(4): 1078-1087.
 10. Waltman, E.L., Venables, B.J. and Waller, W.T. (2006). Triclosan in a North Texas wastewater treatment plant and the influent and effluent of an experimental constructed wetland. *Environmental Toxicology and Chemistry* 25(2): 367-372.
 11. Chun, S., Lee, J., Geyer, R. and White, D.C. (2005). Comparison of three extraction methods for 17 β -estradiol in sand, bentonite, and organic-rich silt loam. *Journal of Environmental Science and Health, Part B* 40: 731-740.
 12. Löffler, D. and Ternes, T.A. (2003). Determination of acidic pharmaceuticals, antibiotics and ivermectin in river sediment using liquid chromatography-tandem mass spectrometry. *Journal of Chromatography A* 1021: 133-144.
 13. Kinney, C.A., Furlong, E.T., Werner, S.L. and Cahill, J.D. (2006). Presence and distribution of wastewater-derived pharmaceuticals in soil irrigated with reclaimed water. *Environmental Toxicology and Chemistry* 25(2): 317-326.
 14. Federle, T.W., Kaiser, S.K. and Nuck, B.A. (2002). Fate and effects of triclosan in activated sludge. *Environmental Toxicology and Chemistry* 21(7): 1330-1337.