

Pharmaceuticals and Personal Care Products (PPCPs), and Endocrine Disrupting Compounds (EDCs) in Runoff from a Potato Field Irrigated with Treated Wastewater in Southern California

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Irrigation of crops with treated wastewater has been employed in many regions of the world. It mitigates the pressure of water demand, however, it also introduces effluent-derived organic contaminants into surface waters *via* agricultural runoff. In this study, a potato field located in southern California was selected as the research site. Runoff samples were collected during irrigation events, and a variety of compounds were identified both in irrigation water and runoff samples. Treatments on the field included polyacrylamide (PAM) application, deep plow, previous-grown Sudan grass, and control (without above treatments). The compounds included pharmaceuticals (*e.g.*, clofibric acid, ibuprofen, naproxen, ketoprofen, diclofenac), personal care product (*e.g.*, triclosan), endocrine disrupting compounds (*e.g.*, bisphenol A, 4-*n*-nonylphenol, 4-*t*-octylphenol), and estrogenic compounds (*e.g.*, estrone, 17 β -estradiol, 17 α -ethynylestradiol). The monitoring results showed the presence of these compounds in runoff samples. They were at concentrations from below limits of quantification (LOQ) to sub $\mu\text{g/l}$ levels. Although their levels were low, their potential to elicit adverse effects in aquatic organisms cannot be overlooked.

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INTRODUCTION

Water reclamation, recycling and reuse are now recognized worldwide as key components in the efficient management of water resources.¹⁾ Landscape and agricultural irrigation with treated wastewater in the United States and many other countries has reduced the demand posed on water supplies. It was estimated that about $9.8 \times 10^6 \text{ m}^3/\text{d}$ treated municipal wastewater (7.4% of the total) was reused in the United States in 2006.²⁾ When enjoying the benefits of treated wastewater reuse, however, people have to face the adverse effects resulted from the effluent-derived organic contaminants during this practice.

Pharmaceuticals and personal care products (PPCPs), and endocrine disrupting compounds (EDCs) are chemicals extensively detected in the effluents of sewage treatment plant (STP), where they can not be efficiently removed.^{3–5)} These emerging chemicals are currently unregulated, but their presence is of growing notoriety and concern.^{6,7)} They have been reported to be transported off-site *via* runoff and drainage.^{6,8)} As a potential non-point pollution source, runoff from agricultural fields may get aquatic systems contaminated from terrestrial ecosystem.

In this study, we examined levels of PPCPs and EDCs from runoffs in a potato field in southern California irrigated with treated wastewater. The potato field has several treatments including polyacrylamide (PAM) application, deep plow, previous-grown Sudan grass, and control (without above treatments). The objective of this study is to determine the presence of effluent-derived compounds in agricultural runoffs and whether the different treatments on the field would affect the runoff compositions.

MATERIALS AND METHODS

Standards and Reagents—All PPCPs and EDCs compounds selected in this study have been detected in surface and ground water susceptible to influences of wastewater treatment plant effluents.^{9–11)} Naproxen (>98%), clofibric acid (>99%), ketoprofen (>98%) and diclofenac

sodium salt (>98%) were purchased from MP Biomedicals (Solon, OH, U.S.A.). Estrone (>99%), 17 β -estradiol (99%), 17 α -ethynylestradiol (>98%) and ibuprofen (99%) were purchased from Acros Organics (Morris Plains, NJ, U.S.A.). 4-tert-octylphenol (97%), bisphenol A (>99%), and the derivatizing reagent, *N*-tert-butyldimethylsilyl-*N*-methyltrifluoroacetamide (MTBSTFA) were purchased from Sigma-Aldrich (St. Louis, MO, U.S.A.). 4-*n*-Nonylphenol (>99%) and triclosan (>97%) were purchased from Sigma-Aldrich (Milwaukee, WI, U.S.A.). The surrogate standard, 2,4-dichlorophenylacetic acid was purchased from Spex CertiPrep (Metuchen, NJ, U.S.A.). Acetone, ethyl acetate and dichloromethane (pesticide grade) were purchased from Fisher (Fair Lawn, NJ, U.S.A.). Anhydrous sodium sulfate (Fisher) was analytical grade. It was baked at 400°C for 4 h and stored in a sealed container. Granular anionic PAM, with an average molecular weight of 10–15 million g/mol, 21% NH₂ group substituted by OH group, was provided by Celanese Corporation (Louisville, KY, U.S.A.).

Potato Field— The potato field locates in western Riverside County, southern California. The climate there belongs to semi-arid condition, with average annual precipitation of 56 mm but evapotranspiration of 1450 mm (Data of 2007. California Irrigation Management Information System, <http://www.cimis.water.ca.gov>). This potato field has a 5-year history of using treated wastewater for irrigation. The field soil was sandy loam soil, with a pH value of 6.5 measured in a 0.005 M CaCl₂ solution, and organic matter content of 0.75% measured by the 450°C combustion method. Particle size analysis was determined by the hydrometer method, and results showed that the soil contained 7.5% of clay, 68.8% of sand, and 23.7% of sand.

The field was divided into 12 plots, each 200 ft long and 30 ft wide. Between every two plots furrows were dredged to introduce runoff to the receptacles located at the end of the plots buried beneath the soil surface. During the experiment, potatoes were growing in the field.

Treatments were as follows. Before the potato planting, two plots were deep-plowed (D); two were previously-grown with Sudan grass (*Sorghum vulgare* var. *sudanense*, the grass was stripped of before potato planting) (S); two were previously-grown Sudan grass and then deep-plowed (S+D); three plots were applied with PAM before irrigation (PAM); the last three plots were as control without

any treatment (control).

Sample Treatment— Procedures for runoff and irrigation water sample treatment were detailed elsewhere.¹² In brief, 1000 ml of water sample was filtered, and the pH was adjusted to 3 with concentrated sulfuric acid. Sample was loaded onto the HyperSep C18 SPE cartridge (500 mg/6 ml, Thermo Electron Corporation, Bellefonte, PA, U.S.A.). The cartridge was eluted with ethyl acetate. The eluate was dried over anhydrous sodium sulfate, and reduced to 0.5 ml, then transferred into the gas chromatography (GC) vial. 100 μ l of MTBSTFA was added, and the volume was brought to 1 ml with ethyl acetate. The GC vials were put into GC oven at 70°C for 60 min for derivatization. The extracts were analyzed with GC-MS.

GC-MS Analysis— Target chemicals were determined using an Agilent 6890N GC with 5975C MSD (Agilent, Palo Alto, CA, U.S.A.) equipped with an Agilent 7683B automatic liquid sampler and an HP-5MS GC column (30 m, 0.25 mm i.d., 0.25 μ m film thickness). Helium was used as the carrier gas, with a column flow rate of 1.2 ml/min in constant-flow mode. Injector temperature was 250°C. The GC-mass selective detector (MSD) interface and the ion source temperatures were set at 280 and 230°C, respectively. The GC oven temperature was kept at 50°C for 1 min, followed by the first ramp at 20°C/min to 120°C, second ramp at 10°C/min to 280°C, and holding for 11 min. The mass spectrometer was operated in the selected ion monitoring mode with electron ionization voltage of 70 eV. A 2- μ l sample was injected in pulsed splitless mode.

RESULTS AND DISCUSSION

Seven-point calibration curves were prepared by spiking corresponding amounts of target compounds into 1000 ml of de-ionized water. The spiked water samples were analyzed as the procedure described above. The calibration curves were quite good for all the target compounds ($R^2 > 0.99$). Limits of quantification (LOQ) were set as the second lowest calibration point within the linear correlation curve, with a signal-to-noise (S/N) ratio of at least 10 using the baseline in the chromatogram. The method recovery for test compounds in runoff samples was between 81–118%, and LOQ ranged from 5 to 75 ng/l depending on the compounds (Table 1).

Table 1. Retention Times and Mass Spectrometric Data for tert-butyl-dimethylsilyl (BDMS) Derivatives of Selected Compounds in GC-MS Analysis and Their Method LOQ

compound	Retention time (min)	Quantification ions, <i>m/z</i>	Confirmation ions, <i>m/z</i>	LOQ, ng/l
clofibric acid	13.34	143	273, 271	7.5
ibuprofen	13.78	263	161, 264	5
4- <i>t</i> -octylphenol	14.10	263	165, 320	40
4- <i>n</i> -nonylphenol	16.79	277	165, 334	7.5
naproxen	18.15	287	185, 288	7.5
triclosan	18.63	347	200, 345	6
ketoprofen	19.29	311	295, 312	7.5
diclofenac	20.14	352	214, 409	10
bisphenol A	21.33	441	207, 456	5
estrone	23.65	327	163, 384	30
17 β -estradiol	23.77	329	386	75
17 α -ethynylestradiol	24.71	353	327, 410	30
2,4-dichlorophenylacetic acid (surrogate standard)	13.65	261	159, 263	

Table 2. Concentrations of PPCPs and EDCs in Irrigation Water and in Runoff Samples from a Potato Field with Different Treatments (ng/l)

Compounds	Irrigation water	S (<i>n</i> = 2)	D (<i>n</i> = 2)	S + D (<i>n</i> = 2)	PAM (<i>n</i> = 3)	Control (<i>n</i> = 3)
clofibric acid	258	113 \pm 23	129 \pm 45	144 \pm 38	188 \pm 23	151 \pm 56
ibuprofen	1154	27 \pm 12	15 \pm 10	16 \pm 12	213 \pm 58	108 \pm 47
4- <i>t</i> -octylphenol	85	<LOQ	80 \pm 23	<LOQ	<LOQ	88 \pm 42
4- <i>n</i> -nonylphenol	329	102 \pm 32	97 \pm 26	81 \pm 33	163 \pm 17	117 \pm 34
naproxen	146	32 \pm 7	43 \pm 25	32 \pm 13	93 \pm 23	53 \pm 18
triclosan	560	75 \pm 15	48 \pm 14	50 \pm 17	95 \pm 52	63 \pm 8
ketoprofen	142	53 \pm 9	56 \pm 24	72 \pm 26	97 \pm 13	53 \pm 22
diclofenac	112	69 \pm 7	36 \pm 21	58 \pm 11	71 \pm 21	47 \pm 18
bisphenol A	457	30 \pm 21	<LOQ	<LOQ	144 \pm 28	66 \pm 25
estrone	63	32 \pm 16	<LOQ	27 \pm 12	75 \pm 36	39 \pm 21
17 β -estradiol	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
17 α -ethynylestradiol	48	22 \pm 10	25 \pm 9	<LOQ	17 \pm 12	55 \pm 15

For each treatment plot, three runoff samples were analyzed. *n* Represents numbers of treatment plot. Refer to section "potato field" in "Materials and Methods" for abbreviations of S, D, etc.

Table 2 summarizes the concentrations of PPCPs and EDCs in the irrigation water and in runoff samples from the potato field under different treatments. As shown in the table, in the irrigation water, ibuprofen has the highest level (1154 ng/l) among all of the selected compounds, and other compounds levels are ranging from 48 to 560 ng/l. The absent detection of 17 β -estradiol in the water samples may be due to its high LOQ with the present method, which is up to 75 ng/l (Table 1). The concentrations of these selected PPCPs and EDCs are typical for effluent-borne contaminants levels compared with other studies.^{11, 13–15)}

Almost all selected compounds were detected in the runoff samples, as shown in Table 2. Previ-

ous studies have proved that irrigation with treated wastewater could introduce human pharmaceuticals, hormones, personal care product ingredients, and other xenobiotic organic compounds to runoffs from fields.^{6, 8)} Data in this study confirmed their results, and also indicated that contaminants compositions of runoff samples altered with different soil treatments. Runoff from the plots treated with PAM application had the highest contaminants levels for most compounds (except for 4-*t*-octylphenol and 17 α -ethynylestradiol) compared with the other four treatments. This may be due to the characteristics of PAM application. PAM works by stabilizing soil surface structure and pore continuity. It can be strongly adsorbed onto the surface of soil particles

and can keep them from dispersion. Thus the adsorbed PAM may form a film on the soil surface, which retards the chemicals to sorption sites inside the soil particles.¹⁶⁾ Lu *et al.* found that PAM treatment could prolong the time for sorption equilibrium of four herbicides on two natural soils.¹⁶⁾ This mechanism can explain the phenomenon that relatively high levels of contaminants occurred in runoff treated with PAM.

Treatments of S, D, and S+D had close contaminants levels in the runoff samples, with some compounds concentrations lower than levels in the control. This result demonstrated that, deep-plow or previously-grown Sudan grass, or both may change some soil physical properties, resulting in the variation of contaminants levels in runoff compositions. The key factor that influences the runoff compositions should be the adsorption coefficients of chemicals onto cropland soils during the irrigation event. Among all treatments, PAM application may have an obvious impact on the adsorption process that retards the sorption of effluent-derived compounds to soil.

In general, in arid/semi-arid areas such as southern California, as more treated wastewater is used for landscape and cropland irrigation, runoff from agricultural fields has become an important non-point source of effluent-borne contaminants. Whereas wastewater reuse may reduce overall impacts to surface waters, irrigation with treated effluent does not eliminate the introduction of organic micro-contaminants into aquatic ecosystem.⁸⁾ Results from the present study indicated the presence of targeted compounds in runoff samples in a potato field irrigated with treated wastewater. Further investigation needs to be conducted to study their ecological impacts to both the aquatic and terrestrial ecosystems.

REFERENCES

- 1) Levine, A. D. and Asano, T. (2004) Recovering sustainable water from wastewater. *Environ. Sci. Technol.*, **38**, 201A–208A.
- 2) Miller, G. W. (2006) Integrated concepts in water reuse: managing global water needs. *Desalination*, **187**, 65–75.
- 3) Takao, Y., Shimazu, M., Fukuda, M., Ishibashi, H., Nagae, M., Kohra, S., Tabira, Y., Ishibashi, Y. and Arizono, K. (2008) Seasonal and diurnal fluctuations in the concentrations of pharmaceuticals and personal care products (PPCPs) in residential sewage water. *J. Health Sci.*, **54**, 240–243.
- 4) Loraine, G. A. and Pettigrove, M. E. (2006) Seasonal variations in concentrations of pharmaceuticals and personal care products in drinking water and reclaimed wastewater in southern California. *Environ. Sci. Technol.*, **40**, 687–695.
- 5) Nikolaou, A., Meric, S. and Fatta, D. (2007) Occurrence patterns of pharmaceuticals in water and wastewater environments. *Anal. Bioanal. Chem.*, **387**, 1225–1234.
- 6) Pedersen, J. A., Yeager, M. A. and Suffet, I. H. (2003) Xenobiotic organic compounds in runoff from agricultural fields irrigated with treated wastewater. *J. Agric. Food Chem.*, **51**, 1360–1372.
- 7) 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. *Environ. Toxicol. Chem.*, **25**, 317–326.
- 8) Pedersen, J. A., Soliman, M. and Suffet, I. H. (2005) Human pharmaceuticals, hormones, and personal care product ingredients in runoff from agricultural fields irrigated with treated wastewater. *J. Agric. Food Chem.*, **53**, 1625–1632.
- 9) 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 US streams, 1999–2000: a national reconnaissance. *Environ. Sci. Technol.*, **36**, 1202–1211.
- 10) Löffler, D. and Ternes, T. A. (2003) Determination of acidic pharmaceuticals, antibiotics and ivermectin in river sediment using liquid chromatography-tandem mass spectrometry. *J. Chromatogr. A*, **1021**, 133–144.
- 11) Wang, Y. Q., Hu, W., Cao, Z. H., Fu, X. Q. and Zhu, T. (2005) Occurrence of endocrine disrupting compounds in reclaimed water from Tianjin, China. *Anal. Bioanal. Chem.*, **383**, 857–863.
- 12) Xu, J., Wu, L. S., Chen, W. P. and Chang, A. C. (2008) Simultaneous determination of pharmaceuticals, endocrine disrupting compounds, and hormone in soils by gas chromatography-mass spectrometry. *J. Chromatogr. A*, **1202**, 189–195.
- 13) Boyd, G. R., Reemtsma, H., Grimm, D. A. and Mitra, S. (2003) Pharmaceuticals and personal care products (PPCPs) in surface and treated waters of Louisiana, USA and Ontario, Canada. *Sci. Total Environ.*, **311**, 135–149.
- 14) Lee, H. B., Peart, T. E. and Svoboda, M. L. (2005) Determination of endocrine-disrupting phenols, acidic pharmaceuticals, and personal-care

- products in sewage by solid-phase extraction and gas chromatography-mass spectrometry. *J. Chromatogr. A*, **1094**, 122–129.
- 15) Soliman, M. A., Pedersen, J. A. and Suffet, I. H. (2004) Rapid gas chromatography-mass spectrometry screening method for human pharmaceuticals, hormones, antioxidants and plasticizers in water. *J. Chromatogr. A*, **1029**, 223–237.
- 16) Lu, J. H., Wu, L. S., Letey, J. and Farmer, W. J. (2002) Anionic polyacrylamide effects on soil sorption and desorption of metolachlor, atrazine, 2,4-D, and picloram. *J. Environ. Qual.*, **31**, 1226–1233.