Presence of Pharmaceutically-Active Compounds in the Rio Grande and Riparian Groundwater

Water Resources Research Institute Project Report

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Introduction

Effects of human activities on local, regional and global biogeochemical cycles have become an issue of growing concern and increased research. Recent studies have clearly documented extensive human alteration of natural systems and processes. These studies range from the increase in global deposition and dispersion of nutrients (e.g. nitrogen) and heavy metals (e.g. mercury), acidification of precipitation, deterioration of the ozone through chlorofluorocarbons (CFCs), persistent organic pollutants (POPs), and the rising temperature of the Earth's surface. Human impacts are ubiquitous and deserve consideration in ecological research. Specifically, impacts that urban areas have on local and regional ecology is a critical area of study to better protect and preserve the diversity of natural ecosystems (Kline et al. 2001, Luck et al. 2001, Paul et al. 2001).

Chemical constituents of streams, rivers and groundwater aquifers are closely linked to the geological and biological dynamics within the catchments in which freshwaters cycle (Hynes 1975, Bartolino and Cole 2002). Freshwater ecosystems also reflect the types of chemical and physical changes humans have on the biosphere (Jackson et al. 2001, Baron et al. 2003). Human effects on freshwater chemistry result from direct inputs such as wastewater treatment effluents to indirect pathways such as non-point sources and climate change (Murdoch et al. 2000, Dahm et al. 2003). Wastewater treatment plant effluents (WTPE) have recently come under scrutiny from several studies reporting on the detection of a suite of trace organic contaminants throughout North American streams that are of human origin (Barber et al. 2000, Kolpin et al. 2002, Singer et al. 2002, Wilson et al. 2003).

These organic wastewater contaminants include an array of human and veterinary pharmaceuticals and personal care products (PPCPs). These compounds range from prescription drugs, to fragrances and sun-screen agents. Kolpin et al. (2002) analyzed water samples collected in 1999 – 2000 from 139 streams across 30 states in North America that they deemed susceptible to contamination from urban, industrial and/or agricultural activities. Anthropogenic organic compounds were found at low concentrations (ng/L to ug/L range), and they were found in 80% of the streams sampled. The frequency of detection and total concentrations differed for different categories of organic compounds (Figure 1).

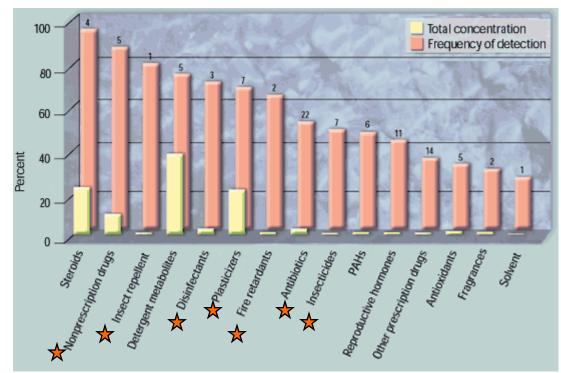


Figure 1. Total concentration and frequency of detection for organic wastewater contaminants by general use category (from Erickson 2002). The number of compounds in each category is shown above bars. Stars indicate categories detected in this study.

Since the study by Kolpin et al. (2002), additional scientific work has addressed national and regional occurrences of specific organic wastewater contaminants and

studies have been carried out to improve analytical procedures for measuring these compounds. Few studies, however, address the environmental fate and ecological impact of these PPCPs compounds. With improved analytical techniques and an increase in nationally coordinated efforts, the occurrence and fate of PPCP compounds has become a major issue of concern and research for the 21st century.

This project focused on two questions: 1) How is the Albuquerque Wastewater Treatment Plant effluent (WTP) altering the nutrient chemistry of the river and the shallow alluvial ground water?, and 2) What types and what concentrations of PPCP compounds are present in Albuquerque's WTPE and shallow alluvial ground water? Addressing these two questions are first steps toward conducting tracer experiments to determine the fate of PPCPs and other inorganic nutrients in the shallow alluvial aquifer of the Rio Grande bosque. When the Rio Grande is at base flow, Albuquerque's effluent water can be the third largest tributary to the Rio Grande. Understanding the characteristics of the organic constituents in WTPE is essential to address potential impacts from these trace organic contaminants.

Methods

Grab samples were collected from the Rio Grande thalweg using a syringe with an inline filter (Ahlstrom glass fiber filters, 0.7 um pore size). Shallow riparian groundwater samples were collected 10 - 15 cm below the water table using air-tight tubing and a Geotech Geopump II. Surface water samples were collected at sites upriver and downriver of Albuquerque WTP (Figure 2). Groundwater samples were collected four times a year at sites 3.11 miles upriver and 4.16 miles downriver of the WTP.

Surface and groundwater samples were analyzed for selected chemical parameters using the following analytical equipment: dissolved oxygen and temperature (YSI 55 and Winkler titration), pH (Orion 260A), alkalinity (Fisher Models 380, 383, 385, 395), conductivity (Accumet 50 Fisher), major cations (Na⁺, Ca⁺², K⁺, Mg⁺²) (Flame AAS, Perkin-Elmer 306), major anions (Cl⁻, Br⁻, SO₄⁻², NO₃⁻) (Ion Chromatograph DX-100), NH₄⁺ and PO₄⁻³ (Technicon Auto Analyzer II), and total/dissolved organic carbon (Shimadzu Total Organic Carbon Analyzer 5050A). The light-dark bottle method using the Winkler method to titrate for dissolved oxygen was used to determine primary production (PP) and community respiration (R) (Wetzel and Likens 2000).

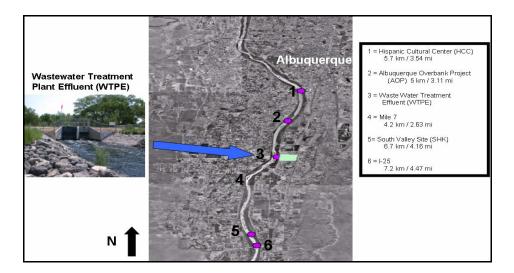


Figure 2. River and groundwater sampling locations. Groundwater sampling occurred at sites 1 and 5.

River and groundwater samples were submitted to MWH Laboratories in California for analysis of a suite of 19 pharmaceuticals and endocrine disruptor compounds using a modified USGS Method 4 as described in Kolpin et al. (2002) (for complete list of compounds see Appendix A). This method applies continuous liquidliquid extraction (CLLE) and CH₂Cl₂ to extract the trace organic compounds from oneliter whole-water samples. Compounds were analyzed using capillary-column gas chromatography/mass spectrometry (GC/MS).

Results

Surface Water

Results from monthly sampling from July 2003 to July 2004 show that Albuquerque WTPE is enriched in nitrate, phosphate and ammonium (Figures 3-5). The Rio Grande downstream of the WTPE (~ 4 miles) is elevated in nitrate and phosphate concentrations, but ammonium concentrations are similar above and below the WTP.

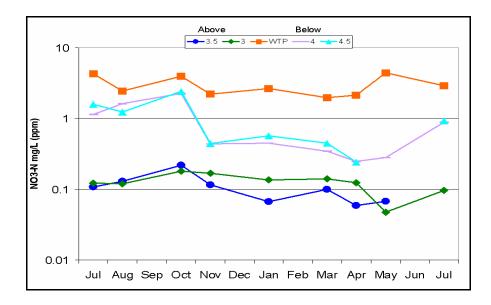


Figure 3. Nitrate (NO₃⁻ - N) concentrations (log scale) above and below (units in miles) the WTP from July 2003 to July 2004.

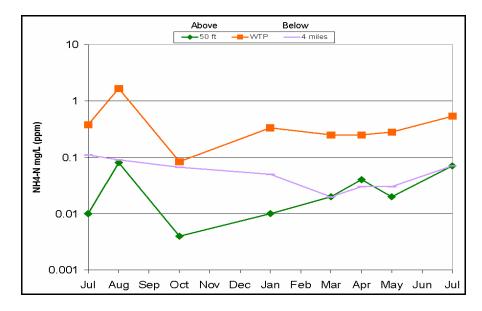


Figure 4. Ammonium (NH₄⁺ - N) concentrations (log scale) above and below the WTP from July 2003 to July 2004.

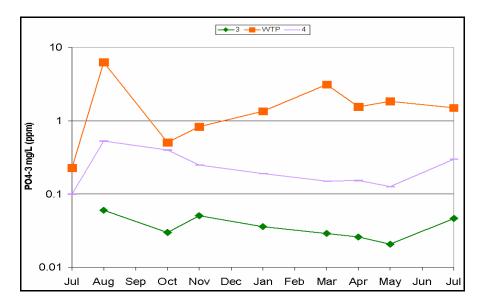


Figure 5. Phosphate (PO₄⁻³) concentrations (log scale) above and below (units in miles) the WTP from July 2003 to July 2004.

The concentration of total dissolved solids (TDS) in WTPE was 1.5 - 3 times greater than the river above the outfall. The largest difference in TDS between the river and WTP occurred during early summer months (data not shown). WTPE has conductivity values of 200 to 500 uS/cm greater than the river (Figure 6). The difference in conductivity between WTPE and the river was greatest in the spring months. Conductivity readings in the river downstream from the WTPE were 55 uS/cm greater on average than above the WTPE outfall. The difference in conductivity between upriver and downriver waters ranged from 20 - 120 uS/cm.

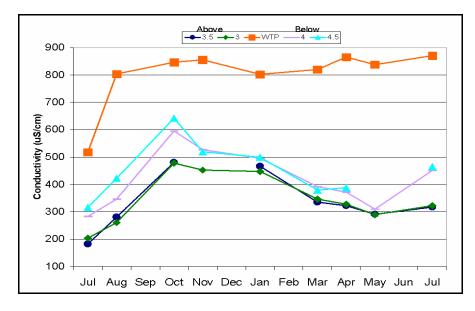


Figure 6. Conductivity (uS/cm) above and below (units in miles) the WTP from July 2003 to July 2004.

Dissolved oxygen (DO) and pH in effluent waters are reduced compared to river concentrations upstream (Figures 7 – 8). The greatest difference in DO concentrations between WTPE and river water was approximately 4 mg/L. This occurred during winter months (Nov – Mar). The difference in DO between WTPE and river water during the non-winter period (April – Oct) averaged 0.9 mg/L DO and ranged from 0.2 to 1.3 mg/L DO.

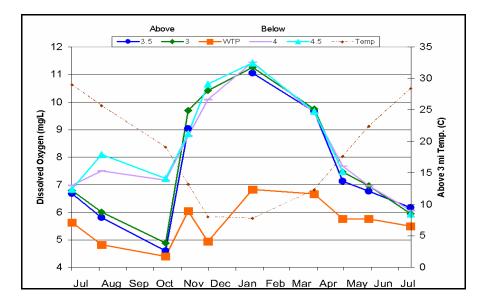


Figure 7. Dissolved oxygen (mg/L) above and below (units in miles) the WTP from July 2003 to July 2004. Dashed line is the temperature readings from 3 miles above WTP outfall.

The pH of the effluent ranges from 6.59 to 7.27, with a mean of 6.9. The average H^+ concentration of effluent waters is 1.2 orders of magnitude lower than the river water above the WTP. The pH of river water above the effluent ranges from 8.26 – 7.93 with a mean of 8.1. The average pH of the river water 4 miles downstream of the WTP is about 0.22 pH units lower than upstream. The pH measurement of the river water upstream of the WTP on March 2004 is not consistent with downstream pH values and is likely an incorrect measurement.

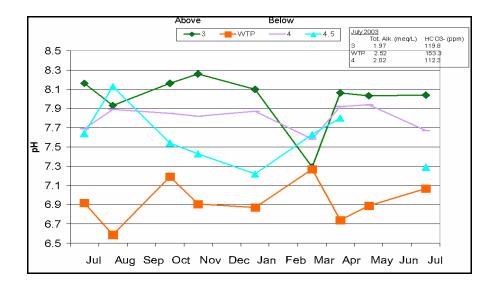


Figure 8. pH above and below (units in miles) the WTP from July 2003 to July 2004. Inset box contains total alkalinity (meq/L) and HCO_3^- (mg/L) of above and below sites during July 2003.

The temperatures of the Rio Grande and the WTPE followed a seasonal pattern ranging from 7.4 to 29.2°C and 19 to 28.5°C, respectively (Figure 9). The temperature of the WTPE was approximately 10°C warmer than the river water above the WTP during the winter months, and approximately 3°C warmer in summer months. The largest temperature difference between the WTPE and the river water above the WTPE occurred in winter months. Interestingly, the river temperatures during summer months 4 miles downriver from the WTPE are 3°C colder than river water above the WTPE on average.

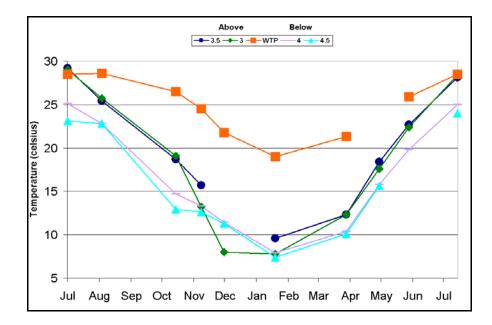


Figure 9. Temperature (°C) above and below (units in miles) the WTP from July 2003 to July 2004.

DOC concentrations in the WTPE ranged from 2.9 to 5.87 mg/L (Figure 10). River water 3.5 miles above the WTPE ranged from 0.71 - 4.08 mg/L DOC. River water concentrations of DOC above the WTPE tend to rise in the spring time periods and are lowest during the winter months. The WTPE increases DOC concentrations in the downriver thalweg by about 1 - 3 mg/L and did not change the concentration of particulate organic carbon (POC) (data not shown).

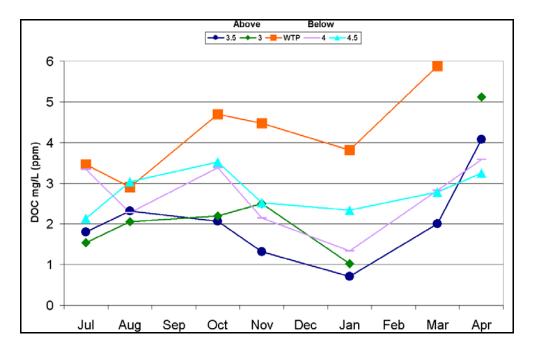


Figure 10. Dissolved organic carbon (mg/L) above and below (units in miles) the WTP from July 2003 to April 2004.

Ground water

Shallow alluvial ground water ~ 4 miles downriver from the WTPE was found to consistently have greater average concentrations of NH_4^+ – N compared to upriver groundwater sites (Figure 11). In groundwater wells ~ 3 miles upriver of the WTPE, concentrations of NH_4^+ – N ranged from below detection to 0.125 mg/L, whereas ~ 4 mile downriver concentrations ranged 0.294 to 0.794 mg/L. Concentrations of NH_4^+ – N in groundwater below the WTPE was on average an order of magnitude greater than sites upriver. The number of groundwater wells sampled for NH_4^+ – N at each site, as for all other chemical parameters, ranged from 3 to 15 wells.

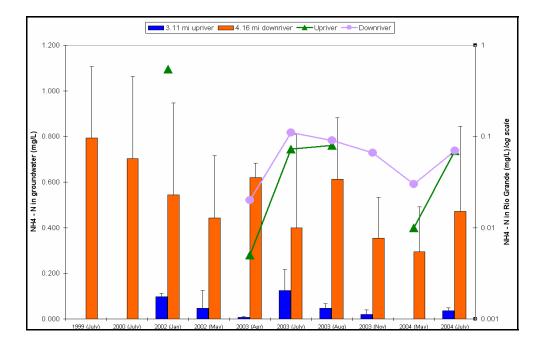


Figure 11. (columns) Average concentrations of NH₄⁺ - N in shallow riparian groundwater wells upriver and downriver (units in miles) from the WTP from July 1999 to July 2004 (3.11 upriver site not sampled in 1999). NH₄⁺ - N concentrations (log scale) in the Rio Grande above (diamonds) and below (circle) the WTP (same distances in miles) also are shown.

Average concentrations of NO_3^- - N in shallow riparian groundwater is not consistently greater downriver of the WTP (Figure 12). Upriver sites ranged from 0.012 to 1.22 mg/L, whereas downriver sites ranged from 0.015 – 2.88 mg/L. The greatest NO_3^- - N concentrations in riparian groundwater occurred in 2002 during the winter (January) and early summer months (May). In 2002, NO_3^- - N concentration in Rio Grande surface water upriver of the WTPE was an order of magnitude greater than 2003 and 2004 (1.41 mg/L compared to an average of 0.1 mg/L).

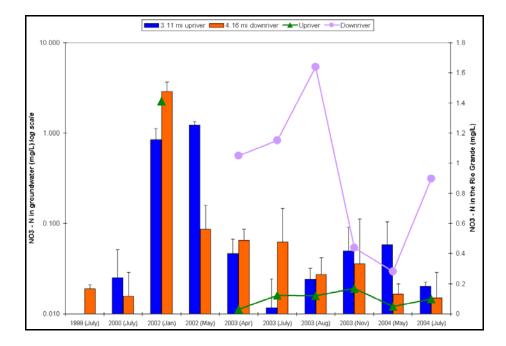


Figure 12. (columns) Average concentration of NO₃⁻ - N (log scale) in shallow riparian groundwater wells upriver and downriver (units in miles) from the WTP from July 1999 to July 2004 (3.11 upriver site not sampled in 1999). NO₃⁻ - N (mg/L) in the Rio Grande upriver (diamonds) and downriver (circles) of the WTP (same distances as groundwater sites) also are shown.

Shallow groundwater ~ 4 miles below the WTPE outfall is consistently enriched in PO_4^{-3} - P compared to sampling sites ~ 3 miles upriver (Figure 13). Concentrations in upriver sites ranged from 0.023 to 0.457 mg/L, and the downriver sites ranged from 0.143 to 0.835 mg/L. On average, the concentration of PO_4^{-3} – P in downriver sites were twice the concentration of upriver sites.

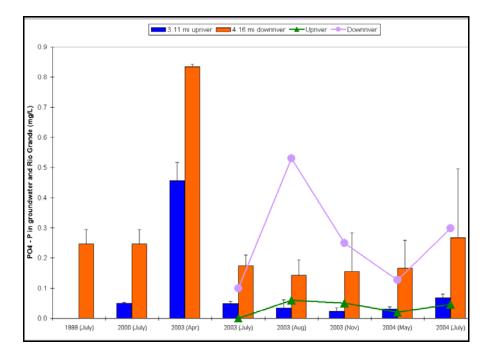


Figure 13. (columns) Average concentration of PO₄⁻³ - P in shallow riparian groundwater wells upriver and downriver (units in miles) from the WTP from July 1999 to July 2004 (3.11 upriver site not sampled in 1999). PO₄⁻³ - P (mg/L) in the Rio Grande upriver (diamonds) and downriver (circles) of the WTP (same distances as groundwater sites) also are shown.

Pharmaceuticals and Endocrine Disruptors

Groundwater Samples

Nineteen types of pharmaceuticals and personal care products (PPCPs) compounds were analyzed (Appendix A). These compounds included some known and suspected endocrine disruptors. Nine compounds were detected in the shallow riparian groundwater (Figure 14). Of the nine compounds detected in the ground water, all compounds, except bis phenol A (BPA)and triphenylphosphate, were detected in both upriver and downriver sampling sites. BPA and triphenylphosphate were detected only in downriver sites. Of those compounds detected in upriver and downriver ground water, DEET, TDCPP, 2-butoxyethyl phosphate and 2-chloroethyl phosphate were at greater concentrations in ground water downriver of the WTP compared to upriver (Figure 14). Concentrations of DEET were an order of magnitude greater in the shallow groundwater compared to most other detected analytes.

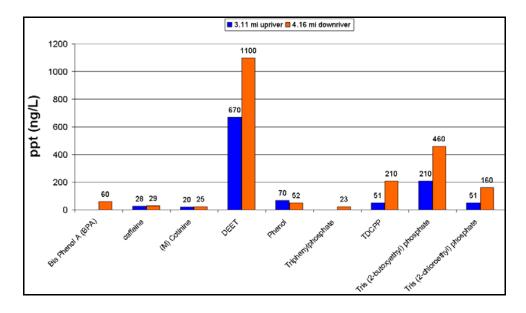


Figure 14. Pharmaceutical and endocrine disruptors from shallow riparian groundwater samples above and below the WTP (units in miles). Samples were collected on October 28, 2004. Concentration units are parts per trillion (ppt).

Effluent samples

Samples from WTPE were collected for analyses of nineteen PPCP compounds at three times throughout the day (6:45 AM, 1:00 PM and 5:45 PM) on October 28, 2004 (Figure 15). Sampling occurred at three different times to get a temporal snapshot of the concentrations of these compounds. Nine of the nineteen compounds were detected in the effluent. Of the nine compounds detected, caffeine, cotinine, diazinon, triclosan and tris (2-butoxyethyl) phosphate showed a temporal pattern in WTPE. The other four compounds, DEET, phenol, TDCPP and Tris (2-chloroethyl) phosphate were detected at consistent concentrations over time. With the exception of TDCPP, the compounds were greater in concentration during the morning sampling compared to the afternoon and early evening. Compared to all detected analytes, TDCPP and tris (2-chloroethyl) phosphate were found to be in the highest concentrations in the WTPE.

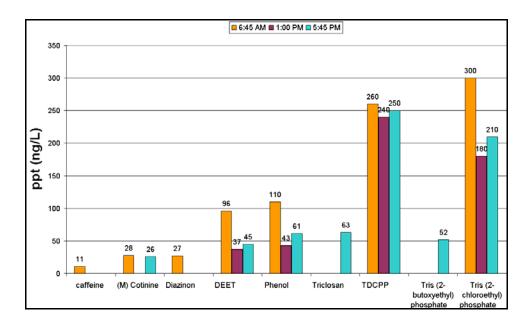


Figure 15. PPCP compounds detected in the WTPE at three different times of the day. Samples were collected on October 28, 2004. Concentrations are in parts per trillion (ppt).

Discussion

Effect of Albuquerque WTPE on the nutrient chemistry of the Rio Grande and riparian

ground water

Albuquerque WTPE is significantly altering the nutrient chemistry of the river and shallow riparian groundwater. As the Rio Grande passes the WTP, the waters become enriched in nitrate, phosphate and ammonium. The Rio Grande continues to show nitrate and phosphate enrichment four miles downstream of the WTPE, but ammonium values in the thalweg return to background levels over this distance. The ammonium ion is positively charged and can be partially deprotonated in basic waters (pH of 8 - 10) and lost to the atmosphere. Deprotonation and adsorption to negatively charged colloidal particles might explain why dissolved ammonium concentrations in the thalweg drop quickly to background levels downriver of the WTP.

Input of inorganic nutrients via WTPE can potentially alter limiting nutrients for aquatic primary producers and decomposers. The WTPE significantly reduces the ratio between primary production (PP) and community respiration (R) in the river (Martinet, unpublished data). The WTPE eliminates riverine primary production at the point of discharge, a classic response downriver from point source pollution. Although productivity of the Rio Grande thalweg is very low, probably due to high turbidity values, algal primary production increases steadily with distance downriver of the WTP. Grab samples taken along the river's edge downriver from the WTP during July 2003 showed nutrient concentrations to be two orders of magnitude lower than thalweg concentrations (Magana, unpublished data). This finding has initiated research examining the spatial pattern of primary production upriver and downriver of the WTPE. River edges may be focal areas for nutrient uptake and utilization by benthic algae.

Enrichment of the Rio Grande with nitrate may be the source of increased in ammonium concentrations in riparian ground water downriver of the WTPE (Figure 3 and Figure 9). Nitrate enriched surface waters enter the shallow subsurface alluvial aquifer of the bosque (induced by the negative hydrologic gradient between the adjacent levee and river surface). Dissolved oxygen (DO) is rapidly removed from surface water recharging the shallow alluvial ground waters (Vinson MS thesis). On average, ground water below the WTP is anoxic or hypoxic (0 < DO < 2 mg/L) throughout the year. Low

DO concentrations, increased DOC, and increased nitrate favor anaerobic pathways of microbial metabolism where nitrate is the electron acceptor. Denitrification (nitrate conversion to N_2 gas) and dissimilatory nitrate reduction to ammonium (DNRA) are two microbial pathways hypothesized to be important in bosque ground waters downriver of the Albuquerque WTP. The presence of significant DNRA activity would explain the high ammonium concentrations in groundwater wells below the Albuquerque WTP.

Shallow ground waters four miles below the WTP are also enriched in phosphate. This is most likely due to the increase in phosphate concentrations in the river (Figure 5 and Figure 11). Studies on the fate of phosphate in the river and shallow alluvial ground water below the Albuquerque WTP are needed.

PPCP compounds present in WTPE and shallow alluvial ground water

Concentrations of the PPCP compounds were all in the parts per trillion (ppt) range, except for DEET, which was found in the parts per billion range. Currently there are reports of about 80 different drugs found in WTPE, surface waters, ground water and even drinking waters (Kümmerer 2001). The compounds detected in this study represent seven of the fifteen categories reported in Kolpin et al. (2002) (see stars in Figure 1). Little information is presently available on the effects that these PPCP compounds have on aquatic organisms and processes. New research suggests, however, that chronic exposure to certain PPCPs at low concentrations can have biological effects on crustaceans, algae and bacteria (Kümmerer 2001).

Some compounds detected in WTPE were also detected in the riparian ground water downriver. Compounds whose concentrations in groundwater are elevated are

DEET, TDCPP, tris (2-chloroethyl) phosphate, and tris (2-butoxyethyl) phosphate. These four compounds were detected in various stream habitats during the recent national reconnaissance study (Kolpin et al. 2002). For example, DEET was detected in 74% of 54 total samples and found to have a maximum concentration of 1.1 ug/L, the same concentration found in the shallow riparian groundwater downriver of the WTPE in this study. Kolpin et al. (2002) detected TDCPP and tris (2-chloroethyl) phosphate, both fire retardants, at a rate 13% and 58%, respectively. The maximum concentration of TDCPP detected in the national survey was 0.16 ug/L, the same amount detected in ground water downriver of the WTPE in this study. The amount of TDCPP detected in the WTPE outfall in three samples were all 1.5 times greater then the maximum concentration found in the national survey. The concentration of TDCPP found in the ground water downriver of the WTPE was slightly lower then concentrations found in the WTPE. Tris (2butoxyethyl) phosphate was detected in about 46% of the national samples. In this study, tris (2-butoxyethyl) phosphate was detected in the WTPE in one sample. Groundwater concentrations of this compound were 4 to almost 10 times greater than detected in the WTPE, with downriver concentrations 2 times greater than upriver. Concentrations of tris (2-chloroethyl) phosphate in the WTPE were greater than median concentrations reported in the national survey, which detected this compound with a 58% detection rate.

Trace anthropogenic organic compounds which were not found to be elevated in the WTPE outfall relative to upstream river water are caffeine, cotinine and phenol. These three compounds also do not show an increase in downriver groundwater samples compared to upriver samples (Figure 14). Concentrations of these compounds in the ground water are similar to those concentrations measured in the WTPE. These three

compounds were detected upriver and downriver at similar concentrations. This might indicate that these compounds are ubiquitous throughout the Rio Grande and that Albuquerque WTPE is not the only source of these compounds to the river ecosystem. Interestingly, these three compounds have the largest water solubility compared to all other compounds detected (see Appendix B). Kolpin et al. (2002) reported caffeine detection in almost 71% of samples, indicating that caffeine is found throughout the water systems of this country. Cotinine and phenol were detected at a rate of 31.5 % and 8%, respectively. Kolpin et al. (2002) indicated that phenol was often detected in laboratory blanks so reported concentrations might be overestimated due to laboratory contamination. The amounts detected in the Rio Grande and alluvial ground water are lower than the median levels detected in the national survey for these three compounds.

Two compounds were detected in the shallow riparian groundwater below the WTPE that were not detected in the WTPE. These compounds were bis phenol A and triphenylphosphate. Concentrations of these compounds in the ground water were lower than median values detected in the national survey. There is insufficient information to determine whether or not these compounds originate from Albuquerque WTPE. Two compounds detected in the WTPE but not detected in the shallow ground water are diazinon and triclosan. The reported effluent concentrations in this study are lower then median levels reported in the national survey. Further sampling will be needed to determine if diazinon and triclosan are truly absent from shallow ground water and whether the Albuquerque WTPE is a source of these compounds to the aquatic environment.

Groundwater accumulation

An interesting outcome of this study was that concentrations of certain organic compounds in the shallow groundwater were greater than concentrations in WTPE. Compounds that followed this pattern were: DEET and tris (2-butoxyethyl) phosphate. The concentrations of DEET in the shallow ground water were more than an order of magnitude greater than concentrations detected in the WTPE.

According to available research on physico-chemical characteristics of DEET, DEET should have moderate mobility through soil sediments based on a organic carbon normalized sorption coefficient (K_{oc}) of 300 (see Appendix B), indicating that this compound tends to adsorb to suspended particulates. Limited available data suggest that DEET does not readily biodegrade under either aerobic or anaerobic conditions in soil or water (National Library of Medicine, Toxnet database - http://toxnet.nlm.nih.gov). If DEET is adsorbing to soil sediments of the bosque and is not readily biodegraded under typical hypoxic or anoxic conditions, the concentration of DEET might accumulate in shallow groundwater, especially downriver of the Albuquerque WTPE. The impact that accumulation of an insect repellent in shallow groundwater might have on biogeochemical processes and riparian plant dynamics is a question that requires further research.

Like DEET, tris (2-butoxyethyl) phosphate will have low to slight mobility in riparian sediments due to relatively high K_{oc} coefficient (2,600). Research conducted in Japan has found that tris (2-butoxyethyl) phosphate is not readily biodegraded (Chemicals Inspection and Testing Institute 1992). Other studies, however, suggest that tris (2-butoxyethyl) phosphate may be utilized by bacteria in river water under some

conditions (Kawai et al 1985). For example, Kawai et al. (1985) showed two out of three tests that a 100% reduction of tris (2-butoxyethyl) phosphate occurred in 30 days in river water samples supplemented with polypeptone. The other river water sample showed no degradation of tris (2-butoxyethyl) phosphate after 30 days. The accumulation of tris (2-butoxyethyl) phosphate and DEET in riparian ground waters warrants further research.

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<u>Appendix A</u> Compounds analyzed for and their reporting detection limit (in ng/L)

2,6-di-tert-butylphenol	5
4-Methylphenol	25
4-Nonyl Phenol	25
Alpha Chlordane	5
Bis Phenol A (BPA)	25
Caffeine	5
Carbaryl	5
Chlorpyrifos	5
(M) Cotinine	10
Diazinon	10
DEET	5
Dieldrin	5
Methyl Parathion	5
Phenol	25
Triclosan	25
Triphenylphosphate	5
TDCPP	5
Tris (2-butoxyethyl) phosphate	25
Tris (2-chloroethyl) phosphate	5

Appendix **B**

Compound	CAS #	Molec. WT.	Water	Water Solubility		Log K (octanol-water)	
Bis Phenol A (BPA)	80-05-7	228.29		120		3.32	
Caffeine	58-08-2	194.19		2.16E+04		-0.07	
(M) Cotinine	486-56-6	176.22		9.99E+05		0.07	
Diazinon	333-41-5	304.35		40		3.81	
DEET	134-62-3	191.28		912		2.18	
Phenol	108-95-2	94.11		8.28E+04		1.46	
Triclosan	3380-34-5	289.55		10 4.7		6, 5.4	
Triphenylphosphate	115-86-6	326.29		1.9		4.59	
TDCPP	13674-87-8	430.91		7		3.65	
Tris (2-butoxyethyl) phosphate	78-51-3	398.48		1100		3.75	
Tris (2-chloroethyl) phosphate	115-96-8	285.49		7000		1.44	
<u>Compound</u>	Henry's Law Constant (atm-m3/mole)			<u>oc</u>		Biological Concentratio	n Factor
Bis Phenol A (BPA)		1.00E-	-11 mo	derate to low mob	ility	<100	
Caffeine		1.90E-	19 18	to 22			
(M) Cotinine		3.33E-	12				
Diazinon	1.13E-07			191-1,842 3-20		3-200 low to moderate	
DEET	2.08E-08			300		0.8-2.4 low	
Phenol	3.33E-07			<100		unlikely	
Triclosan	4.99E-09			9,200		2.7 to 90 low to moderate	
Triphenylphosphate	3.31E-06			moderate to low mobility		132-573 high	
TDCPP	2.61E-09			1,500 0.3 to 113 low to m		0.3 to 113 low to moderate	
Tris (2-butoxyethyl) phosphate	1.20E-11			2,600 <5.8 low			
Tris (2-chloroethyl) phosphate	3.29E-06				140	0.3 to 3.3 low	