Division of Science, Research and Environmental Health

Research Project Summary

March 2016

Occurrence of Antibiotic Compounds Found in the Water Column and Bottom Sediments from a Stream Receiving Two Wastewater Treatment Plant Effluents in Northern New Jersey

Authors
Jacob Gibs Ph.D. [1]

Prepared By
R. Lee Lippincott Ph.D. (Project Manager) [2]

Abstract

An urban watershed in northern New Jersey was studied to determine the presence of antibiotic compounds above and below the discharges of two wastewater treatment plants (WWTP). Many antibiotic compounds are not completely removed by conventional wastewater treatment plants which results in these compounds entering receiving waters. The antibiotic compounds which enter waterways from WWTP discharges are assumed to be resistant to biologically mediated degradation.

Twenty-five antibiotic compounds and six antibiotic compound degradates were analyzed at nine sample locations on two days in September 2008. Two of the nine sampling locations were background sites upstream of the WWTP discharge locations on the Hohokus Brook. Another background site was located upstream of a source-water intake for potable water on the Saddle River above the confluence of the Saddle River and the WWTP discharge receiving stream, the Hohokus Brook. At low stream flows, the drinking-water source-water intake can receive Hohokus Brook water.

A total of 8 antibiotic compounds and one degradate were detected in the water samples from the sites downstream of the WWTP discharges. Concentrations of 6 of the 8 detected compounds decreased downstream of the WWTP discharges as the distance from the WWTP discharges increased. There were no detections of any of the 25 target antibiotic compounds or six degradates at two of the three background sites in either water or sediment samples. One background site had a detection of one compound in a sediment sample.

Four compounds were detected in sediments. Two fluoroquinolones and azithromycin were found in their respective highest concentration at the nearest sampling site downstream of the WWTP discharges. Trimethoprim was only detected in the sediments of one of the background sites. Pseudo-partition coefficients normalized for sediment organic carbon concentration were calculated for the three compounds identified in the downstream sediment samples to evaluate the affinity for certain compounds to partition into the sediment.

Introduction

Two Wastewater Treatment Plants (WWTP) discharge into the Hohokus Brook, a tributary of the Saddle River. A raw water intake for drinking water is located on the Saddle River approximately 1,600 feet upstream of the confluence of the two streams. Downstream of the confluence is a weir to maintain a minimum water level for the intake. Hohokus Brook water can enter the drinking water intake at stream baseflow levels. The land use of the Saddle River watershed is 74 percent urban, of which the majority of the area is sewered (New Jersey Department of Environmental Protection [NJDEP], 2010). The remaining watershed land uses are undeveloped and water bodies. Stackelberg et al. (2007) found that one antibiotic compound and one antibiotic compound degradate were present in the raw water of a drinking water treatment plant that was downstream from several WWTPs. Thus, it is important to determine the changes in antibiotic compound and degradate concentrations with distance downstream from WWTP discharges, and changes in concentrations in stream bottom sediments which originate from the water column.

The combined Hohokus Brook and Saddle River watershed was investigated for the presence of antibiotic compounds because two WWTP discharges are located on Hohokus Brook and a diversion for potable water is located on the Saddle River. Under baseflow conditions, the diversion for potable water has a high probability of collecting the Hohokus Brook water and the compounds associated with the subsequent WWTP discharges.

Methods

Sample Collection

Samples were collected from nine locations on two days in September 2008. Three sites upstream of wastewater treatment plants and drinking water intakes were considered background for this study. Two of the three background sites were on the Hohokus Brook and the other was upstream of the Saddle River-Hohokus Brook confluence. Of the other six sites, three were on the Hohokus Brook and three were downstream of the confluence on the Saddle River. Sites 8 and 9 were downstream of the Sprout Brook tributary. Figure 1 shows the study area.

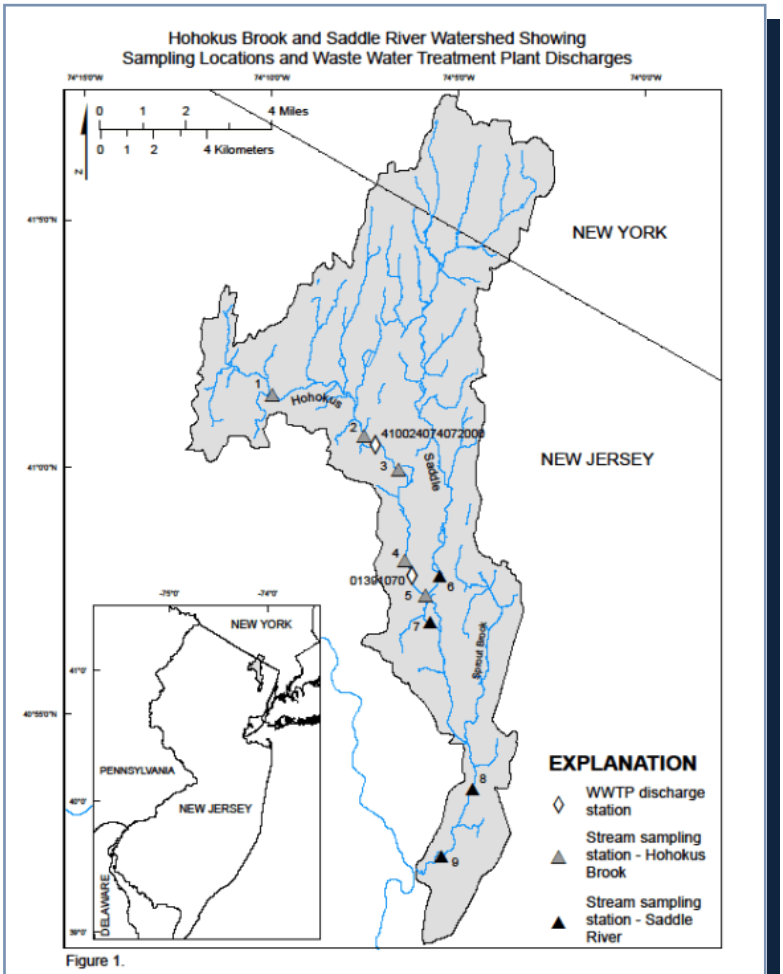

Figure 1.

Field methods for the collection of water-quality data are described in the USGS National Field Manual (U.S. Geological Survey, variously dated). A surface-water sample was collected from the center of flow in an amber, glass bottle that had been cleaned and baked in the laboratory at 450°F. Streambed sediment was collected from several areas of deposition at each site and composited in a methanol-rinsed stainless steel container. The bed sediments were mixed well and sieved to retain a less than 2 millimeter fraction. The stainless steel sieves were cleaned using a soap and water, de-ionized water rinse, and then methanol-rinsed and air dried. The sediment samples were placed in a baked, amber glass jars. All samples were preserved by chilling on ice and shipped on ice for overnight delivery to the USGS Kansas Water Science Center, Organic Geochemistry Research Laboratory.

Laboratory Analysis

Isolation

Twenty-five antibiotic compounds and six antibiotic compound degradates were targeted in this study (Table 1). Samples were extracted using the HLB Prospekt cartridges (Waters Corp., Milford, MA). Clinafloxacin, $^{13}C_2$-erythromycin, $^{13}C_2$-erythromycin-H_2O, meclocycline, simatone, and $^{13}C_6$-sulfomethoxazole are used as internal standards while demeclocycline, nalidixic acid, oleandomycin, and $^{13}C_6$-sulfamethazine were used as the surrogate standards. An internal standard solution containing 0.062 ng/µl of simatone and 0.25 ng/µl of each of the other internal standard was placed in an amber 2-ml chromatography vial and placed on the LC autosampler tray.

Instrumental Analysis

The laboratory analysis is currently an evolving research method that was developed at the Kansas Water Science Center, Organic Geochemistry Research Laboratory that was modified from a liquid chromatography/tandem mass spectrometry (LC/MS/MS) version of the on-line solid-phase extraction (OLSPE) LC/MS method in Meyer and others (2007). Water samples were analyzed for the analytes listed in Table 1. LC/MS/MS with electrospray ionization (ESI) used multiple-reaction monitoring (MRM). Samples were analyzed in positive-ion mode.

Table 1: Antibiotics Measured In This Research

Antibiotic Class	Reporting Limit (ppb)
Fluoroquinolines	
Ciprofloxacin	0.005 µg/L
Enrofloxacin	0.005 µg/L
Lomefloxacin	0.005 µg/L
Norfloxacin	0.005 µg/L
Ofloxacin	0.005 µg/L
Sarafloxacin	0.005 µg/L
Macrolides	
Azithromycin	0.005 µg/L
Erythromycin	0.008 µg/L
*Erythromycin-H_2O	0.008 µg/L
Roxithromycin	0.005 µg/L
Tylosin	0.010 µg/L
Virginiamycin	0.005 µg/L
Sulfonamides	
Sulfachloropyridazine	0.005 µg/L
Sulfadiazine	0.100 µg/L
Sulfadimethoxine	0.005 µg/L
Sulfamethoxazole	0.005 µg/L
Sulfamethazine	0.005 µg/L
Sulfathiazole	0.005 µg/L
Tetracyclines	
Chlorotetracycline	0.010 µg/L
Oxytetracycline	0.010 µg/L
Tetracycline	0.010 µg/L
Doxycycline	0.010 µg/L
*Epi-chlorotetracycline	0.010 µg/L
*Epi-iso-chlorotetracycline	0.010 µg/L
*Epi-oxytetracycline	0.010 µg/L
*Epi-tetracycline	0.010 µg/L
*Iso-chlorotetracycline	0.010 µg/L
Miscellaneous antibiotic compounds	
Chloramphenicol	0.100 µg/L
Lincomycin	0.005 µg/L
Ormetoprim	0.005 µg/L
Trimethoprim	0.005 µg/L

*Degradation Products

Results and Discussions

Upstream Background Sites

There were no detections of any of the 25 target antibiotic compounds or six degradates at the three background sites in the water column. Trimethoprim was detected in the sediments at Site 1, a background site. However, this compound was not detected in the water samples collected at this site. The detection of trimethoprim currently cannot be explained using the available data, but its ubiquitous use as an antibacterial agent could be a possibility for this random detection.

Downstream Water Samples

A total of eight antibiotic compounds (azithromycin, erythromycin, ciprofloxacin, enrofloxacin, ofloxacin, trimethoprim, sulfamethazine and sulfamethoazole) and one degradate (erythromycin-H2O) were detected in the water samples from the sites downstream of the WWTP discharges. The concentrations of 6 of the 8 detected compounds and the one degradate decreased downstream of the WWTP discharges as the distance from the WWTP discharges increased. Table 2 summarizes the results of the water column investigation.

Downstream Sediments

As previously noted, trimethoprim was detected at one background site. The other three compounds detected were azithromycin, a macrolide, and two fluoroquinolines: ciprofloxacin, and ofloxacin. The highest concentrations of azithromycin, ciprofloxacin, and ofloxacin detected in sediments were found at the nearest sampling site located downstream of the WWTP discharges. The azithromycin concentration was the highest of the four antibiotics detected. Table 3 shows the results for the four antibiotic compounds detected in the stream bottom sediments.

Organic Carbon Concentrations in Sediments

The stream bottom sediment organic carbon concentrations ranged from 0.6 to 4.4 g/kg (Table 3). Organic-carbon normalized pseudo-partitioning coefficients (P-PC_{OC}) (Gibs et al. 2013) were averaged for all sites for an antibiotic compound when a quantified concentration in water, sediment, and an organic carbon concentration existed. The order of the average normalized organic carbon P-PC_{OC}s, from highest to lowest was as follows: (azithromycin) > (ciprofloxacin) ~ (ofloxacin) (Table 4). Lou et al. (2011) detected 10 antibiotic compounds in the bottom sediments of the Haihe River, China and estimated the P-PC but did not normalize for the organic carbon content. For comparison, the organic carbon concentrations of the Haihe River bottom sediments ranged from 15.5 to 38.1 g/kg; an order of magnitude higher than organic carbon concentrations found in the sediments of this study. Work by Massey et al. (2010), which detected nine antibiotic compounds in the bottom sediments of waterways in Arkansas, supports the strong relative affinity for the antibiotics identified in this study to partition into the sediment.

Conclusion

An abundance of literature reflects the presence of antibiotics in waterways, especially in waterways receiving wastewater effluent. The literature also supports the result that many of the studied antibiotic compounds partition into the sediments resulting in trace quantities present in the water column. The results of this investigation were among the first examples of antibiotic compounds detected in both the water column and sediment using analytical methodology developed and refined during this investigation by the USGS Kansas Water Science Center, Organic Geochemistry Research Laboratory. Pseudo-partition coefficients were developed to explain the affinity of certain antibiotics for the organic carbon compartment in the sediments. A published journal article describes this research in more detail (Gibs et al. 2013).

References

Gibs, J., Heckathorn, H., Meyer, M., Klapinski, F., Alebus, M., Lippincott, R.L. 2013. Occurrence and partitioning of antibiotic compounds found in the water column and bottom sediments from a stream receiving two wastewater treatment plant effluents in Northern New Jersey, 2008. Science of the Total Environment.v458-460:107-116.

Lou, Y., Lin, X., Rysz, M., Wang, Y., Zhang, H., and Alvarez, P.J.J. 2011. Occurrence and transport of Tetracycline, Sulfonamide, Quinolone, and Macrolide Antibiotics in the Haihe River Basin, China. Environmental Science and Technology, 45:1827-1833.

Massey, L.B., Haggard, B.E., Galloway, J.M., Loftin, K.A., Meyer, M.T., and Green, W.R. 2010. Antibiotic fate and transport in three effluent-dominated Ozark streams. Ecological Engineering, 36:930-938.

Meyer, M.T., Lee, E.A., Ferrell, G.M., Bumgarner, J.E., and Varns, J. 2007. Evaluation of offline tandem and online solid-phase extraction with liquid chromatography/electrospray ionization-mass spectrometry for analysis of antibiotics in ambient water and comparison to an independent method. U.S. Geological Survey Scientific Investigations Report 2007-5021, 28 p.

NJ Department of Environmental Protection (NJDEP), Office of Information Resources Management (OIRM), Bureau of Geographic Information System (BGIS), 2010. NJDEP 2007 Land Use/Land Cover Update.

Stackelberg, P. E., Gibs, J., Furlong, E. T., Meyer, M. T., Zaugg, S. D., and Lippincott, R. L. 2007. Efficiency of conventional drinking-water-treatment processes in removal of pharmaceuticals and other organic compounds. Science of the Total Environment, 377:255-272.

U.S. Geological Survey. variously dated. National Field Manual for the Collection of Water-Quality Data: U.S. Geological Survey Techniques of Water-Resources Investigations, book 9, chaps. A1–A9, available online at http://pubs.water.usgs.gov/twri9A.

This project was funded by the NJDEP, Division of Science, Research and Environmental Health.
Contract number SR08-050

PRINCIPAL INVESTIGATORS:

[1] U.S. Geological Survey

PREPARED BY:

[2]New Jersey Department of Environmental Protection, Division of Science, Research and Environmental Health

Table 2: Concentration of target antibiotic compounds detected in the water column for the study stations downstream of the waste water treatment plants on the Hohokus Brook and Saddle River. Refer to Figure 1 for site locations.

Station ID	Sample Date	Azithromycin	Ciproflaxacin	Enrofloxacin	Erythromycin	Erythromycin-H2O*	Ofloxacin	Sulfamethazine	Sulfamethoxazole	Trimethoprim
3	9/23/2008	0.109	0.039	<0.005	0.013	0.052	0.086	<0.005	0.139	0.049
3	9/25/2008	0.096	0.024	<0.005	<0.008	0.033	0.072	<0.005	0.085	0.069
4	9/23/2008	0.056	0.020	<0.005	<0.008	0.041	0.070	<0.005	0.100	0.017
4	9/25/2008	0.081	0.037	0.015	0.014	0.044	0.098	<0.005	0.121	0.047
5	9/23/2008	0.134	0.027	<0.005	<0.008	0.059	0.436	<0.005	0.250	0.051
5	9/25/2008	0.237	0.076	<0.005	0.024	0.084	0.915	<0.005	0.145	0.140
7	9/23/2008	0.082	<0.005	<0.005	0.011	0.035	0.120	<0.005	0.149	0.005
7	9/25/2008	0.077	0.012	<0.005	<0.008	0.022	0.096	<0.005	0.128	0.045
8	9/23/2008	0.025	<0.005	<0.005	0.009	0.031	0.072	<0.005	0.174	0.006
8	9/25/2008	0.039	<0.005	<0.005	<0.008	0.015	0.076	<0.005	0.122	0.034
9	9/23/2008	<0.005	<0.005	<0.005	<0.008	0.017	0.054	0.018	0.126	0.014
9	9/25/2008	0.023	<0.005	<0.005	<0.008	0.014	0.057	0.018	0.100	0.024

*Degradation Product

Table 3. Concentration of detected antibiotic compounds (ug/kg) in streambed sediments and organic carbon (g/kg) for the nine study stations.

Station number	Sample date	Azithromycin	Ciprofloxacin	Ofloxacin	Trimethoprim	Organic carbon
1	9/23/2008	<1	<1	<1	11	2.8
2	9/23/2008	<1	<1	<1	<1	3.6
3	9/23/2008	<1	9.2	9.5	<1	4.4
4	9/23/2008	--	--	--	--	2
5	9/23/2008	44	10	21	<1	3
6	9/23/2008	<1	<1	<1	<1	0.6
7	9/23/2008	23	3.4	9.9	<1	1.6
8	9/23/2008	29	2.5	7.7	<1	1.3
9	9/23/2008	--	--	--	--	3.3

-- No antibiotic samples collected

Table 4. Organic carbon normalized pseudo-partition coefficients (L/kg) determined from samples collected September 23, 2008.

Station Number	Azithromycin	Ciprofloxacin	Ofloxacin
3	ND	5,360	2,510
5	10,950	12,350	1,610
7	17,530	ND	5,160
8	89,230	ND	8,230
Average	39,240	8,860	4,380

ND, non-detect in either the water or sediment

RESEARCH PROJECT SUMMARY

Please send comments or requests to:
Division of Science, Research and Environmental Health
Mail code 428-01, P.O. Box 420
Trenton, NJ 08625

Phone: (609) 984-6070
Visit the Division of Science, Research & Environmental Health web site @ www.state.nj.us/dep/dsr/

Division of Science, Research & Environmental Health
Dr. Gary Buchanan, Director

State of New Jersey
Chris Christie, Governor

Department of Environmental Protection
Bob Martin, Commissioner