AWRA 2007 SUMMER SPECIALTY CONFERENCE
Vail, Colorado
June 25-27, 2007

EVALUATION OF WASTEWATER IMPACT ON DRINKING WATER SOURCES USING CAFFEINE, CARBAMAZEPINE, AND PRIMIDONE AS TRACERS

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Abstract: Wastewater impact on drinking water supplies was assessed using several approaches, including analysis of three pharmaceuticals and personal care products--caffeine, carbamazepine, and primidone--as tracers, and determination of precursor loadings for the disinfection by-product N-nitrosodimethylamine (NDMA) using formation potential (FP) tests. Samples were collected in rivers impacted by wastewater treatment plant (WWTP) discharges, at drinking water treatment plants (DWTPs) upstream or downstream of these discharges, and from a WWTP effluent in one watershed. The levels (minimum – maximum [median]) of caffeine, carbamazepine, primidone, and NDMAFP were 7-687 (130) ng/L, 2-188 (22) ng/L, 2-66 (9) ng/L, and 11-261 (36) ng/L, respectively. The highest concentrations of caffeine and NDMA precursors were detected at a river heavily impacted by treated wastewater discharges, whereas the highest concentrations of carbamazepine and primidone were from the WWTP effluent. The lowest concentrations of the three PPCPs were from a DWTP influent upstream of a metropolitan urban area. The results show that the three PPCPs and NDMAFP tests can be used to evaluate wastewater impact in different watersheds and to assess precursor loadings for nitrogenous disinfection by-products.

Key terms: Pharmaceuticals and personal care products (PPCPs), N-nitrosodimethylamine (NDMA), formation potential (FP), tracers, drinking water, wastewater impact.

INTRODUCTION

Wastewater treatment plant (WWTP) discharges are a source of various micropollutants (Kolpin et al.; 2002; Snyder et al., 2003; Glassmeyer et al., 2005), including pharmaceuticals and personal care products (PPCPs), and disinfection by-products (DBPs) and their precursors. The occurrence of PPCPs in surface waters affected by treated wastewater discharges has been reported by the U.S. Geological Survey and other research groups (Kolpin et al. 2002; Glassmeyer et al., 2005). As part of a project on the occurrence and formation of nitrogenous DBPs (N-DBPs), wastewater impact on drinking water supplies was assessed using several approaches, including analysis of three PPCPs--caffeine, carbamazepine, and primidone--as tracers, and determination of precursor loadings for the DBP N-nitrosodimethylamine (NDMA). Caffeine has been identified as an anthropogenic marker for wastewater contamination of surface waters, however it can undergo biodegradation (Buerge et al.; 2003). The anticonvulsants carbamazepine and primidone are stable in the environment and are considered conservative tracers (Sedlak et al., 2004; Glassmeyer et al., 2005; Krasner et al., 2006). All three PPCPs have been detected in treated wastewaters at levels considerably higher than the analytical method's minimum reporting levels (MRLs); therefore their fate, transport, and attenuation in watersheds can be followed. Treated wastewater discharges are also a source for NDMA precursors. An NDMA formation potential (FP) test under reactivity-based chloramination conditions has been shown as a useful tool to evaluate NDMA precursor levels and to better understand the impact of treated wastewater discharges on downstream drinking water sources (Krasner et al., 2004).

ANALYTICAL METHODS

The three PPCPs were analyzed by solid-phase extraction of a 500-mL sample followed by liquid chromatography/tandem mass spectrometry under electrospray positive ionization mode (Vanderford et al., 2003) on an Applied Biosystems API 4000 triple quadrupole mass spectrometer coupled with an Agilent 1100 liquid chromatograph. Two isotopically labeled compounds, caffeine-$^{13}C_3$ and carbamazepine-d_{10}, were used as internal standards and added to the initial sample prior to extraction to compensate for extraction variations and matrix effects (Vanderford et al., 2006). The analysis of matrix-spiked samples was used to adjust primidone results for their recovery. The MRLs were 1 ng/L each.

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NDMAFP tests were conducted according to the protocol developed during a previous study (Krasner et al., 2004). After a 3-day hold time, the chloramine residuals were quenched and the samples were then extracted with dichloromethane using a micro-liquid-liquid extraction method (Guo et al., 2004) and analyzed by gas chromatography/tandem mass spectrometry for NDMA under chemical ionization mode, with an MRL of 10 ng/L. The instrument used was a Varian Saturn 2200 ion trap mass spectrometer coupled with a Varian CP-3800 gas chromatograph.

RESULTS AND DISCUSSION

Samples were collected in rivers impacted by treated wastewater discharges, at drinking water treatment plants (DWTPs) upstream or downstream of these discharges (DWTP 4 used water from an effluent-impacted lake), and from a WWTP effluent in one watershed. The results are summarized according to different watersheds (states sampled) in Table 1. The levels (minimum – maximum [median]) of caffeine, carbamazepine, primidone, and NDMAFP were 7-687 (130) ng/L, 2-188 (22) ng/L, 2-66 (9) ng/L, and 11-261 (36) ng/L, respectively. Because the scope of work of the overall project focused on the occurrence and formation of N-DBPs at DWTPs, WWTP effluents were not sampled in this study except for one, resulting in 66 ng/L for primidone, 188 ng/L for carbamazepine, and 202 ng/L for caffeine. In a previous study, primidone concentrations in WWTP effluents (some of which were in the watersheds in the current study) typically ranged from 100 to 200 ng/L (Krasner et al., 2006).

Table 1. Occurrence of Three PPCPs and NDMAFP in the Watersheds Studied.

State	Site Description	Caffeine	Carbamazepine	Primidone	NDMAFP
CA	WWTP* effluent	202	188	66	NA‡
	River A downstream of other WWTPs	26	125	62	NA
PA1	River B upstream of DWTP† 1	133	18	5	17
	DWTP 1 influent	140	26	10	37
	DWTP 2 influent	130	18	4	27
PA2	River C upstream of DWTP 3	86	14	6	36
	DWTP 3 influent	78	16	6	35
OK	DWTP 4 influent	55	48	28	22
NJ	DWTP 5 influent	99	156	35	75
CO	River D upstream of DWTP 6	687	116	37	261
	River E upstream of DWTP 6	176	22	8	94
	DWTP 6 influent	207	5	9	53
	DWTP 7 influent	7	2	2	11

*WWTP=wastewater treatment plant; †DWTP=drinking water treatment plant; ‡NA=not analyzed.

In one watershed in Pennsylvania (PA1), primidone was detected at 5 ng/L at River B upstream of DWTP 1. The concentration of primidone increased to 10 ng/L at DWTP 1 due to treated wastewater discharges in a tributary that entered River B near the intake for DWTP 1 (Figure 1). The concentration of primidone at DWTP 2 was similar (4 ng/L) to that of River B upstream of DWTP 1, indicating that the wastewater-impacted tributary did not appear to impact DWTP 2 (DWTP 2 is on the other side of the river). These data were consistent with the NDMAFP results from the corresponding sites, as the concentrations of the three PPCPs and NDMA FP were the highest at DWTP 1. The concentrations of caffeine in this watershed, however, were not significantly different at the different sites sampled.

In a watershed in Colorado (Figure 2), significantly higher levels of tracers (37 ng/L primidone, 116 ng/L carbamazepine, and 687 ng/L caffeine) and NDMAFP (261 ng/L) were detected at River D upstream of DWTP 6. Another sample site at River E upstream of DWTP 6 had lower levels of tracers (8 ng/L primidone, 22 ng/L carbamazepine, and 176 ng/L caffeine) and NDMA FP (94 ng/L), suggesting less impact from treated wastewater. The concentrations of the three PPCPs in River D were 4-5 times higher than in River E and the NDMAFP was three times higher. DWTP 7 took water from River F in the same watershed, but upstream of the metropolitan urban area. This DWTP had the lowest levels of the three PPCPs and NDMAFP of all samples studied, suggesting that the wastewater impact was minimal.

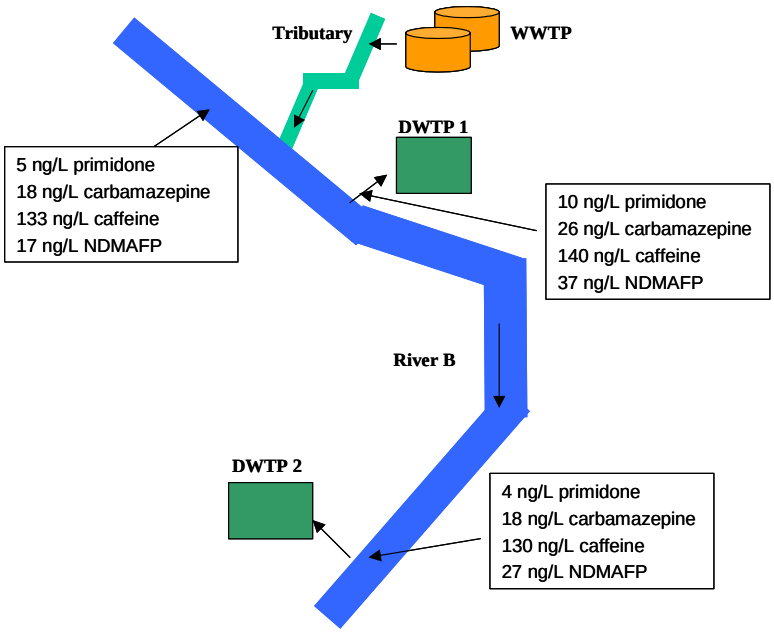

Figure 1. Sampling locations and concentrations of the three PPCPs and NDMAFP in watershed PA1.

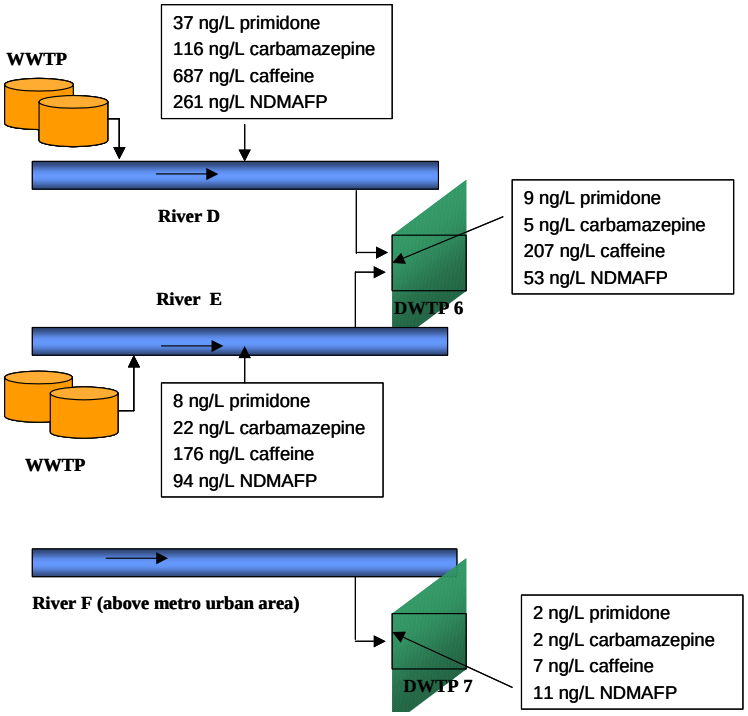

Figure 2. Sampling locations and concentrations of the three PPCPs and NDMAFP in watershed CO.

Excluding the one WWTP effluent sampled and the DWTP 7 influent upstream of a metropolitan area, the other samples--located downstream of WWTPs--represent surface waters with various degrees of treated wastewater impact. The distributions of the three PPCPs and NDMAFP in these effluent-impacted surface waters are shown in box-and-whisker plots below (Figure 3).

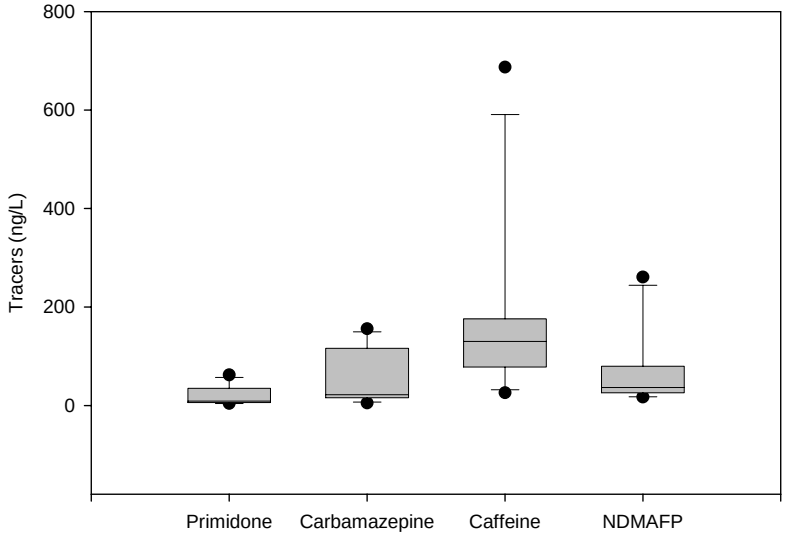

Figure 3. Concentrations of the three PPCPs and NDMA precursors in effluent-impacted surface waters. Top and bottom of box = 75th and 25th percentiles, respectively; top and bottom of whiskers = 90th and 10th percentiles, respectively; line across inside of box = median (50th percentile); and points beyond whiskers = outliers.

Because primidone had been demonstrated previously (Krasner et al., 2006) to be a conservative indicator of treated wastewater impact, the concentrations of carbamazepine and caffeine were plotted against that of primidone to identify any correlations among the three PPCPs (Figure 4). The correlation between the two anticonvulsants, carbamazepine and primidone, is good (R^2=0.86), whereas there is no correlation between caffeine and primidone (R^2=0.04). The lack of correlation between caffeine and other pharmaceuticals had also been noted by Glassmeyer et al. (2005).

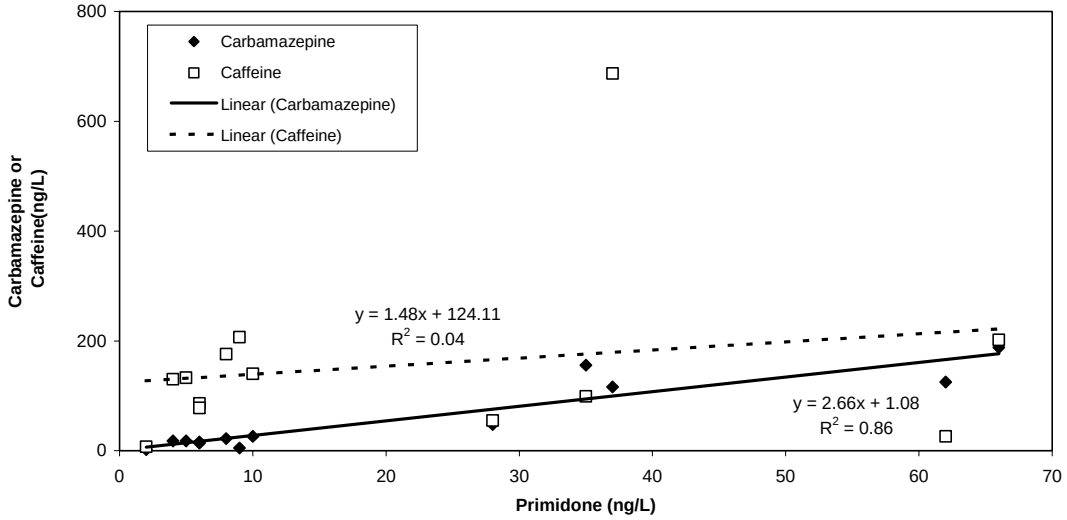

Figure 4. Correlations of concentrations of carbamazepine and caffeine to that of primidone.

CONCLUSIONS

The three PPCPs and NDMA precursors were present in all effluent-impacted drinking-water samples investigated to date. In previous research, the concentration of primidone was a quantitative indicator of the degree of treated wastewater impact. The correlation between the concentrations of carbamazepine and primidone suggest that either pharmaceutical can be used as conservative wastewater tracers, whereas the concentration of caffeine did not appear to provide the same degree of information. More samples are being collected and analyzed for the project. Because treated wastewaters are a source of NDMA precursors, the measurement of PPCPs in drinking-water supplies can be used in evaluating water quality in drinking water sources downstream of treated wastewater discharges.

ACKNOWLEDGMENTS

The authors gratefully acknowledge that the Awwa Research Foundation is the joint owner of the technical information upon which this publication is based. The authors thank the Foundation and the U.S. government, through the Environmental Protection Agency (USEPA) for its financial, technical, and administrative assistance in funding and managing the project through which this information was discovered. The comments and views detailed herein may not necessarily reflect the views of the Awwa Research Foundation, its officers, directors, affiliates or agents, or the views of the U.S. Federal Government. The project manager is Djanette Khiari. The authors also would like to acknowledge other co-investigators of the overall project: Dr. William Mitch (Principal Investigator, Yale University), Dr. Paul Westerhoff (Co-Investigator, Arizona State University), and Mike Sclimenti (Co-Investigator, Metropolitan Water District of Southern California). In addition, the participating utilities are acknowledged for their invaluable assistance. Finally, the authors would like to thank Metropolitan staff, Tiffany Lee and Eduardo Garcia, for their assistance in NDMAFP analysis.

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