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Dairy-Impacted Wastewater Is a Source of Iodinated Disinfection Byproducts in the Environment

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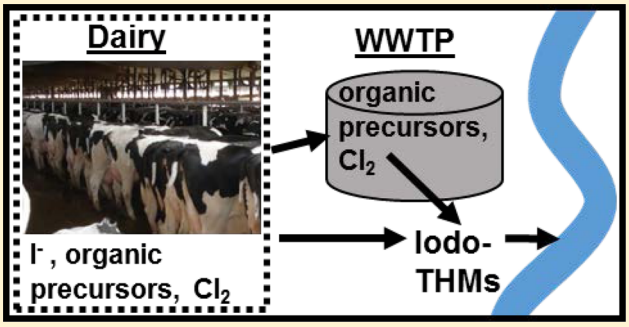
Supporting Information

ABSTRACT: Iodinated disinfection byproducts (DBPs) are among the most toxic DBPs, but they are not typically measured in treated water. Iodinated DBPs can be toxic to humans, and they also have the potential to affect aquatic communities. Because of the specific use of iodine and iodine-containing compounds in dairies, such livestock operations can be a potential source of iodinated DBPs in corresponding receiving water bodies. DBPs [trihalomethanes (THMs), including iodinated THMs] were measured within dairy processing facilities (milking and cheese manufacturing) and surface waters that receive dairy-impacted effluents [either directly from the dairy or through wastewater treatment plants (WWTPs)] in three areas of the United States (California, New York, and Wisconsin). Iodo-THMs comprised 15−29% of the total THMs in surface water near WWTP effluents that were impacted by dairy waste and 0−100% of the total THMs in samples from dairy processing facilities.



INTRODUCTION

Disinfection byproducts (DBPs) from wastewater sources are poorly understood and could constitute an important source of these contaminants in the aquatic and terrestrial environment. In contrast to the more commonly studied bromo-chloro DBPs, the presence of iodinated DBPs (iodo-DBPs) has been measured less frequently, but they may be an important class of DBPs, particularly from sources such as dairy discharges. Most DBP research has focused on drinking water; however, these compounds are also formed when wastewater is disinfected, including wastewaters from municipal areas, animal agriculture, and energy extraction.[1−3] These other sources of DBPs could have deleterious effects on aquatic organisms through discharge to streams and impacts on terrestrial organisms through biosolids and manure land application; however, the toxicity of DBPs in these settings has been understudied.

Types of DBPs formed from these various wastewater sources can vary substantially in chemical composition from those found in drinking water because of a range of different precursors, residual disinfectant levels, and other operational factors. A range of DBPs, including aliphatic compounds [trihalomethanes (THMs), haloacetic acids, haloacetonitriles, haloacetaldehydes, and *N*-nitrosodimethylamine][1−3] and aromatic compounds (halopyrroles and halobenzenesulfonic acids),[4−6] have been documented in wastewater effluent sources and are a potential risk to downstream water quality. In particular, bromine incorporation was consistently documented because of the relatively high levels of bromide found in treated wastewater effluents,[1] especially those influenced by produced water from oil and gas production.[2]

Iodine incorporation, while less studied than bromine incorporation, is of particular importance because iodo-DBPs are generally more cytotoxic and genotoxic than their chlorinated and brominated analogues.[7−9] Naturally occurring iodide, believed to be the primary source of iodo-DBPs, has been detected in drinking water[10] and wastewater.[1−3] Iodine-containing molecules, such as medical imaging compounds, can also form iodo-DBPs such as iodo-THMs and iodo-acids.[11]

Dairy waste is another potential, yet underinvestigated, source of iodo-DBPs in the environment. Iodine is used in the sanitation process in dairies, and iodine sanitizers (usually as iodophors; teat dips are typically 1% iodine) are used extensively in filling/packaging machines, culture processing equipment, drop hoses, and hand dipping stations.[12,13] Iodine and other iodinated compounds, in conjunction with chlorine

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disinfection within the dairy processing facility or further downstream at a municipal wastewater treatment plant (WWTP), could lead to the formation of iodo-DBPs, particularly iodo-THMs. Given the lack of inclusion of iodo-DBPs in treated water studies, the goal of this study was to document iodo-DBP concentrations in waste streams in and near dairy activities to confirm their importance as a source of iodo-DBPs. Samples were collected during 2014 and 2015 from two surface water sites below wastewater effluent that included dairy waste, five milking facilities, and three cheese processing facilities in California, New York, and Wisconsin.

EXPERIMENTAL METHODS

Field Sampling. Grab samples were collected midstream (where possible) for surface water and end-of-pipe or in-line for dairy (milking and cheese) processing facilities. Samples were collected using prebaked 1 L amber glass bottles. Bottles were filled without headspace and immediately placed on ice for transport; no preservatives were required as samples were analyzed within 24 h of collection.

Samples were collected in three states, California, New York, and Wisconsin. Two surface water stream sites were sampled in California below discharges of WWTP effluent. Both WWTPs receive some portion of dairy waste (up to 50%) and undergo tertiary treatment (filtration) and chlorine disinfection (and subsequent dechlorination before waste is discharged). The WWTP 1 effluent follows a drain for approximately 8 km with no significant water inputs before being discharged to a river. WWTP 1 receives approximately half of its waste from dairy and food processing. Four samples were collected between September 2014 and September 2015 from a site just downstream from where the drain discharges to the river (Table S1 and Figure S1). At one sampling time (October 2014), two additional samples were collected longitudinally along the drain before it enters the river (Figure S1). At WWTP 2, samples were collected in September 2015: one sample of surface water just downstream of the WWTP effluent discharge and another sample ~0.8 km downstream (Figure S1). WWTP 2 receives ~10% of its waste from dairy and food processing.

Dairy processing samples from both milking and cheese facilities (noted as "MF" for milking facility and "CP" for cheese processing; total of eight different processing facilities) were collected in Wisconsin and New York. A wastewater composite sample was collected from CPs; however, MF samples were collected as either a composite or several grab samples during the milking machine cleaning and sanitation process (Figure S2). Many of the steps within the MFs included chlorination at the rinse, wash, acid, and sanitize cycles. Grab samples were collected either directly from the end of a pipe [MF 1 and 3 (Table S1)] or from a holding tank/composite [MF 2, 4, and 5 (Table S1)]. Cheese processing samples were collected in Wisconsin [CP 1−3 (Table S1)] from the end of a pipe that discharges into a nearby stream. If possible, direct effluent (before being mixed with surface water) and stream samples both upstream and downstream of the CP effluent were collected.

DBP Analysis. Twenty-nine DBPs were measured in the water samples via solid phase extraction (SPE) and gas chromatography/mass spectrometry using a previously published method[2] though only the 10 THMs will be discussed further because this was the only target group of compounds that contained the iodo-DBPs. The THMs discussed include four bromo-chloro THMs (chloroform, bromodichloromethane, dibromochloromethane, and bromoform) and six iodo-THMs [dichloroiodomethane (DCIM), bromochloroiodomethane (BCIM), chlorodiiodomethane (CDIM), dibromoiodomethane (DBIM), bromodiiodomethane (BDIM), and iodoform (TIM)]. Further details of the analytical method, along with quality assurance procedures, can be found in the Supporting Information.

RESULTS AND DISCUSSION

WWTP Effluents That Receive Dairy Waste. Of the six iodo-THMs measured, four (BCIM, CDIM, DBIM, and DCIM) were detected at both WWTP 1 and WWTP 2 (Table S1). WWTP 1 was sampled on four different occasions over a period of one year, while WWTP 2 was sampled only once; concentrations at WWTP 1 were averaged over the four sampling times. Total THM concentrations were lower at WWTP 1 (1.06 ± 0.62 μg/L) than at WWTP 2 (4.91 μg/L) (Table S1). The percentages of iodo-THMs were similar between the two WWTPs (23 ± 5.6% at WWTP 1 and 19% at WWTP 2). The maximal concentrations of iodo-THMs at either site decreased in the following order: DCIM (0.55 μg/L) > BCIM (0.22 μg/L) > DBIM (0.13 μg/L) ≈ CDIM (0.12 μg/L).

At a single sampling date at WWTP 1 (October 6, 2014) and WWTP 2 (September 14, 2015), both surface water and either two within-drain samples (WWTP 1; up to 8 km up-drain) or a downstream sample (WWTP 2; 0.8 km downstream) were also collected (Figure 1). The total THM and iodo-THM concentrations decreased as the distance from the source increased; for example, the concentration of DCIM at WWTP 1 decreased from 0.38 to 0.15 μg/L along the 8 km drain. These longitudinal data indicate that the THMs may be experiencing partial attenuation due to various environmental processes (e.g., volatilization, photolysis, etc.) but were conservative enough to be transported downstream through the length of the reaches studied (dilution was not considered to be a major factor in this attenuation as there were no major inputs of other surface water or groundwater between the sampling points). The percentages of iodo-THMs were similar when moving downstream; the percent iodo-THMs decreased from 22 to 20% at WWTP 1 and from 19 to 16% at WWTP 2.

Dairy Processing Samples. Four iodo-THMs were detected in various stages of milk processing from five MFs (Table S1 and Figure 2), three of which were also detected at the WWTP sites. Overall, total THM concentrations ranged from 0.11 to 92 μg/L (Table S1). Similar to the WWTP sites, DCIM was still the most frequently detected iodo-THM (detected in at least one sample at 60% of the sites) and was detected at the highest concentrations [maximal concentration of 5.4 μg/L (Table S1)]. The MFs also had one detection (20% of sites) of BCIM (maximal concentration of 0.33 μg/L) and multiple detections (60% of sites) of CDIM (maximal concentration of 0.72 μg/L). The one iodo-THM detected at the MFs (40% of sites) that was not detected at the WWTPs was TIM; concentrations were lower than those of the other iodo-THMs (maximal concentration of 0.20 μg/L). Iodo-THMs made up 0−100% of the total THMs in the MF samples; this iodo-THM distribution varies more than the percentage [from 15 to 29% (Table S1)] of iodo-THMs below the WWTPs.

When multiple samples were collected at various points in the milking cleaning and sanitization process at the same MF, it

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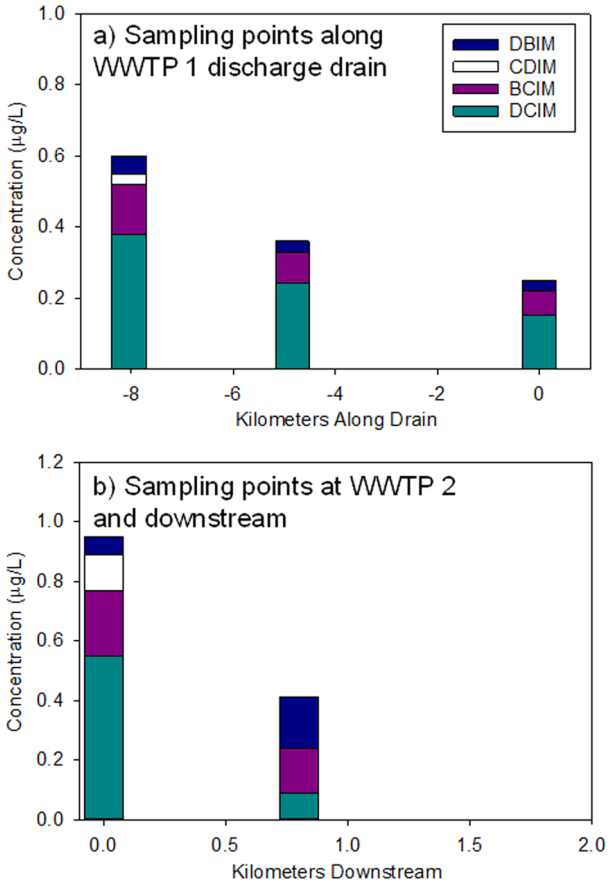

Figure 1. Concentrations of iodo-THMs before or after being discharged to surface water (river). (a) Sampling points along the drain for WWTP 1 (that received ~50% of its waste from dairy and dairy food processing) before reaching the surface water discharge point. (b) Sampling surface water (river) below WWTP 2 (that received ~10% of its waste from dairy and dairy food processing) and one point further downstream. Abbreviations: DBIM, dibromoiodomethane; CDIM, chlorodiiodomethane; BCIM, bromochloroiodomethane; DCIM, dichloroiodomethane.

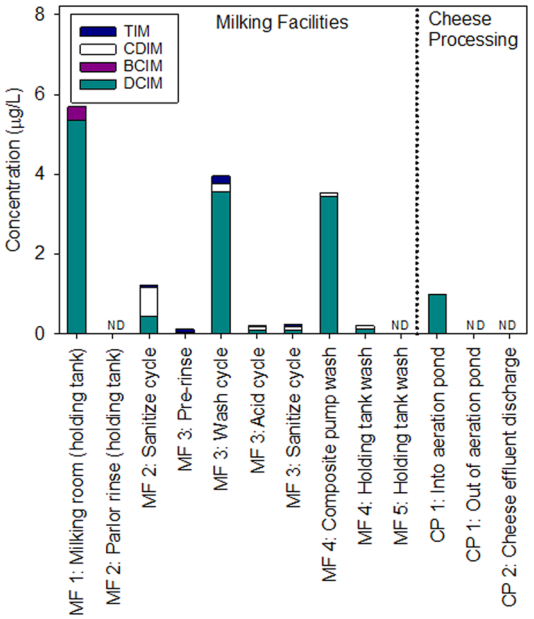

Figure 2. Concentrations of iodo-THMs in water from various spatial locations within the dairy processing cycle at five milking (MF 1–5) and two cheese processing facilities (CP 1–2). Abbreviations: DCIM, dichloroiodomethane; BCIM, bromochloroiodomethane; CDIM, chlorodiiodomethane; TIM, iodoform.

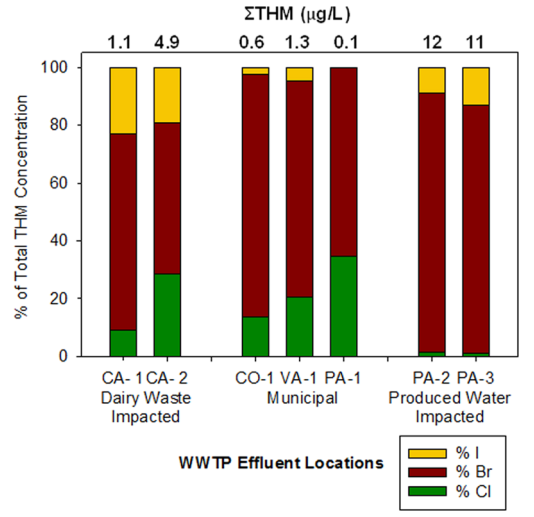

Figure 3. Percentages of chlorinated, brominated, and iodinated THMs in streams and rivers that received WWTP effluent in California (CA), Colorado (CO), Virginia (VA), and Pennsylvania (PA). In addition to municipal waste, the two CA sites also receive dairy waste and the two PA sites receive produced waters. Total THM concentrations are listed above the bars. The CA site data are from this study; the CO, VA, and PA site data are from refs 2 and 3.

was shown that THMs can form, degrade, and be re-formed throughout the entire facility (MF 3 in Figure 2; Table S1). The breakdown and formation of these compounds depends on the chemical conditions of the current process (i.e., wash vs sanitize cycle in MF 3), and the addition of chlorination can impact the THMs formed; more sampling and disinfectant levels would need to be known to further describe the conditions under which certain iodo-THMs form.

For the three CPs, there were fewer detections and lower concentrations of THMs, including iodo-THMs, when compared to the MFs (Table S1 and Figure 2). One effluent (CP 1) had one iodo-THM (DCIM, 1.0 µg/L) detected (Table S1); CP 2 had no iodo-THMs detected but did have detections of bromo-chloro THMs. CP 3 had no THMs detected, and it was determined after sampling that no chlorination was used for disinfection in contrast to the other facilities sampled. Depending on the type of disinfection used in the CPs, they can form THMs, including iodo-THMs. Nevertheless, no THMs were detected in stream samples collected downstream of CP effluent discharges.

Comparison to Previous WWTP Research. The dairy-impacted WWTP effluent results were compared to those of other WWTP effluent samples collected in previous studies[2,3] (Figure 3); for all types of WWTP effluents, total THMs varied substantially (from 0.1 to 12 µg/L). In addition, the dairy-impacted WWTPs had a higher level of iodo-THMs (19–23%) compared to those of three other municipal WWTPs (0–5%) and two WWTPs that received (high bromide) produced waters (9–13%).[2,3] A larger number of WWTP sites that do and do not receive dairy waste would have to be sampled to determine if the higher percentage of iodo-THMs in dairy-impacted waste observed in this study is statistically significant; however, these results indicate that there may be substantial

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differences in the occurrence of iodo-THMs in facilities that accept dairy waste, suggesting that such facilities may be unrecognized sources of these contaminants.

Of the iodo-THMs detected at municipal WWTPs not impacted by dairy, DCIM and BCIM were the most frequently detected, with lower levels of CDIM and DBIM detected;[3] this same pattern is found at the dairy-impacted WWTPs, even though total iodo-THM concentrations are higher at the dairy-impacted WWTPs (Figure 3). Other research has detected DCIM as the only iodo-THM after chlorination at WWTPs,[1] and in drinking water studies, DCIM was the most commonly observed iodo-DBP.[8,10]

The produced water-impacted WWTPs had higher total THM levels (up to 12 μg/L) and a different iodo-THM profile compared to those of dairy-impacted WWTPs. Below WWTPs that received produced waters (high in bromide), DBIM (the most brominated iodo-THM) was detected at concentrations greater than those of the other iodo-THMs; overall, five of six iodo-THMs were detected, and the only iodo-THM not detected was CDIM.[2]

Dairy waste can form iodo-THMs in water during food processing (milk and cheese) and at WWTPs that receive dairy waste where they may be mixed with other DBPs before being discharged to receiving streams. Results of this study show the fraction of iodo-THMs is greater in dairy-impacted waste than in other treated municipal waste, including produced water-impacted waste. More research needs to be conducted to improve our understanding of other components in wastewater (e.g., iodide concentration, disinfectant dosages, pH, and organic carbon content) and how these factors affect iodo-DBP formation in dairy waste.

While the surface water samples analyzed in this study were collected from targeted watersheds where they were not originally treated for drinking water consumption, these results are indicative of the potential for more highly iodinated (but unregulated) DBPs to form at drinking water treatment plants or wherever these source waters undergo more treatment and disinfection. Though iodo-THMs are among the more toxic forms of DBPs known,[7] the relative pathways of iodo-THMs to the environment and potential impacts on exposed biota remain poorly understood. These results highlight the potential significance of these environmental contaminants and need for further study.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.estlett.6b00109.

Details of the analytical method (extraction and quantitation), concentrations of individual THMs (Table S1), and schematics of WWTP and dairy sample collection (Figures S1 and S2, respectively) (PDF)

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Notes

The authors declare no competing financial interest.

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