



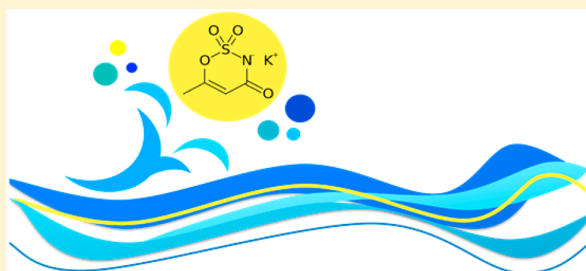
## Sweetened Swimming Pools and Hot Tubs

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### S Supporting Information

**ABSTRACT:** Nitrogenous organics in urine can react with chlorine in swimming pools to form volatile and irritating N-Cl-amines. A urinary marker is desirable for the control of pool water quality. The widespread consumption of acesulfame-K (ACE), a stable synthetic sweetener, and its complete excretion in urine, makes it an ideal urinary marker. Here we report the occurrence of ACE and its potential application in swimming pools and hot tubs. First, we developed a new method for achieving high-throughput analysis of ACE without preconcentration or large-volume injection. Analysis of more than 250 samples from 31 pools and tubs from two Canadian cities showed ACE in all samples. Concentrations ranged from 30 to 7110 ng/L, up to 570-fold greater than in the input tap water. The level of dissolved organic carbon was significantly greater in all pools and tubs than in the input water. Finally, we determined the levels of ACE over 3 weeks in two pools (110000 and 220000 U.S. gallons) and used the average ACE level to estimate the urine contribution as 30 and 75 L. This study clearly shows the human impact in pools and tubs. This work is useful for future studies of the human contribution to DBP formation, epidemiological assessment of exposure, and adverse health effects in recreational facilities.



### INTRODUCTION

The recent news article “Chemical reactions taking place in your pools”<sup>1</sup> and the overnight color change of the water from blue to green in the 2016 Rio Olympic pools<sup>2</sup> highlight the need to monitor water quality in swimming pools. A variety of chemicals can be introduced into recreational waters via body fluids<sup>3</sup> that can react with disinfectants. Recently, a study identified more than 100 disinfection byproducts (DBPs) in swimming pools and hot tubs and found that organic extracts from those samples were more mutagenic than corresponding tap water extracts.<sup>4</sup> Epidemiological studies have found a potential association of an increased risk of bladder cancer with long-term DBP exposure via drinking water,<sup>5</sup> but association via exposure through swimming pools has been inconsistent.<sup>6,7</sup>

Human urinary input into swimming pools is a public health concern, although urine itself is sterile. Urine contains many nitrogenous compounds such as urea, ammonia, amino acids, and creatinine. These compounds can react with disinfectants (e.g., chlorine) in swimming pools to form DBPs, including trihalomethanes, haloacetic acids, haloamines, and halonitromethanes.<sup>8,9</sup> Exposure to volatile DBPs, specifically trichloramine, in indoor swimming facilities can lead to eye and respiratory irritation<sup>10–12</sup> and has been linked to occupational asthma.<sup>13</sup> Although considered a taboo, 19% of adults have admitted to having urinated in a swimming pool at least once.<sup>14</sup> The average urine excretion per swimmer in pools is approximately 70 mL.<sup>15</sup> Dissolved organic carbon (DOC) in swimming pools has been associated with both bather load and formation of trihalomethanes.<sup>16,17</sup> The potential negative health

effects associated with DBPs led us to investigate a marker for urine in swimming pools and hot tubs.

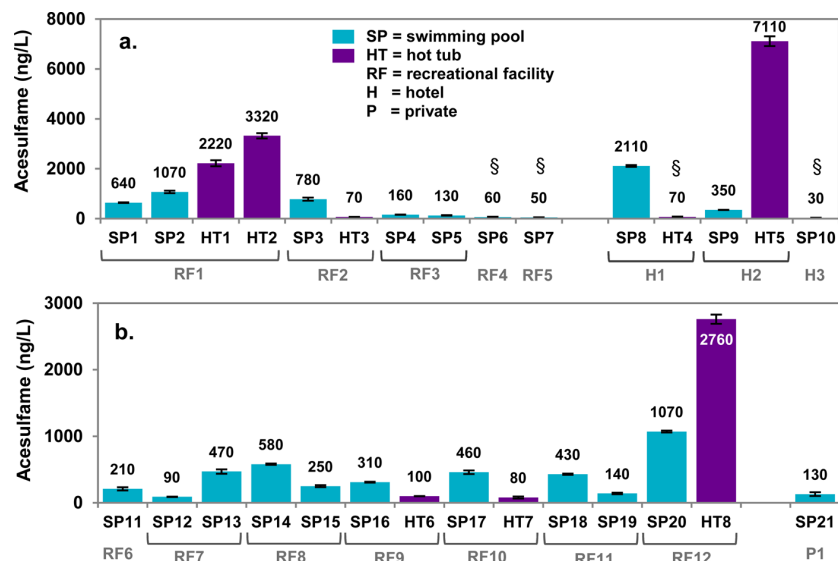
Artificial sweeteners are consumed in large quantities because of their negligible calories and low impact on blood sugar.<sup>18</sup> Found pervasively in natural water bodies,<sup>19–23</sup> they have been recognized as emerging environmental contaminants.<sup>23,24</sup> Non-nutritive artificial sweeteners, including acesulfame-K (ACE),<sup>25,26</sup> sucralose (SUC), saccharin (SAC), and cyclamate (CYC), have been recognized as indicators of wastewater in environmental waters.<sup>27,28</sup> ACE, used in prepackaged foods,<sup>18,29,30</sup> is not metabolized by humans; it is completely absorbed and excreted exclusively in the urine,<sup>29,31</sup> whereas SUC is excreted mainly in feces.<sup>32</sup> The average concentration of ACE in urine is approximately 4000 ng/mL.<sup>33</sup> Several studies have shown that ACE is stable at varying pHs and high temperatures<sup>30</sup> and is resistant to microbial action in aerobic soils.<sup>34</sup> Furthermore, ACE is much more resistant to wastewater treatment processes than SAC or CYC.<sup>25,35,36</sup> Because of its widespread consumption, stability, and persistent nature, we hypothesized that ACE may serve as an indicator of urinary input in swimming pools. The occurrence of any artificial sweetening agents in swimming pools has not been studied previously. The objective of this study was to determine the

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**Figure 1.** Average ACE concentration ( $N = 3$ ) detected in swimming pool (SP) and hot tub (HT) samples collected from public recreational facilities (RF), hotels (H), and a private residence (P) in (a) city 1 and (b) city 2. Samples indicated by the silcrow (§) were analyzed at a 1/10 dilution, rather than 1/20, because of their low ACE concentration.

occurrence of the artificial sweetener ACE in swimming pools and hot tubs compared to input tap water.

The assessment of ACE in water typically includes separation by ion or liquid chromatography (LC) and detection using electrospray ionization mass spectrometry (ESI-MS), with<sup>37</sup> or without<sup>27</sup> solid phase extraction (SPE). Recently, a method capable of detecting ACE at a concentration of 0.2 ng/L without preconcentration was developed.<sup>38</sup> However, the need for specialized equipment or sample preconcentration makes these methods impractical for monitoring studies. To allow the assessment of ACE in the complex matrices of pool and hot tub water samples, without preconcentration, we have developed a rapid, high-throughput method using high-performance liquid chromatography (HPLC) with tandem mass spectrometry (MS/MS). The method was applied to assess ACE in more than 250 samples collected from 31 pools and hot tubs and more than 90 corresponding input tap water samples.

## MATERIALS AND METHODS

### Collection of Swimming Pool and Hot Tub Samples.

We collected samples from two Canadian cities between May and August 2014. In city 1, samples were collected from 10 swimming pools (SP) and 5 hot tubs (HT) from 5 recreational facilities (RF) and 3 hotels (H). In city 2, samples were collected from 11 SPs and 3 HTs from 7 RFs and one private pool (P). All facilities used municipal tap water as the input source. Triplicate grab samples were collected using new, sterile, 15 mL polystyrene vials. In swimming pools and hot tubs, samples were collected away from the jets, approximately 30 cm from the edge and 15 cm below the surface. Municipal tap water was collected on the same day, in triplicate, at each site.

Samples were stored at 4 °C until they were analyzed. ACE is stable and resistant to decomposition, showing no detectable decrease in concentration after being stored for 10 years at room temperature.<sup>39</sup> Samples were filtered through disposable 0.45  $\mu\text{m}$  Millipore filters (PVDF, 25 mm). An analysis blank was injected into the HPLC-MS/MS instrument after each set

of samples to detect and avoid any carryover or contamination during sequential analysis. No ACE was detected in the analysis blanks.

**Case Study Sample Collection.** Samples were collected over 3 weeks from two swimming pools, SP $x$  and SP $z$ , in city 2 in August 2016. SP $x$  and SP $z$  have volumes of 110000 and 220000 U.S. gallons, respectively (roughly 420000 and 840000 L, respectively). Both SPs are on a closed water filtration system with new water only being added to replace losses due to evaporation or splash out. Both pools are disinfected with  $\text{Cl}_2$  gas and shocked with  $\text{CaOCl}_2$ . Each day, 6 SP samples and 3 tap water samples were collected from the same locations at the same time. Human urine samples ( $N = 20$ ) with equal volume were pooled and homogenized. The mixture was diluted 100000-fold with Optima water through serial dilution. The diluted sample was analyzed in triplicate to obtain the average concentration of ACE.

**HPLC-MS/MS Analysis of ACE.** Details regarding the purchase and preparation of materials, standards, and stock solutions can be found in the [Supporting Information](#). An Agilent (Santa Clara, CA) 1100 HPLC system was used with an Inspire C18 column (100 mm  $\times$  3.0 mm, 3  $\mu\text{m}$  particle size; Dikma Technologies, Lake Forest, CA) at room temperature. The flow rate was set to 0.5 mL/min with the autosampler injection volume set to 100  $\mu\text{L}$ . Solvent A consisted of acidified water [0.1% formic acid (FA)] and solvent B acidified methanol (0.1% FA).

A triple quadrupole tandem mass spectrometer (5500 QTRAP, AB Sciex, Concord, ON) with multiple-reaction monitoring (MRM) mode was used for the detection and quantification of ACE and the internal standard, ACE- $d_4$ . For ACE, the Q1 and Q3 mass-to-charge ratios for primary and secondary transitions were 162.1 Da > 81.9 Da and 162.1 Da > 77.9 Da, respectively; for ACE- $d_4$ , transitions of 166 Da > 85.9 Da and 166 Da > 77.9 Da, respectively, were used. Retention times were matched with authentic standards. Detailed HPLC-MS conditions are presented in the [Supporting Information](#).

ACE- $d_4$  was prepared in LC–MS-grade methanol. Each sample was spiked with ACE- $d_4$  at a concentration of 10 ng/L. All samples had a final 9:1 H<sub>2</sub>O:MeOH composition. The relative peak area of the primary transition for ACE to ACE- $d_4$  was used for quantification. The secondary transition peak confirmed the identity of ACE in the samples. A calibration curve was prepared with each batch to account for variation in instrument signal intensity.

**Determination of Dissolved Organic Carbon.** Swimming pool, hot tub, and input tap water samples collected from city 1 were analyzed for their DOC content. DOC was measured at the Biogeochemical Analytical Service Laboratory of the University of Alberta. U.S. Environmental Protection Agency (U.S. EPA) Method 415.1 for Determination of Total Organic Carbon in Water was used with a Shimadzu TOC-5000A Total Organic Carbon Analyzer.

## RESULTS AND DISCUSSION

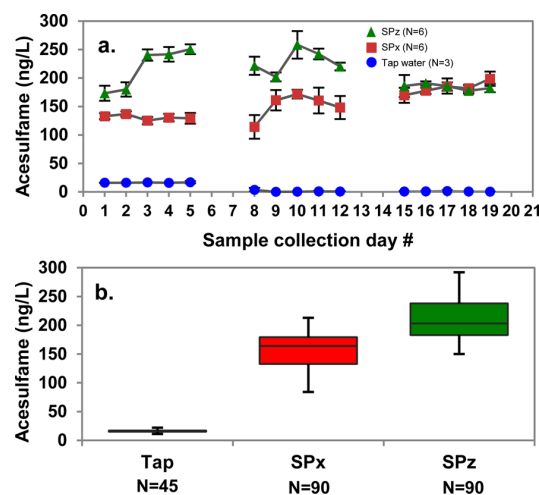
**Concentration of ACE in Swimming Pools and Hot Tubs.** Figure 1 shows the concentrations of ACE determined in the pools and hot tubs. In city 1, the concentration of ACE in the pool samples ranged from 30 ng/L in SP10 to 2110 ng/L in SP8 (Figure 1a). In city 2, the concentration of ACE ranged from 90 to 580 ng/L in all the pools except SP20, where 1070 ng/L ACE was found (Figure 1b). ACE concentrations in all hot tub samples ranged from 70 to 100 ng/L (HT3, HT4, HT6, and HT7) and from 2220 to 7110 ng/L (HT1, HT2, HT5, and HT8). HT5 contained the highest ACE concentration (7110 ng/L), more than double that of any other sample. These samples were collected at one time and represent only a snapshot in time. The large variation in the concentration of ACE in the pools and tubs may be explained by the water change cycling time point, the number of users and events, and facility management practices. Typically, fresh water is added to swimming pools only to maintain water levels, whereas hot tub water in community facilities is replaced frequently to prevent health issues associated with heavy use.<sup>40,41</sup>

ACE was detected in all tap water samples at concentrations significantly lower than those in the pools and tubs in both cities. ACE in tap water samples ranged from 6 to 12 ng/L (Figure S1a) in city 1 and from 12 to 15 ng/L (Figure S1b) in city 2. The difference in ACE concentration in the two cities' tap waters is statistically significant ( $p < 0.001$ ; unpaired  $t$  test). This is expected, as the source water for each city is unique. The ACE concentrations in swimming pools and hot tubs were 4 (SP10) to 571 (H4) times greater than that in the corresponding input tap water (Table S1). The ACE concentrations determined in the tap water samples in this study are comparable to those of some Albertan well water samples (0.9–1530 ng/L ACE)<sup>38</sup> and lower than those in Swiss tap waters (20–70 ng/L ACE).<sup>18,42</sup>

**Concentration of Dissolved Organic Carbon in City 1 Samples.** To examine the potential human impact on the water quality in the pools and hot tubs, we determined DOC in all samples collected in city 1 (Figure S2). The average DOC ranged from 4.8 to 6.3 mg/L in the tap waters and from 6.7 to 40.5 mg/L in the pools and tubs. For controls, the DOC of input tap waters was significantly greater ( $p < 0.001$ ; unpaired  $t$  test) than the blanks (LCMS Optima water). In the paired samples, the DOC of all SP and HT samples, except HT4, was significantly greater ( $p < 0.01$ , or  $p < 0.001$ ; unpaired  $t$  test) than those of the respective input tap water samples. An

increase in the DOC in the pools and hot tubs suggests human impact on water quality. Previous studies have observed the association of the increasing DOC in swimming pools with an increasing bather load.<sup>16,17</sup> An increased DOC is linked with enhanced formation of DBPs (e.g., trihalomethanes and halobenzoquinones).<sup>16,17,43</sup> Natural organic matter (NOM) is the primary source of DOC in tap water, whereas human inputs such as personal care products and body fluids introduced by swimmers (e.g., urine and sweat) may contribute to DOC in recreational waters.

**Case Study: ACE Variability in Swimming Pools over Time.** To investigate the degree of variation of ACE in pool water, we collected samples from two different sized swimming pools, SPx (110000 U.S. gallons) and SPz (220000 U.S. gallons), over 3 weeks. The concentration of ACE in the tap water control samples ranged from 12 to 20 ng/L (Table S2) during the collection period ( $N = 45$ ). The average concentrations of ACE in SPx and SPz were 156 and 210 ng/L, respectively (Figure 2). The concentration of ACE in



**Figure 2.** (a) Average ACE concentration detected in SPx, SPz ( $N = 6$ ), and tap water ( $N = 3$ ) samples per day over 3 weeks. (b) Box and whisker diagram for the average ACE concentration detected in SPx, SPz ( $N = 90$ ), and tap water ( $N = 45$ ) samples over 3 weeks.

both pools varied similarly. The percent relative standard deviation (%RSD) values for ACE determined in SPx and SPz were 18 and 15%, respectively. On the basis of the volume of each pool, the total mass of ACE present was estimated to be 65 mg in SPx and 176 mg in SPz (see Calculation 1 in the Supporting Information and Table S3).

To estimate the total urinary input in SPx and SPz, we determined the average ACE concentration in a pooled Canadian human urine sample ( $N = 20$ ) to be 2360 ng/mL with 4% RSD (Figure S3). Although this is lower than the mean concentration of ACE in Chinese human urine samples ( $N = 54$ ), reported as 4070 ng/mL,<sup>33</sup> both values have the same order of magnitude. Using approximate pool volumes and the ACE concentration determined in Canadian urine samples, we estimated the total urinary input in SPx and SPz to further illustrate the feasibility of ACE as an indicator (see Calculation 2 in the Supporting Information and Table S3). We calculated the volume of urine to be approximately 30 and 75 L in SPx and SPz, respectively.



**HPLC–MS/MS Method Development and Optimization.** The successful and rapid determination of the concentration of ACE in more than 350 samples is due to the new method we developed. This method eliminates the need for preconcentration and provides sensitive and rapid analysis for a wide range of concentrations of ACE in swimming pool, hot tub, and tap water samples. The method can achieve an instrument limit of detection (LOD) of 0.5 ng/L and a method LOD of 2.2 ng/L. Additional method validation details, including intraday and interday variation and matrix effects, can be found in the [Supporting Information](#). Compared to previous methods requiring manual injection of 500  $\mu$ L or SPE,<sup>37,38</sup> the new method, with a 100  $\mu$ L autosampler injection volume allowing high-throughput analysis, makes the analysis of many samples feasible.

This is the first reported occurrence study of ACE in swimming pools and hot tubs. The high concentration of ACE with 100% occurrence in pools and hot tubs demonstrates the human impact on recreational water quality. The association of occupational asthma in swimmers with volatile N-DBPs (e.g., trichloramine) highlights the need to control the water quality of swimming pools. Several studies have reported that increased DOC in swimming pools results in enhancement of DBP formation. To reduce exposure to N-DBPs and their negative health impacts in swimming pools, we should monitor and control water quality. Public education on personal hygiene in the pools is important as demonstrated in the *Chemical & Engineering News* cover story.<sup>1</sup>

## ■ ASSOCIATED CONTENT

### 📄 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/acs.estlett.7b00043](https://doi.org/10.1021/acs.estlett.7b00043).

Materials, method development and validation, and sample calculations; average ACE in input tap water (Figure S1); average DOC in city 1 samples (Figure S2); chromatogram of ACE in urine (Figure S3); chromatogram of ACE at the LOD (Figure S4); ACE calibration curve (Figure S5); ACE reproducibility (Figure S6); matrix dilution (Figure S7); ACE fold increases (Table S1); ACE in case study pools (Table S2); urine in case study pools (Table S3); and ACE percent spike recovery (Table S4) ([PDF](#))

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### Notes

The authors declare no competing financial interest.

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