Environmental Science & Technology Letters

Letter

pubs.acs.org/journal/estlcu

The Presence of Pharmaceuticals and Personal Care Products in Swimming Pools

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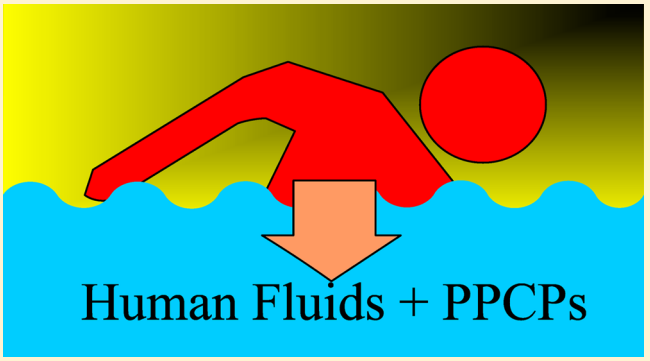
Supporting Information

ABSTRACT: The introduction of pharmaceuticals and personal care products (PPCPs) into the environment can be partially attributed to discharges of human wastes, which is also relevant in swimming pool settings. Little or no information exists to address this issue in the literature. Therefore, experiments were conducted to examine the presence and behavior of PPCPs in swimming pools. Among 32 PPCPs amenable to analysis by an available method, *N*,*N*-diethyl-*m*-toluamide (DEET), caffeine, and tri(2-chloroethyl)-phosphate (TCEP) were found to be present in measurable concentrations in pool water samples. Examination of the degradation of selected PPCPs by chlorination illustrated differences in their stability in chlorinated pools. These results, as well as literature information regarding other attributes of PPCPs, indicate characteristics of these compounds that could allow for their accumulation in pools, including slow reaction with chlorine, little potential for liquid → gas transfer, and slow metabolism by humans (among orally ingested PPCPs). The findings of this study also suggest the potential for accumulation of topically applied PPCP compounds in pools. More generally, the results of this study point to the importance of proper hygiene habits of swimmers. The potential for the accumulation of PPCPs in pools raises questions about their fate and the risks to swimming pool patrons.



INTRODUCTION

The potential for pharmaceuticals and personal care products (PPCPs) to bring about changes in water supplies has been recognized since the late 1990s.[1] PPCPs comprise a broad range of chemicals that are used for personal health, cosmetic, or agricultural purposes. They have been found in many aquatic environments[2] and have the potential to yield adverse impacts on natural ecosystems.[3] The fate of PPCPs in municipal wastewater and drinking water systems has been studied extensively. In general, most treatment systems have not been designed to remove or degrade PPCPs, so the presence of these chemicals represents a potential future challenge for water treatment systems.[4−6] The sources of PPCPs in water supplies include discharges of human and animal wastes, as well as the improper disposal of pharmaceuticals.[7] Some PPCPs are effectively removed or degraded in treatment processes, while others are persistent.[8−11] The persistent PPCPs are likely to be discharged to the environment, where they have the potential to cause harm.

In swimming pool settings, the discharge of human body fluids (especially urine and sweat) is known to introduce a wide range of chemicals into the water.[12−14] In addition, the potential exists for lotions and other externally applied PPCPs to be released as a result of swimmer immersion. Moreover, because some pharmaceuticals are not completely metabolized in humans, they can be excreted in an unchanged form by humans via urine.[15,16] As a result, the potential exists for PPCPs to be introduced into pools, where three routes of exposure are possible: ingestion, inhalation, and dermal uptake.

In the United States, it is common practice to recirculate swimming pool water continuously (a closed-loop system) with little or no replacement for months or years. Water treatment in pool facilities generally involves filtration and chlorination, which are usually included as part of the external recirculating loop. As such, once PPCPs have been introduced into pool water, their fate will be largely determined by reaction and transfer processes that take place within the pool system.

Received: April 14, 2014
Revised: October 23, 2014
Accepted: October 24, 2014
Published: October 24, 2014

   dx.doi.org/10.1021/ez5003133 | Environ. Sci. Technol. Lett. 2014, 1, 495−498

Processes that can influence the fate of chemicals in pool systems include liquid ↔ gas transfer and reactions with chemical oxidants (e.g., chlorine). However, some PPCPs react slowly with free chlorine and are essentially nonvolatile and are therefore likely to persist in swimming pools. Therefore, the potential exists for the accumulation of PPCPs in pool systems. A search of the refereed literature revealed little information about this subject. The objective of this study was to examine the presence and behavior of PPCPs in public swimming pools. In addition, because one of the target pools had recently installed a medium-pressure UV (MPUV) system, sample collection and analysis were performed in a manner that allowed examination of the effects of MPUV for degradation of these compounds in pools.

METHODS AND EXPERIMENTS

Field Experiments. Water samples were collected during periods of typical use from three indoor swimming pools in January 2013 (winter) and July 2014 (summer). The pools will be identified simply as pools A–C. Pools A and B are included as part of university natatoria in Georgia and Indiana, respectively. The primary users of these pools are college students, but both pools are open to the public. Pool C is located in a high school in Indiana and is used by physical education classes, school swimming teams, and age-group swimming clubs. For winter sampling, samples from pool C were collected immediately before and 1 month after a medium-pressure UV reactor was installed. The sample collected before installation of the UV system (before UV) was stored at 5 °C until it was analyzed. The pH of all the pool water samples was between 7.0 and 7.5.

The PPCP analytical method was adopted from ref 11. For all samples that were collected, residual chlorine was quenched by adding a sodium thiosulfate solution (250 mg/L) with a volume sufficient to apply a slight stoichiometric excess, relative to the free chlorine concentration. Sample extraction was conducted within 3 days of collection, except for the before UV sample from pool C (all samples were extracted at the same time). In addition, one laboratory blank (i.e., laboratory-grade deionized water to assess the potential for sample contamination in the laboratory), one deionized water spike recovery sample, and one pool water spiked recovery sample (i.e., water sample spiked with the target PPCPs to check the method performance) were analyzed along with the samples. The filtered water samples were adjusted to pH 2–2.5 by addition of HCl and extracted by solid-phase extraction (SPE) using 6 mL, 500 mg hydrophilic–lipophilic balance (HLB) cartridges (Waters Corp., Milford, MA). The extraction volume was 800 mL, and a batch of 10 samples was extracted simultaneously using an extraction station. The water samples were passed through the SPE cartridge at a flow rate of <20 mL/min. The analytes were eluted from the cartridges by methanol. An aliquot was taken and directly analyzed by liquid chromatography and tandem mass spectrometry (LC/MS/MS) for the detection of benzophenone-3 (BP-3) and 6-acetyl-1,1,2,4,4,7-hexamethyltetralin (ATHN). The rest of the methanol elute was blown down to dryness with pure nitrogen gas, reconstituted in a formic acid solution/methanol mixture [95:5 (v:v)] to a volume of 1.0 mL, and analyzed by LC/MS/MS for the detection of other PPCPs. BP-3 and ATHN were analyzed before being blown down to avoid volatile loss. Details of the LC/MS/MS method are provided in the Supporting Information.

Reaction Kinetics of Chlorination with Selected PPCPs. Batch, bench-scale experiments were conducted to investigate the degradation kinetics by chlorination of selected PPCPs, including naproxen (Sigma-Aldrich), ibuprofen (≥98%, Sigma), caffeine (Reagentplus, Sigma-Aldrich), *N*,*N*-diethyl-*m*-toluamide (DEET, 97%, Aldrich), and acetaminophen (≥99.0%, Sigma-Aldrich). Compounds were selected for inclusion in this experiment on the basis of previous reports of their chemical accessibility and usage, as well as their frequency of detection in the environment.[2,4–6,11] These compounds were presumed to be those that were most likely to be present in swimming pool water samples. The initial concentration of each target compound was 1.8×10^{-5} M, and free chlorine was added in form of NaOCl (10–15% aqueous solution, Aldrich) with a chlorine:precursor ratio (Cl:P) of 10 (i.e., 12.78 mg/L as Cl_2) under a phosphate-buffered system (0.1 mM, pH 7). Time course sampling was applied over a 24 h period. Samples were analyzed by a high-performance liquid chromatography system equipped with a photodiode array detector (Surveyor system, Thermo Scientific). The mobile phase consisted of water and acetonitrile (80:20) at a flow rate of 0.2 mL/min (isocratic), and a reverse-phase C18 column was used (Altima HP C18 ESP 3 μm column, Grace) for analysis.

RESULTS AND DISCUSSION

The LC/MS/MS method used for analysis of swimming pool water samples was designed to detect and quantify 32 PPCPs that are common to water samples or are relevant to swimming pool settings (Table S1 of the Supporting Information). Among the pool water samples, DEET was the only chemical that was identified in the first round of sampling and three PPCPs (DEET, caffeine, and TCEP) were found in the second round of sampling, in which all were present at a concentration above their respective limits of detection. As shown in Figure 1, the

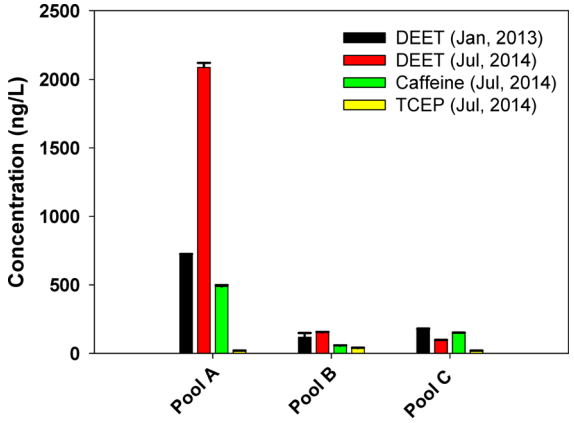


Figure 1. Concentrations of three PPCPs (DEET, caffeine, and TCEP) in three swimming pools. Error bars represent the standard deviation of three measurements for each pool water sample.

sample from pool A (located in Georgia) contained the highest concentration of DEET of the three pools, 721 ± 3.7 ng/L in winter and 2087 ± 32 ng/L in summer, which were substantially higher than the concentrations observed in samples from the pools in Indiana at the same sampling times. The differences in DEET concentration among samples from the three pools could probably be attributed to the time of year when the samples were collected and the locations of the pools (Georgia and Indiana). Specifically, use of insect

dx.doi.org/10.1021/ez5003133 | *Environ. Sci. Technol. Lett.* 2014, 1, 495–498

repellents in winter months is uncommon in northern, temperate states such as Indiana, whereas insect repellent use in Georgia may continue through the winter; large differences in DEET concentration were observed among the three pools collected during the summer. The samples from pool C collected before UV and after UV had nearly identical DEET concentrations, which suggests that UV irradiation has little or no effect on DEET (data shown in Figure S1 of the Supporting Information). Moreover, given that the before UV sample was collected roughly one month prior to the after UV sample, these results suggest that degradation of DEET in pool water is a very slow process.

DEET is a commonly used active ingredient in commercial insect repellents. Although DEET has a relatively low toxicity toward aquatic organisms (96 h LC_{50} = 71.25−150 mg/L), the concentrations found in swimming pool samples are comparable to those found in municipal wastewater and are higher than those found in surface water.[17,18] Caffeine and TCEP were found in the summer samples collected from the three pools. Caffeine could be introduced by human excretions (e.g., sweat and urine), but the route of introduction of the flame retardant TCEP is unclear. Assuming that the concentration of the PPCPs in swimming pools is largely influenced by use pattern and bather loading, more studies are needed to clarify the introduction mechanisms for these compounds.

As described above, most pools include filtration and chlorination as components of their recirculating water treatment systems. Of these processes, chlorination has been judged to be the most likely to yield changes in the structures and concentrations of PPCP compounds. Therefore, batch experiments were conducted to examine the kinetics of decay of five PPCP chemicals that were identified as being the most likely to accumulate in pools. These five chemicals included naproxen, ibuprofen, caffeine, DEET, and acetaminophen. The results of time course monitoring of chlorination of these compounds for 24 h are shown in Figure 2. These data indicate

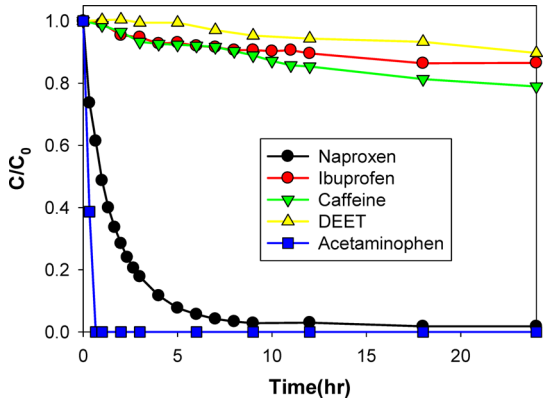


Figure 2. Time course concentration profiles for naproxen, ibuprofen, caffeine, DEET, and acetaminophen after exposure to free chlorine at an initial free chlorine:precursor ratio of 10 (12.78 mg/L as Cl_2).

that acetaminophen and naproxen are susceptible to chlorination; more than 90% of both compounds degraded within the first 6 h of chlorine exposure. These results are consistent with those of Bedner and MacCrehan[19] and Boyd et al.[20] On the other hand, DEET, caffeine, and ibuprofen reacted more slowly to chlorination; more than 80% of these three compounds remained after chlorination for 24 h. Similar results have been reported for these compounds under near-neutral pH conditions by Gould and Richards,[21] Westerhoff et al.,[8] and Acero et al.[22]

The results presented in Figure 2 explain the absence of chlorine-susceptible PPCPs (e.g., acetaminophen and naproxen) in swimming pool water samples, where the pool allows continuous exposure to chlorine and indefinite exposure time for the reaction to occur. Although reactions of the susceptible PPCPs with chlorine can generate transformation products as disinfection byproducts (DBPs),[19] the fate of the chlorine-susceptible PPCPs' transformation products was not investigated in this study. However, the results of chlorine degradation experiments alone do not explain the absence of chlorine-persistent PPCPs (e.g., ibuprofen and caffeine) other than DEET. The data presented in Figure 2 indicate that these three chemicals degrade at similar rates upon being exposed to free chlorine.

The fate and behavior of PPCPs in pools will also be influenced by their routes of introduction. DEET is likely to be introduced to a pool directly by rinsing from skin, whereas caffeine and ibuprofen (as well as other ingestible chemicals) are likely to be introduced via urine from swimmers. However, these orally ingested PCPPs are largely metabolized by humans before excretion via urine. Tang-Liu et al.[23] reported that only 3% of ingested caffeine remains in the unmetabolized form in urine. Mills et al.[24] illustrated that ibuprofen is metabolized into several small fragment compounds before excretion and only 2−3% of ingested ibuprofen was excreted as its unchanged form or its isomer.[16] As such, human metabolism will diminish the mass loading of these parent pharmaceuticals to swimming pool water. However, despite the small fraction of caffeine that remained unchanged after metabolism, quantifiable concentrations of caffeine were observed in the swimming pool samples, possibly because of the large amounts of caffeine that are consumed by humans. On the other hand, direct rinsing from skin may represent the most efficient pathway for introduction of PPCPs into swimming pool water.

Other evidence of introduction of PPCPs into pool water from topical PPCPs has been reported. Lambropoulou et al.[25] and Zwiener et al.[26] identified constituents from sunscreen agents in swimming pools. Wang et al.[27] found a group of halobenzoquinones in a swimming pool, which were identified as derivatives of constituents in lotions that formed in pools as a result of reactions with chlorine. These chemicals could function as DBP precursors and could be ingested, inhaled, or absorbed by swimmers, all of which raise questions about their fate and the risks they may pose to swimming pool patrons.

Collectively, the results of these experiments and previous research allow for identification of the characteristics of PPCPs that would permit accumulation in chlorinated swimming pools. Specifically, compounds that express low potential for liquid → gas transfer, slow reaction rate with chlorine (or other oxidants used in pools), and inefficient metabolism in humans (among ingestible compounds) have the potential to accumulate in pools.

The results of this study support the importance of showering before entering a swimming pool, as a part of an overall hygiene program among swimmers. Other externally applied medications or other topical agents (e.g., lotions, perfumes, and cosmetics, which were not investigated in this study) may also be expected to enter pools via a similar pathway.[28] The effects of introduction of these chemicals into pools are largely undefined but may merit investigation. Moreover, the operating conditions that are employed in

dx.doi.org/10.1021/ez5003133 | Environ. Sci. Technol. Lett. 2014, 1, 495−498

most pools, which typically involve recirculation of chlorinated water for long periods (months or longer), provide an opportunity for slow reactions with chlorine (or other chemical agents) to yield disinfection byproducts that are different than those that are found in drinking water settings. Given the routes of exposure that are available to swimmers in pools, additional research in this area may be warranted.

■ ASSOCIATED CONTENT

Supporting Information

Description of the LC/MS/MS method for identification and quantification of PPCPs in water samples, target PPCPs selected for study, and measured concentrations of DEET before and after inclusion of a UV system at one of the pools from which samples were collected. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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