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# Illicit drugs and pharmaceuticals in swimming pool waters

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## HIGHLIGHTS

- Four illicit drugs and eleven pharmaceuticals were found in swimming pools.
- Ibuprofen was found in all the investigated pool waters.
- Human Risk Assessment (HRA) was performed for different classes of age
- No health risk was found for humans via swimming pool waters

## GRAPHICAL ABSTRACT


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## ABSTRACT

The occurrence of illicit drugs (cocaine, opioids, amphetamines and cannabis derivatives), some of their metabolites and 48 pharmaceuticals, was investigated in pool and source waters in ten Italian indoor swimming pools. The samples were analyzed by highperformance liquid chromatography-tandem mass spectrometry (HPLC-MS/MS), after solid phase extraction (SPE). Cocaine and its metabolites were found in nine swimming pools, at concentrations from 0.3 to 4.2 ng/L for cocaine, 1.1 to 48.7 ng/L for norcocaine, 0.7 to 21.4 ng/L for benzoylecgonine and 0.1 to 7.3 ng/L for norbenzoylecgonine. Opioids, amphetamines and cannabis derivatives were never detected. The most frequent pharmaceuticals were anti-inflammatory drugs: ibuprofen was found in all the pool waters, with a maximum 197 ng/L and ketoprofen was detected in 9/10 samples (maximum 127 ng/L). Among anticonvulsants, carbamazepine and its metabolite, 10,11-dihydro-10,11dihydroxycarbamazepine, were frequent in swimming pool water (8/10 samples) at concentrations up to 62 ng/L. The cardiovascular drug valsartan was also found frequently (8/10 samples), but at lower concentrations (up to 9 ng/L). Other pharmaceuticals were detected occasionally and at lower concentrations (atenolol, enalapril, paracetamol, hydroclorothiazide, irbesartan and dehydro-erythromycin). Carbamazepine, irbesartan and dehydroerythromycin were detected at very low levels (up to 5 ng/L) in only one of the four source water samples. A quantitative risk assessment showed that the health risk for humans to these substance in swimming pool waters was generally negligible, even for vulnerable subpopulations such as children and adolescents.



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## 1. Introduction

There is growing concern about the presence of emerging chemical contaminants in swimming pools and similar environments. Chemicals in pool water can come from a number of sources, namely the source water (polluted in origin), deliberate additions such as disinfectants, and bathers who continuously release organic matter mainly through sweat and urine (WHO, 2006).

Most of the studies on the chemical risk in swimming pools are focused on disinfection by-products (DBPs) in pool water and on the mechanisms of their formation as a result of the reaction between the chlorine used as a disinfectant and the organic substances present in the waters (Zwiener et al., 2007; Richardson et al., 2010). Some hundreds of DBPs have been identified in chlorinated water of swimming pools, some being of particular importance to human health because they are toxic and/or have suspected carcinogenic or mutagenic activity (Richardson et al., 2012).

Other chemical contaminants recently found in swimming pool waters include sunscreen agents, personal care products, pharmaceuticals and other chemicals. However, up to now, the occurrence of pharmaceuticals in swimming pool waters has been scarcely investigated. (Zwiener et al., 2007; Wang et al., 2013; Bottoni et al., 2014; Teo et al., 2016).

Weng et al. (2014) studied 32 pharmaceuticals and personal care products in three swimming pools in USA and detected N, N-diethyl-m-toluamide (DEET), caffeine, and tri(2-chloroethyl)-phosphate (TCEP) in pool water. DEET, a commonly used active ingredient in commercial insect repellents, was found at very different levels. In pool A (in Georgia, USA) the concentration of DEET was highest 721 ± 3.7 ng/L in winter and 2087 ± 32 ng/L in summer, while in pool C (in Indiana, USA) DEET was found at about 200 ng/L. The authors examined the kinetics of decay of five chemicals (naproxen, ibuprofen, caffeine, DEET, and acetaminophen) identified as being the most likely to accumulate in pools. Acetaminophen and naproxen were susceptible to chlorination; >90% of both compounds degraded within the first 6 h of chlorine exposure while DEET, caffeine, and ibuprofen reacted more slowly to chlorination and >80% of these three compounds were still detectable after 24 h.

Ekowati et al. (2016) observed atenolol, carbamazepine, hydrochlorothiazide, metronidazole, ofloxacin, sulphamethoxazole, acetaminophen, ibuprofen, ketoprofen and phenazone in the waters of 17 swimming pools in Catalonia, Spain. The highest concentration was found for the diuretic hydrochlorothiazide (904 ng/L), while the most frequently detected pharmaceutical was carbamazepine, observed in 53% of the pool waters.

In Australia, Teo et al., 2016 investigated the occurrence and daily variability of 30 pharmaceuticals and personal care products in pool waters. Ibuprofen was above the LOQ in seven swimming pools, ranging from 16 to 83 ng/L.

The main sources of these chemicals and/or their metabolites in pool waters are swimmers who eliminate organic substances, urine and sweat during their sport activities (WHO, 2006). Furthermore, when pharmaceuticals are used topically (anti-inflammatory drugs, for instance), they too can be released into pool waters from the skin. Once these substances have entered the water, their fate will be largely determined by reaction and transfer processes within the pool system. If not completely removed by chlorination, these chemicals continuously accumulate and increase in pool waters with time, due to the widespread practice of recirculating pool water continuously with little or no replacement for months or years.

Bathers can release other chemicals such as drugs of abuse and/or their metabolites in urine. To date, there is no information in the literature, to our knowledge, about illicit drugs in swimming pool waters, although these chemicals are continuously found in other aquatic environments. Previous studies in Europe and Italy reported cocaine, opioids, amphetamines, cannabis and their metabolites in waste, surface and ground waters and also in drinking waters (Zuccato et al., 2000; Castiglioni et al., 2006; Zuccato et al., 2008; van der Aa et al., 2013; Mendoza et al., 2014).

Pharmaceuticals and illicit drugs, documented in chlorinated drinking water at concentrations in the order of ng/L, can further react with chlorine and DBPs already formed and present, becoming in turn additional by-products, with greater toxicity than the original compounds (González-Mariño et al., 2012).

Besides other chemicals in pool waters, such as disinfection by-products (DBPs) from chlorine-based water treatment, swimmers may be exposed to pharmaceuticals and illicit drugs through ingestion of small amounts of water while swimming or by skin contact and even by inhalation of aerosols; the amount of water ingested depends on various factors including experience, age, skill and type of activity (Aggazzotti et al., 1995; WHO, 2006).

In view of the potential hazards of pharmaceuticals and illicit drugs and the scarcity of data in the literature on their levels in swimming pool waters, this study investigated for the first time the occurrence of these substances and some of their metabolites in pool and source waters in a sample of Italian indoor swimming pools. The aim was to quantify pharmaceuticals and illicit drugs actual amounts in pool waters and to link them to the different water treatments such as disinfection and filtration. Another aim was to assess the potential exposure for swimmers, taking into account sensitive subpopulations.

## 2. Material and methods

### 2.1. Sample collection

The study was done in ten public indoor swimming pools in the Emilia-Romagna Region (Northern Italy). One indoor swimming pool from the major cities of the Region (ten cities) was sampled. Each pool was visited once and information about the pool water treatments and disinfection procedures was collected. All sampling sessions were carried out in May 2016 in order to obtain waters that had been in the pools a long time, as the complete draining and filling with fresh water is generally done at the end of the summer. The time since the last complete change of water was collected. During each session, source (only in four swimming pools) and pool waters were sampled according to the EPA sampling procedure (USEPA, 2016). A grab sample of source water was collected as close as possible to the point where source water was added to the recirculating pool water. Individual samples of pool water (100 mL) were collected for trihalomethanes (THMs) determination at three different points, at a depth of 20 cm, and 40 cm from the edge of the pool. Samples for the determination of illicit drugs and pharmaceuticals were collected in 1000 mL polypropylene bottles, and were frozen and stored at −20 °C until analysis.

### 2.2. Analysis of swimming pool water physico-chemical parameters

Temperature, pH, free and total chlorine, were analyzed in water samples on the poolside. Water temperature was taken with a digital thermometer, pH and oxidation reduction potential (ORP) were measured with a portable pH meter (pH 110 EUTECH Ins, USA). Free and combined chlorine were evaluated at the poolside using a colorimetric method based on N,N-diethyl-*p*-phenylendiamine (DPD) (PC compact – Aqualityc, USA).

THMs, considered the most representative of the DBPs, were examined in order to link any by-products deriving from chlorination to other chemicals in the waters (WHO, 2006). Triplicate water samples for the determination of THMs (chloroform, bromodichloromethane, dibromochloromethane and bromoform) were collected in screw-capped glass vials (40 $cm^3$) with Teflon faced septa. Five mg of sodium thiosulfate were added to the vials to quench residual chlorine reactions. The analysis were done within a few days, according to the EPA sampling procedure (USEPA, 2016).