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Organic micropollutants (OMPs) in natural waters: Oxidation by UV/H_2O_2 treatment and toxicity assessment

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ABSTRACT

Organic micropollutants (OMPs) are ubiquitous in natural waters even in places where the human activity is limited. The presence of OMPs in natural water sources for human consumption encourages the evaluation of different water purification technologies to ensure water quality. In this study, the Biobío river (Chile) was selected since the watershed includes urban settlements and economic activities (i.e. agriculture, forestry) that incorporate a variety of OMPs into the aquatic environment, such as pesticides, pharmaceuticals and personal care products. Atrazine (herbicide), caffeine (psychotropic), diclofenac (anti-inflammatory) and triclosan (antimicrobial) in Biobío river water and in different stages of a drinking and two wastewater treatment plants downstream Biobío river were determined using solid phase extraction (SPE) and liquid chromatography/tandem mass spectrometry (LC-MS/MS) and electrospray ionization (ESI). Quantification of these four compounds showed concentrations in the range of 8 ± 2 to 55 ± 10 ng L^{-1} in Biobío river water, 11 ± 2 to 74 ± 21 ng L^{-1} in the drinking water treatment plant, and 60 ± 10 to $15{,}000 \pm 1300$ ng L^{-1} in the wastewater treatment plants. Caffeine was used as an indicator of wastewater discharges.

Because conventional water treatment technologies are not designed to eliminate some emerging organic pollutants, alternative treatment processes, UV and UV/H_2O_2, were employed. The transformation of atrazine, carbamazepine (antiepileptic), diclofenac and triclosan was investigated at laboratory scale. Both processes were tested at different UV doses and the Biobío river water matrix effects were evaluated. Initial H_2O_2 concentration used was 10 mg L^{-1}. Results showed that, the transformation profile obtained using UV/H_2O_2 at UV doses up to 900 mJ cm^{-2}, followed the trend of diclofenac > triclosan > atrazine > carbamazepine. Furthermore acute toxicity tests with Daphnia magna were carried out after UV/H_2O_2 treatments of the OMPs mixture studied. At the lower UV doses tested (300 mJ cm^{-2}) a higher toxicity was observed, suggesting the formation of toxic intermediates in the course of the reaction. As expected, at higher UV doses the toxicity declined. Considering the treatment of the mixture of ATZ, CBZ, DCL and TCS with a UV dose of 1200 mJ cm^{-2} and 10 mg L^{-1} of H_2O_2 the acute toxicity results exhibits values for Daphnia magna immobilization equal to 20 and 42% evaluated after 24 and 48 h, respectively.

1. Introduction

In the recent years, as analytical chemistry technology improves, the number of studies reporting the occurrence of OMPs at μg to ng L^{-1} levels in surface water (Kolpin et al., 2002; Sodré et al., 2010), groundwater, drinking water, even in stages of drinking water treatment plants (DWTP) (Boleda et al., 2011) and

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wastewater treatment plants (WWTP) (Blair et al., 2015) has increased. The reported evidence has brought increasing concern to public and scientific community throughout the world.

The importance of surface waters covers from the ability to sustain life and biodiversity as we know it and the many human activities. Nowadays the increasing human and economic activities like agriculture, forestry, aquaculture, industry, tourism and the growing population in urban areas in the surroundings of the Biobío river basin (36°42′–38°49′ S, 71°–73°20′ W) have possibly caused the incorporation of a variety of organic micropollutants (OMPs) to the environment (water, soil and air) (Chiang et al., 2014). The Biobío river has a surface area of 24,625 km^2 and has the second largest flow in Chile (1943 $m^3\ s^{-1}$ during winter) (Parra et al., 2009). Furthermore, it is a hotspot of freshwater biodiversity (Habit et al., 2006).

These OMPs include persistent organic pollutants like pesticides and emerging contaminants like pharmaceuticals and personal care products (PPCPs). The pollutants have many inputs routes: (1) domestic and municipal wastewater discharge, (2) transport through irrigation and runoff in agricultural and forestry activities, (3) leaching into groundwater by authorized and unauthorized landfills (Díaz-Cruz et al., 2003), (4) some OMPs like pesticides have the property of atmosphere dispersion (Campbell et al., 2006). OMPs are of increasing attention and awareness because of their continuous and uncontrolled release to the environment and the potential risk to human health and environment even at trace level concentrations (ppb) (Kümmerer, 2009). This kind of pollutants present hydrophobic and hydrophilic properties, therefore may be present in water, sediment and soil, and can also bioaccumulate in plants and other organisms (human or animal) (Meredith-Williams et al., 2012).

The OMPs are active compounds impacting organisms through all the food chain e.g. birds, fishes, amphibians, aquatic plants and microorganisms (Crane et al., 2006; Oaks et al., 2004). Furthermore, some PPCPs and herbicides are known as endocrine disrupting compounds (EDCs) that cause adverse effects on human and wildlife, and can also act as carcinogenic compounds (Birnbaum and Fenton, 2003).

It is known that one of the main pathways to incorporate PPCPs and EDCs into the aquatic environment is from WWTP effluents. WWTPs commonly use the activated sludge process to biologically degrade organic compounds, but a wide amount of PPCPs and EDCs are recalcitrant compounds and cannot be partially or completely degraded by this process (Vieno and Sillanpää, 2014; Ziylan and Ince, 2011). The presence of OMPs in surface waters is a concern because of its wide use as a source of drinking water (Ternes et al., 2015). Conventional DWTPs include a physico-chemical process such as coagulation-flocculation, sand filtration and chlorination, which are not enough to remove this type of contaminants and can even increase their endocrine disrupting capacity by chlorination (Snyder et al., 2007; Postigo and Richardson, 2014). Several studies have reported the presence of OMPs in DWTPs and tap water (TW) because of the recalcitrance of certain refractory compounds (Benotti et al., 2009). Conventional drinking water treatment is a process that currently is designed only for the removal of known pathogens and priority pollutants. Therefore, new process stages are needed in DWTPs to effectively remove PPCPs and EDCs. Moreover, research of an adequate technology for the treatment of emerging contaminants is of primary importance because, water is a vital and scarce resource that nowadays is limited due to pollution problems, improper distribution policies, population growth, and climate change (Rodriguez-Mozaz and Weinberg, 2010). One option is to include an advanced oxidation process (AOPs) in the DWTPs, which are defined as any oxidation process in which the hydroxyl radical (HO•), a short-lived, extremely potent oxidizing agent, is the dominant species. Studies have shown that AOPs successfully degrade several OMPs (Kim and Tanaka, 2009).

These treatments use reagents like H_2O_2 or O_3 combined with radiation, other oxidants or a heterogeneous catalyst. Hydroxyl radicals are capable of oxidizing organic compounds mostly by hydrogen abstraction. The most common AOPs studied are UV/H_2O_2, O_3/OH^-, O_3/UV, Fe(II)/H_2O_2, UV-A/Fe^{+2}/H_2O_2 and heterogeneous photocatalysis (TiO_2/UV, ZnO/UV) (Klavarioti et al., 2009).

For water treatment, the UV/H_2O_2 process is an important barrier against OMPs, where these compounds are degraded by photon (direct UV photolysis) and HO• attack (Postigo and Richardson, 2014; Wols and Hofman-Caris, 2012). However, the UV/H_2O_2 degradation efficiency depends on the characteristics of the water matrix, such as turbidity, alkalinity, among others (Wols et al., 2013).

Degradation of OMPs under different UV and UV/H_2O_2 conditions were investigated. Canonica et al. (2008) showed 27% of diclofenac degradation using a UV dose of 40 mJ cm^{-2}. Kim and Tanaka (2009) indicated an 8 and 100% carbamazepine and diclofenac reduction employing 230 mJ cm^{-2}, respectively. Using UV/H_2O_2 in natural water, Pereira et al. (2007b) obtained carbamazepine complete degradation at 1700 mJ cm^{-2} and 10 mg L^{-1} of H_2O_2. Sanches et al. (2010) showed around 60% atrazine degradation in single solute and mixtures experiments with surface water applying UV and UV/H_2O_2 treatments at a UV dose of 1500 mJ cm^{-2}. Carlson et al. (2015) obtained 90% triclosan degradation at a UV dose of 700 mJ cm^{-2} in laboratory grade water. The detection of OMPs and the efficacy of UV/H2O2 on OMPs transformations has been evaluated in surface waters, however, considering the importance to determine the presence of OMPs in aquatic environments and treatment systems, no systematic studies have been performed within the Biobío river basin.

The present study evaluates the occurrence of OMPs in the Biobío river, in a drinking water treatment plant and in a wastewater treatment plant. Atrazine (ATZ, herbicide), caffeine (CAF, psychotropic), diclofenac (DCL, anti-inflammatory) and triclosan (TCS, antimicrobial) were found in all studied systems. Advanced oxidation process UV/H_2O_2 was evaluated as an alternative treatment for the founded OMPs. Carbamazepine (CBZ, antiepileptic) was included as a fourth model compound in AOPs studies. To evaluate the degradation extent, experiments were carried out for individual compounds and in mixture using both ultrapure water and Biobío river natural water. Moreover, toxicity tests with *Daphnia magna* were performed to assess the effects of the UV/H_2O_2 process in OMPs mixture.

2. Materials and methods

2.1. Standards and reagents

Atrazine (ATZ) was purchased from Pestanal®, Fluka and Sigma-Aldrich, USA (St. Louis, MO, USA). Caffeine (CAF), carbamazepine (CBZ), diclofenac (DCL) and triclosan (TCS) were purchased from Sigma-Aldrich, USA (St. Louis, MO, USA). The purity of all standards was ≥97%. The UV and UV/H_2O_2 experiments with ATZ were performed with Atranex (90% purity). Table 1 shows physico-chemical properties of the OMPs studied.

Hydrogen peroxide (H_2O_2) 30% p.a. was obtained from Merck (Darmstadt, Germany). A solution of sodium bisulfite and sodium metabisulfite (NaHSO3 and Na2S2O5 mixture, Sigma Aldrich, St. Louis, MO, USA) was used to quench the H2O2. Only in samples used for *Daphnia magna* bioassays the H2O2 was quenched with catalase (Sigma Aldrich, St. Louis, MO, USA).

Acetonitrile, methanol and nitric acid were purchased from Lichrosolv, Merck (Darmstadt, Germany). $NaH_2PO_4 \times 2H_2O$,