Science of the Total Environment 487 (2014) 763–770

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

# Ozonation of wastewater: Removal and transformation products of drugs of abuse

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## HIGHLIGHTS

- The ozonation of six drugs of abuse and one human drug metabolite was carried out.
- Drug removals vary between 3 and 50% for the ozone doses tested.
- The main transformation products of the drugs of abuse were identified.
- The most plausible structure of a transformation product of MDMA was elucidated.

## ARTICLE INFO

*Article history:*
Received 30 July 2013
Received in revised form 18 October 2013
Accepted 4 November 2013
Available online 7 December 2013

*Keywords:*
Drugs of abuse
Wastewater
Ozone
Cocaine
Amphetamines
High resolution mass spectrometry

## ABSTRACT

In this study amphetamine, methamphetamine, methylenedioxymethamphetamine (MDMA), cocaine (COC), benzoylecgonine (BE), ketamine (KET) and oxycodone (OXY) in wastewater at concentrations of 100 $\mu g L^{-1}$ were subjected to ozone to determine their removals as a function of ozone dose and to identify significant oxidation transformation products (OTPs) produced as a result of ozonation. A method based on high resolution mass spectrometry and differential analysis was used to facilitate and accelerate the identification and structural elucidation of the transformation products. The drug removal ranged from 3 to 50% depending on the complexity of the matrix and whether a mixture or individual drugs were ozonated. Both transient and persistent oxidation transformation products were identified for MDMA, COC and OXY and their chemical formulae were determined. Three possible structures of the persistent transformation product of MDMA (OTP-213) with chemical formula $C_{10}H_{16}O_4N$, were determined based on $MS^n$ mass spectra and the most plausible structure (OTP-213a) was determined based on the chemistry of ozone. These results indicate that ozone is capable of removing drugs of abuse from wastewater to varying extents and that persistent transformation products are produced as a result of treatment.



## 1. Introduction

Wastewater treatment plants (WWTPs) have been designed to reduce carbon and nitrogen loads in sewage water. Recently however, several classes of micropollutants have been detected in wastewaters but the treatment systems are not equipped to remove them and they are therefore discharged to receiving waters either unaltered or as metabolites, making wastewater effluents important point sources of contamination (Pedrouzo et al., 2011b; Valcárcel et al., 2012).

Although much work has been done to determine the occurrence of pharmaceuticals and other contaminants of emerging concern (CECs) in wastewater and their fate during wastewater treatment (Boxall et al., 2012; Camacho-Muñoz et al., 2010; de Jongh et al., 2012; Kolpin et al., 2002; Metcalfe and Koenig, 2003; Ternes, 1998), the data available for drugs of abuse (DOAs) and their metabolites are far more scarce. It is well known however, that the use of psychoactive substances is essentially universal and that they are one of the most recent additions to the list of contaminants of emerging concern in the environment (Boleda et al., 2009; Kasprzyk-Hordern et al., 2010). It is clear from the studies that have identified these compounds in wastewater effluents and surface waters at the nanogram and in some cases, microgram per liter level, that they and many of their main human metabolites, are ubiquitous in the environment (Baker and Kasprzyk-Hordern, 2011; Bartelt-Hunt et al., 2009; Bijlsma et al., 2012, 2013; Castiglioni et al., 2006a; Gheorghe et al., 2008; González-Mariño et al., 2011; Hummel et al., 2006; Jones-Lepp et al., 2004; Kasprzyk-Hordern et al., 2009; Metcalfe et al., 2010; Pedrouzo et al., 2011a; Postigo et al., 2011; Zuccato et al., 2005). In fact, these compounds, like many other contaminants of emerging concern have been shown to be resistant to physicochemical and biological treatment at WWTPs and are therefore continuously introduced into the aquatic environment (Boleda et al., 2009; Bolong et al., 2009; Chiaia et al., 2008; Huerta-Fontela et al., 2008; Pal et al., 2013; Postigo et al., 2010; Valcárcel et al., 2012; Yargeau et al., 2013;

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http://dx.doi.org/10.1016/j.scitotenv.2013.11.023

Zuccato et al., 2008). These compounds have also been detected in surface waters in many countries (Boleda et al., 2011; Gonzalez-Marino et al., 2010; Martínez Bueno et al., 2011; Terzic et al., 2010; Valcárcel et al., 2012) and since illicit drugs have psychoactive properties, their presence in the aquatic environment raises concern (Huerta-Fontela et al., 2012). In addition, the potential for adverse effects exists due to the presence of these and other compounds as complex mixtures in the environment and multi-generational exposure of aquatic organisms (Kantiani et al., 2010). There also exists a potential for negative effects on humans since surface waters are often used as raw sources of drinking water as well as concerns in water reuse since these compounds can accumulate if they are not properly removed (Bolong et al., 2009; Halling-Sørensen et al., 1998). The above knowledge on the presence and potential impact of contaminants of emerging concern demonstrates the need to upgrade wastewater treatment plants and improve wastewater treatment technologies.

One approach to reduce the load of these compounds released in the environment is to treat contaminants of emerging concern at their major entry point which is the effluent from WWTPs (Joss et al., 2008). In order to reduce the loads of these compounds in wastewater effluent, the conventional wastewater treatment process must be improved by implementing new treatment technologies that are capable of efficiently removing these, and other, compounds of interest. Such technologies include, among others: UV disinfection, activated carbon adsorption, ion exchange, electrodialysis, membrane filtration and separation and advanced oxidation processes (AOPs). These treatment systems have been shown to efficiently remove compounds that remain in wastewater after secondary treatment, such as: pharmaceuticals, endocrine-disrupting chemicals, iodinated X-ray contrast media and musk fragrances (Huber et al., 2003; Larcher and Yargeau, 2013; McDowell et al., 2005; Nakada et al., 2007; Rodayan et al., 2010; Ternes et al., 2003; Zwiener and Frimmel, 2000). Due to the strong oxidizing power of hydroxyl radicals, AOPs such as photocatalysis, ozonation and photo-Fenton systems are of particular interest for the removal or transformation of contaminants of emerging concern (Akmehmet Balcıoğlu et al., 2003; Boleda et al., 2011; Comninellis et al., 2008; Gogate and Pandit, 2004; Nasuhoglu et al., 2012; Valcárcel et al., 2012).

Ozone ($O_3$) is a selective oxidant that is reactive towards double bonds, aromatic systems, non-protonated secondary and tertiary amines, and reduced sulfur species (Hollender et al., 2009). In addition, hydroxyl radicals that are formed by the decomposition of ozone also add to the oxidizing potential of the ozonation process (von Gunten, 2003). From an economic standpoint, Joss et al. (2008) considered the implementation of an ozonation treatment setup to be quite feasible in terms of energy and cost given that the total estimated cost of ozonation is between 0.05 and 0.20 € per $m^3$ of wastewater which does not consist a large part of the total cost of maintaining a WWTP (of course depending on the size of the plant and the level of dissolved organic carbon remaining in the treated water). Hollender et al. (2009) showed that operational costs for ozone treatment systems can be estimated based on the ozone doses determined at the laboratory scale, therefore making such experiments essential to the understanding of ozone application at WWTPs.

Ozonation of drinking water and wastewater for disinfection is well established in some parts of the world, especially Europe, but its potential to remove contaminants of emerging concern has only been investigated more recently (Rosal et al., 2010). It has already been shown that ozonation is effective at removing several micropollutants to more than 95% that are not typically removed during conventional activated sludge treatment, therefore making it a promising option to remove these compounds (Huber et al., 2005; Nakada et al., 2007; Rodayan et al., 2010; Ternes et al., 2003; Wert et al., 2009). Rosal et al. (2010) investigated the removal of the DOA codeine in wastewater during ozonation and found that a dose of <50 μM was required to decrease the concentration of the drug to below 5 $\mu g L^{-1}$ which was the limit of quantification (LOQ) of the method used. To our knowledge, no other study has investigated the potential to remove DOAs in wastewater using ozone.

An issue that arises from the application of ozonation and other oxidation techniques to treat wastewater is the potential transformation products that are produced as a result of incomplete mineralization of the organic compounds in aqueous solution and their potential toxicity (Klavarioti et al., 2009). Huerta-Fontela et al. (2012) showed that disinfection by-products are produced after chlorine oxidation of amphetamine-type compounds at a drinking water treatment plant but in most studies the fate of the parent compound is monitored and the transformation products are generally not identified nor quantified (Celiz et al., 2009). It has been shown however that degradation by-products often persist after the parent compound has been completely removed and in some cases they are more toxic to aquatic organisms than the parent compound (Dantas et al., 2007; Gomez-Ramos et al., 2011; Rosal et al., 2010). Since it is not economically feasible to implement an ozonation system to supply enough ozone for complete mineralization, before ozone is implemented at WWTPs for either disinfection purposes or for the removal (or transformation) of CECs, the potential oxidation transformation products (OTPs) must first be investigated. It must be proven that these OTPs are either nontoxic (or at least less toxic than the parent compound) or are easily degraded (Joss et al., 2008).

The objective of this work was to obtain the first removal profiles of selected drugs of abuse in pure water (reverse osmosis water) and wastewater effluent as a function of ozone dose and to investigate the presence of OTPs in the treated water using high-resolution multi-stage tandem mass spectrometry ($HRMS^n$) and differential analysis. The chemical structures of the six drugs of abuse and one human metabolite considered in this study are shown in Fig. 1 along with some physicochemical properties of the selected compounds. These DOAs were selected based on their worldwide consumption (UNODC, 2008) and detection in wastewater effluents in a previous Canadian study as well as in studies conducted in other countries (Boleda et al., 2007; Bones et al., 2007; Castiglioni et al., 2006b; Gheorghe et al., 2008; Huerta-Fontela et al., 2007; Hummel et al., 2006; Irvine et al., 2011; Kasprzyk-Hordern et al., 2009; Metcalfe et al., 2010; Pedrouzo et al., 2011a; Postigo et al., 2011; Zuccato and Castiglioni, 2009). In addition, it has been shown that COC has cyto-genotoxic effects on *Dreissena polymorpha* (zebra mussel) at environmentally relevant concentrations. To our knowledge, ecotoxicity results have not been reported for the other DOAs considered in this study.

## 2. Methodology

### 2.1. Chemicals and reagents

Analytical standards of all compounds studied and their stable isotopes are listed in Table 1. The deuterated stable isotope standards of each compound were used as surrogates to correct for extraction recoveries and, in the case of wastewater, matrix effects as well. All standards were supplied by Cerilliant (Austin, TX, USA) with purity higher than 99%. Standards of compounds and surrogates were obtained at 1 g $L^{-1}$ and 100 μg $mL^{-1}$ respectively, in methanol with the exception of cocaine which was supplied in acetonitrile at the same concentrations. All standards and working solutions were stored in amber glass bottles at −20 °C. Working solutions were allowed to thaw in the fridge prior to use but standards were used directly from the freezer since they were in pure solvent.

Ultrapure water obtained using a Milli-Q water purification system from Millipore (Bedford, MA, USA) was used to prepare working solutions and drug stock solutions. Optima liquid chromatography–mass spectrometry (LC–MS) grade methanol, acetonitrile, and water, high performance liquid chromatography (HPLC grade or equivalent) acetone as well as ACS reagent grade sulfuric acid (96%) and formic acid (88%) and trace metal grade ammonium hydroxide (88%) were purchased from Fisher Scientific (Ottawa, ON, Canada).