



Investigation of degradation products of cocaine and benzoylecgonine in the aquatic environment

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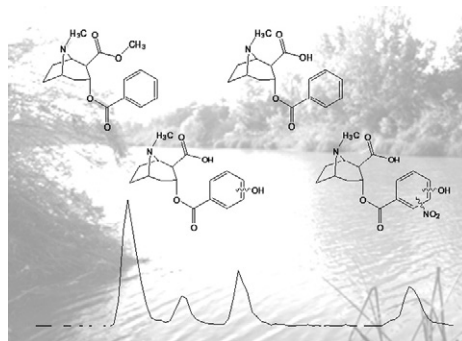
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HIGHLIGHTS

- ▶ Cocaine and benzoylecgonine degradation/transformation products investigated in water
- ▶ Hydrolysis, chlorination and photo degradation studied under laboratory conditions
- ▶ Several TPs discovered and tentatively elucidated by high resolution MS
- ▶ Structures of non-previously reported TPs have been suggested.
- ▶ Several reported/known TPs but also new TPs were found in sewage and surface water.

GRAPHICAL ABSTRACT



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ABSTRACT

In this work, ultra-high-performance liquid chromatography (UHPLC) coupled to a hybrid quadrupole time-of-flight mass spectrometer (QTOF MS) has allowed the discovery and elucidation of degradation products of cocaine and its main metabolite benzoylecgonine (BE) in water. Spiked surface water was subjected to hydrolysis, chlorination and photo-degradation (both ultraviolet irradiation and simulated sunlight). After degradation of cocaine, up to sixteen compounds were detected and tentatively identified (1 resulting from hydrolysis; 8 from chlorination; 7 from photo-degradation), three of which are well known cocaine metabolites (BE, norbenzoylecgonine and norcocaine). Regarding BE degradation, up to ten compounds were found (3 from chlorination; 7 from photo-degradation), including one known metabolite (norbenzoylecgonine). Since reference standards were available for the major metabolites, they could be confirmed using information on retention time and fragment ions. The other degradates resulted from chlorination, dealkylation, hydroxylation and nitration, or from a combination of these processes. Several influent and effluent sewage water, and surface water samples were then screened for the identified compounds (known and unknown) using UHPLC–tandem MS with triple quadrupole. BE, norcocaine and norbenzoylecgonine were identified in these samples as major metabolites. Four previously unreported degradates were also found in some of the samples under study, illustrating the usefulness and applicability of the degradation experiments performed in this work.

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1. Introduction

Cocaine use has increased during the last decade and is the illicit drug with the second-highest consumption in Europe, behind only cannabis (EMCDDA, 2010). After consumption and excretion, cocaine enters the sewage treatment plants (STPs) as the parent drug or as human

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metabolites (mainly benzoylecgonine (BE)) and may end up in the receiving surface waters as a consequence of incomplete elimination in the STPs. In most studies, if the presence of cocaine in the aquatic environment is reported, only the parent compound and a few relevant metabolites, commonly BE and cocaethylene or ecgonine methyl ester are included (Baker and Kasprzyk-Hordern, 2011). Occasionally, in monitoring studies dealing with sewage- and surface water, some minor metabolites have been found, such as norBE and norcocaine (e.g. Chiaia et al., 2008; Zuccato et al., 2008; Bijlsma et al., 2009; Bisceglia et al., 2010). Although concentrations reported in surface water are generally low (i.e. 7–60 ng/L for cocaine and 15–191 ng/L for BE (Huerta-Fontela et al., 2008; Gheorghe et al., 2008)), there is a potential negative impact of their presence in the aquatic ecosystem (Binelli et al., 2012). Especially, the effects of combined exposure to multiple compounds are of potential concern.

In order to evaluate the hazard in the water cycle, not only removal of the parent compounds and metabolites in the treatment processes must be taken into account, but also the possible formation of degradation/transformation products (TPs). In some countries (e.g. Italy), chlorination is progressively abandoned because of its potential for generating unwanted TPs and replaced by UV irradiation (Antonelli et al., 2008). Furthermore, after incomplete elimination during chlorination (Huerta-Fontela et al., 2008; Boleda et al., 2011), cocaine and BE which ended up in surface water may be exposed to natural sunlight and produce photo-degradation products. The same would occur for cocaine and BE still present in treated wastewater when no tertiary treatment is applied in the STP (e.g. Gheorghe et al., 2008; Huerta-Fontela et al., 2008; Bijlsma et al., 2009; Bisceglia et al., 2010). Despite the fact that some TPs are more persistent or might exhibit similar toxicity than their parent compounds (Farré et al., 2008; Kern et al., 2009; Fatta-Kassinos et al., 2011; Metz et al., 2011), the research on TPs of illicit drugs has received little attention. Nevertheless, investigation of TPs is of importance to know the overall contribution of chemicals in the environment. Information on potential TPs that may be present in the environment can be used to set-up monitoring studies in order to get a wider and more realistic view on the impact of cocaine on the aquatic environment.

The identification of TPs in the aquatic environment, especially unknown ones, is a challenging task for analytical chemists and commonly various techniques and/or analytical reference standards are necessary for a reliable confirmation (Wick et al., 2011). An important analytical tool in the elucidation of TPs is high resolution mass spectrometry (HRMS), with analyzers like Orbitrap and time-of-flight (TOF). The accurate mass full-spectrum acquisition and the possibility to obtain fragment ions by coupling HRMS to ion trap or quadrupole analyzers is highly suitable and helpful for the proposal of convincing molecular structures (Ibañez et al., 2004; Farré et al., 2008; Quintana et al., 2010; Metz et al., 2011).

Laboratory degradation experiments in combination with HRMS are one of the most useful tools to identify TPs that can be formed in the aquatic environment. They have been applied mainly to elucidate pesticide and pharmaceutical TPs formed in water (Ibañez et al., 2004; Hernández et al., 2008; Quintana et al., 2010; Wick et al., 2011). Treatment conditions applied by STPs, e.g. chlorination and UV irradiation, can be simulated, as well as natural sunlight. The most important TPs identified can subsequently be included in multi-residue LC tandem MS methods with triple quadrupole. This has allowed the detection of parent compounds and of their related TPs in sewage-, surface- and/or drinking water (Hernández et al., 2008; Quintana et al., 2010; Wick et al., 2011), and illustrates the importance of investigating TPs.

The use of MS^E is an attractive option, which is feasible working with hybrid QTOF MS instruments. Using this approach, information on both (de)protonated molecules and their fragment ions is acquired simultaneously in a single injection (Hernández et al., 2011). The accurate mass

measurement of the (de)protonated molecule generally allows the assignment of a highly probable molecular formula. Subsequently, fragment ions as well as neutral losses can be investigated in order to elucidate the structure of the TPs detected. Available software for the detection of metabolites and TPs is usually offered by MS manufacturers. They compare and contrast data of a presumptive positive sample with a control or blank sample. This facilitates data processing and might even detect (low abundant) compounds overlooked by visual inspection.

The objective in this paper was to perform a study on TPs of cocaine and BE that might be found in the aquatic environment. Several laboratory controlled degradation experiments (i.e. hydrolysis, chlorination, and photo-degradation under ultraviolet (UV) irradiation and simulated sunlight) have been carried out and the TPs formed investigated by LC-QTOF under MS^E mode. To the best of our knowledge, several unknown TPs reported in this study have not previously described in the literature. In a subsequent step, influent and effluent sewage water, and also surface waters, were searched for the identified TPs.

2. Materials and methods

2.1. Reagents and chemicals

Cocaine, norcocaine, BE and norbenzoylecgonine (norBE) reference standards were purchased from the National Measurement Institute (Pymble, Australia) and Cerilliant (Round Rock, TX, USA). Standard solutions of cocaine and BE were prepared at 500 mg/L in acetonitrile (ACN) and methanol (MeOH), respectively. Intermediate work solutions (50 mg/L) were made by diluting the solution ten times with MeOH.

HPLC-grade MeOH, ACN and formic acid (FA) were acquired from Scharlau (Barcelona, Spain). Sodium hypochlorite solution (available chlorine 10%) was obtained from Sigma-Aldrich. A Milli-Q ultra-pure water system from Millipore (Bedford, MA, USA) was used to obtain the HPLC grade water. Leucine enkephalin and imazalil were purchased from Sigma-Aldrich and Dr. Ehrenstorfer (Augsburg, Germany), respectively.

Solid-phase extraction (SPE) cartridges (Oasis-HLB; 3 mL, 60 mg) were purchased from Waters (Milford, MA, USA). Prior to use, the SPE cartridges were conditioned by washing and rinsing with 3 mL of MeOH and 3 mL of Milli-Q water.

2.2. Degradation experiments

Blank surface water from the Mijares River (Castellón, Spain) was collected in November 2010 and used for all laboratory controlled experiments. Surface water (pH 8.1) was selected in order to simulate reality, as it contains matrix components which may affect degradation.

Surface water used for hydrolysis, chlorination and photo-degradation experiments was spiked with cocaine or BE at a concentration of 0.5 mg/L. This relatively high concentration allowed better evaluation of degradation products, and especially facilitated the detection of minor TPs. Non-spiked surface water samples were subjected to the same degradation processes and used as control samples.

The hydrolysis and chlorination experiments were performed at room temperature and in darkness. Regarding chlorination, 40 µL of ten-fold diluted sodium hypochlorite solution was added to 50 mL of each surface water sample. During the experiment, 2 mL aliquots of the water sample were collected at several time intervals (0, 30 min, 1, 3, 10 h, 1, 3, 7, 11 and 15 days for hydrolysis; and 0, 30 min, 1 and 3 h for chlorination), after stirring of the water solutions, and were immediately stored at –20 °C until analysis.

Photo-degradation experiments were carried out under UV irradiation and simulated sunlight. UV irradiation was performed using a mercury lamp with its main output at 254 nm. 250 mL surface water samples were kept in quartz glass vessels at a distance of ~15 cm

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