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Spatial and temporal variations in the occurrence of cocaine and benzoylecgonine in waste- and surface water from Belgium and removal during wastewater treatment

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ABSTRACT

Estimates of cocaine consumption are currently resulting from population surveys, consumer interviews and crime statistics. A new approach (''sewage epidemiology'') based on the analysis of cocaine (COC) and its metabolite, benzoylecgonine (BE), in water samples was applied to 10 river sites and 30 wastewater treatment plants (WWTPs) in Belgium. Each river site was sampled twice, during the summer of 2007 and the winter of 2007–2008, while each WWTP was sampled on a Sunday and a Wednesday, during the summer–autumn of 2007 and the winter of 2007–2008. This sampling strategy allowed for the evaluation of spatial and seasonal variations in the occurrence of COC and BE in waste- and surface water. WWTP Brussel-Noord was sampled for 19 consecutive days to evaluate daily and weekly variations in the presence of COC and BE in wastewater. For 7 WWTPs, influent and effluent water samples were collected to investigate the removal of COC and BE during the wastewater treatment process. Analysis of water samples was performed using solid-phase extraction and liquid chromatography coupled to tandem mass spectrometry. Measured concentrations were further converted into an amount of used cocaine, called cocaine equivalents, as previously described in the literature. Results showed no significant difference in cocaine use between the investigated seasons. A constant cocaine consumption was observed during the week (Monday–Friday) with peaks during the weekend for WWTP Brussel-Noord. The COC/BE ratio in water samples was significantly higher during winter, most probably due to a slower hydrolysis of cocaine in low-temperature water. COC and BE were removed in the investigated WWTPs with a removal efficiency of >93%.

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1. Introduction

Illegal cocaine consumption has increased significantly since 2000 and cocaine is now the second most used illicit drug worldwide after cannabis (EMCDDA, 2007). Cocaine is snorted (intranasally), injected (intravenously) or inhaled (smoked). It enhances monoamine neurotransmitter activity in the central and peripheral nervous systems by blocking the presynaptic reuptake pumps for these neurotransmitters (dopamine, norepinephrine and serotonin) (Rothman et al., 2001; White and Kalivas, 1998). The stimulating psychological effects of cocaine are considered to be due to the enhancement of the brain dopamine activity, especially in the dopamine reward circuit of the brain. This is ultimately also responsible for its addictive properties (Dackis and O'Brien, 2001). Cocaine is unique among stimulant drugs in having a second action of blocking voltage-gated membrane sodium ion channels, which accounts for its local anaesthetic effect and may contribute to cardiac arrhythmias (Gorelick, 2008).

Estimates for prevalences and trends of cocaine use at national scale are currently obtained only from socio-epidemiological studies. Such studies use crime statistics, medical records, population surveys and consumer interviews to give estimates of the prevalence of cocaine use (EMCDDA, 2002). These indicators are general and indirect and can give only rough estimations about cocaine use, because most of the information comes from the consumers themselves (Zuccato et al., 2008a) or the population is biased (Sloboda, 2005). To obtain more precise information of cocaine use, there is a need for novel, more objective and less time consuming approaches to monitor cocaine use at local and (inter)national scale (UNODC, 2007).

Recently, a new approach based on the measurement of urinary excreted cocaine (COC) and its major metabolite, benzoylecgonine (BE), in waste- and surface water was proposed by Zuccato et al. (2005,2008a). This approach, called sewage epidemiology, has already been applied in a number of studies investigating the occurrence of cocaine and metabolites in aquatic systems (Bones et al., 2007; Chiaia et al., 2008; Frost et al., 2008; Huerta-Fontela et al., 2008a; Postigo et al., 2008; van Nuijs et al., 2009; Zuccato et al., 2005; Zuccato et al., 2008a). Together with socio-epidemiological studies, sewage epidemiology could give more precise estimates about patterns and trends in cocaine consumption.

Previously, we have validated an analytical method for the analysis of COC and metabolites in waste- and surface water (Gheorghe et al., 2008). Further, we have shown the potential of sewage epidemiology to estimate cocaine abuse at local and national scale (van Nuijs et al., 2009). In the present manuscript, we investigated the environmental fate of COC and BE in waste- and surface water and during wastewater treatment in Belgium. We investigated the effect of the temperature and pH of the water samples on the degradation of COC and BE by calculating the COC/BE ratio for each water sample. By collecting influent and effluent samples for 7 selected WWTPs, we evaluated the efficiency of the applied wastewater treatment process to remove COC and BE from wastewater. We also evaluated seasonal differences in cocaine use through collection of samples in two different seasons. By sampling the WWTP Brussel-Noord for 19 consecutive days, we evaluated daily and weekly variations in the cocaine consumption in the region of Brussels.

2. Materials and methods

2.1. Sample collection

2.1.1. Wastewater

Influent 24-h flow dependent composite wastewater samples (1.5 L) were collected from 30 wastewater treatment plants (WWTPs) in Belgium. All WWTPs serve more than 27 000 inhabitants. The composite samples were collected volume-proportional and there was taken care that no samples were collected during heavy rain or storm weather to avoid losses due to overflow. For every WWTP, a sample on Wednesday and Sunday was collected to evaluate daily variations in occurrence of COC and BE in wastewater. This sampling procedure was executed during the summer–autumn of 2007 (sampling campaign I) and was repeated during the winter of 2007–2008 (sampling campaign II) to evaluate seasonal variations in the occurrence of COC and BE in wastewater. The temperature and pH of all collected samples were recorded. For WWTP Brussel-Noord, 24-h flow dependent composite influent wastewater samples were collected on 19 consecutive days to investigate daily and weekly variations in COC and BE in wastewater. For 7 WWTPs also 24-h flow dependent composite water samples of the effluent were collected to evaluate removal efficiencies for COC and BE during wastewater treatment. All samples were collected in glass bottles, their pH was adjusted to 2 with 37% HCl and stored at −20 °C in the dark until analysis to prevent degradation of COC and BE during storage (Chiaia et al., 2008; Gheorghe et al., 2008).

2.1.2. Surface water

Grab samples (2.5 L) were collected from 10 sites on 6 rivers and brooks in Belgium. Each site was sampled during the summer of 2007 (sampling campaign I) and during the winter of 2007–2008 (sampling campaign II) to evaluate seasonal variations in occurrence of COC and BE in surface water. The temperature and pH of the samples were measured after sample collection. Sampling was performed in dry weather. All samples were collected in glass bottles, their pH was adjusted to 2 with 37% HCl and stored at −20 °C in the dark until analysis to prevent degradation of COC and BE during storage (Chiaia et al., 2008; Gheorghe et al., 2008).

2.2. Analysis of cocaine and its metabolites

The same materials and methods are used as described in Gheorghe et al. (2008) and van Nuijs et al. (2009). Briefly, water samples (influent/effluent waste- and surface water samples) were first filtered over a glass filter and afterwards brought to pH = 6 with NH_4OH. Deuterated internal standards for each compound were then added to the samples. Solid-phase extraction with Oasis HLB® cartridges was performed and the methanolic eluates were dried and