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Fate of cocaine drug biomarkers in sewer system: the role of suspended solids in biotransformation and sorption

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Biochemical processes determining the fate of micropollutants in wastewater are not limited to treatment plants (WWTPs), occurring also in sewer systems after discharge by excretion. In-sewer processes are associated mainly to the presence of biofilm attached on pipelines and suspended solids in raw sewage. Among existing micropollutants, in-sewer fate assessment is specifically relevant to illicit drugs, impacting the calculation of consumption levels in catchments according to the wastewater-based epidemiology approach (Zuccato et al., 2005). However, there is still a knowledge gap on the fate of illicit drugs in sewer systems. This study aims at assessing the role of suspended solids on the biotransformation and sorption in raw sewage of eight illicit drug biomarkers (cocaine, heroin, methadone, mephedrone, ketamine, methamphetamine, MDMA and THC and their urinary metabolites).
Separate sets of batch experiments were performed to assess biotransformation and sorption of illicit drugs under aerobic and anaerobic conditions, prevailing in sewer systems. Biotransformation experiments were started by spiking a mixture of standards in methanol to batch reactors (final concentration of 10 μg L^{-1}). Nine samples (240 ml) were taken over 48 h. Immediately after collection, samples were spiked with deuterated standards (final concentration 360 ngL^{-1}) and stored at -20°C. Control experiments were also performed using mineral water under same experimental conditions of biotransformation experiments. Sorption experiments were performed according to the same procedure and with inactivation of biomass using sodium azide (0.05% v/v). Sample preparation and analysis consisted of solid phase extraction (SPE) with Oasis HLB cartridges followed by liquid chromatography coupled to high resolution mass spectrometry. The Activated Sludge Model for Xenobiotics (ASM-X) (Plósz et al., 2013) was used to simulate biotransformation and sorption of spiked chemicals. Monte Carlo method employing Latin Hypercube Sampling (LHS) of parameter space was used to estimate first-order abiotic ($k_{abiotic}$, d^{-1}) and pseudo-first-order biotransformation rate constants (k_{bio}, L g^{-1} d^{-1}), with root mean square normalized error as objective function. Sorption coefficients (K_d) were calculated from the decrease of aqueous concentrations during experiments.
Experimental and modelling results are illustrated in Figure 1 and Table 1, which summarize experimental results and estimated parameter values for cocaine (COC) and its major metabolites benzoylecgonine (BE), ecgonine-methyl-ester (EME) and cocaethylene (CE). Our results suggest the formation of BE from COC and CE. COC transformation to CE and EME was assumed negligible (Plósz et al., 2013; Bisceglia and Lippa, 2014). A comparison of results from different experiments showed that abiotic transformation was overall prevalent under both redox conditions. Under anaerobic condition, in particular, transformation was almost completely associated to abiotic processes. Biotransformation rate constants (k_{bio}) could not be estimated and should be considered negligible. These evidences are in agreement with earlier studies illustrating that chemical hydrolysis plays a major role in the transformation of cocaine biomarkers (Bisceglia and Lippa 2014). In addition, limited sorption for EME (K_d=0.7 L g^{-1}) and BE (K_d=0.1 L g^{-1}) and no sorption for COC and CE were observed.

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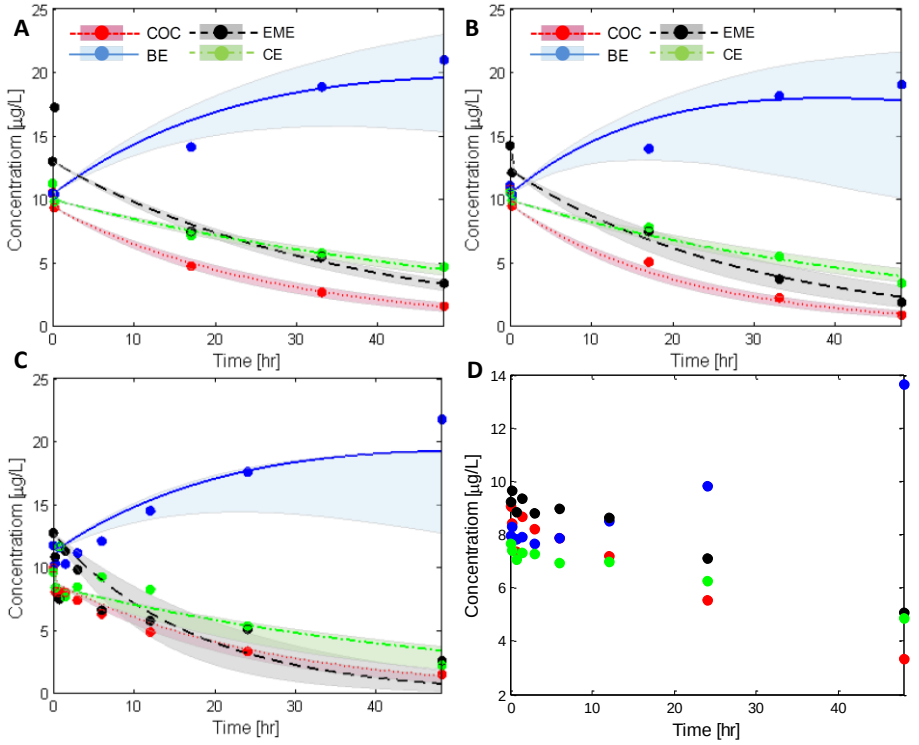

Figure 1. Concentration profiles of COC and its major urinary metabolites in different batch experiments: (A) abiotic transformation under aerobic conditions; (B) abiotic transformation under anaerobic conditions; (C) biotransformation under aerobic conditions; (D) biotransformation under anaerobic conditions. Circles are measured data and lines are simulation results. The shaded area shows standard deviation of the mean.

Table 1. Values of the abiotic and biotic transformation rate parameters estimated are shown in tables to the right (n.e. = not estimated; *=assumed; Transf. Prod.=transformation product).

	$\mathbf{k_{abiotic}}$ $(\mathbf{d^{-1}})$		$\mathbf{k_{bio}}$ $(\mathbf{L\, g^{-1} d^{-1}})$	
	Aerobic	Anaerobic	Aerobic	Anaerobic
COC → BE	1±0.09	1.27±0.1	0.08±0.3	n.e.
COC → EME	0*	0*	0*	0*
BE → Transf. Prod.	0.14±0.09	0.22±0.18	0±0.3	n.e.
EME → Transf. Prod.	0.68±0.04	0.96±0.12	2.2±1	n.e.
CE → BE	0.45±0.05	0.49±0.05	0.2±0.4	n.e.
CE → Transf. Prod.	0*	0*	0*	0*