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Distribution of antidepressant residues in wastewater and biosolids following different treatment processes by municipal wastewater treatment plants in Canada

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ABSTRACT

The fate of 14 antidepressants along with their respective *N*-desmethyl metabolites and the anticonvulsive drug carbamazepine (CBZ) was studied in 5 different sewage treatment plants (STPs) across Canada. Using two validated LC-MS/MS analytical methods, the concentrations of the different compounds were determined in raw influent, final effluent and treated biosolids samples. Out of the 15 compounds investigated, 13 were positively detected in most 24-h composite raw influent samples. Analysis showed that venlafaxine (VEN), its metabolite *O*-desmethylvenlafaxine (DVEN), citalopram (CIT), and CBZ were detected at the highest concentrations in raw influent (up to 4.3 $\mu g\ L^{-1}$ for DVEN). Cumulated results showed strong evidence that primary treatment and trickling filter/solids contact has limited capacity to remove antidepressants from sewage, while activated sludge, biological aerated filter, and biological nutrient removal processes yielded moderate results (mean removal rates: 30%). The more recalcitrant compounds to be eliminated from secondary STPs were VEN, DVEN and CBZ with mean removal rates close to 12%. Parent compounds were removed to a greater degree than their metabolites. The highest mean concentrations in treated biosolids samples were found for CIT (1033 $ng\ g^{-1}$), amitriptyline (768 $ng\ g^{-1}$), and VEN (833 $ng\ g^{-1}$). Experimental sorption coefficients (K_d) were also determined. The lowest K_d values were obtained with VEN, DVEN, and CBZ (67–490 $L\ kg^{-1}$). Sorption of these compounds on solids was assumed negligible ($\log K_d \leq 2$). However, important sorption on solids was observed for sertraline, desmethylsertraline, paroxetine and fluoxetine ($\log K_d > 4$).

1. Introduction

There is a growing concern over the presence of pharmaceutically active compounds (PhACs) in urban wastewater and the aquatic environment (Halling-Sørensen et al., 1998; Daughton and Ternes, 1999). PhACs and their metabolites enter the waste stream after disposal and excretion (Halling-Sørensen et al., 1998; DeVane, 1999) and are not efficiently removed by sewage treatment plants (STPs) where limited removal yields are often observed (Ternes, 1998; Heberer,

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2002). Among the most prescribed PhACs throughout the world are the psychiatric drugs that include the antidepressants family annually dispensed to patients (2007) at more than 22,000 kg in Canada (Calisto and Esteves, 2009; Metcalfe et al., 2010). These neuroactive compounds from the classes of selective serotonin reuptake inhibitors (SSRIs) and serotonin noradrenergic reuptake inhibitor (SNaRI) have been detected in surface waters and municipal wastewaters in North America (Kolpin et al., 2002; Vanderford et al., 2003; Schultz and Furlong, 2008; Lajeunesse et al., 2008; Metcalfe et al., 2010; Schultz et al., 2010), Europe and Asia (Lamas et al., 2004; Weigel et al., 2004; Gómez et al., 2006; Himmelsbach et al., 2006), and Scandinavia (Vasskog et al., 2006, 2008). Since the presence of antidepressants in municipal wastewaters could lead to physiological and behavioral effects on aquatic organisms (Fong, 2001; Mennigen et al., 2010; Lajeunesse et al., 2011; Lazzara et al., 2012), sensitive and reliable analytical methods are therefore needed to monitor such substances in various complex environmental matrices.

The tendency for antidepressants and their metabolites to be only partially removed by STPs contributes in part to their constant load in receiving waters and ecosystems at the high ng L^{-1} level (Rúa-Gómez and Püttmann, 2012). In addition to effluent discharges, treated biosolids are now attracting more attention from the scientific community since they are frequently used as fertilizers in agriculture (Ternes et al., 2004). Indeed, the scarcity of current data regarding the chemical constituents in treated biosolids led the US National Research Council (NRC) to produce a report in 2002. Among the NRC's recommendations was the need for investigating the occurrence of pharmaceuticals in such sewage sludge samples (Jones-Lepp and Stevens, 2007). As yet, much less scrutiny has been given to the environmental fate of pharmaceuticals adsorbed on particulate matter. To date, only a few analytical methods have been published on the extraction of PhACs in wastewater solids samples (raw sludge and treated biosolids) (Ternes et al., 2005; Göbel et al., 2005; Englert, 2007; Carballa et al., 2007; Nieto et al., 2007; Barron et al., 2008; Chenxi et al., 2008; Jelić et al., 2009; Radjenović et al., 2009; Vasskog et al., 2009; Viglino et al., 2011; Bergersen et al., 2012). These methods are mostly based on liquid chromatography or gas chromatography-tandem mass spectrometry (LC-MS/MS, GC-MS/MS) and involve sequential or single-step extraction techniques composed of pressurized liquid extraction (PLE) (Ternes et al., 2005; Nieto et al., 2007), PLE combined to solid-phase extraction (SPE) (Barron et al., 2008; Jelić et al., 2009; Radjenović et al., 2009), and liquid–liquid extraction (LLE) often accompanied with ultrasonic stages (Carballa et al., 2007; Chenxi et al., 2008). However, the majority of the available methods did not include any antidepressant groups in their lists. In fact, only one existing method allowed the extraction of 5 antidepressants (citalopram, sertraline, paroxetine, fluvoxamine, fluoxetine) along with 4 related metabolites (desmethylcitalopram, didesmethylcitalopram, desmethylsertraline, norfluoxetine) in sewage sludge using an adapted extraction method known as hollow fibre supported liquid phase microextraction (HF-LPME or LPME) (Vasskog et al., 2009). Other methods allowed the non-specific extraction of fluoxetine alone (Kinney et al., 2006), fluoxetine and paroxetine (Radjenović et al., 2009), or fluoxetine and carbamazepine (Englert, 2007) in treated biosolids.

Our previous work completed on antidepressants residues in wastewater and surface water has demonstrated the limited capability of a primary treatment process to remove and/or degrade these emerging contaminants (Lajeunesse et al., 2008). Since the fate of antidepressants in wastewater and treated biosolids remained largely unknown, the impact of conventional or advanced wastewater treatment processes also needs to be clarified.

The main goals of this study were three-fold: i) present a novel reliable analytical method for the specific analysis of 14 antidepressants along with their respective *N*-desmethyl metabolites and the antiepileptic drug carbamazepine in treated biosolids samples by LC-MS/MS, ii) estimate the fate of antidepressants in wastewaters and biosolids based on a set of concentration data compiled from a survey at 5 Canadian STPs employing different treatment modes (e.g. primary physicochemical treatment and secondary biological treatment), iii) determine experimental phase partitioning coefficients (K_d) values of antidepressants and metabolites to better assess the sorption and distribution of such active substances in sewage and biosolids.

2. Experimental

2.1. Chemicals and materials

Certified standard (>98% purity grade) fluoxetine (FLX), norfluoxetine (NFLX), paroxetine (PAR), sertraline (SER), (S)-citalopram (CIT), fluvoxamine (FLV), desmethylfluvoxamine (DFLV), mirtazapine (MIR), and desmethylmirtazepine (DMIR) were provided by Toronto Research Chemical Inc. (North York, Ontario, Canada). Desmethylsertraline (DSER), venlafaxine (VEN), O-desmethylvenlafaxine (DVEN), and bupropion-*d*9 (BUP) were obtained from Nanjing Jinglong PharmaTech (Nanjing, China). Amitriptyline (AMI), nortriptyline (NTRI), carbamazepine (CBZ), and 10,11-dihydrocarbamazepine (DHC) were purchased from Sigma–Aldrich Co. (St. Louis, Missouri, USA), while cis-tramadol^{13}C-*d*3 (TRA) was purchased from Cerilliant Corp. (Round Rock, Texas, USA). The high-performance liquid chromatography–grade solvents (methanol and acetonitrile) and ammonium hydroxide were provided by Caledon Laboratories Ltd. (Georgetown, Ontario, Canada). Reagent-grade hydrochloric acid, acetic acid, ammonium bicarbonate, and ACS grade ethyl acetate were provided by American Chemicals Ltd. (Montreal, Quebec, Canada). Solid-phase extraction (SPE) cartridges of 6 mL, 200 mg Strata™X-C were purchased from Phenomenex (Torrance, California, USA). Stock solutions of 100 mg L^{-1} of each substance were prepared in methanol and stored at 4 °C in amber glass bottles. Target antidepressants were selected due to their occurrence and ubiquity in the aquatic environment, according to the information found in literature reported, as well as their high human consumption in Canada. All corrosive and pure standard chemicals were handled carefully under a ventilated fume hood wearing appropriate protection.