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Persistence and dissipation pathways of the antidepressant sertraline in agricultural soils

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HIGHLIGHTS

- The antidepressant drug sertraline is carried in biosolids used as fertilizers.
- The persistence of this drug in agricultural soils was determined using radioisotope methods.
- The half-life ranged from about 50 to 85 days.
- Hydroxylated transformation products accumulated to less than 10% of the concentration of the added parent.

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ABSTRACT

Sertraline is a widely-used antidepressant that is one of the selective serotonin reuptake inhibitors. It has been detected in biosolids and effluents from sewage treatment plants. Since sertraline can reach agriculture land through the application of municipal biosolids or reclaimed water, the persistence and dissipation pathways of ^{3}H-sertraline were determined in laboratory incubations using three agriculture soils varying in textures and properties. The total solvent extractable radioactivity decreased in all three soils with times to dissipate 50% of material (DT_{50}) ranging from 48.1 ± 3.5 (loam soil) to 84.5 ± 13.8 (clay soil) days. Two hydroxylated sertraline transformation products were identified in all three soils by high performance liquid chromatography with time-of-flight mass spectrometry (HPLC–TOF-MS), but the accumulation did not exceed 10% of the initial parent concentration. The addition of liquid municipal biosolids to the loam soil had no effect on the rate of sertraline dissipation, or production of transformation products. In summary, sertraline was persistent in agricultural soils with major dissipation pathways including the production of non-extractable soil-bound residues, and accumulation of hydroxylated transformation products. The biologically active sertraline transformation product norsertraline was not detected in soil.

1. Introduction

Emerging pollutants including pharmaceuticals, personal care products and endocrine disrupting substance are now widely detected in aquatic and terrestrial environments, and the potential environmental and public health impact of these chemicals is of some scientific and regulatory concern (Li et al., 2010; Monteiro and Boxall, 2010; Kümmerer, 2009; Kleywegt et al., 2007; Fent et al., 2006; Kolpin et al., 2002). Sources of environmental exposure to these chemicals include sewage treatment plant effluents, leakage from land fertilized with biosolids or irrigated with reclaimed municipal wastewater, and landfill leachate (Topp et al., 2010; Eggen et al., 2010; Chefetz et al., 2008; Metcalfe et al., 2010; Kinney et al., 2006).

Municipal biosolids have been widely used in agriculture as a source of crop nutrients and organic matter for soil improvement (O'Connor et al., 2005). In a series of field experiments, we have been characterizing the movement of micropollutants from biosolids-fertilized land that are transported in effluents via surface runoff or tile drainage (Edwards et al., 2009; Sabourin et al., 2009; Topp et al., 2008). In more recent work we have evaluated the uptake of micropollutants into various vegetable crops grown in land fertilized with biosolids (Sabourin et al., 2012). The biosolids used in these experiments contained 497 ng sertraline g dry weight^{-1}, but no sertraline residues were detected in crop tissues (Sabourin et al., 2012). Sertraline is expected to readily adsorb to organic matter during sewage treatment (Styrishave et al., 2011). A survey of anaerobically-treated biosolids from five different Canadian sewage treatment plants detected sertraline at concentrations ranging from 203 to 528 ng g dry weight^{-1} (Lajeunesse et al., 2012). Sertraline ((1S,4S)-4-(3,4-dichlorophenyl)-1,2,3,4-tetrahydro-*N*-methyl-1-naphthalenamine hydrochloride; Fig. 1) is a potent second generation selective serotonin reuptake inhibitor with antidepressant properties. In

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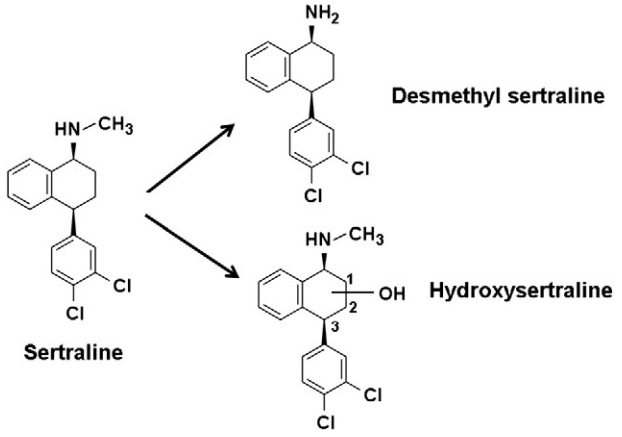

Fig. 1. Structures of the antidepressant sertraline, and potential transformation products. The radiolabelled parent was *N*-methyl tritiated.

addition to its use for the treatment of depression, sertraline is also used to treat panic disorders, social phobia, obesity, and obsessive–compulsive disorders (DeVane et al., 2002; MacQueen et al., 2001; Warrington, 1992). Sertraline acts by modulating the levels of the neurotransmitter serotonin (DeVane et al., 2002; MacQueen et al., 2001; Warrington, 1992). Approximately 5000 kg of the drug is used annually in Canada (McLaughlin and Belknap, 2008).

A number of antidepressants have been identified in water and in tissues of aquatic organisms (Calisto and Esteves, 2009). Sertraline has been detected at ng L^{-1} concentrations in surface water and in wastewater effluent (Metcalfe et al., 2010; Schultz et al., 2010; Lajeunesse and Gagnon, 2008; Vasskog et al., 2008). Brooks et al. (2005) found sertraline concentrations in the range of 0.15–8 ng g^{-1} in muscle, liver and brain tissues of four fish species in a municipal effluent-dominated stream in Texas, USA. Sertraline persisted in an outdoor microcosm study in Guelph, Ontario Canada with a half-life of 6.3 ± 0.2 days (Lam et al., 2004). Given the very large volume of sertraline used, its widespread detection in surface water, detection in biosolids and their use in agriculture, the objective of the present study was to elucidate the persistence characteristics and dissipation pathways of sertraline in agricultural soils. Furthermore, given that micropollutants will reach agricultural land through the application of biosolids, the effect of this material on soil dissipation was examined. To our knowledge this is the first study of the persistence of sertraline in agricultural soil.

2. Material and methods

Sertraline-[*N*-methyl-^{3}H] hydrochloride (radioactive purity >99%; specific activity 80 Ci $mmol^{-1}$) was purchased from American Radiolabeled Chemicals, Inc. (St. Louis, MO). Sertraline hydrochloride (purity >98%) was purchased from AK Scientific Inc. (Union City, CA). Desmethylsertraline (norsertraline) hydrochloride (purity >98%) was purchased from SynFine Research, Inc. (Richmond Hill, ON). Structures of sertraline and derivatives are presented in Fig. 1. HPLC grade acetonitrile, ethanol and methanol were purchased from Caledon Laboratories Ltd. (Georgetown, ON). All other chemicals were obtained from Sigma-Aldrich, Canada (Mississauga, ON). Stock solutions of ^{3}H-labeled (final radioactive concentration of 1500 k dpm 100 μL^{-1}) and unlabeled (1 mg mL^{-1}) chemicals were prepared in ethanol and stored at −20 °C until used.

Three agriculture soils (sampling depths 0–20 cm) that varied in texture and chemical properties were used in this study; a loam obtained from the Agriculture and Agri-Food Canada (AAFC) research farm at London, Ontario (42°59′N, 81° 15′W), a sandy loam soil obtained from the AAFC research farm at Delhi, Ontario (42°51′N, 80°29′W), and a clay loam soil obtained from the Essex Region Conservation Authority research farm in Holiday Beach, Ontario (42°2′N, 83°3′W). Key properties of these soils have been described in Al-Rajab et al. (2010). All soils were obtained from areas that were under sod and had never received biosolids. Soils were sieved to a maximum particle size of 2 mm and were stored at −7 °C prior to experimentation.

The liquid municipal biosolids (LMB) used in the present study were obtained from the Adelaide pollution control plant in London, Ontario. They were returned activated sludge from secondary treatment and had been aerobically digested. The LMB used had the following key characteristics: pH 7.0; dry matter content 0.5%; organic matter content 0.4%; carbon to nitrogen ratio 6:1.

2.1. Laboratory incubations

Fifty-gram portions of soils were incubated in laboratory microcosms as described in Al-Rajab et al. (2010) and Li et al. (2013). Briefly, microcosms consisted of 150 mL baby-food jars incubated in sealable glass 1 L Mason jars. A scintillation vial containing 10 mL of water was placed in each jar to maintain soil moisture and prevent desiccation of the soil. Soils were supplemented with ^{3}H-labeled and unlabeled sertraline by adding stock solutions in ethanol to 1-g aliquots of pulverized air-dried soil, allowing the solvent to evaporate and thoroughly mixing this into 49 g (moist weight) of soil to give a total of 50 g. Soils received 1 μg sertraline g^{-1} and 30 k dpm g^{-1} moist soil and soil moisture were normalized to 15% in all treatments. Triplicate microcosms were prepared for each treatment and these microcosms were incubated in darkness at 30 °C, unless otherwise indicated. The effects of LMB (10% V/V) on drug dissipation were evaluated only in the loam soil.

In preliminary experiments the efficiency of various solvent mixtures (acetonitrile + 2% NH_4OH; hexane/ethyl acetate/NH_4OH (90:8:2); hexane/isopropranol/NH_4OH (94:4:2)) for extraction of ^{3}H-sertraline from soils (loam, sandy loam, clay loam) was determined. Since sertraline is basic (p*K*a 9.47) (Kosjek and Heath, 2010), NH_4OH was added to the organic solvent to improve the extraction efficiency. Acetonitrile with 2% NH_4OH was considered to be satisfactory for the extraction of sertraline from the three soils. Using the methods described below the recovery of sertraline (triplicate incubations) from the sandy loam soil was 66.8 ± 1.5%, from the loam soil, 69.5 ± 3.1% and from the clay soil 67.5 ± 1.3%.

Four-gram portions of soil were removed periodically from each microcosm with a spatula and stored at −20 °C until extraction. Soils were extracted three times with 15 mL of organic solvent each time. For each extraction, samples were vigorously shaken for 20 min on a wrist-action shaker (Burrell Corporation, Pittsburgh, PA). The samples were then centrifuged for 15 min at 3000 rpm in an HL-4 swinging bucket rotor in a Sorvall GLC-1 centrifuge (Fisher Scientific, Ottawa, ON). The supernatants were transferred to a clean glass vial, reduced to dryness under nitrogen in a 35 °C water bath, reconstituted in 200 μL of acetonitrile–water mixture (1:1, v/v) and stored at −20 °C until analyzed. In order to determine what portion of sertraline had been mineralized, some extracts were counted before and after drying. It was assumed that any difference in radioactivity was due to evaporative loss of ^3H_2O due to mineralization of the N-C^3H_3.

2.2. Analytical methods

Radioactivity in soil extracts was determined by liquid scintillation counting (LSC) using a Beckman Coulter Model LS 6500 instrument (Irvine, CA). Each sample was added to 10 mL UniverSol scintillation cocktail (ICN Biomedicals, Inc., Costa Mesa, CA) in plastic scintillation vials. Data were corrected automatically for quenching.

^{3}H-Sertraline and potential radioactive transformation products in 50 μL portions of soil extracts were analyzed by high performance liquid chromatography (HPLC), consisting of an Agilent 1260 Infinity