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Interactions of triclosan, gemfibrozil and galaxolide with biosolid-amended soils: Effects of the level and nature of soil organic matter

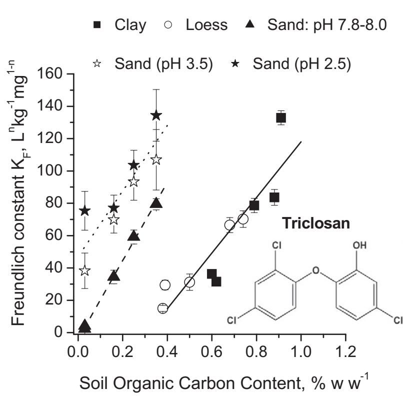
Alla Usyskin [a,b], Nadezhda Bukhanovsky [b], Mikhail Borisover [b,*]

[a] Robert H. Smith Faculty of Agriculture, Food and Environment, The Hebrew University of Jerusalem, Rehovot 76100, Israel
[b] Institute of Soil, Water and Environmental Sciences, Agricultural Research Organization, The Volcani Center, Bet Dagan 50250, Israel

HIGHLIGHTS

- 45 sorption isotherms of three PPCPs were studied on various soil–biosolid mixtures.
- Soil organic matter (SOM) in sand-based sorbents shows an enhanced sorptivity.
- A "critical" SOM content may be needed to promote organic compound–soil interactions.
- Molecular and anionic triclosan species may be comparable in their sorptive affinity.
- Enhanced soil sorption will reduce the pollutant release from biosolid-amended soils.

GRAPHICAL ABSTRACT



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ABSTRACT

Triclosan, gemfibrozil and galaxolide, representing acidic and non-ionized hydrophobic organic compounds, are biologically active and can be accumulated during wastewater treatment in sewage sludge. The interactions of these substances with the soils amended by sewage sludge-originating biosolids may control their environmental fate. Therefore, the sorption of three organic compounds was studied in dune sand, loess soil, clay soil and mixtures of these media with three different sewage sludge-originating biosolids that were incubated under aerobic conditions for 6 months. For each compound, 15 sorption isotherms were produced at pH 7.8–8.0. The sorption of triclosan and gemfibrozil on sand-containing sorbents was examined also under acidic conditions. In some soil series, the compound's Freundlich constants (K_F) are linearly related to the soil organic carbon (OC) content. Notably, for a given OC content, the sand-containing sorbents tend to demonstrate enhanced interactions with triclosan and galaxolide. This may be related with more hydrophobic and/or less rigid soil organic matter (SOM) as compared with the clay-containing soils, implying indirect effects of minerals. Generally the OC-normalized K_F vary among different soil–biosolid combinations which is explained by the differences in the composition and properties of SOM, and is also contributed by the non-zero intercepts of the linear K_F upon soil OC dependencies. The negative intercepts suggest that below a certain OC level no considerable organic compound–soil interactions would occur. Interactions of molecular and anionic forms of triclosan with a

* Corresponding author at: Institute of Soil, Water and Environmental Sciences, Agricultural Research Organization, The Volcani Center, P.O. Box 6, Bet Dagan 50250, Israel.
E-mail addresses: alla.usyskin@mail.huji.ac.il (A. Usyskin), nadia@volcani.agri.gov.il (N. Bukhanovsky), vwmichel@volcani.agri.gov.il (M. Borisover).

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sand-containing sorbent may be comparable, but interactions involving gemfibrozil molecules could be stronger than interactions involving its anion.

1. Introduction

Pharmaceuticals and personal care products (PPCPs) form a large group of organic pollutants and include chemical compounds of various classes (EPA US, 2010). In the course of wastewater treatment, PPCP compounds and the products of their transformations may accumulate in sewage sludge (Heidler et al., 2006; McClellan and Halden, 2010). Therefore, the land application of biosolids from sewage sludge may contribute to the presence of PPCP contaminants in soils and their further transport to groundwater and surface water (Gottschall et al., 2012; McClellan and Halden, 2010). Since the environmental fate of organic compounds is strongly influenced by sorption interactions at soil–water interfaces, the factors and mechanisms controlling the soil sorption of PPCPs are of great interest.

This study is focused on three representatives of the PPCP family: galaxolide (a synthetic polycyclic musk), triclosan (an antibacterial and antifungal agent) and gemfibrozil (a lipid-regulating agent). These organic compounds were selected for the following reasons. First, all three compounds are found at environmentally significant concentrations in sewage sludge from wastewater treatment plants (WWTP; Stevens et al., 2003; Stevens-Garmon et al., 2011; Hyland et al., 2012). Second, the selected PPCPs demonstrate variable biological effects, such as phytotoxicity (D'Abrosca et al., 2008; An et al., 2009) and toxicity to aquatic microorganisms (Orvos et al., 2002; El-Bassat et al., 2012). They accumulate in edible parts of plants (Macherius et al., 2012; Pannu et al., 2012), soil organisms (Kinney et al., 2008) and aquatic biota (Bester, 2004; Coogan et al., 2007; Ramirez et al., 2007). Gemfibrozil may also cause endocrine disruption in fish (Mimeault et al., 2005). Importantly, widespread use of triclosan is thought to lead to the development of microbial resistance to antibiotics (McNamara et al., 2014; Pycke et al., 2014). Third, the three PPCPs selected all include hydrophobic moieties, but differ dramatically in their ability to undergo ionization in aqueous solutions; thus they represent both non-ionized (galaxolide) and variously ionized (gemfibrozil and triclosan) PPCPs. Both of these factors (i.e., the presence of a hydrophobic backbone and the ability to ionize in aqueous solutions) are of importance if we want to better understand the mechanisms controlling organic compound–soil interactions.

In general, the studies examining sorption of PPCPs on soils amended with sewage sludge-originating biosolids have been relatively limited (Barron et al., 2009) and, in particular, more work is needed to be done under basic soil pH conditions, which are relevant for multiple environmental scenarios, for example, when soils contain natural or added calcium carbonate. Specifically, little work was done on sorption of galaxolide and gemfibrozil by soils that have been amended with sewage sludge-borne biosolids. Wu et al. (2009) studied interactions between triclosan and biosolid-amended soils at acidic pH. Agyin-Birikorang et al. (2010) examined triclosan interactions in a series of soils, biosolids and biosolid-amended soils (but apparently no sufficient details on solution pH range and variability were reported). Also, the studies are needed to determine the sorption of triclosan on soils amended with the sewage sludge-based compost, which is actually used in agricultural systems. Hence, the objective of this work was to examine the sorption of selected PPCPs on native and biosolid-amended and incubated agricultural soils.

2. Material and methods

2.1. Chemicals

Triclosan (5-chloro-2-[2,4-dichlorophenoxy]-phenol, >97% – the HPLC-grade) was purchased from BioChemika (Sigma, Germany). Gemfibrozil (5-[2,5-dimethylphenoxy]-2,2-dimethyl-pentanoic acid, ⩾99%) was obtained from Sigma (Italy). Galaxolide (1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethylcyclopenta-gamma-2-benzo pyran, 99.6%) was obtained from Agan Chemical Manufacturers, Ltd. (Ashdod, Israel). Chemical structures and selected physico-chemical properties of these three organic compounds are presented in Table S1 (The Supplementary Data). Specifically, triclosan and gemfibrozil are characterized by pK_a values such as 7.9 and 4.7, respectively (Toxnet, 2009) whereas galaxolide is not ionized in aqueous solutions. The $\log K_{ow}$ (i.e., log octanol–water partitioning coefficients; $L\,L^{-1}$) of triclosan, gemfibrozil and galaxolide are as following: 4.76, 4.77 (Toxnet, 2009) and 5.90 (Balk and Ford, 1999).

Sodium azide (99%), calcium chloride dihydrate (99%) and acetonitrile (gradient grade for liquid chromatography, >99.9%) were purchased from Merck (Darmstadt, Germany). The hydrochloric acid (AR, 36.46%) used for adjusting pH and water (ULC/MS purity) were purchased from Bio-Lab, Ltd. (Jerusalem, Israel).

2.2. Soils and biosolids

Two representative cultivated soils were obtained from regions where sewage sludge-based amendments are in use or may be applied in the future (i.e., the clay soil from Kibbutz Revadim and loess (sandy clay loam) from the Oz Stream, located in southwest Israel). The dune sand representing a natural clay-poor (and relatively "inert") medium was obtained from the Ashkelon–Palmahim seashore. The clay, silt, sand, moisture, organic carbon (OC), total nitrogen (TN) and calcium carbonate contents of the soils; their cation exchange capacities, exchangeable sodium and potassium percentages and the pH levels of aqueous soil extracts are presented in Table S2 (The Supplementary Data). The soil samples were air-dried, passed through a 2.0-mm sieve and stored at room temperature (~25 °C) for further experiments.

Three types of sewage sludge-originating biosolids were used: (1) anaerobically digested Class B sludge (SB) from WWTP in Herzliya (Israel), (2) a secondary aerated Class A sewage sludge (SA) from WWTP Shafdan, and (3) sewage sludge compost (SC, from mixed organic sources) obtained from the Dalila site (the Dalila Materials Recycling Agriculture Cooperative Society, Kibbutz Nahshon). Immediately after sampling, the organic biosolids were frozen and stored at −18 °C. The OC and TN contents of organic amendments are presented in Table S3 (The Supplementary Data).

2.3. Soil–biosolid incubation procedure

Based on three soils and three biosolids, nine soil–biosolid combinations were incubated and used for the further sorption experiments. For the incubation study, a 50-g soil portion was mixed with a portion of a biosolid (i.e., 0.59, 0.74 and 1.27 g of SA, SB and SC, respectively) such that the biosolid to soil ratio was equivalent to the land application rate of 1.5 Mg of N ha^{-1}. This is higher than the application rate recommended by Israeli regulations,