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Impact of sludge treatments on the extractability and fate of acetyl sulfamethoxazole residues in amended soils

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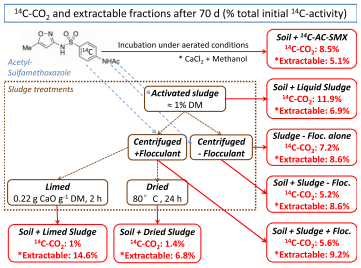
HIGHLIGHTS

- The fate of AC-SMX brought with different treated sludges was investigated in soil.
- The extractability of AC-SMX residues decreased most in the first 14 days.
- Water-extractability of AC-SMX residues in soil was the highest for limed sludge.
- Liming and drying sludge decreased the mineralization of AC-SMX residues in soils.
- The mineralization rates of ^{14}C-AC-SMX residues and sludge organic C were correlated.

GRAPHICAL ABSTRACT



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ABSTRACT

Sludge recycled in agriculture may bring antibiotics into cropped soils. The nature, total amount, and availability of the antibiotics in soil partly depend on the sludge treatments. Our paper compares the fate of N-acetyl sulfamethoxazole (AC-SMX) residues between soils incubated with the same sludge but submitted to different processes before being added in soil.

The fate of ^{14}C-AC-SMX residues was studied in mixtures of soil and sludges at different treatment levels: 1) activated and 2) centrifuged sludges, both enriched with ^{14}C-AC-SMX, and 3) limed and 4) heat-dried sludges obtained by treating the previously contaminated centrifuged sludge. The evolution of the extractability of ^{14}C residues ($CaCl_2$, methanol) and their mineralization were followed during 119 days.

More than 80% of the initial ^{14}C-activity was no longer extractable after 14 days, except in soil with limed sludge. Liming and drying the centrifuged sludge decreased the mineralized ^{14}C fraction from 5.7-6.4% to 1.2–1.8% and consequently, the corresponding soils contained more ^{14}C residues after 119 days. Although ^{14}C residues were more $CaCl_2$-extractable in soil with limed sludge, they seemed to be poorly bioavailable for biodegradation. For all solid sludges, the mineralization rate of ^{14}C-AC-SMX residues was strongly correlated to that of sludge organic carbon, with a coefficient three times lower for the limed and dried sludges than for the centrifuged sludge after 14 days.

1. Introduction

The recycling of sewage sludge in agriculture is conditioned by both its agronomic value as a fertilizer and/or an amendment and

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its innocuousness as sludge may contain different types of potentially transferable contaminants (Alvarenga et al., 2015). The periodic introduction in soil of small amounts of potentially bioactive contaminants, such as antibiotics (Du and Liu, 2012), could increase the abundance of some antibiotic-resistance genes in soil (Bondarczuk et al., 2016; Chen et al., 2016) and, depending on the antibiotic concentration, change the diversity of soil microbial communities to some extent (Liu et al., 2012; Cleary et al., 2016).

Different families of antibiotics and their derivatives can be quantified in sludge (Verlicchi and Zambello, 2015). Their total content mainly relies on the amounts prescribed to humans (Van Boeckel et al., 2014), their metabolization and excretion rates by organisms (Jjemba, 2006), and the effectiveness of their removal and/or transformation by wastewater (Tuc et al., 2017) and sludge treatments (Verlicchi and Zambello, 2015). As an example, the concentrations of sulfamethoxazole, a bacteriostatic antibiotic representative of the sulfonamides, can vary between 1 and 178 μg kg^{-1} sludge dry mass (DM) (Nieto et al., 2010). There are very few data for N-acetyl sulfamethoxazole (e.g., <1.5 μg kg^{-1} DM in the sludge of a membrane bioreactor; Le-Minh et al., 2012). This human metabolite of sulfamethoxazole is present in the liquid phase of sewage, and it may be transformed back to sulfamethoxazole during water treatments (Göbel et al., 2005). The sludge treatments, like liming and thermal drying, may also influence the availability of N-acetyl sulfamethoxazole and its derivatives inside the sludge prior to spreading in fields (Geng et al., 2016).

Following sludge incorporation into the soil, sulfamethoxazole is not always detected in soil (Walters et al., 2010); its total content should be in the range of 0.01–1 μg kg^{-1} soil DM, considering also soils amended with manure (Hu et al., 2010) and compost of sludge and green waste (Ferhi et al., 2016). There is little information for its metabolites. However, the risk assessment should account for both the parent pharmaceuticals and their metabolites that can persist in the environment (Celiz et al., 2009). Although the acetylated form, N-acetyl sulfamethoxazole, is inactive, it can be transformed back to sulfamethoxazole as mentioned before.

Sulfamethoxazole applied with biosolids was rapidly dissipated in non-sterile soil under aerobic conditions with a 2-day half-life (Liu et al., 2010). Sulfamethoxazole and N-acetyl sulfamethoxazole were found to be poorly adsorbed on a soil amended with manure; after 102 days, only 0.3% of the sulfamethoxazole was mineralized compared to 11% of the N-acetyl sulfamethoxazole in soil amended with contaminated sludge (*vs* 2 and 3% in soil alone; Höltge and Kreuzig, 2007). Additionally, non-extractable residues were rapidly formed after 7 days (>45% in the soil alone and >75% in the presence of sludge). Less than 5% of the non-extractable residues of sulfonamide antibiotics were remobilized in the soil when the antibiotics were initially added in liquid manure, and less than 1% were transferred either to the plant or to earthworms (Heise et al., 2006). The uptake by plants of sulfamethoxazole (e.g., Herklotz et al., 2010; Chitescu et al., 2013) has often been reported in fertilized soils or under hydroponic conditions at relatively high concentrations, where some phytotoxic effects were observed with possible detoxification pathways.

Consequently, the (bio)availability and the fate of sulfonamides in the soil appears to depend on the way by which the antibiotics are introduced into the soil (e.g., alone in water, with liquid manure/sludge, etc.). The sludge treatments may influence the fate of pharmaceuticals in soil after spreading (Lachassagne et al., 2015; Verlicchi and Zambello, 2015), and the possibility to direct treatments towards limited environmental and ecotoxicological risks is at stake. There is still limited knowledge for antibiotics, e.g., sulfonamides, about the link between the availability of the compounds in treated sludge and their availability and fate in the soil. This topic is additionally challenging due to the low concentrations expected.

The objectives of this work were to study the impacts of the chemical and physical processes of sludge treatments on the fate and extractability of the residues of N-acetyl sulfamethoxazole once the sludge is incorporated into the soil. This paper follows our previous work (Geng et al., 2016) that focused on the fate of ^{14}C-labelled N-acetyl sulfamethoxazole after different sludge treatments: centrifugation, liming and heat-drying. Different sludges produced from Geng et al. (2016) and containing the ^{14}C-labelled N-acetyl sulfamethoxazole were added to soil for incubation in microcosms under controlled aerated conditions. The proportions of easily and less extractable ^{14}C-labelled N-acetyl sulfamethoxazole residues were characterized at specific dates until day 119, while their mineralization and the mineralization of sludge organic carbon were followed over the entire period.

2. Materials and methods

2.1. Chemicals and reagents

[ring-^{14}C] N_4-acetyl sulfamethoxazole (AC-SMX; specific activity: 2849 MBq $mmol^{-1}$, purity: 99.0%) was purchased from American Radiolabeled Chemicals, Inc. (Saint Louis, MO, USA). A stock solution (820.9 kBq mL^{-1}), stored at 4 °C, was prepared from the initial solution in ethanol by dilution in Milli-Q water (18.2 MΩ; Millipore, Molsheim, France).

Sodium hydroxide (NaOH, 32%) and methanol (MeOH, 99%) were purchased from CarloErba (Val de Reuil, France); calcium oxide (CaO, 99.9%) and chloride ($CaCl_2$, 98.0%) from Sigma Aldrich (Saint-Quentin-Fallavier, France) and Prolabo (Paris, France). The flocculant solution (50% of active compound) used for sludge centrifugation was provided free of charge by the manager of the wastewater treatment plant (WWTP) (section 2.3).

2.2. Soil

The horizon 0–28 cm of a Luvisol soil (Feucherolles, Parisian Basin, France), cultivated with either maize or wheat, and receiving a compost of green waste and sludge in September every two years since 1998, was sampled in March 2013. It was dried at ambient temperature to reach 0.115 g water g^{-1} DM, sieved to 4 mm, and then stored at 4 °C. Its main characteristics were (pH unit or g kg^{-1} DM): pH_{water}, 6.9; clay, 152; silt, 787; sand, 62; organic C (ISO 10694 standard), 15.6; total N (ISO 13878 standard), 1.47; and P_2O_5 (Olsen method), 0.18. Sulfamethoxazole has been sometimes detected but not quantified either before the compost application or a few weeks after (<1 μg kg^{-1} soil DM; Ferhi et al., 2016).

2.3. Sludge and sludge treatments

The sludges were all produced from the same activated sludge, sludge 1 (pH, 6.7; dry matter, 5 ± 0.03 g DM L^{-1} (n = 6)), sampled in April 2013 at a domestic WWTP (45,000 equivalent inhabitants; Villepreux, France). Between mid-October and mid-December 2012, sulfamethoxazole was quantified both in the liquid and solid phases of sludge 1 with concentrations respectively at 0.18–0.42 μg L^{-1} and 131–172 μg kg^{-1} DM.

The sludge treatments performed in this WWTP, i.e. centrifugation and liming, and also thermal drying were reproduced at a laboratory scale. We considered realistic treatment conditions and looked for contrasted availability levels of ^{14}C-labelled residues (Geng et al., 2016). The sludge 1 was first centrifuged in the presence/absence of the flocculant at the WWTP dose to obtain the sludges 2A/2B (Fig. 1). Then 0.6 mL and 0.4 mL of the ^{14}C-AC-SMX