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Assessing the fate of antibiotic contaminants in metal contaminated soils four years after cessation of long-term waste water irrigation

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ABSTRACT

Spreading of urban wastewater on agricultural land may lead to concomitant input of organic and inorganic pollutants. Such multiple pollution sites offer unique opportunities to study the fate of both heavy metals and pharmaceuticals. We examined the occurrence and fate of selected antibiotics in sandy-textured soils, sampled four years after cessation of 100 years irrigation with urban wastewater from the Paris agglomeration. Previous studies on heavy metal contamination of these soils guided our sampling strategy. Six antibiotics were studied, including quinolones, with a strong affinity for organic and mineral soil components, and sulfonamides, a group of more mobile molecules. Bulk samples were collected from surface horizons in different irrigation fields, but also in subsurface horizons in two selected profiles. In surface horizons, three quinolones (oxolinic acid, nalidixic acid, and flumequine) were present in eight samples out of nine. Their contents varied spatially, but were well-correlated one to another. Their distributions showed great similarities regarding spatial distribution of total organic carbon and heavy metal contents, consistent with a common origin by wastewater irrigation. Highest concentrations were observed for sampling sites close to irrigation water outlets, reaching 22 μg kg^{-1} for nalidixic acid. Within soil profiles, the two antibiotic groups demonstrated an opposite behavior: quinolones, found only in surface horizons; sulfamethoxazole, detected in clay-rich subsurface horizons, concomitant with Zn accumulation. Such distribution patterns are consistent with chemical adsorption properties of the two antibiotic groups: immobilization of quinolones in the surface horizons ascribed to strong affinity for organic matter (OM), migration of sulfamethoxazole due to a lower affinity for OM and its interception and retention in electronegative charged clay-rich horizons. Our work suggests that antibiotics may represent a durable contamination of soils, and risks for groundwater contamination, depending on the physicochemical characteristics both of the organic molecules and of soil constituents.

1. Introduction

The elimination of antibiotics present in wastewater by sewage treatments is often incomplete. Low removal rates after wastewater treatments were reported for some compounds such as sulfamethoxazole, trimethoprim or some macrolides, ascribed to their low degradation and potential sorption on soil constituents (McArdell et al. 2003; Paxeus 2004; Lindberg et al. 2005). The discharge of treated wastewater into surface waters was recognized as a major source of antibiotics contamination (Miao et al. 2004; Siemens et al. 2008) and, consequently, cautious management of urban wastewater is essential.

Spreading of urban wastewater on soil surfaces is widely considered as an alternative way to decrease such an organic contamination discharged by wastewater (Ternes et al. 2007). The purpose of such a proceeding is to complete in a natural way the purification of wastewater by using the specific filtering and purifying characteristics of coarse textured soils, before their recharge to the groundwater. Such land management, however, may lead to a diffuse organic or inorganic contamination of soils depending on the quality of wastewater. Frequently, mineral contamination relates to the introduction and accumulation of heavy metals in soils. Although organic contaminants generally are more degradable, the fate of their long-term input in soils is not well known. Yet, such active compounds are designed to act upon soil microorganisms at low concentrations and, therefore, represent serious environmental risk (Westergaard et al. 2001; Schauss et al. 2009). Furthermore, heavy metals and antibiotic are suspected to act together in bacterial

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resistance selection or maintaining (Baker-Austin et al. 2006; Matyar et al. 2008), and many questions remain about long-term impacts on living organism by sub-inhibitory exposure in real field situations of multi organic and inorganic soil contamination.

Such concern is particularly important for antibiotics exhibiting high adsorbing properties, and for which accumulation in soil on the surface of either mineral or organic soil constituents has been assessed (Chang et al. 2009; Zhang et al. 2009). On the other hand, migration to deeper horizons of more mobile compounds represents additional risk regarding contamination of groundwater resources (Kinney et al. 2006; Ternes et al. 2007; Heberer et al. 2008; Siemens et al. 2010).

Moreover, some antibiotic compounds were shown to display relatively long half-lives, reaching several months in soils (Marengo et al. 1997), while others undergo a rapid biodegradation occurring within a few days (Burkhardt and Stamm 2007; Kotzerke et al. 2008). The sorption of antibiotics on soil constituents was shown to play a significant role in such persistence, related to a reduced biodegradability (Ingerslev and Halling-Sørensen 2001). It has been shown that the fate and impact of such compounds depend to a large extent on the nature of the molecules (Kinney et al. 2006; Ternes et al. 2007; Carrasquillo et al. 2008; Siemens et al. 2010) and on the nature and characteristics of the main soil constituents (Vasudevan et al. 2009; Zhang et al. 2009). However, in situ research on the distribution and accumulation of antibiotics at the field scale remains scarce, thus restricting sustainable land management regarding past or future spreading of wastewater.

Therefore, in this work we aimed at 1) investigating antibiotic contamination in agricultural soils irrigated for more than 100 years with untreated urban wastewater of the Paris area, previously studied for consequent heavy metal contamination; 2) assessing in situ the importance of the nature of the antibiotic molecules on their fate in soil profiles and 3) comparing the in situ fate of non-biodegradable trace elements to that of a priori biodegradable antibiotic molecules. We focused on two antibiotic groups exhibiting contrasting properties: i) the quinolones, known for their strong adsorption properties on soil constituents, and ii) the sulfonamides, with more mobile characteristics. Since metals and antibiotics were mentioned to be detected together (Lee et al. 2009; Oyetibo et al. 2010), we hypothesized that some inorganic and organic pollutants added to soils by wastewater irrigation might display similar distribution patterns, according to their physicochemical characteristics. Our sampling strategy of surface and subsurface horizons was based on previous field survey on heavy metal contamination (Lamy et al. 2006; Bourennane et al. 2006).

2. Materials and methods

2.1. Site presentation

The study site (Fig. 1) is located ≈65 km downstream of the center of Paris and approximately 6 km from the Seine Aval wastewater treatment plant, treating most of the Paris city and close suburbs wastewater (van Oort et al. 2008), estimated at about 300×10^6 m^3/day at the end of the 1990s.

Since the 1890s, and for more than one century, raw wastewater has been transported to different irrigation fields, totalizing more than 5000 ha at the beginning of the 20th century, and still ~2000 ha in 2000 (Védry et al. 2001). Irrigation was done by flooding, with soils being immerged for one or more days, several times a year. The soils of these fields were chosen because of their coarse texture, allowing high water infiltration rates. Such irrigation practices enhanced agricultural use for market garden of the low fertile soils by strongly increasing crop yields, recognized as soon as 1895 (Risler 1897).

The actual irrigation perimeter, approximately 1200 ha, is located at the extremity of the general emissary of the Paris conurbation sewer network, ≈20 km NE of Paris. The irrigated perimeter is divided in five irrigation sectors, delivering irrigation water to about 60 irrigation fields, each field being bordered by a series of water outlets. The irrigation by gravitational flooding of wastewater is favored by annual plowing parallel to topography. During the 1990s the soils of this area still received annual rates of about 2000 mm of urban wastewater (Védry et al. 2001). Several reports stressed the strong accumulation of heavy metals leading to the stop of food crop production in 2000, while ongoing irrigation with wastewater clarified by flocculation was recommended for maize growth assigned to animal breeding. On the studied irrigation fields, irrigation was stopped during 2005.

2.2. Sampling

Based on the hypothesis that multi-pollution added in the soils by wastewater would lead to comparable distribution patterns, we used previous studies on distribution of concentrations of organic carbon and heavy metals in the surface horizons of the irrigated site (Bourennane et al. 2006) to select one characteristic irrigated parcel. In this parcel, on September 21st 2008, we collected nine bulk samples (P1–P9) in the middle of the plow layer, between 15 and 25 cm depth, following a 1 km wide topographical transect (Fig. 1). Sampling sites were selected in upslope (P9), middle or down slope positions (P1), and at various distances of wastewater irrigation

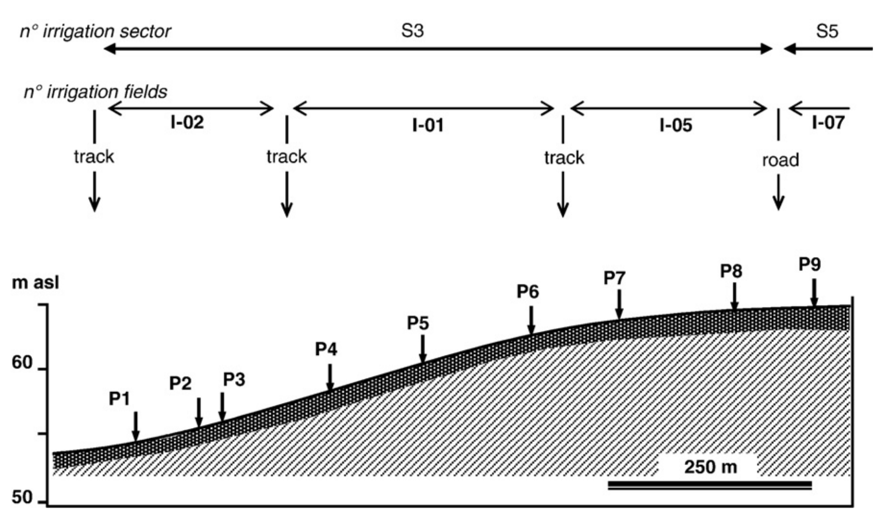

Fig. 1. Schematic presentation of the sampling locations P1 to P9, with respect to the irrigation fields and wastewater distribution sectors along a topographical transect.