Institut für Nutzpflanzenwissenschaften und Ressourcenschutz

Binding and mobilization of pharmaceuticals in wastewater-irrigated soils and sediments of the Mezquital Valley, Mexico

Dissertation

zur Erlangung des Grades

Doktor der Agrarwissenschaften (Dr.agr.)

der

Landwirtschaftlichen Fakultät

der

Rheinischen Friedrich-Wilhelms-Universität Bonn

von

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aus

Mexiko-Stadt

Bonn 2017

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Tag der mündlichen Prüfung: 15. 12. 2016

Erscheinungsjahr: 2017

Angefertigt mit Genehmigung der Landwirtschaftlichen Fakultät der Universität Bonn

Abstract

The irrigation of crop fields with treated or untreated wastewater has been an ancient practice in many cities around the world and is still a common practice nowadays. In doing so, wastewater is disposed and at the same time the water and eventually also nutrients as valuable resource are reused, which is particularly important in regions where water scarcity evolved by dry climate, high demographic density, or both. The irrigated soils retain wastewater derived compounds, which, however, also leads to an accumulation of pollutants with the time. This unintended reserve of pollutants can represent a risk if the regular conditions of the wastewater-irrigation-system changes, as in Mezquital Valley, Mexico, where fields formerly receiving untreated wastewater now face irrigation with treated wastewater of different chemical quality. The overall aim of my theses was, therefore, to elucidate the role of changed wastewater quality on potential release of pharmaceuticals. In detail I hypothesized that (i) sorption of surfactants competes with the sorption of sulphonamides, but not with strongly sorbing fluoroquinolones, that (ii) sediments from the Endhó reservoir provide a historical record of the pollutant inputs and thus a potential release of antibiotics by changing water quality, and that (iii) a treatment of wastewater, as anticipated in the region by the construction of the recently built Atotonilco wastewater treatment plant, will promote the desorption of antibiotics from wastewater-irrigated soils, maybe facilitated by anionic surfactants. To test these hypotheses, I focused on the sorption and desorption of a fluoroquinolone (ciprofloxacin) and a sulphonamide (sulfamethoxazole) from soils and sediments from the Mezquital Valley, which have been exposed for several decades to untreated wastewater, and I added linear alkyl sulfonates (LAS) to batch sorption studies in order to understand their impact on the binding of the pharmaceuticals.

The experiments revealed a strong bonding of ciprofloxacin through a cation-exchange mechanism and small desorption that prevailed independently from the presence of surfactants and from water quality. In contrast, sorption of sulfamethoxazole was reduced when the surfactant was present due to its competition with the surfactant for sorption sites. However, this effect was only noticeable in soils poor in organic matter, which excludes wastewater-irrigated soils. In wastewater-irrigated soils, the accumulation of organic matter ensured sufficient sorption sites for both antibiotics and surfactants. Sulfamethoxazole binding and desorption depended also on water quality. The effects were soil specific, largest net desorption occurred from Leptosols and Phaeozems. Sediments of the Endhó reservoir acted as a sink for ciprofloxacin and other pharmaceuticals, particularly for bezafibrate, diclofenac and trimethoprim. Concentrations of these agents in the upper sediment layers were much larger than those found in wastewater-irrigated soils. In deeper layers concentrations declined, presumably also due to degradation under anaerobic conditions that likely explained the lacking detection of sulfamethoxazole.

The results of this thesis indicate that switching from irrigation with untreated wastewater to irrigation with treated wastewater can lead to a mobilization of compounds that are bound with moderate strength, like sulfamethoxazole, whereby the desorption might be promoted by surfactants. Yet, degradation of sulfamethoxazole under anaerobic conditions makes its mobilization from sediments unlikely. The strong sorption of ciprofloxacin prevents its mobilization from soils and sediments also after the introduction of treated wastewater in the irrigation system. This applies most likely also for other strongly sorbing pharmaceuticals. For risk control, I recommend the establishment of a permanent monitoring system for concentrations of pharmaceuticals in soils, crops, irrigation water and groundwater.

Kurzfassung

Seit Jahrhunderten sind Ackerfelder rund um Städte weltweit mit Abwasser bewässert worden. Heutzutage ist das immer noch eine gewöhnliche Praxis. Mit der Abwasserbewässerung wird das Abwasser entsorgt und gleichzeitig wird das Wasser und eventuell Nährstoffe wiederverwendet, was von großer Bedeutung ist, vor allem in Regionen wo Wasser wegen eines trockenen Klimas, einer hohen demographischen Dichte, oder beidem, ein knappes Gut ist. Aber nicht allein Nährstoffe, auch im Abwasser enthaltenen Schadstoffe gelangen in die bewässerten Böden und werden dort in unter-schiedlichem Maße zurückgehalten, was zu einer Schadstoffakkumulation führt. Diese unbeabsichtigte Akkumulation von Schadstoffen und der Aufbau eines Schadstoffvorrates im Boden stellt ein Risiko dar, insbesondere wenn die Randbedingungen des Bewässerungssystems geändert werden. Das ist im Mezquital Valley, Mexiko, der Fall, wo die bisher mit Abwasser bewässerten Felder in Zukunft behandeltes Abwasser erhalten werden. Das allgemeine Ziel meiner Dissertation ist deshalb, den Einfluss der Wasserqualitätsveränderung auf die potenzielle Freisetzung von akkumulierten Arzneimitteln aufzuklären. Ich formulierte die Hypothesen, dass (i) die Sorption von Tensiden mit der Sorption von Sulfonamiden konkurriert, aber nicht mit der Sorption der stark sorbierenden Fluorchinolonen, dass (ii) die Sedimente aus dem Endhó Stausee eine historische Aufzeichnung des Eintrages von Schadstoffen enthalten und dadurch auch eine potentielle Quelle von Arzneimitteln unter den neuen Bewässerungs-bedingungen darstellen, und dass (iii) die Abwasserbehandlung kurz vor der Inbetriebnahme stehenden Atotonilco Kläranlage zu einer Desorption von akkumulierten Arzneimitteln aus den mit Abwasser bewässerten Böden führt, die eventuell auch von anionischen Tensiden gefördert wird. Um die Hypothesen zu prüfen, habe ich Sorptions- und Desorptionsversuche mit einem Fluorchinolonwirkstoff (Ciprofloxacin), einem Wirkstoff der Gruppe der Sulfonamide (Sulfamethoxazole), und mit Tensiden (Lineare Alkylsufonate, LAS) mit Böden und Sedimenten aus dem Mezquital Valley durchgeführt.

Die Ergebnisse zeigen eine starke Sorption durch einen Kationaustausch-Mechanismus und eine geringe Desorption von Ciprofloxacin, die unabhängig von der Anwesenheit der Tenside und von der Wasserqualität ist. Im Gegensatz wurde die Sorption von Sulfamethoxazol durch eine Konkurrenz mit dem Tensid für Sorptionsplätze vermindert. Diese Wirkung trat jedoch nur bei den humusärmen Böden auf. In langjährig mit Abwasser bewässerten Böden, waren infolge der Akkumulation von organischer Bodensubstanz, für beide Stoffe Sorptionsplätze in einer ausreichenden Mange vorhanden. Die Sorption und Desorption von Sulfamethoxazol war von der Wasserqualität abhängig, wobei die Wirkung bodenspezifisch war. Die höchste Desorption geschah aus Proben eines Leptosols und eines Phaeozems. Die Sedimente des Endhó Stausees wirkten als Arzneimittelsenke, insbesondere für Ciprofloxacin, Bezafibrat, Diclofenac und Trimethoprim. Im Vergleich zu den mit Abwasser bewässerten Böden waren die Konzentrationen dieser Stoffe in den oberflächennahen Sedimentschichten viel höher als in den bewässerten Böden, wobei die Konzentrationen mit steigender Sedimenttiefe abnahmen. Vermutlich fanden in den Sedimenten anaerobe Abbauprozesse der Arzneimittel statt, die auch die Abwesenheit von Sulfamethoxazole erklären.

Die Ergebnisse dieser Dissertation beweisen die potentielle Freisetzung von schwach bis moderat gebundenen Stoffen, wie Sulfamethoxazol, infolge einer Veränderung des Bewässerungsregimes (von unbehandeltem zu behandeltem Abwasser). Diese Freisetzung kann auch von Tensiden gefördert werden. Eine Mobilisierung von Sulfamethoxazole aus Sedimenten wird jedoch durch einen anaeroben Abbau unwahrscheinlich. Die starke Sorption von Ciprofloxacin an Böden und Sedimente verhindert eine Mobilisierung des Stoffes auch bei der Bewässerung mit behandeltem Abwasser, was wahrscheinlich auch für weitere stark sorbierende Arzneimittel gilt. Zur Kontrolle von Risiken im Zuge der Umstellung eines Abwasserbewässerungssystems schlage ich ein permanentes Überwachungssystem der Arzneimittelkonzentrationen in Böden, Ernten, Grund- und Bewässerungswasser vor.

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List of abbreviations

ASE	Accelerated Solvent Extraction
BEZ	Bezafibrate
CAR	Carbamazepine
CIP	Ciprofloxacin
CLA	Clarithromycin
DIC	Diclofenac
d.m.	Dry matter
DOC	Dissolved Organic Carbon
DOM	Dissolved Organic Matter
ENR	Enrofloxacin
HESI	Heated Electrospray Ionization
HPLC	High Performance Liquid Chromatography
LC-MS/MS	Liquid Chromatography – Tandem Mass Spectrometry
LAS	Linear Alkylbenzene Sulfonate
MCMA	Mexico City Metropolitan Area
MRM	Multiple Reaction Monitoring
MS	Mass Spectrometer
NAP	Naproxen
OC	Organic Carbon
OM	Organic Matter
RLOQ	Routine Limit of Quantification
SAX	Strong Anion Exchange
SMX	Sulfamethoxazole
SPE	Solid phase extraction
TRI	Trimethoprim
WWTP	Wastewater Treatment Plant
XRF	X-Ray Fluorescence

I. General introduction

1. Rationale

Water supply is closely related to crucial needs of the population, like food production and sanitation. However, as world population is rising, water availability in areas with a high demographic density has become a major problem. Particularly in urban and peri-urban areas, population growth demands an intensive use of high quality water while at the same time large volumes of wastewater are produced (Jiménez et al., 2010). In an attempt to satisfy these needs and to mitigate the pressure on water resources, the irrigation of crop fields with treated or untreated wastewater has been an ancient practice in many cities (Asano and Levine, 1996). Nowadays many farmers still grow crops with this system, particularly in many exploited countries (Pedrero et al., 2010; Qadir et al., 2010). Considering that 70% of the water taken from natural sources like rivers and groundwater is destined to agriculture globally (FAO, 2002), this practice seems to be a convenient alternative for the reuse of wastewater with some additional advantages: when irrigated with wastewater, crop fields do not only receive water, but also an important input of nutrients (Siebe, 1998). Besides, many pollutants are removed from wastewater when percolating through soil (Drewes, et al., 2003).

Irrigation with wastewater has, however, some drawbacks, such as the accumulation of pollutants in soil (Gibson et al., 2010; Xu et al., 2010; Fatta-Kassinos et al., 2011), the increase in soil salinity (Rusan et al., 2007), and the exposure of farmers and final consumers to pathogens (Gupta et al., 2009; Ferrer, et al., 2012). These risks should not be overlooked when implementing wastewater-irrigation practices (Pereira et al., 2002; Fatta-Kassinos et al., 2011).

Among the pollutants commonly present in wastewater from urban centres, pharmaceuticals are often found at relatively high concentrations (Kümmerer, 2001; Heberer, 2002), because most of them are not completely metabolised when consumed and are excreted in urine and faeces (Heberer, 2002). Some pharmaceuticals are innocuous once released, but many others have detrimental effects on the environment (Arnold et al., 2014; Kümmerer, 2009). Soils are able to remove a considerable load of pollutants from wastewater, but they have a limited capacity for the retention of solutes, and

therefore the risk of aquifer contamination is always present. This retention limit can be exceeded especially if soils receive a high and continuous load of pollutants. Therefore, having an historical record of the input of pollutants can be useful to get a better estimation of the risk and prevent the groundwater contamination. Another undesired effect of the accumulation of antibiotics in soil is the development of resistance against these pharmaceuticals by microorganisms in sewage and soils as a consequence of their constant exposure to that class of compounds (Dalkmann et al., 2012). This issue represents a major epidemiological risk that has gained importance in the last decades (Bondarczuk et al., 2016; Fletcher, 2015).

Surfactants are also a class of pollutants commonly present in wastewater from urban centres, as they are mainly used as household cleaners (Edser, 2006). Due to their amphiphilic properties they can interact with both, polar and non-polar, moieties of other compounds, either in solution or on solid surfaces. These properties make them able to influence sorption processes and mobility of pollutants in soil (Abu-Zreig et al., 1999; Peña et al., 2011). Such phenomena have been observed for hydrophobic compounds, but little is known regarding the interactions between surfactants and hydrophilic pollutants like many pharmaceuticals are.

In order to achieve a comprehensive understanding of the factors that influence the behaviour and fate of pharmaceuticals in wastewater-irrigated soils, studies regarding their interaction with other pollutants play a major role.

2. State of the art

2.1 Wastewater irrigation

In many regions over the world water has been such a limited resource that the reuse of wastewater for irrigation of crop fields has been implemented in many cities since antiquity (Asano and Levine, 1996). This is still common nowadays, particularly in many exploited countries, either because farmers find this convenient or because they do not have access to unpolluted fresh water (Pedrero et al., 2010; Qadir et al., 2010). Irrigation is an attractive alternative for the reuse of municipal wastewater, considering that in this way fields receive not only water, but also an important input of nutrients (Siebe, 1998). As an additional advantage, many pollutants are either transformed or retained in soil as water percolates through the vadose zone in a process known as soil-aquifer treatment (Mahmood et al., 2013), which contributes to the recharge of aquifers with relatively high-quality water (Drewes, et al., 2003; Fox et al., 2005), offering a practical and low-cost disposal of wastewater. All these factors make it an attractive practice particularly in arid and semiarid areas, where water is scarce and soils often show a nutrient deficiency (Xu et al., 2010; Babayan et al., 2012).

Irrigation with wastewater has of course associated drawbacks. One of the most worrying issues is the exposure of farmers and final consumers of crops to pathogens (Gupta et al., 2009; Ferrer, et al., 2012). The most common health problems among farmers who use wastewater for irrigation are intestinal nematode infections, skin and nail problems, as well as intoxication due to the long-term exposure to organic and inorganic trace pollutants (Qadir et al., 2010; Raschid-Sally et al., 2005). The risk of exposure to pathogens for final consumers is especially high when edible parts of plants are in direct contact with wastewater (Manshadi et al., 2013; Mara and Sleigh, 2010), but this is not a necessary condition as some human pathogens can enter the plant through the roots and then translocate and survive in aerial plant tissues (Bernstein, 2011).

Even when some farmers are not completely aware in detail of health and environmental risks, mainly due to their poor access to adequate information (Qadir et al., 2010), Mojid et al. (2010) nicely showed

that irrespective of their educational level, many farmers in Bangladesh are well aware of the general health risks of such practice, but nevertheless, they consider wastewater irrigation a good option. This is because the fertile wastewater is reliably available during the whole year, at little if any costs. Only some farmers would avoid the use of wastewater if they had access to freshwater. On the other hand, some farmers in Faisalabad, Pakistan, refuse to use treated wastewater from oxidation ponds because that would require additional fertilizer inputs (Raschid-Sally et al., 2005).

Regarding the soil and water pollution, irrigation with wastewater leads to an accumulation of a wide variety of pollutants in soil (Fatta-Kassinos et al., 2011) as well as to an increase in soil salinity (Rusan et al., 2007; Xu et al., 2010). The accumulation of heavy metals in wastewater-irrigated soils has been well documented in the last decades (Massaquoi et al., 2015; Salehi and Tabari, 2008; Flores et al., 1997), but recent research confirms that organic pollutants also tend to accumulate in wastewater-irrigated soils (Petousi et al., 2014; Zeng et al., 2011; Wang et al., 2010; Gibson et al., 2010).

Due to the high input of dissolved and particulate organic matter, wastewater irrigation leads to a progressive increase of soil organic matter (Xu et al., 2010), which can promote the sorption and retention of organic pollutants in soils. On the other hand, the dissolved organic matter in wastewater can interact with sorbed pollutants creating stable soluble complexes, which can be mobilized to groundwater or absorbed by plants (Graber and Grestl, 2011).

Appropriate controls of health and environmental impact are necessary to reduce such risks when irrigating crop fields with wastewater (Pereira et al., 2002, Fatta-Kassinos et al., 2011). All these phenomena necessitate appropriate controls of health and environmental impacts to reduce all the risks associated with wastewater-irrigation (Pereira et al., 2002, Fatta-Kassinos et al., 2011).

2.2 Mexico City Metropolitan Area – Mezquital Valley wastewater system

Mexico City is located inside an endorheic basin, i.e. water has no natural outflow path. Tenochtitlan, the capital city of the Aztecs, was built over a lake inside this basin, with its buildings and streets connected with each other via small islands and to the shore by a system of roads (Mundy, 2015). This situation led to several floods of the city over the centuries, being particularly devastating after the Spaniards took control of the city in the sixteenth century (García-Acosta, 2007). The first attempts to take water out of the basin started in 1607 with the construction of the tunnel of *Huehuetoca*, which would let water run out of the basin to the north (Legorreta, 2004). Since then, additional works have been performed to construct new channels or to expand the existing ones, with the last major works done in the 1970s (Burns, 2009). At the beginning of the twentieth century, the city sewage system was connected to these exit channels in order to take the wastewater out from the basin and conduct it to the Mezquital Valley (Siebe and Cifuentes, 1995), a semiarid region located 80 km north of Mexico City in the state of Hidalgo (Figure I-1). Nowadays the megacity produces between 45 and 300 m^3 s^{-1} of wastewater, with a maximum during the rainy season, as it has a mixed sewage system that collects both, rain and wastewater (Jiménez and Chávez, 1997). This amount is high enough to irrigate an area of approximately 900 km^2 in Mezquital Valley, the largest contiguous wastewater-irrigated area worldwide (Jiménez et al., 2010). Farmers grow there mainly alfalfa and maize and in a smaller extend also other fodder plants, wheat, beans, and potato among other crops (Burns, 2009). These crops satisfy, at least in part, Mexico City's demand for food (Ramírez-Fuentes et al., 2002).

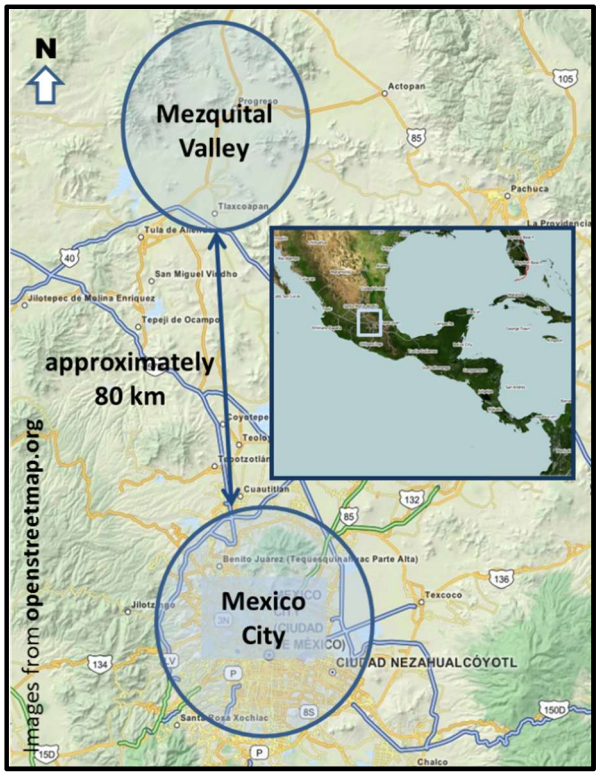


Figure I-1. Location of Mezquital Valley, which receives wastewater from Mexico City

Farmers from Mezquital Valley get the above discussed advantages like access to cheap water —a very valuable resource in arid regions as Mezquital Valley— with an additional input of nutrients, while the recharge of the aquifer and the low cost treatment of wastewater by the soil are achieved (soil-aquifer-treatment). Regarding this last point, an interesting phenomenon has been observed in the Mezquital Valley. Here the artificial rate of recharge is so high that the water table has risen in the last century producing several new springs (Jiménez and Chávez, 2004). Thanks to sorption and retention processes of metals (Guedron et al., 2014) and organic pollutants like phthalates and nonylphenols (Murillo-Torres et al., 2012) in soils, the concentrations of pollutants in groundwater of Mezquital Valley are very low, many of them smaller than the official regulations limits for drinking water (Chavez et al., 2011). Nevertheless, many emerging pollutants are not yet regulated and further studies are needed to consider it as “pure” drinking water. Although soils in Mezquital Valley work like an efficient filter for many pollutants, some have been found in low, but not negligible concentrations in groundwater (Navarro et al., 2015; Chavez et al., 2011).

As a consequence of the excessive nutrients input from wastewater in the Mezquital Valley, crops are not able to uptake them completely, so nitrogen losses from soil are to be expected. One of these losses is in the form of nitrate, which has a high mobility in soils and represents therefore a high risk of groundwater contamination and eutrophication (Siebe, 1998).

On the other side, the most tangible problem associated with wastewater irrigation in Mezquital Valley is the high incidence of gastrointestinal infections among farmers and their families (Cifuentes et al., 2000). Many chemical species like heavy metals (Guedron et al., 2014; Flores, 1997; Siebe and Fischer, 1996, Cajuste et al., 1991) and organic pollutants have accumulated in soils (Dalkmann et al., 2012; Murillo-Torres et al., 2012), leading to a health risk for the farmers and the final consumers if crops are able to uptake and translocate them to edible parts (Lara-Viveros et al., 2015). Before reaching the crop fields, untreated wastewater is collected in the Endhó reservoir to ensure the availability of the resource during the dry season. The reservoir has a capacity of 190 Mm^3 and occupies an area of 10.26 km^2. People living in the surroundings of the reservoir claim to have often illnesses and that part of their cattle and even some people have died due to the wastewater (Muñoz, 2014).

In order to improve the quality of the water used for irrigation, the Atotonilco wastewater treatment plant is currently being constructed and expected to start operating in 2016. With an operational capacity of 35 m s^{-1}, this plant will treat approximately 65 % of the wastewater coming from Mexico City before it reaches the fields. This will expose soils and sediments to wastewater of different properties, but it is not clear whether pollutants will still accumulate or whether the soils will become a net source of the sorbed substances —such as antibiotics— if the change in water quality promotes desorption processes.

2.3 Pharmaceuticals in the environment

When consumed, pharmaceuticals are not completely metabolized; so they commonly reach the sewage via urine and faces (Beausse, 2004; Giger et al., 2003). The fraction of excreted compound may vary depending on the pharmaceutical and the mode and time of administration, but up to 90 % of the

original compound can be found in excretions, in many cases together with metabolites (Monteiro and Boxall, 2010; Kümmerer, 2009; Heberer, 2002). Similar values are observed for veterinary medicaments (Kemper, 2008). Although the pharmaceutical industry hardly acknowledges its contribution to the environmental contamination with pharmaceuticals, the manufacturing units are also an important source of pharmaceuticals to the environment (Larsson, 2014).

Conventional treatments eliminate pharmaceuticals only partially from wastewater, so the effluents of wastewater treatment plants still contain a considerable load of antibiotics (Giger et al., 2003). In the case of veterinary pharmaceuticals, they can additionally reach soils directly when manure is used as fertilizer or by direct faecal shedding on grassland (Kemper, 2008).

Kolpin et al. (2002) confirmed the presence of several antibiotics and other drugs in many of the 139 monitored streams across the United States of America. Despite the usually very low concentrations in surface and ground water (Giger et al., 2003), attention must be paid regarding their adverse effects on ecosystems even at such low concentrations (Arnold et al., 2014), considering that for many of them there are not yet regulation guidelines established, that the effects of the metabolites are in many cases unknown, and that little is known about possible interactive effects, such as synergistic toxicity (Kolpin et al., 2002). Antibiotics in the environment are getting more attention in the last decades as the evidence of a major epidemiological risk, caused by the development and transfer of antibiotic resistance by microorganisms in wastewater, sewage sludge and soil, accumulates (Bondarczuk et al., 2016; Tahrani et al., 2015; Fletcher, 2015).

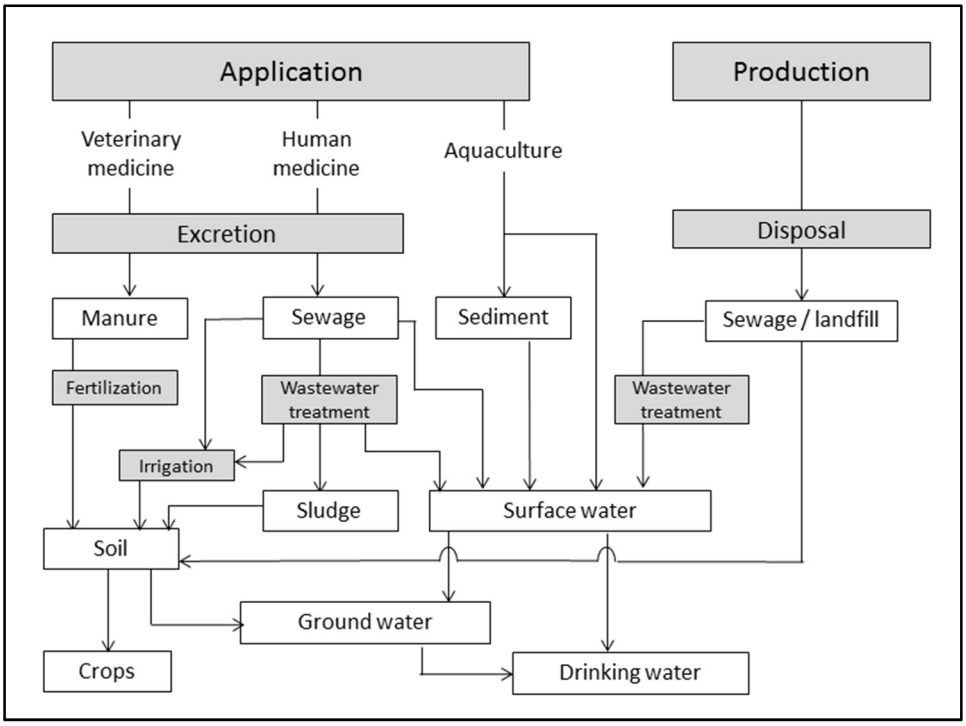


Figure I-2. Possible fate of antibiotics in the environment (modified from Hirsch et al., 1999)

Figure I-2 summarizes the routes pharmaceuticals can follow in the environment. Diverse processes govern their fate in the environment. Once the pharmaceuticals reach the soils, either transported by wastewater, manure or sewage sludge, their sorption and mobility depend on the compound and soil properties, but many of the most consumed pharmaceuticals have acidic properties, a limited solubility in water and a low volatility, therefore, it is expected to observe a tendency to sorb onto soils or sediments (Beausse, 2004). Sorption tends to increase with increasing organic matter or clay contents (Beausse, 2004).

2.4 Selected antibiotics

The most prevalent antibiotics present in the environment are macrolides, fluoroquinolones and sulphonamides (Beausse, 2004). From these two latter groups I selected ciprofloxacin and sulfamethoxazole as test compounds because they are among the most consumed antibiotics in Mexico, with 16 045 and 70 164 kg per year, respectively (data from 2003 and 2004; IMS 2008). Although hospitals are a point source of antibiotics, the main sources of these pollutants are

communities and urban centres (Kümmerer, 2009), especially the irregular settlements (Ngumba et al., 2016).

2.4.1 Ciprofloxacin

Developed in the 1980s, ciprofloxacin became the most widely used fluoroquinolone mainly because it shows a wide spectrum of activity and a higher potency compared to other antibiotics (Sharma et al., 2009). Ciprofloxacin has two protonable atoms (pK_{a1}=6.2; pK_{a2}=8.8), which make it a zwitterion at environmentally relevant pH ranges (usually between 6 and 8).

Up to 72 % of the ingested ciprofloxacin can be excreted unmetabolized from the target organism (Daughton and Ternes, 1999). It has been found in wastewater and surface water in levels of tens to hundreds of ng L^{-1} in different regions worldwide (Speltini et al., 2010; Li and Zhang, 2011), even after wastewater treatment (Larsson et al., 2007). During aerobic wastewater treatment, most of the antibiotic (> 70 %) is removed by sorption to the sewage sludge (Lindberg et al., 2006; Giger et al., 2003). This highlights the importance of a proper disposal of the sludge, as its final destination is often the agricultural fields. Ciprofloxacin is among the most often found contaminants in this kind of waste (Verlicchi and Zambello, 2015).

Once released into the environment, there are several paths for the dissipation of ciprofloxacin. For example, it was naturally removed (66 % of the dissolved fraction) from a river stream in Switzerland in summer (Giger et al., 2003). It is susceptible to photodegradation by natural sunlight in aqueous solution, in soil, and in an aqueous suspension of soil —the most common situation in natural streams—, even when the strong sorption to mineral clay and the hindering of light by solid particles reduce the efficiency of the process (Sturini et al., 2013). Under simulated solar radiation it presented a half-life of 14 minutes in natural water (Batchu et al., 2014). The biodegradation of ciprofloxacin in soil is not expected as it sorbs rapid and tightly to clay minerals (Wu et al., 2010), making it unavailable for microorganisms. The strong sorption of ciprofloxacin contributes at the same time to a low mobility. Like other fluoroquinolones, ciprofloxacin is efficiently removed from the aqueous phase in

clayey soils and tend to accumulate when applied as sewage sludge (Beausse, 2004). Sorption/desorption batch experiments have shown a rapid, strong and largely irreversible sorption of ciprofloxacin on soils from Mezquital Valley, Mexico, irrespective of the organic matter content and how long they have received wastewater (Dalkmann et al., 2014a; Dalkmann et al., 2014b).

2.4.2 Sulfamethoxazole

Since its introduction into the market in the 1960s, sulfamethoxazole has been used to treat uncomplicated infections of skin, soft-tissues and the urinary tract, commonly in combination with trimethoprim (Cassir et al., 2014).

It has been detected in the influent and effluent of wastewater treatment plants in the range of few to several hundreds of ng L^{-1} (Gros et al., 2013). Its concentration in surface water is comparatively lower (Couperus et al., 2016; Nannou et al., 2015), although it has been detected in several rivers (Nguyen Dang Giang et al., 2015) and even in drinking water sources in China (Sun et al., 2015). The predominant form of sulfamethoxazole at the pH of most of surface and natural waters is as anion (pKa_1=1.7; pKa_2=5.6). The main elimination mechanism of sulfamethoxazole in a wastewater treatment plant is biodegradation (Li and Zhang, 2010; Pérez et al., 2005), but some studies have shown that sulfamethoxazole is resistant to common wastewater treatment processes (Xu et al., 2007; Lindberg et al., 2005).

Sulfamethoxazole appears to be quite sensitive to photodegradation (Batchu et al., 2014). Under simulated sunlight radiation it was degraded in more than 85 % in the first 24 hours in water (Periša et al., 2013). Experiments show that sulfamethoxazole dissipates rapidly in soils, where not only microorganisms seem to be responsible for this process (Srinivasan and Sarmah, 2014).

Particularly in soils from Mezquital Valley, Mexico, sulfamethoxazole sorbs mainly to soil organic matter, where its quality, rather than its quantity seems to have a larger influence on the sorption process (Dalkmann et al., 2014b). The long-term effect of wastewater irrigation reduces the sorption of sulfamethoxazole, likely due to competition with the already sorbed antibiotic or due to other

dissolved organic species present in wastewater (Dalkmann et al., 2014b). Nevertheless, these processes do not seem to have a significant effect on the overall dissipation rate as could have been assumed from potential microbial adaptation mechanisms of microorganisms in soil (Dalkmann et al., 2014a).

A singular and important aspect of soils contaminated with sulfamethoxazole is the potential uptake of the antibiotic by crops. The contamination of lettuce with this pharmaceutical under wastewater-irrigation regime was confirmed, where the leaves contained up to 125 ng g^{-1} (fresh weight) of sulfamethoxazole (Sallach et al., 2015).

2.5 Surfactants in wastewater

Synthetic surfactants are widely used in household cleaning detergents, personal care products, textile, paints, polymers, pesticide formulations, pharmaceuticals, oil recovery activities and pulp and paper industries (Ying, 2006). Among the different synthetic surfactants, linear alkylbenzene sulfonates (LAS) have been the most used surfactants since the 1960s (Scheibel 2004), when they were introduced to the market to replace the poorly biodegradable branched alkylbenzene sulfonates (Berna et al., 1991).

Because of their widespread use and high consumption it is common to find LAS and other synthetic surfactants at various concentrations in surface waters, sediments and sludge-amended soils (Ying, 2006). In sewage systems LAS have been found in concentrations up to 31.8 mg L^{-1} (Holt et al., 1995) and in effluents from wastewater treatment plants in the range of 2 – 21 mg L^{-1} (Clara et al., 2007; Gomez et al., 2011; Temmink und Klapwijk, 2004; Scott and Jones, 2000; Holt et al., 1995). The LAS concentration in rivers and lakes depends on the season and distance to residential districts, but their presence in surface water is quite common (Cserháti et al., 2002). This reflects that conventional treatment processes are not always efficient in completely removing LAS from wastewater, which leads to a potential contamination of natural water or soil. In the case of Mexico City Metropolitan Area, concentrations in the range of 1.3 - 35 mg L^{-1} of methylene blue active substances (MBAS) in

wastewater are reported (Mazari 1992). This parameter includes not only LAS, but also other types of anionic surfactants. Nevertheless, these values are in good agreement with the previously mentioned studies, especially when taking into account, that LAS are actually the most-used surfactants. According to Fytianos et al. (1998), the risk of groundwater pollution with LAS is low, as these compounds sorb readily to organic matter in soil, but little is known about the influence they might have on the sorption and mobilization of other compounds.

Due to their high concentration in wastewater and their sorption properties, the LAS content of sewage sludge is usually high, with typical values of 100 – 500 mg kg^{-1} dry weight, when the treatment is aerobic and even much higher (5000 – 15000 mg kg^{-1} dry matter) in sludge from anaerobic treatment (Ying, 2006). The difference is due to the poor biodegradability of LAS under anaerobic conditions. In contrast, LAS have a half-life of 7-33 days in well aerated soils and less 3 days in river water (Ying, 2006).

Besides their toxicity and negative effects on organisms and ecosystems (Cserháti et al., 2002), their amphiphilic character is of particular interest for the present study. This means that they are able to interact with both, polar and non-polar moieties, either in solution or as part of solid phases. These properties play a significant role regarding their fate in soils and their influence on the sorption of other pollutants. LAS sorb readily to organic matter in soil, showing an increasing affinity with increasing alkyl chain length (Westall et al., 1999). They can sorb also to soil inorganic phases (Rico-Rico et al., 2009), but they sorb preferentially to organic matter if it is available (Westall et al., 1999).

Regarding their influence on other substances, LAS can enhance the sorption of organic pollutants, acting like a bridge between the sorbate and the solid phase, but they can also hinder the sorption, either by direct competition for sorption sites or by facilitating the transfer of the sorbed species to the aqueous phase by forming soluble complexes. A nice example of these opposing effects is the influence of surfactants on the sorption of naphthalene in soil (Brickell and Keinath, 1991). The authors observed both effects and concluded that the clay mineralogy of the soil determines whether the

surfactants increase or hinder the sorption of naphthalene. Jones-Hughes and Turner (2005) observed a reduced sorption of phenanthrene to estuarine sediments in the presence of sodium dodecyl sulfate, while desorption of pesticides and explosives was enhanced by anionic surfactants (Cserháti et al., 2002). Similarly, the anionic surfactant dodecylbenzene sulfonate has the ability to reduce the sorption (Gao et al., 2012) and to promote the desorption (Banerji et al., 1993) of phenolic compounds.

Several studies on sorption and transport of pharmaceuticals have been carried out (e.g., Gielen et al., 2009), but only few have focused on the influence of dissolved organic matter (Haham et al., 2012) or surfactants (Hari et al., 2005; Yu et al., 2012) on the sorption processes. The aim of the present study is to offer some insight into the understanding of such complex processes.

3. Objectives and hypothesis

Although the environmental effects and fate of antibiotics and other emerging contaminants have been recurrent topics in the last decades, there are many aspects that remain unclear. The interactions of antibiotics with other components commonly present in wastewater and the effects they can have on each other have been scarcely investigated. This work focuses on the influence of dissolved organic substances like surfactants and organic matter on the sorption processes of two selected antibiotics in soil and sediment from Mezquital Valley, the largest wastewater-irrigated area worldwide. For more than 100 years, the fields have received untreated wastewater, but soon this will change as the Atotonilco wastewater treatment plant starts operating. As the sediments of the Endhó reservoir are a sink of many compounds present in wastewater, they are a potential net source of pharmaceuticals if the physicochemical conditions change and desorption processes are enhanced, as it could be after the wastewater treatment. Therefore, a better knowledge of the type and quantities of the sorbed pharmaceuticals would help to have a better understanding of the potential risk the sediments represent. The same applies to long-term irrigated soils, which accumulated antibiotics for decades (Dalkmann et al., 2012). To get an insight on how the change in water quality might affect the

sorption/desorption processes of antibiotics in wastewater-irrigated soils, I performed desorption experiments with water of different qualities.

With the performed experiments I hypothesized that:

i) **Surfactants may have an influence on the sorption of antibiotics, hindering the sorption of sulfamethoxazole by competition, but not of ciprofloxacin due to the strong sorption of the fluoroquinolone.** Sorption batch experiments of the antibiotics were performed in the presence of surfactants using wastewater irrigated soils and soils from rain fed agriculture to compare the effect of the long-term wastewater irrigation.

ii) **Antibiotics present in wastewater from Mexico City sorb to suspended particles, so sediments from the Endhó reservoir contain an historical record of the input of those pollutants into the crop fields in Mezquital Valley.** Sediment cores were analysed for selected pharmaceuticals, heavy metals and radionuclides. The purpose of the last class of contaminants was for dating purposes.

iii) **Treatment of the wastewater before reaching the crop fields would lead to new conditions that promote the desorption of antibiotics from wastewater-irrigated soils, a process also enhanced by anionic surfactants that compete directly for sorption sites with sulfamethoxazole.** We performed desorption batch experiments with three soils from Mezquital Valley and one sediment from the Endhó reservoir exposing them to water of different qualities.

II. Materials and methods

1. Materials

1.1 Study area

Mezquital Valley is a semiarid region located in the central part of Mexico (geographic coordinates 20.1189, -99.2898) that receives currently approximately 60 m^3 s^{-1} of untreated wastewater from Mexico City distributed over an area of 900 km^2. This makes it the largest contiguous wastewater irrigated area worldwide. The extension of the irrigated area in the Mezquital Valley has increased gradually over the past century parallel to Mexico City´s population growth, creating a chronosequence of soils that have received wastewater for different time lengths from 0 to 100 years of irrigation.

In order to have enough water for irrigation during the dry season (November – May), untreated wastewater is collected in the Endhó reservoir, which has a capacity of 190 000 m^3. Wastewater is then distributed from the reservoir to the fields by a system of canals. The residence time for wastewater in the reservoir is around three months, which serves unintentionally as a primary treatment where an important load of suspended particles settle. Therefore, the sediments from the Endhó reservoir can offer an historical record of the contaminant input if pollutants sorb to settled particles and show a low mobility and enough stability in sediments.

1.2 Soils

We performed experiments with selected soils from the chronosequence to compare the sorption properties of irrigated and non-irrigated soils (Chapter III) and also the potential release of sorbed antibiotics from different soil types (Chapter V).

Composite samples were always used. Each individual field was subdivided into four parcels, two on the wastewater inflow side and two on the wastewater outflow side of the field. From each parcel we got a sample composed of 12 to 16 single cores, taken with an auger at a depth of 0–30 cm. Soil samples were collected in plastic bags, transported to the laboratory in cooling boxes (around 4 °C), sieved to

a grain size of <2 mm and stored at -21 °C in darkness. The properties of the selected soils are detailed in the chapter of the corresponding experiment.

1.3 Sediment

To evaluate the potential release of sorbed pharmaceuticals from sediments (Chapter V) we collected surface sediments (0-30 cm depth) from the Endhó reservoir with a dredge sampler. Sediments were transported to the laboratory in cooling boxes (around 4 °C), freeze-dried and stored at -21 °C.

For the reconstruction of the historical input of pharmaceuticals into the Mezquital Valley (Chapter IV) we took sediment samples from the reservoir with a core sampler. They were transported to the laboratory and sectioned in 1-cm segments. Each section was freeze-dried, homogenized and stored at -21 °C.

1.4 Chemicals and reagents

All solvents used were HPLC-grade, inorganic salts and acids were of analytical grade and water was purified by a Millipore Synergy water treatment system (Schwallbach, Germany). According to the consumption data of Mexico (IMS 2008) and their ecotoxicological relevance, we selected ciprofloxacin (CIP) and sulfamethoxazole (SMX) as our model antibiotics for the sorption/desorption experiments. They were obtained from Sigma-Aldrich (Schnelldorf, Germany). For the quantification of the pharmaceuticals isotope-labeled compounds were used. Ciprofloxacin (carboxyl-$^{13}C_3$, quinoline-^{15}N, ≥98% pure), enrofloxacin hydrochloride (ethyl-d_5, ≥98% pure), sulfamethoxazole (ring-$^{13}C_6$, ≥98% pure), trimethoprim (methyl-$^{13}C_3$, ≥98% pure), and carbamazepine (phenyl-d_{10}, ≥98% pure) were supplied by LGC Standards (Wesel, Germany) as internal standards. Labeled bezafibrate (phenyl-d_4, >98% pure) and clarithromycin (methyl-d_3, 98% pure) were obtained from Toronto Research Chemicals (North York, Canada). Labeled naproxen (methyl-d_3, 98% pure) and diclofenac (phenyl-d_4, 99% pure) were purchased from Dr. Ehrenstorfer (Augsburg, Germany). The internal standard solution was prepared in acetonitrile at a concentration of 1 ng mL^{-1} and stored in the dark at -20 °C. Sodium dodecyl benzenesulfonate was selected as model surfactant because it is widely used in household cleaning

products. It was purchased from TCI (Eschborn, Germany) as a mixture of four linear isomers (chain length C_{10}-C_{13}). All substances had a declared purity of >95%.

2. Methods

2.1 Extraction of pharmaceuticals

Pharmaceuticals were extracted from solid matrices by accelerated solvent extraction (ASE) following a modification of the methods of Golet et al. (2002) and Gobel et al. (2005). Samples were mixed thoroughly with purified sea sand in a ratio of 1:1 (w/w) and extracted in stainless steel 34-mL cells first with a mixture of aqueous 50 mM phosphoric acid and acetonitrile (1:1, v/v) (Golet et al., 2002) and then with a methanol/water solution (1:1, v/v) (Gobel et al., 2005), collecting both extracts in the same flask. The conditions of the extraction programs are detailed in Table A-1 and extraction recoveries are provided in Table A-2, both in Appendix A.

2.2 Solid phase extraction

Samples were concentrated and cleaned up by means of solid phase extraction (SPE). Liquid samples, including wastewater samples and supernatant of sorption/desorption experiments were directly processed. In the case of solid matrices (see section II-2.1), an aliquot of 25 mL of the mixed extract was diluted to a volume of 300 mL with Millipore water. This extract was processed then as liquid sample. Before passing them through the SPE-columns, the samples were acidified with HCl 1 M to a pH of 2.4 and 50 µL of the internal standard solution were added. The SPE was conducted using a strong anion exchange (SAX) cartridge (Chromabond SB; Macherey-Nagel; Germany) and an HLB cartridge (Oasis HLB, Waters; UK). The cartridges were serially connected in such a way the extract flowed first through the SAX cartridge and then through the HLB cartridge immediately after. The analytes were retained and collected in the solid matrix of the HLB cartridges, while the purpose of the SAX cartridge was to provide an additional sample clean-up and to prevent the HLB cartridge from clogging. A recovery experiment proved negligible retention of the analyzed pharmaceuticals on the

SAX cartridges (less than 0.5% of the target compounds were lost, Table A-2). Recoveries from the Oasis HLB cartridges are also shown in Table A-2 from Appendix A.

Analytes were eluted sequentially from the Oasis HLB cartridges with 5 mL methanol, 5 mL acetonitrile, and 5 mL acidified acetonitrile (0.1% 12M HCl). The eluents were combined and concentrated to approximately 0.5 mL with a rotary evaporator at 40 °C and a gradually decreasing pressure from 200 to 160 mbar. One mL of 50 mM phosphoric acid/acetonitrile solution (80:20 v:v) was added to the residue and sonicated for 2 minutes to redissolve any possible precipitate. The liquid was transferred to an Eppendorf tube and centrifuged at 15 000 g for 20 minutes. The liquid was transferred to 2 mL amber autosampler vials and stored at -21 °C until the measurements.

2.3 Quantification of pharmaceuticals

Concentrations of pharmaceuticals were measured using liquid chromatography tandem mass spectrometry (LC-MS/MS) with a TSQ Quantum Ultra spectrometer (Thermo Finnigan, Dreieich, Germany) equipped with a heated electrospray ionization ion source (HESI). For the chromatographic separation of pharmaceuticals we used an XBridge C18 (3.5 µm, 2.1 x 150 mm) column (Waters, Milford, MA, USA) together with a guard column (Sentry 2.1 x 10 mm, Waters, Milford, MA, USA) and a gradient of methanol (A) and Millipore water (B), both with a 0.1 % content of formic acid, and a flow of 300 µL min^{-1}. The gradient started with 5 % of A, increasing linearly to 60 % in the first 5 minutes. The fraction of A was then increased linearly to 80 % in the next 9 minutes. For one minute it was increased up to 90 % and then held for one minute more. From the minute 16 to 17 the % A was reduced linearly to 5 % and held for five minutes more to take the system to the initial condition. The total run time was 22 minutes. Pharmaceuticals were measured in positive ion mode with a discharge current of 4.0 kV, a vaporizer and capillary temperatures of 390 and 217 °C respectively, nitrogen as sheath gas and argon as collision gas (0.2 Pa). Details regarding the detected ions and collision energies are shown in Table A-3. Routine Limits of Quantification (RLOQ = lowest concentration of standard used) were 250 ng kg^{-1} for CIP and 25 ng kg^{-1} for SMX.

2.4 Quantification of surfactants

A Kromasil 100 C18 (5 µm, 4.6 x 250 mm) column and a Kromasil 100 C18 (5 µm, 4.6 x 10 mm) guard column, both from MZ Analysentechnik (Mainz, Germany) were used for the quantification of the surfactants. A gradient of methanol (A) and an aqueous solution of 5 mM formic acid and 5 mM triethylamine (B) with a flow of 1000 µL min^{-1} was used. The gradient started with 40 % of A, which was increased linearly up to 100 % in the first seven minutes. This percentage was held until the end of the analysis for a total run time of 15 minutes. Surfactants were measured in negative mode with a discharge current of 4.0 kV, a vaporizer and capillary temperatures of 390 and 217 °C respectively, nitrogen as sheath gas and argon as collision gas (1.5 mTorr). The analysis of the LAS standard in the scan mode showed four peaks at m/z 297.2 (retention time: 9.44 min.), m/z 311.2 (9.72 min.), m/z 325.3 (10.03 min), and m/z 339.2 (11.84 min). All four compounds produced only one fragment with m/z 182.8 in the MRM mode of the MS. The four compounds were therefore detected by monitoring the mass transitions 297.2 $\rightarrow$ 182.8 for the C_{10} LAS, 311.2 $\rightarrow$ 182.8 for the C_{11} LAS, 325.3 $\rightarrow$ 182.8 for the C_{12} LAS, and 339.2 $\rightarrow$ 182.8 for the C_{13} LAS. Assuming that the compounds had similar ionization efficiency in the HESI source, we first calculated the concentrations of all four compounds in the supernatant. Subsequently the concentrations of the four individual compounds were summed up to give the total concentration of LAS in solution.

2.5 Quantification of metals

Total metal content in sediments were determined by X-ray fluorescence (XRF). 5 g of sample were mixed with 1 g of wax used as binding agent, grinded and mixed thoroughly in a ceramic mortar and then turned into a pellet with a press. The pellets were measured with a XRF spectrometer (Axios, PANalytical).

III. Competitive sorption of linear alkylbenzene sulfonate (LAS) surfactants and the antibiotics sulfamethoxazole and ciprofloxacin in wastewater irrigated soils of the Mezquital Valley, Mexico

Modified on the basis of:
Carrillo M, Siebe C, Dalkmann P, Siemens J (2016) Journal of Soils and Sediments 16:2186-2194

1. Introduction

Water supply is closely related with other crucial needs of people, like food production and sanitation. Particularly in urban and peri-urban areas the population growth demands an intensive use of high quality water and -at the same time- produces a large volume of wastewater (Jiménez et al. 2010). The irrigation of arable fields with untreated wastewater has been an ancient practice in many cities (Asano and Levine 1996). Many pollutants in wastewater are either transformed or retained in soil as water percolates through the vadose zone in the so-called Soil Aquifer Treatment (SAT), which contributes to the recharge of aquifers (Drewes et al. 2003), offering a practical and low-cost disposal of wastewater.

Several drawbacks are linked to wastewater irrigation too, like an accumulation of pollutants in soil (Gibson et al. 2010; Fatta-Kassinos et al. 2011), an increase in soil salinity (Rusan et al. 2007), and an exposure of farmers and crop consumers to pathogens (Gupta et al. 2009). Among the diversity of pollutants that wastewater from urban centres carries, pharmaceuticals are present because most of them are not completely metabolised and are excreted in urine and faeces (Kümmerer 2009). Surfactants are also commonly present in wastewater because they are a component of many household cleaners (Edser 2006). Due to their amphiphilic properties they can interact with both, polar and non-polar species in solid phases and in solution as well. These interactions can affect sorption processes and mobility of pollutants in soil (Abu-Zreig et al. 1999; Peña et al. 2011). Such phenomena have already been observed for hydrophobic compounds (Jones-Hughes and Turner 2005), but little is known regarding the interactions between surfactants and hydrophilic pollutants like many pharmaceuticals.

The largest contiguous wastewater irrigated area worldwide is the Mezquital Valley, which receives wastewater from the Mexico City Metropolitan Area (MCMA) since more than 100 years (Jiménez et al. 2010) and is used for crop irrigation, mainly of alfalfa and maize. Several antibiotics have been found in the wastewater (Siemens et al. 2008; Gibson et al. 2010) and have accumulated in soils over time (Dalkmann et al. 2012). Batch experiments evidenced a weaker sorption of the anionic

sulfamethoxazole, but not of the cationic and zwitterionic ciprofloxacin in irrigated soil compared to non-irrigated soil (Dalkmann et al. 2014b). A possible competition with other compounds present in wastewater like dissolved organic matter (DOM) including surfactants was suggested by the authors as a possible explanation for the weaker sorption in wastewater-irrigated soil. Linear alkylbenzene sulfonates (LAS) have been the most used surfactants since the 1960s (Scheibel 2004). Typical concentrations of LAS in treated and untreated wastewater from urban centers ranged from 2 mg L^{-1} to 32 mg L^{-1} (Gomez et al. 2011; Clara et al. 2007; Temminik and Klapwijk 2004; Scott and Jones 2000; Holt et al. 1998; Holt et al. 1995).

According to Fytianos et al. (1998), the risk of groundwater pollution with LAS is low, as these compounds sorb readily to OM in soil, but only few studies have focused on the influence of DOM (Haham et al. 2012) or of surfactants (Hari et al. 2005; Yu et al. 2012) on the sorption processes of pharmaceuticals.

We studied the sorption of anionic LAS to soils from the Mezquital Valley that were either irrigated or not with wastewater for more than 100 years. We also investigated the effect of LAS on the sorption of two commonly used antibiotics, ciprofloxacin and sulfamethoxazole. We hypothesized that:

i) higher soil OM contents in long-term irrigated soils increase LAS sorption and

ii) sorption of anionic LAS competes with sorption of anionic sulfamethoxazole, but not with the strong sorption of cationic or zwitterionic ciprofloxacin.

2. Materials and methods

2.1 Soils

We used two soils from rainfed agriculture and two wastewater-irrigated soils that received wastewater for 100 years. The soils were collected as described in Section II-1.2 and their properties are detailed in Table III-1.

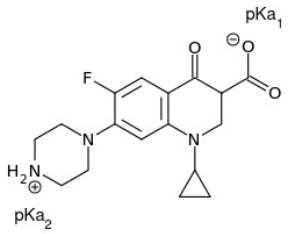
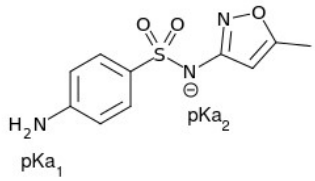
Table III-1. Properties and irrigation regime of the tested soils

Soil	Site	Irrigation regime	Composition % weight			org. C g kg^{-1}	pH ($CaCl_2$)
			Sand	**Silt**	**Clay**		
Rnf1	Tezontlale	Rainfed	24	41	35	9.5	7.22
Rnf2	El Tigre	Rainfed	12	40	48	18.4	7.22
Irr1	Ulapa	Wastewater (100 years)	45	45	39	25.9	7.27
Irr2	Juandhó	Wastewater (100 years)	47	47	29	28.2	7.29

2.2 Chemicals

Ciprofloxacin and sulfamethoxazole were our model antibiotics. Their structures and some chemical properties are summarized in Table III-2. We selected sodium dodecyl benzenesulfonate as model surfactant because it is used widely in household cleaning products. It was purchased from Tokyo Chemical Industries (TCI, Eschborn, Germany).

Table III-2. Properties of the tested pharmaceuticals

Compound	CAS Number	Water solubility g L^{-1}	log K_{OW}	K_{OC} L kg^{-1}	pK_a[c]	Precursor ion m/z	Fragment ions m/z	Collision energy eV
 Ciprofloxacin (CIP)	85721-33-1	0.5[a, b]	1.63[b]	3.49[d]	6.2; 8.8	332.09	245.06 288.11	24 17
 Sulfamethoxazole (SMX)	723-46-6	2.8[a, b]	0.66[b]	219[e]	1.7; 5.6	254.02	108.03 155.97	23 15

[a] At pH=7 and 25 °C
[b] Data from SciFinder Database
[c] Data from Chen et al. (2011)
[d] Data from Figueroa-Diva et al. (2010)
[e] Data from Barron et al. (2009)

2.3 Batch experiments

Sorption experiments were carried out in 25-mL borosilicate glass bottles in duplicate. The soils were weighted inside the bottles and then sterilized with an autoclave (121 °C and 100 kPa for 15 minutes) to avoid the biodegradation of the surfactant. The soil to solution ratio was 1:50 for the experiments with ciprofloxacin and 1:5 for those with sulfamethoxazole, based on former studies (Dalkmann et al., 2014b) and attending the guidelines for the testing of chemicals in adsorption - desorption batch experiments (OECD 2000). Soils were mixed with a 0.01 M $CaCl_2$ aqueous solution and shaken with a rotatory agitator for 24 hours to reach a pre-equilibrium, then the mixtures were spiked with a mixture of LAS and one of the tested antibiotics. Nominal surfactant concentrations of 0, 5, 10 and 30 mg L^{-1} were established, according to the typical LAS-concentrations in wastewater (Clara et al. 2007; Scott and Jones 2000; Holt et al. 1995). The concentration of pharmaceuticals was 1.0 mg L^{-1} in all the experiments according to the procedure described by Dalkmann et al. (2014b). Once spiked, the bottles were shaken in the dark with a rotatory agitator for 48 hours and then centrifuged at 15 000xg for 20 minutes to separate the liquid from the solid phase. An aliquot from the supernatant was taken, spiked with the corresponding antibiotic internal standard, and then analyzed by LC-MS/MS for both, surfactants and pharmaceuticals as described in sections II-2.3 and II-2.4. Controls of LAS solutions with the background electrolyte ($CaCl_2$) and the corresponding pharmaceutical without soil were incubated to evaluate the formation of insoluble Ca^{2+}-LAS complexes.

2.4 Data evaluation

The data for the sorption of the pharmaceuticals were fitted to the Freundlich model, described by the following equation:

$$Q = K_F C^N \qquad \text{(III-1)}$$

where Q is the amount of sorbed compound (mg kg^{-1}), C is the amount of this compound in solution after equilibrium (mg L^{-1}), K_F is the Freundlich sorption constant related to the sorption strength (mg^{1-}

^{N} L^{N} kg^{-1}) and *N* is related to the heterogeneity of sorption sites (dimensionless). We used the software SigmaPlot version 11 (Systat, Erkrath, Germany) for the fitting.

3. Results

Measured concentrations of LAS in the controls with background electrolyte (0.01 M aqueous $CaCl_2$) without soil were smaller than the nominal concentrations of 5, 10, and 30 mg L^{-1} after the equilibration period. As the media were sterile and protected from light, we discarded the possibility of a degradation of the surfactant. The observed reduction in LAS-concentrations was thus likely caused by LAS complexation and precipitation with Ca^{2+} (see Table B-1, Appendix B). Since sorbed amounts of LAS were calculated as difference between spiked and measured LAS concentrations, this complexation has to be considered when interpreting the isotherms and the observed reduction in LAS concentrations must be mathematically corrected for complexation-precipitation effects.

Independently of the presence of antibiotics, LAS was in almost all cases bound more strongly to wastewater-irrigated soils (Irr1 and Irr2) than to non-irrigated (rain fed) soils (Rnf1 and Rnf2), as shown by the slope of the isotherms (Fig. III-1 and III-2) and by their K_F values (Table III-3). At a soil-solution ratio of 1:50 we observed almost linear sorption isotherms with *N* values close to 1 when ciprofloxacin was not present (Fig. III-1a) (Table III-3). With a soil-solution ratio of 1:5 in the absence of sulfamethoxazole we got also nearly-linear isotherms for the soil with a OC content >28 g kg^{-1} (Fig. III-2a). In both systems, when the antibiotic was present, the linearity of the LAS sorption isotherms was reduced (Figs. III-1b and III-2b), which was more pronounced with ciprofloxacin (Fig. III-1b; soil-solution ratio of 1:50). At a soil to solution ratio of 1:5 in the presence of sulfamethoxazole the isotherm for soil Irr1 showed an increase in LAS sorption for the spiking concentration of 30 mg LAS L^{-1}, leading to an *N* Freundlich exponent larger than 1 (Fig. III-2b, Table III-3).

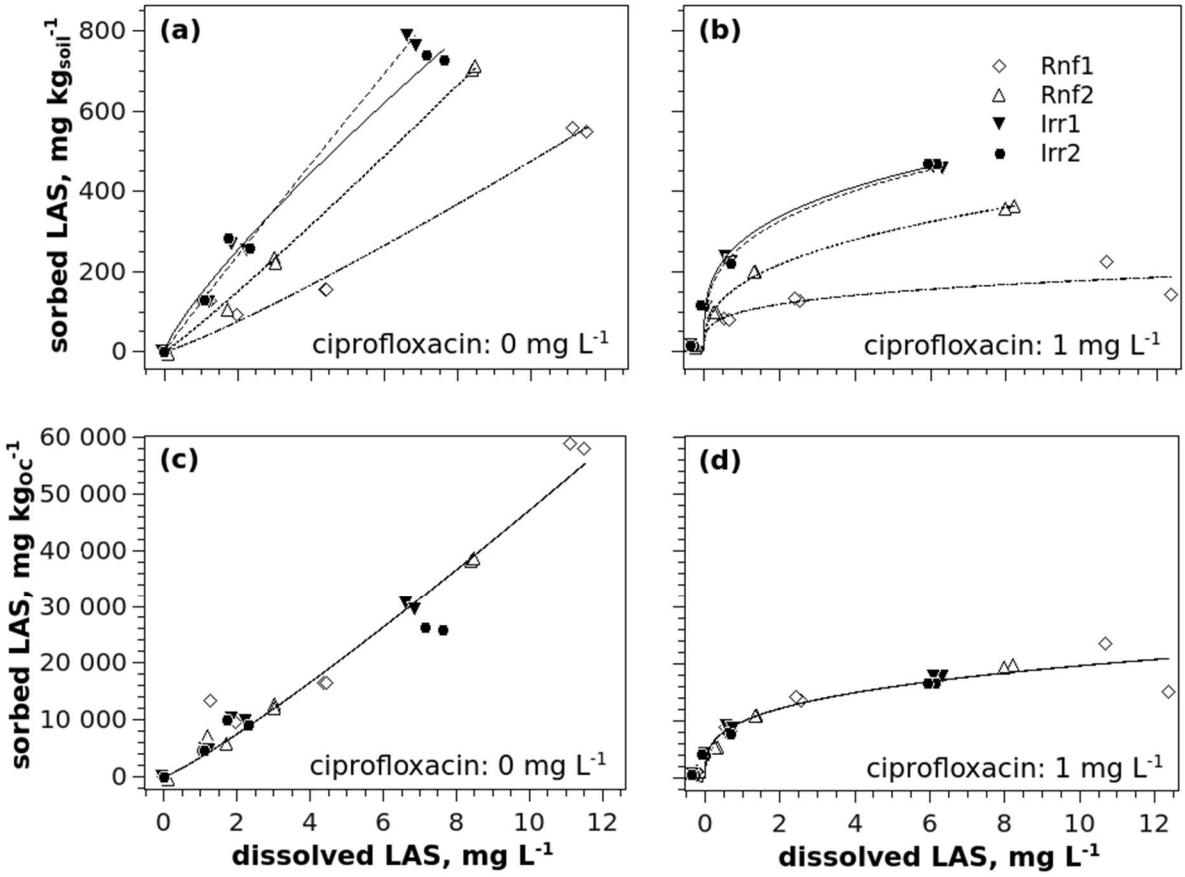


Figure III-1. Comparison of Freundlich sorption isotherms of linear alkylbenzene sulfonates (LAS) on rainfed (open symbols) and wastewater-irrigated (closed symbols) soils (soil to solution ratio 1:50) in the absence, (a) and (c), and in the presence, (b) and (d), of ciprofloxacin (1 mg L^{-1}). The lower panels, (c) and (d), show the LAS sorption normalized to the organic carbon (OC) content of the four soils. The two replicates for each point of the isotherms are included in the plots, therefore, no error bars are displayed.

In the presence of ciprofloxacin (soil-solution ratio of 1:50), K_F values ranged from 100-276 mg^{1-N} L^N kg^{-1} (Table III-3), exceeding the K_F coefficients in the range of 29-124 mg^{1-N} L^N kg^{-1} that were found in the presence of sulfamethoxazole for a soil-solution ratio of 1:5. When normalized to the OC content, the isotherms for all soils showed a similar pattern and the whole set of data fell on a single isotherm for LAS sorption in the presence of sulfamethoxazole or ciprofloxacin and one single isotherm in the absence of the antibiotics (Figs. III-1c, III-1d, III-2c and III-2d).

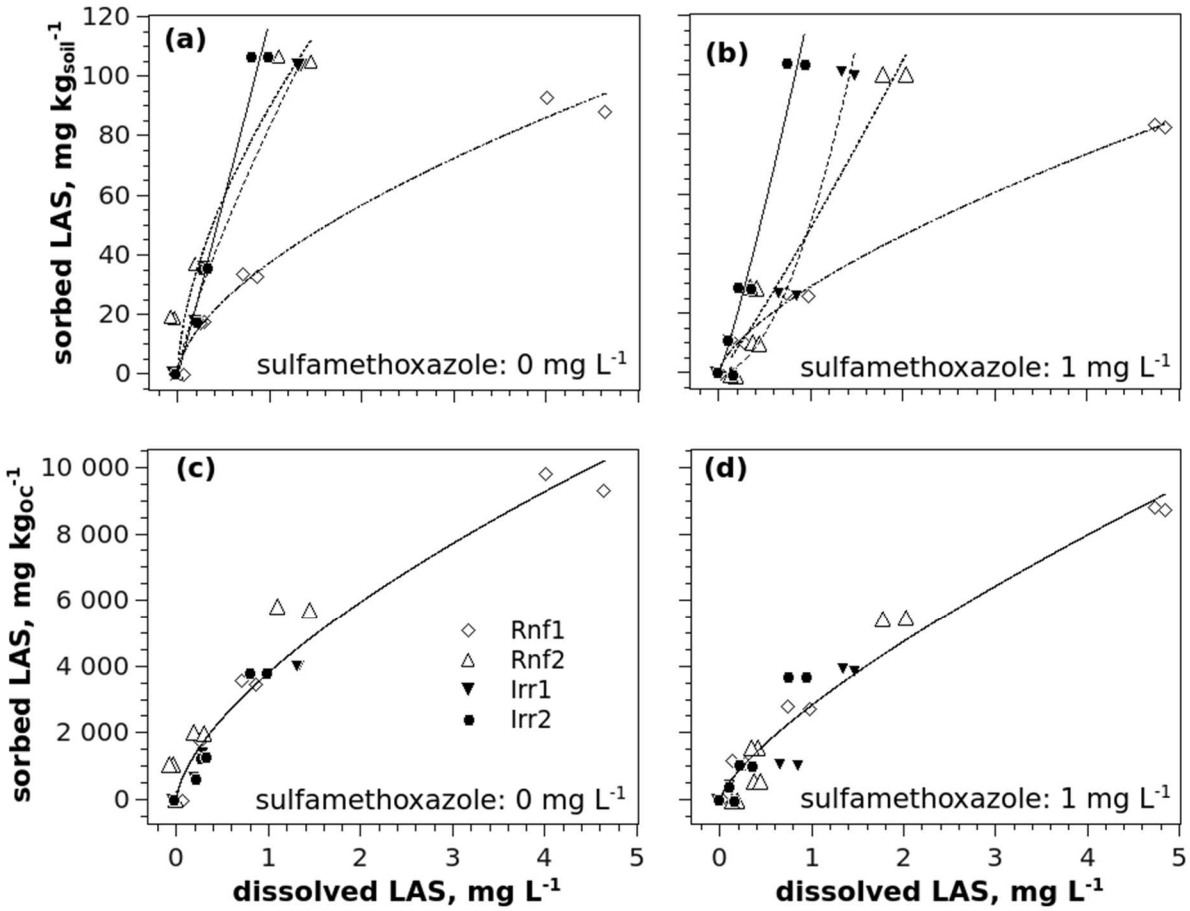


Figure III-2. Comparison of Freundlich sorption isotherms of linear alkylbenzene sulfonates (LAS) on rainfed (open symbols) and wastewater-irrigated (closed symbols) soils (soil to solution ratio 1:5) in the absence, (a) and (c), and in the presence, (b) and (d), of sulfamethoxazole (1 mg L^{-1}). The lower panels, (c) and (d), show the LAS sorption normalized to the organic carbon (OC) content of the four soils. The two replicates for each point of the isotherms are included in the plots, therefore, no error bars are displayed.

Concentrations of dissolved organic carbon (DOC) in equilibrium with the soils differed widely between the treatments. After equilibration with 0.01 M $CaCl_2$ at a soil to solution ratio of 1:50, small concentrations of 1.3-3.8 mg L^{-1} DOC were found prior to the addition of LAS and ciprofloxacin, while concentrations of 7.4-15.8 mg L^{-1} DOC were found in the supernatant at a soil to solution ratio of 1:5 prior to the addition of LAS and sulfamethoxazole, which was an effect of dilution. The addition of LAS and sulfamethoxazole to the OM-rich soils Rnf2, Irr1 and Irr2 induced a further release of OM from soil to the liquid phase, increasing concentrations of soil-borne DOC (LAS carbon subtracted from total DOC) in the solution to values in the range of 31.3 to 47.2 mg L^{-1}.

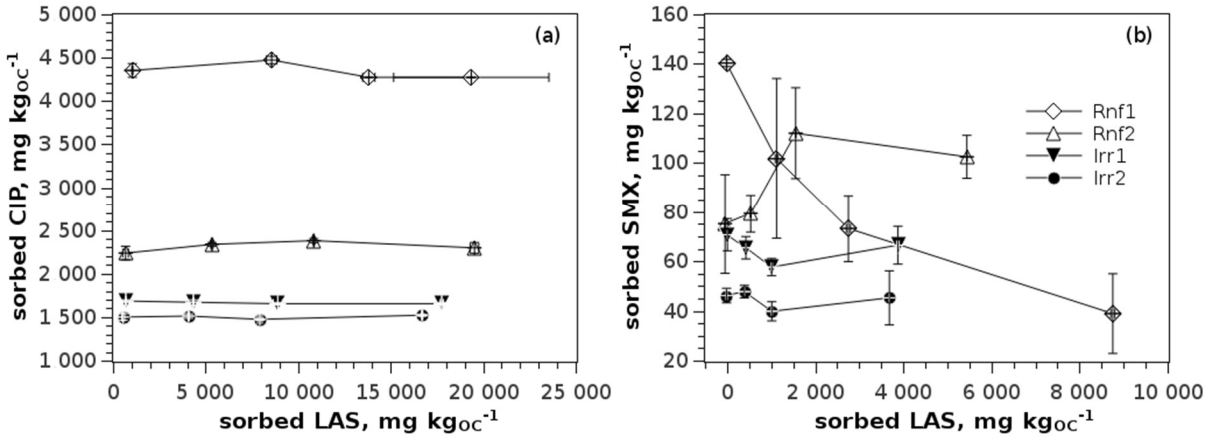


Figure III-3. Sorption of ciprofloxacin (CIP) (a) and sulfamethoxazole (SMX) (b) as a function of the sorbed amount of linear alkylbenzene sulfonates (LAS). Both quantities are normalized to the organic carbon (OC) content in soil. Error bars represent the standard deviation

As hypothesized, the sorption of ciprofloxacin was not affected by the presence of LAS (Fig. III-3a), but other than expected, the sorption of the anionic sulfamethoxazole did not decrease with increasing amounts of sorbed LAS in soils Rnf2, Irr1, and Irr2 (Fig. III-3b).

Table III-3. Freundlich parameters and the associated standard deviation obtained for LAS binding in wastewater-irrigated and rainfed soils in presence or absence of ciprofloxacin (CIP) or sulfamethoxazole (SMX)

Soil	K_F $mg^{1-N}L^Nkg^{-1}$	*N*	K_F $mg^{1-N}L^Nkg^{-1}$	*N*
	Without CIP (soil to solution ratio 1:50)		**In presence of CIP** (soil to solution ratio 1:50)	
Rnf1	34 ± 12	1.14 ± 0.15	100 ± 14	0.25 ± 0.07
Rnf2	71 ± 9	1.07 ± 0.06	169 ± 5	0.36 ± 0.02
Irr1	123 ± 13	0.97 ± 0.06	263 ± 5	0.31 ± 0.01
Irr2	144 ± 16	0.81 ± 0.06	276 ± 15	0.29 ± 0.03
Normalized to OC (K_{FOC}; four soils)	3 431 ± 506	1.14 ± 0.07	9 886 ± 387	0.30 ± 0.03
	Without SMX (soil to solution ratio 1:5)		**In presence of SMX** (soil to solution ratio 1:5)	
Rnf1	37 ± 3	0.60 ± 0.05	29 ± 2	0.67 ± 0.04
Rnf2	90 ± 4	0.60 ± 0.08	49 ± 6	1.12 ± 0.17
Irr1	83 ± 3	0.79 ± 0.05	51 ± 7	1.94 ± 0.38
Irr2	119 ± 7	1.02 ± 0.12	124 ± 11	1.14 ± 0.19
Normalized to OC (K_{FOC}; four soils)	3 809 ± 158	0.64 ± 0.04	2 830 ± 166	0.75 ± 0.05

OC: organic carbon

Only for the soil with the lowest OC content, Rnf1, sorbed amounts of sulfamethoxazole significantly decreased with increasing amounts of sorbed LAS indicating a reduced sorption due to competition for sorption sites (Fig. III-3b).

4. Discussion

4.1 LAS Sorption

Independent of the presence or absence of the antibiotic, the type of added antibiotic or the soil to solution ratio, sorption of LAS was stronger to irrigated soils than to non-irrigated soils. This can be related to the higher OM contents of the irrigated soils, since normalization of the sorbed amounts of LAS to the OC contents of the different soils produced superposed sorption isotherms for all investigated soils (Figs. III-1c, III-1d, III-2c and III-2d). We also found a positive correlation between the K_F parameter for LAS sorption and the OC content in the presence of ciprofloxacin (Pearson correlation coefficient R = 0.994, p = 0.006). This kind of correlation for LAS sorption has already been observed for sediments (Westall et al. 1999) and soils (Fytianos et al. 1998). Although sorption of anionic surfactants by clay minerals has been reported (Harendra and Vipulanandan 2012), LAS sorbs mainly to the soil organic phases (de Wolf and Feijtel 1998). Only when concentrations of LAS are small (<< 1 mg L^{-1}), inorganic phases such as clay minerals or oxyhydroxides had a significant effect on LAS sorption (Rico-Rico et al. 2009). This explains why the Rnf2 soil, the most clayey soil, did not show a higher affinity for LAS than the OC-rich soils (K_F values in Table III-3) as we used always LAS concentrations larger than 1 mg L^{-1}. The large OM content of the soils Irr1 and Irr2 is a consequence of the long-term irrigation in the Mezquital Valley (Dalkmann et al. 2014b). Our results thus illustrate that long-term irrigation indirectly increases LAS sorption in soils as a consequence of soil OM accrual over time.

We suggest that the weaker sorption of LAS at a soil to solution ratio of 1:5 compared to a soil to solution ratio of 1:50 is mainly a consequence of larger DOC concentrations. Although at a smaller soil to solution ratio smaller K_d values for soil organic matter could be expected (You et al. 1999; Yin et al. 2002), the total content of soil and therefore of soil organic matter is larger at the 1:5 soil to solution

ratio. This led to a larger concentration of dissolved organic matter released from soil into the solution, which was also indicated by the noticeable darker coloration of the supernatant. This dissolved organic matter might have reduced LAS sorption by *i)* direct competition with the surfactant molecules for sorption (Yu et al. 2011) and *ii)* interactions with dissolved LAS by forming soluble associations as Yu et al. (2014) suggest for an anionic biosurfactant.

A sorption isotherm with $N > 1$ was observed for soil Irr1 at a soil to solution ratio of 1:5 in the presence of sulfamethoxazole (Fig. III-2b). Such isotherms are typical when solute-solute interactions induce cooperative sorption (Hinz 2001). At an early stage, surfactant molecules attach to the mainly mineral (e.g., Ou et al. 1996) solid surface. As the density of sorbed molecules on soil surfaces increases, the intermolecular forces among the hydrophobic moiety contribute additionally to the sorption process. Hence, the isotherm shows a strong increase at larger dissolved and sorbed concentrations (Zhang and Somasundaran 2006).

4.2 LAS influence on sorption of pharmaceuticals

We observed a noticeable reduction in the linearity of LAS sorption in all the investigated soils when ciprofloxacin was present (Fig. III-1b). This indicated a reduction of the homogeneity of sorption sites for LAS when the antibiotic was sorbed. In the presence of ciprofloxacin, sorption of LAS was described with smaller N values, but larger K_F constants implying enhanced sorption of LAS at low LAS concentrations. Potential mechanisms causing enhanced sorption at low LAS concentrations could be the formation of ciprofloxacin-LAS associations via cation bridges or the masking of negatively charged clay mineral surfaces by sorbed ciprofloxacin. At higher LAS concentrations (nominal concentration = 30 mg L^{-1}) the surfactant was sorbed in a very similar degree with and without ciprofloxacin (Fig. III-1a and III-1b). It seems that at higher LAS concentrations the intermolecular forces among the hydrophobic moieties of LAS and also between them and the soil solid phase play an increasing role for sorption, so that interactions with ciprofloxacin become less important.

The present study confirmed the expected small effect of LAS on the strong sorption of the fluoroquinolone ciprofloxacin to the Mezquital Valley soils. Similarly, a negligibly small effect of LAS on the leaching of enrofloxacin (also a fluoroquinolone) in column experiments was observed (Yu et al. 2012). Ciprofloxacin sorbs mainly by a cation exchange mechanism (Wu et al., 2010; Wu et al. 2013), hence anionic surfactants like LAS do not compete directly with ciprofloxacin for sorption sites. Although we only performed tests with the anionic surfactant LAS, neither cationic nor non-ionic surfactants had an effect on the sorption of the fluoroquinolone norfloxacin onto an aquifer material studied by Hari et al. (2005). The results of Hari et al. (2005) for norfloxacin can likely be extrapolated to other fluoroquinolones, because the different substituent groups in the chemical structure of fluoroquinolones have little influence on sorption interactions with soil so that they exhibit similar sorption behaviour (Figueroa-Diva et al. 2010). Sorption of fluoroquinolones is strongly influenced by their pH-dependent chemical speciation (e.g. Vasudevan et al. 2009). The four studied soils have a pH in the range of 7.22 – 7.29 (Table III-1), but the pH in the sorption experiments were always lower. The pH of the supernatant after the sorption process were in the range of 6.41 – 6.81 with a mean value of 6.57 (n=32). At pH values larger than 9, the anionic form of ciprofloxacin predominates (pKa_2 = 8.7), and its overall sorption to negatively charged surfaces is strongly reduced. Therefore, competition between fluoroquinolones and anionic surfactants for sorption sites could take place at pH values larger than their pKa_2.

Except for the soil with the lowest OM content (Rnf1), we did not find an evident trend of decreasing sulfamethoxazole sorption with increasing LAS concentrations. Only soil Rnf1 sorbed decreasing amounts of sulfamethoxazole with increasing concentrations of sorbed LAS (Fig. III-3b), suggesting that in organic matter-poor soils competitive sorption with LAS might reduce sulfamethoxazole sorption. In addition, the formation of soluble LAS-sulfamethoxazole associations might have limited the sulfamethoxazole sorption in the organic matter-poor Rnf1 soil. The inhibition of sorption of hydrophobic compounds, such as chlorophenols, in sediments in the presence of LAS was attributed to the formation of associations of the hydrophobic compounds with LAS in the aqueous phase (Gao

et al. 2012). On the other hand, a similar effect of sodium dodecyl sulfate on the sorption of phenanthrene was explained by the competition of both sorbates for sorption sites (Jones-Hughes and Turner 2005).

5. Conclusions

We conclude that OM is the main sorbent of LAS in the Mezquital Valley soils. In addition to sorption, complexation with Ca^{2+} significantly contributes to the removal of free LAS from the solution phase. Interactions of LAS with other dissolved organic compounds released from soils reduce LAS sorption. Significant reduction of sulfamethoxazole sorption due to competition with LAS for sorption sites likely occurs only in soils with small OM contents. The accumulated OM in wastewater-irrigated soils offers enough sorption sites for both LAS and sulfamethoxazole so that they no longer compete for sorption sites and the sorption of the antibiotic is not hindered. The effect of the anionic LAS on the sorption of ciprofloxacin in the clayey circumneutral soils of the Mezquital Valley is negligible.

IV. Accumulation and persistence of pharmaceuticals in sediment of the Endhó reservoir, Mezquital Valley, Mexico

1. Introduction

Along human history the release of pollutants into the environment has increased at different rates, with a marked increase from the Industrial Revolution onwards. Several periods in the last centuries were characterized by the release of a particular class of pollutants. For example, during the last part of the nineteenth century a dramatic increase in the hydrocarbons and heavy metals emission took place. Then in the middle of the twentieth century the usage of synthetic fertilizers and pesticides had a boom as part of the Green Revolution, resulting in the emissions of those compounds in the environment. In an attempt to reduce the negative impact of these pollutants on the environment, several regulations have been implemented by the governments. In the last decades, research has focused on the so-called emerging pollutants, which are chemicals without regulatory status and for which impacts on the environment and human health are poorly understood (Deblonde et al., 2011). In the last decades, medicine experienced an important advancement with the development of many novel synthetic antibiotics (Coates and Hu, 2007), but as their environmental effects, behaviour and fate are not well known yet, they are considered emerging pollutants too.

Sediment records can offer valuable information about environmental conditions in the past (Xiang et al., 2013), major environmental events and natural disasters (Miller et al., 2013; Bruins et al., 2008) and human activities, either from ancient civilizations (Binford et al., 1997) or from recent times (Turner and Rabalais, 2003). Geochronological investigations on aquatic sediment archives provide insights into the initial appearance of a contamination and its subsequent behaviour (Heim and Schwarzbauer, 2013). With the appropriate additional information, e.g. usage rates of compounds and input sources, it is possible to expand the knowledge of historical contamination.

In some cases the sediment records allow the reconstruction of pollutant emissions for very long periods. A nice example is the reconstruction of lead emissions to the atmosphere in northern Europe for the last 3000 years from analyses of sediment cores from lakes in Sweden (Brännvall et al. 1999). Historical reconstruction of recent emissions using sediment cores is also possible, like the case of the

contamination of a San Francisco Bay marina with trace metals, petroleum hydrocarbons and radionuclides derived from industrial wastewater discharges (Love et al., 2003).

Regarding pharmaceuticals, sorption to particles and the subsequent sedimentation, where sediments act as a bank or sink (Acuña et al., 2015; Arias-Andrés et al., 2014; Hu et al., 2012), also provide a data basis for reconstructing pharmaceutical inputs into environment, if not even for detecting older pools of antibiotic-resistance genes (Devarajan et al., 2015). Ciprofloxacin was found frequently and in high concentrations in sediments of three major rivers in China, in contrast to sulfonamides, which were only found in low frequencies and small concentrations (Zhou et al., 2011). Generally speaking, sediments are a sink of tetracyclines and fluoroquinolones due to their strong sorption to solid particles. Sulfamethoxazole persisted in sediments from the Seine River for more than 30 to 40 years (Tamtam et al., 2011a). All these studies highlight the value of sediment analysis as an archive of environmental pollution and also the potential of sediments as long-term source of pollutants (Tamtam et al., 2011b). In the case of Mezquital Valley, pharmaceuticals have accumulated in soils in the range of several $\mu g\ kg^{-1}$ (Dalkmann et al., 2012), but little is known about their accumulation in sediments of the Endhó reservoir, were untreated wastewater from Mexico City is stored for the dry season before it is distributed to the crop fields. Here the suspended particles had the chance to settle, offering a storage pool and at the same time a potential record of the historical input of antibiotics from Mexico City to the Mezquital Valley. As the Atotonilco wastewater treatment plant will start soon delivering treated wastewater to the reservoir, the risk of a release of pharmaceuticals from sediments is plausible.

A better knowledge regarding the accumulation and historical input of pharmaceuticals in the Mezquital Valley wastewater irrigation system is therefore crucial for the assessment of the long-term risk of contamination. We performed analyses of a sediment core from the Endhó reservoir to compare the role of the two kind substrates -soil and sediment- as sink of pharmaceuticals in the environment. We hypothesized that:

i) Due to the sorption of pharmaceuticals they bind to solid particles in wastewater, settle, and accumulate in the sediments of the Endhó reservoir,

ii) as the Endho reservoir has received wastewater since 1972, the sediments contain a record of the input of pharmaceuticals into the crop fields from Mexico City for the last forty years, and therefore

iii) with the appropriate analyses and dating techniques of a sediment core from this reservoir it is possible to reconstruct the historical input of pharmaceuticals from Mexico City to Mezquital Valley.

2. Materials and Methods

2.1 Sediments

We took an 86-cm core from the sediments of the Endhó reservoir, Mezquital Valley in May 2013. The entire core was transported to the laboratory and segmented in 1-cm thick slices, which were freeze-dried and kept at -21 °C until the analyses.

2.2 Analyses of pharmaceuticals

Pharmaceuticals were extracted from sediment samples by Accelerated Solvent Extraction as described on section II-2.1. These extracts were cleaned by Solid Phase Extraction as described in section II-2.2 before measuring the pharmaceuticals concentration by LC-MS/MS (section II-2.3)

2.3 Analyses of heavy metals

Metals were quantified by X-ray fluorescence as described in section II-2.5

2.4 Measurement radionuclides´ activity

The activity of the isotopes ^{137}Cs, ^{214}Pb, ^{212}Pb, ^{210}Pb, ^{214}Bi, ^{235}U, ^{208}Tl and ^{40}K was measured by gamma-ray spectroscopy. The gamma radiation of 15 grams of sample was measured for 48 hours with the gamma spectrometer.

2.5 Sediment dating

The technique used for the sediment core dating was based on the ^{210}Pb radioisotope. One of the daughter radioisotopes of ^{238}U is ^{226}Ra, with a half-life of 1600 years. Soils and rocks contain ^{226}Ra, which decays to ^{222}Rn (half-life of 3.8 days), an inert gas. A fraction of the gas escapes to the atmosphere, where it decays to ^{210}Pb through a series of short-lived daughters. The particulate ^{210}Pb returns to the ground or water surface, usually washed in by rainfall or by dry deposition. The fraction of ^{210}Pb that reaches a water body sorbs usually to suspended particles and settles in the sediments. Once there, it decays to ^{210}Bi ($t_{1/2}$= 5 days) and it to ^{210}Po ($t_{1/2}$= 138 days), which yields the stable isotope ^{206}Pb.The vertical distribution in the sediments of ^{210}Pb coming from the atmosphere, commonly termed unsupported ^{210}Pb, can be used to determine the age of the sediments.

The sediments contain also a fraction of ^{210}Pb that is produced by the in-situ decay of ^{226}Ra. This ^{210}Pb is known as supported ^{210}Pb and must be differentiated from the unsupported ^{210}Pb. This can be done measuring the total ^{210}Pb activity, and then subtracting the activity of the supported ^{210}Pb. As the supported ^{210}Pb is considered being in equilibrium with ^{226}Ra, its activity can be measured indirectly through the daughters ^{214}Pb and ^{214}Bi. The unsupported ^{210}Pb activity and the sedimentation rate are related by means of the following equations according to the Constant Flux Constant Sedimentation Rate model (CF:CS):

$$A_x = A_0 e^{-bx} \quad \text{(IV-1)}$$

$$v = \frac{\lambda}{b} \quad \text{(IV-2)}$$

where A_x is the unsupported ^{210}Pb activity at depth x [Bq kg^{-1} d.m.], A_0 is the activity of the unsupported ^{210}Pb in the surface layer [Bq kg^{-1} d.m.], b is the slope from the regression fitted with the data, x is the depth [cm], v is the sedimentation rate [cm year^{-1}] and λ is the ^{210}Pb radioactive decay constant (0.03114 year^{-1}).

3. Results

3.1 Radionuclide activities

Figure IV-1 shows the activity of the unsupported ^{210}Pb as a function of the depth. This activity is not measured directly, but calculated from the difference between the activities of the total ^{210}Pb and ^{214}Pb. In the case of the studied sediments, this difference was not very large, but large enough to calculate the activity of the unsupported ^{210}Pb. Although relatively large uncertainties arose from this situation, a trend can be noticed in the profile. The activity of unsupported ^{210}Pb decreased from the upper layers of sediment to the bottom of the core. The solid line represents the adjusted model (Equation IV-1) for the unsupported ^{210}Pb activity along the profile, from which we got a sedimentation rate of 2.19 cm year^{-1}. With this rate and considering that the core was sampled on May 2013, a correspondence between the depth and the year was established, with the bottom of the core dating at 1974.

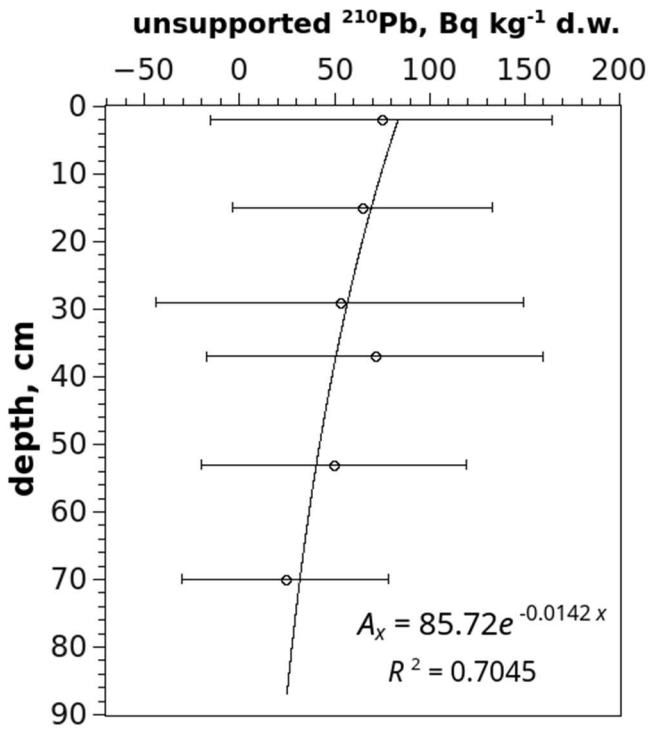


Figure IV-1. Profile of the unsupported ^{210}Pb activity in the sediment core (the horizontal bars represent the standard error)

3.2 Total lead content

The content of total lead in the core samples showed a large variability with depth, probably because of variations in the inputs of Pb with Mexico City wastewater during the rainy season and the dry season over time. Despite these large variations a trend could still be recognized. While at larger depths than 50 cm (older sediments) the concentrations oscillated in the range of 71.11 – 442.09 mg kg^{-1} (dry mass), from 45 cm to the top of the sediments total Pb content tends to diminish clearly, showing variations within a narrower range of 20.33 to 195.21 mg kg^{-1} (dry mass) (Figure IV-2).

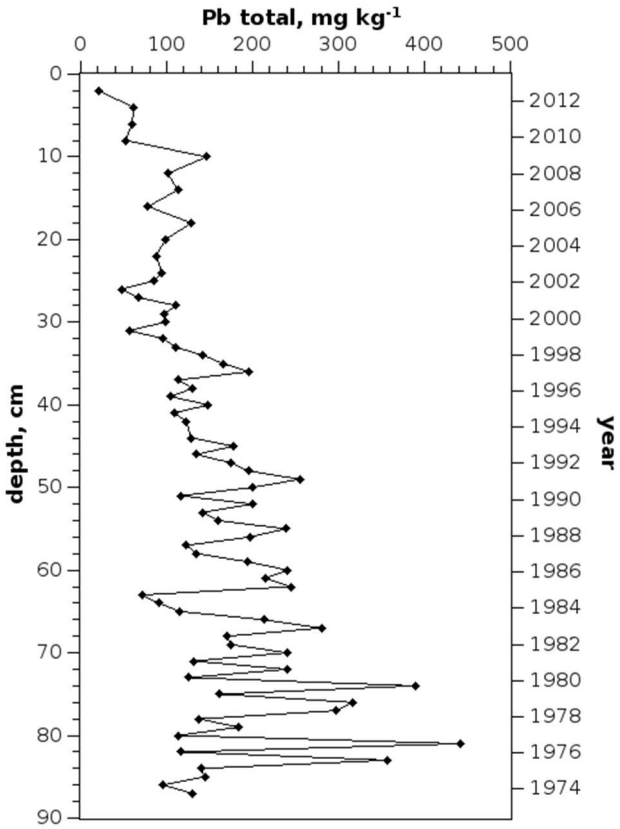


Figure IV-2. Depth profile of total lead (dry mass) in the sediment core from the Endhó reservoir with the corresponding chronology based on the ^{210}Pb method

3.3 Concentrations of pharmaceuticals in the sediment

From the nine pharmaceuticals we analysed, clarithromycin, naproxen and sulfamethoxazole were not detected in the sediment column, diclofenac was found in large quantities (up to 250 µg kg^{-1}) and the rest of the pharmaceuticals were found in the order of few µg kg^{-1} (Table B-2). For most of the

compounds there was not a clear trend of the concentration as a function of depth, but for bezafibrate, ciprofloxacin and trimethoprim larger concentrations were found close to the surface, showing a decrease with increasing depth (Figure IV-3).

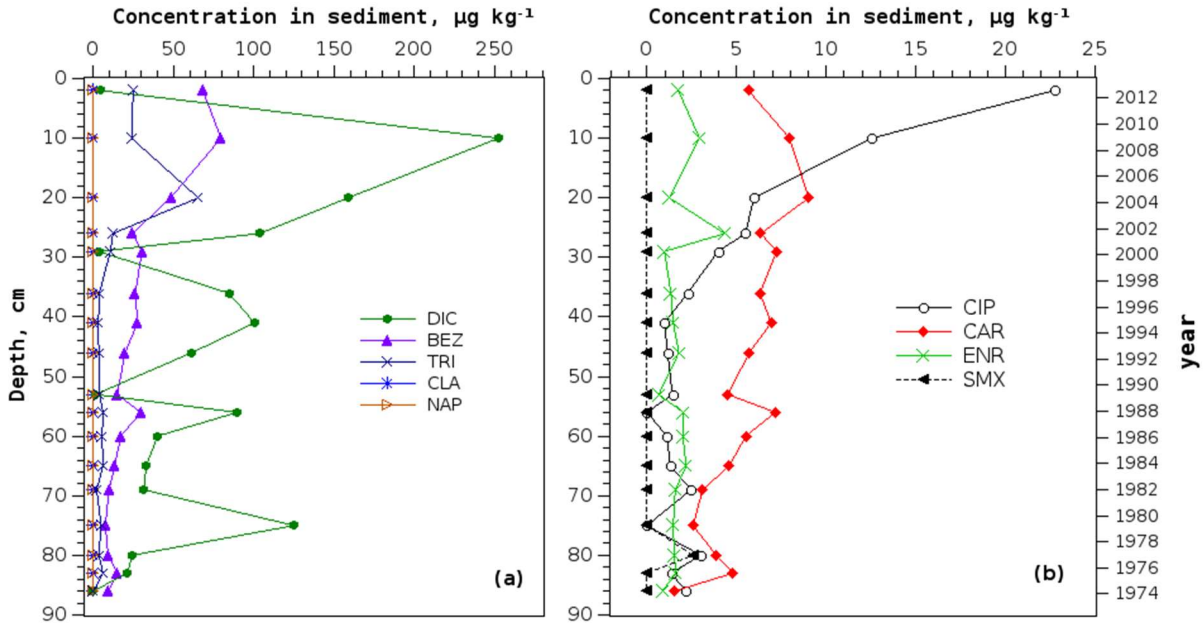


Figure IV-3. Concentration of pharmaceuticals in the sediment profile (dry mass). a) DIC – diclofenac; BEZ – bezafibrate; TRI – trimethoprim; CLA – clarithromycin; NAP – naproxen. b) CIP – ciprofloxacin; CAR – carbamazepine; ENR – enrofloxacin; SMX – sulfamethoxazole. The chronology is based on the ^{210}Pb-dating method

Figure IV-3b shows in an amplified scale the concentrations of ciprofloxacin, carbamazepine, enrofloxacin and sulfamethoxazole in sediments as a function of depth. With the exception of the point at 80 cm, sulfamethoxazole was not detected in sediments. Ciprofloxacin shows the highest concentrations close to the surface -with a maximum of 22.72 µg kg^{-1}- and a clear trend of decreasing concentrations as the depth increases.

4. Discussion

4.1 Dating of the sediment core

The activity of the supported ^{210}Pb was estimated indirectly from the activity of a gamma emitter among the ^{238}U daughters, which was subtracted from the activity of the total ^{210}Pb in sediments to estimate the activity of unsupported ^{210}Pb. In our case, the activities of the ^{238}U-daughter isotopes

^{214}Pb and ^{214}Bi showed atypically high values, in some cases with ^{214}Bi activities exceeding those of total ^{210}Pb. This hampered the calculation of the activity of unsupported ^{210}Pb using the ^{214}Bi activities, as we would get negative values. Therefore, only the values of ^{214}Pb were used for the unsupported ^{210}Pb calculations. Although they were also high, a regression of the ln ^{210}Pb as function of the depth could be fitted (Figure IV-1). The small differences between the activities of the two lead isotopes, and the act that the excess ^{210}Pb was calculated by subtracting only the ^{214}Pb activity increased the uncertainty of estimated unsupported ^{210}Pb, its depth distribution and sedimentation rates.

Atypically high activities of the radionuclides from the ^{238}U series can arise from an additional input of the isotopes, which interferes with the assumptions underlying ^{210}Pb-dating methods, i.e. a secular equilibrium between ^{210}Pb and ^{226}Ra, which typically comes from local soil and bedrock particles transported mainly to the water body by colluviation and alluviation (Brenner et al., 2004). This extra input of nuclides can be anthropogenic, as found in a marina in San Francisco, USA, where high activities of ^{226}Ra and its daughter nuclides obscured the excess ^{210}Pb values, making the dating of a sediment core difficult (Love et al., 2003). The source of the additional ^{226}Ra in the San Francisco Bay was presumably a painting facility, where luminescent painting operations during the World War II took place.

However, additional inputs of radionuclides that interfere with the ^{210}Pb dating come sometimes from natural sources, as Brenner et al. (2004) discussed for some lakes in Florida, USA. In the middle of the 60s the lakes began receiving groundwater supplements from a deep aquifer to maintain their water levels. As the geologic deposits in the area contained carbonate fluorapatite rich in ^{238}U, it was highly probable that additional ^{226}Ra was introduced into the lakes with the groundwater. The radium adsorbed rapidly to suspended particles and settled in the lake, explaining the observed high activity of this radionuclide in sediment. In Mexico City, drinking water has been a scarce resource and approximately 70% of the water the city consumes comes from aquifers, some of them with a depth of hundreds of meters (Ortega-Guerrero et al., 1997; Birkle et al., 1998). It is well possible that this

deep groundwater also contains elevated levels of radionuclides that obscure the use of depth profiles of ^{210}Pb for dating the sediment cores.

4.2 Total lead content in sediments

Total lead content shows large variations through the whole profile of sediments, but the range in which they oscillate is wider and located at larger concentrations in the lower half of the sediment core (Figure IV-2). From 45 cm to the top of the core a decreasing trend in the total lead content can be recognized. At the beginning of the 1990s lead-free gasoline was introduced in Mexico and then in 1998 leaded gasoline was completely banned and withdrawn from the market (Gleeson Hanna and Jiménez García, 2008). The reduction of the amplitude of total Pb concentrations and decreasing average concentrations might well reflect a reduction in the total input of lead from Mexico City from the 1990s to the present, which is in good agreement with the dating of the sediments by the ^{210}Pb method described above.

4.3 Accumulation of pharmaceuticals in sediment

The analysed pharmaceuticals showed a different behaviour in sediments of the Endhó reservoir (Figure IV-3a), based on their differing chemical properties. Clarithromycin, sulfamethoxazole and naproxen are absent in the sediment, other show a more or less constant concentration along the profile (carbamazepine and enrofloxacin) and others show a trend of decreasing concentrations with increasing depths (ciprofloxacin, trimethoprim and bezafibrate). Based on the calculated average sedimentation rate (2.19 cm $year^{-1}$), the average density of the sediments along the profile, and the dimensions of the core sampler, it was possible to calculate a deposition rate for each pharmaceutical for the recent years i.e., taking into account the concentration in the upper centimetres of sediment (Table IV-1). Diclofenac shows the highest input rate into the sediments with more than 2 mg per square meter of sediment per year. The deposition rate of bezafibrate, trimethoprim and ciprofloxacin are in the range of hundreds of µg m^{-2} $year^{-1}$ and those for carbamazepine and enrofloxacin below 100 µg m^{-2} $year^{-1}$.

Dalkmann et al. (2012) performed a survey of a variety of pharmaceuticals in soils from crop fields that are irrigated with wastewater from the Endhó reservoir. A comparison between the content of pharmaceuticals in both matrices offers an interesting picture (Table IV-1). Generally speaking, concentrations of pharmaceuticals in the sediment are higher or much higher than in soils, even 118 and 630 times higher (bezafibrate and diclofenac, respectively). As wastewater is stored in the Endhó reservoir before being distributed among the crop fields, our findings suggest that a considerable fraction of the pharmaceuticals transported by wastewater from Mexico City sorbs to suspended particles and settle in the Endhó reservoir, supporting the postulate that sediments are a sink for pharmaceuticals (Acuña et al., 2015; Arias-Andrés et al., 2014; Hu et al., 2012). This would imply that sediments are also a potential source of such compounds if the conditions are favourable for desorption processes, like a change in the water quality after treatment (see chapter V), as some pharmaceuticals seem to be stable enough in sediments of the Endhó reservoir.

Table IV-1. Deposition rate of pharmaceuticals in the Endhó reservoir and comparison of the their concentrations in sediments and in wastewater-irrigated soils from Mezquital Valley

Pharmaceutical	Deposition rate in sediment $\mu g\ m^{-2}\ year^{-1}$	Maximum concentration found $\mu g\ kg^{-1}$		Factor of enrichment in sediment compared to soil
		Sediment	Soil[a]	
Diclofenac	2 244.61	252.18	0.40	630
Bezafibrate	854.39	79.48	0.67	118
Trimethoprim	496.59	65.33	2.40	27.2
Ciprofloxacin	179.75	22.72	2.82	8.1
Carbamazepine	98.77	9.03	6.96	1.3
Enrofloxacin	25.77	4.34	0.64	6.8
Clarithromycin	---	n.d.	3.89	---
Naproxen	---	n.d.	2.86	---
Sulfamethoxazole	---	n.d.	2.40	---

n.d.=not detected
[a] from Dalkmann et al., 2012.

Clarithromycin, naproxen and sulfamethoxazole were not detected in sediments, but they were found in soils (Table IV-1). This suggests either that they were not transported by suspended particles to the bottom of the reservoir or that they went through a dissipation process in the water column or in the sediments. In contrast to the soils, sediments are permanently under anaerobic conditions, which play a major role in the dissipation of the pharmaceuticals (Radke and Maier, 2014). The decreasing concentrations of ciprofloxacin, trimethoprim and bezafibrate with increasing depths might also reflect a dissipation of the pharmaceuticals under anaerobic conditions.

Figure IV-3b show the profile of sulfamethoxazole and ciprofloxacin in the sediment core in an amplified scale. These two antibiotics were selected as representatives of the sulphonamide and the fluoroquinolone families respectively and were used for sorption and desorption experiments in the present work (see chapters III and V), so their behaviour will be discussed in more detail. Sulfamethoxazole was not detected in the sediment core except at a depth of 80 cm. This sulphonamide tends to sorb to solid particles, especially if they are rich in organic matter (Leal et al., 2013), so it is expected to sorb to the suspended particles in wastewater and settle together with the sediments, as sediments in the Endhó reservoir have a large organic matter content (C_{org} = 88 g kg^{-1}). Its absence in the core can be explained by a possible anaerobic degradation or transformation. Sulfamethoxazole was detected in larger frequencies and concentrations compared with other sulphonamides in a national survey in the USA (Kolpin et al., 2002), which reflects its persistence in sediments. Several studies regarding the degradability of sulfamethoxazole have been published, but they offer contradictory information about the most appropriated conditions for the transformation. Some studies suggest that aerobic conditions are needed for sulfamethoxazole´s degradation (Drilla et al., 2005; Xu et al., 2011), while others suggest that anoxic or anaerobic conditions are also favourable (Mohring et al., 2009; Narumiya et al., 2013). Long-term experiments of sulfamethoxazole degradation under different redox regimes showed that this antibiotic is more effectively degraded under aerobic conditions, but it is still degradable under anoxic or anaerobic conditions (Baumgarten et al. 2011). The authors argue that the poor biodegradability found in some studies relies on the long time needed for

a sufficient bacterial growth or microbial adaptation. The Endhó reservoir has received wastewater since 1972 and sulfamethoxazole was introduced into the market in the 1960s. Therefore, the microbial community in the sediments of the Endhó reservoir might had enough time to adapt to sulfamethoxazole, so the biodegradation of the antibiotic is feasible. Further degradation experiments with sediments from the reservoir would be needed to confirm this.

Sulphonamides were found in small concentrations and frequencies in sediments of several rivers in China, and sulfamethoxazole in particular was not detected at all (Zhou et al., 2011). In a 100-cm sediment core from the Seine River sulfamethoxazole was detected at small concentrations along the profile, with a maximum of approximately 16 µg kg^{-1} at a depth of 31 cm, which corresponds to the year 1988 (Tamtam et al., 2011a). Although the redox conditions and dynamics of sediments from a river and a reservoir can be substantially different, this offers a comparison of the behaviour of sulfamethoxazole in sediments.

Ciprofloxacin shows a different behaviour, with high concentrations at shallow depths and a trend to decrease in deeper sediments (Figure IV-3b). This trend can indicate an increase in the prescription of the antibiotic in recent time, which was developed and introduced into the market in the 1980s. The curve of the ciprofloxacin profile can be also due to a degradation of the antibiotic in sediments. In the upper more recent sediments the progress of the degradation process is not so advanced as in the older deeper sediments, so the concentrations are higher. Although ciprofloxacin is considered poorly degradable, Liu et al. (2013) found evidence of biotransformation of the antibiotic under denitrifying conditions. Nevertheless, they found no transformation under methanogenic conditions in agreement with a previous study (Golet et al., 2003), which are probably the dominant conditions in sediments of the Endhó reservoir, as the high input of organic matter from wastewater would deplete the oxidizing species. Trimethoprim and bezafibrate showed a similar decreasing pattern in sediments of the Endhó reservoir. The former was degraded almost completely (> 90%) during anaerobic digestion of sewage sludge (Narumiya et al., 2013) so we can consider the anaerobic degradation of the pharmaceuticals as plausible. A migration of ciprofloxacin from the upper part of sediments to deeper layers is unlikely, as

it is well known that it is strongly sorbed (Tolls, 2001). A similar pattern would be expected for other fluoroquinolones as enrofloxacin, nevertheless this antibiotic is of veterinary use and its concentration in sediments and soils from the Mezquital Valley are not as high as those of ciprofloxacin.

The concentrations of ciprofloxacin in sediments of the Endhó reservoir were in the range of 0.97 - 22.72 µg kg^{-1}, with the maximum at the top of the sediment core. This order of magnitude is in good agreement with other measurements of pharmaceutical in sediments in several rivers in China, where ciprofloxacin was found in high frequencies and in concentrations of some tens of µg kg^{-1} with a maximum concentration of 1290 µg kg^{-1} at the Hai River (Zhou et al., 2011).

5. Conclusions

With the exception of the not detected compounds, the concentration of the tested pharmaceuticals was higher in sediments of the Endhó reservoir than in the wastewater-irrigated soils by a factor up to 630 times. The Endhó reservoir serves therefore like a sink of pharmaceuticals before they reach the crop fields in the Mezquital Valley, which is advantageous as it prevents a larger input of pharmaceuticals to the soils, but at the same time it implies that sediments are a potential source of them if the compounds are stable enough to persist and if the conditions in the reservoir favour desorption processes, as a change in water quality could be. Naproxen, clarithromycin and sulfamethoxazole were not detected in sediments, presumably due to an anaerobic dissipation. Apparently other pharmaceuticals like ciprofloxacin, trimethoprim and bezafibrate go also through a dissipation process in sediments of the Endhó reservoir but at a lower rate, as they were detected in larger concentrations in the upper sediments. The reconstruction of the historical input of pharmaceuticals to Mezquital Valley´s soils from Mexico City turned out difficult because of the possible degradation of the pharmaceuticals and the unexpected high activities of supported ^{210}Pb in the sediments.

V. Desorption of sulfamethoxazole and ciprofloxacin from long-term wastewater-irrigated soils of the Mezquital Valley as affected by water quality

Modified on the basis of:
Carrillo M, Braun GC, Siebe C, Amelung W, Siemens J (2016) Journal of Soils and Sediments 16:966-975

1. Introduction

Due to the health risks that wastewater-irrigation represents for farmers and final consumers, an appropriate treatment of municipal wastewater is recommended before using it for growing crops (FAO, 1992). Although conventional wastewater treatment removes an important fraction of the pollutants and pathogen agents, the removal efficiency of some contaminants like antibiotics is not always satisfactory (Deblonde et al., 2011).

Soils that have received constantly wastewater for long periods of time can accumulate contaminants through sorption processes, becoming potential sources of those pollutants. The sorbed compounds could be released as consequence of a change in the water quality the fields receive or can be also facilitated by other agents like dissolved organic matter or surfactants, which are commonly present in municipal wastewater. Due to their amphiphilic properties, surfactants can interact with hydrophobic organic compounds and polar solvents as well, which can enhance the mobility of some organic pollutants, like it has been reported for pesticides (Cserháti et al., 2002), polycyclic aromatic hydrocarbons (Jones-Hughes and Turner, 2005) and phenolic compounds (Gao et al., 2012). Little is known however, about such effect over pharmaceuticals.

Mezquital Valley has used since more than 100 years the untreated wastewater from Mexico City Metropolitan Area to grow alfalfa, maize and beans among other crops. Part of the wastewater coming from Mexico City is directed to the Endhó reservoir, where it is stored to ensure water availability during the dry season. This serves unintentionally as a primary wastewater treatment, where the suspended particles settle down. The sediments of the reservoir might have in consequence a fraction of sorbed pollutants and could be also a potential source of them.

A few years ago a wastewater treatment plant was built to treat approximately 65% of the wastewater from Mexico City before it reaches the fields. This will change markedly the properties of the soil solution from the irrigated fields. The sorption equilibria might be therefore affected, leading to an unknown dynamic of the pharmaceuticals.

To have a better understanding of such consequences we performed desorption batch experiments with three soils from Mezquital Valley and one sediment from the Endhó reservoir exposing them to water of different qualities. We hypothesized that:

(i) the smaller concentrations of pharmaceuticals in treated wastewater compared to untreated wastewater promote the desorption of antibiotics,

(ii) anionic surfactants enhance desorption of pharmaceuticals because of competition for sorption sites and their solubilizing effect and

(iii) the overall desorption process can be subdivided into an instantaneous and a kinetic rate-limited process.

2. Materials and Methods

2.1 Soils

We used a surface sediment sample and three soil types, namely a Vertisol, a Leptosol and a Phaeozem for the desorption experiments. They were collected as described in Section II-1.2 and their properties are described in Table V-1.

Table V-1. Properties of the tested soils and sediment

Substrate	Irrigation period	pH ($CaCl_2$)	Clay content	Organic carbon	Fe oxides [c]
	years		g kg^{-1}	g kg^{-1}	g kg^{-1}
Phaeozem	99	6.76	226 [a]	20.7 [b]	1.41
Vertisol	85	7.37	435 [a]	23.0 [b]	1.50
Leptosol	85	6.82	316 [a]	20.0 [b]	0.68
Sediment	42	7.48	175	88.0	---

[a] From Siebe (1994)
[b] From Dalkmann et al. (2012)
[c] Oxalate extractable, from Siebe (1994)

2.2 Chemicals

Ciprofloxacin (CIP) and sulfamethoxazole (SMX) were our model antibiotics. Their structures and some chemical properties are summarized in Table III-2. We selected sodium dodecyl benzenesulfonate as

model surfactant because it is used widely in household cleaning products. It was purchased from Tokyo Chemical Industries (TCI, Eschborn, Germany).

2.3 Extraction solutions

The sediment and soil were extracted with tree different solutions: *i*) artificial wastewater prepared in the laboratory with inorganic salts, *ii*) artificial wastewater spiked with linear alkylbenzene sulfonate (100 µg L^{-1}) and *iii*) treated wastewater (effluent) from a treatment plant located in Mexico City. For a detailed composition of the artificial wastewater see Table A-4 from Appendix A.

The treated wastewater was collected from the treatment plant *Cerro de la Estrella*, located in Mexico City on May 2014. The plant receives municipal wastewater from the metropolis and after a tertiary treatment it is used to recharge the Xochimilco lakes located in the southern part of the city. We considered this a good model to emulate the water the fields in Mezquital Valley will receive in the near future when the Atotonilco wastewater treatment plant starts operating. After sampling the wastewater it was transported to the laboratory in a cooling box (approx. 4 °C) and then kept at -21 °C until required for the experiments.

2.4 Desorption batch experiments

The experiments were performed in triplicate. The batch desorption experiments were conducted according to the OECD Guideline 106 for the testing of chemicals' adsorption/ desorption (OECD 2000). We chose a soil/solution ratio of 1:5 (m/m) and performed a sequential extraction of five steps within a total period of 336 h.

Before adding 25 mL of the corresponding extracting solution the solid samples were sterilized with an autoclave (121 °C, 20 min) in the centrifugation tubes to minimize microbial activity. This was necessary to prevent LAS degradation. The mixture was shaken with an overhead shaker for the defined time for the corresponding extraction step, namely 24, 48, 72, 144, and 336 h. Subsequently, we separated supernatant and solids by centrifugation (2500×g, 40 min). The liquid phase was decanted for further

analysis and replaced with enough fresh extracting solution in order to have again 25 mL of liquid phase for the following extraction step. The tubes were weighted before and after each extraction step to quantify the amount of added or withdrawn liquid.

2.5 Desorption kinetics

We used the following model to describe the desorption kinetics of the antibiotics desorption:

$$d[Y_e]_{total}/_{dt} = Y_o + (Y_e - Y_o)(1 - e^{-kt}) \quad \text{(V-1)}$$

where t is the elapsed time since the solid and liquid phases got in contact (h); Y_o is the amount of instantly desorbed antibiotic at an infinitesimal time, which can be read as the point of intersection with the y-axis (µg kg^{-1}); Y_e is the total desorbable fraction at an infinite time (µg kg^{-1}); and $(Y_e - Y_o)$ is the amount of pharmaceutical desorbed via a rate-limited process with a rate constant k (h^{-1}). The cumulative amounts of desorbed antibiotic in the subsequent extraction steps were used to plot them as a function of time and fitting them to equation (V-1) using SigmaPlot version 11.0 (Systat Inc.).

3. Results

3.1 SMX desorption as affected by water quality

Artificial wastewater with and without the anionic surfactant extracted a total of 1115–2004 ng SMX kg^{-1} from the three soils after the five desorption steps (Fig. V-1). The content of SMX extracted during each extraction step from soils with these extractants was always relatively low (<1000 ng kg^{-1}), and there was no clear difference in the total amount of SMX extracted with or without surfactant, except for the Phaeozem (Fig. V-1a).We observed no SMX desorption from the sediment with these extractants, because sediment did not contain significant amounts of SMX (Table V-1). With the treated wastewater as extractant, a net sorption, indicated as “negative desorption” in Fig. 1, was observed during some extraction steps, particularly for the Vertisol and the sediment sample. For all samples, we observed a net sorption of SMX during the second extraction step (Fig. V-1a, b, c). From the third extraction onward, the behaviour was different for the four substrates: we observed a net

desorption from the three soils at least at one step, but not from the sediment. For the Phaeozem, we found a steady increase in the amount of desorbed SMX from the third step onward. For the Leptosol and Vertisol, we saw an increase at the third step followed by an irregular pattern by the last two steps. The sediment showed a different trend: we observed for every extraction step a SMX sorption from treated wastewater.

Table V-2. Content of ciprofloxacin (CIP) and sulfamethoxazole (SMX) in the tested substrates

Substrate	ASE-extractable ciprofloxacin	ASE-extractable sulfamethoxazole	Fraction of sulfamethoxazole extracted (%)		
	µg kg^{-1}	µg kg^{-1}	w/ artificial wastewater	w/ LAS-spiked artificial wastewater	w/ treated wastewater
Phaeozem	1.51 ± 0.44 [a]	5.30 ± 1.19 [a]	21	38	98
Vertisol	1.54 ± 0.58 [a]	5.00 ± 0.97 [a]	40	32	36
Leptosol	1.62 ± 1.15 [a]	4.62 ± 0.80 [a]	39	40	91
Sediment	13.33 ± 8.18	n.d.	n.d.	n.d.	n.d.

n.d. not detected

[a] From Dalkmann et al. (2012)

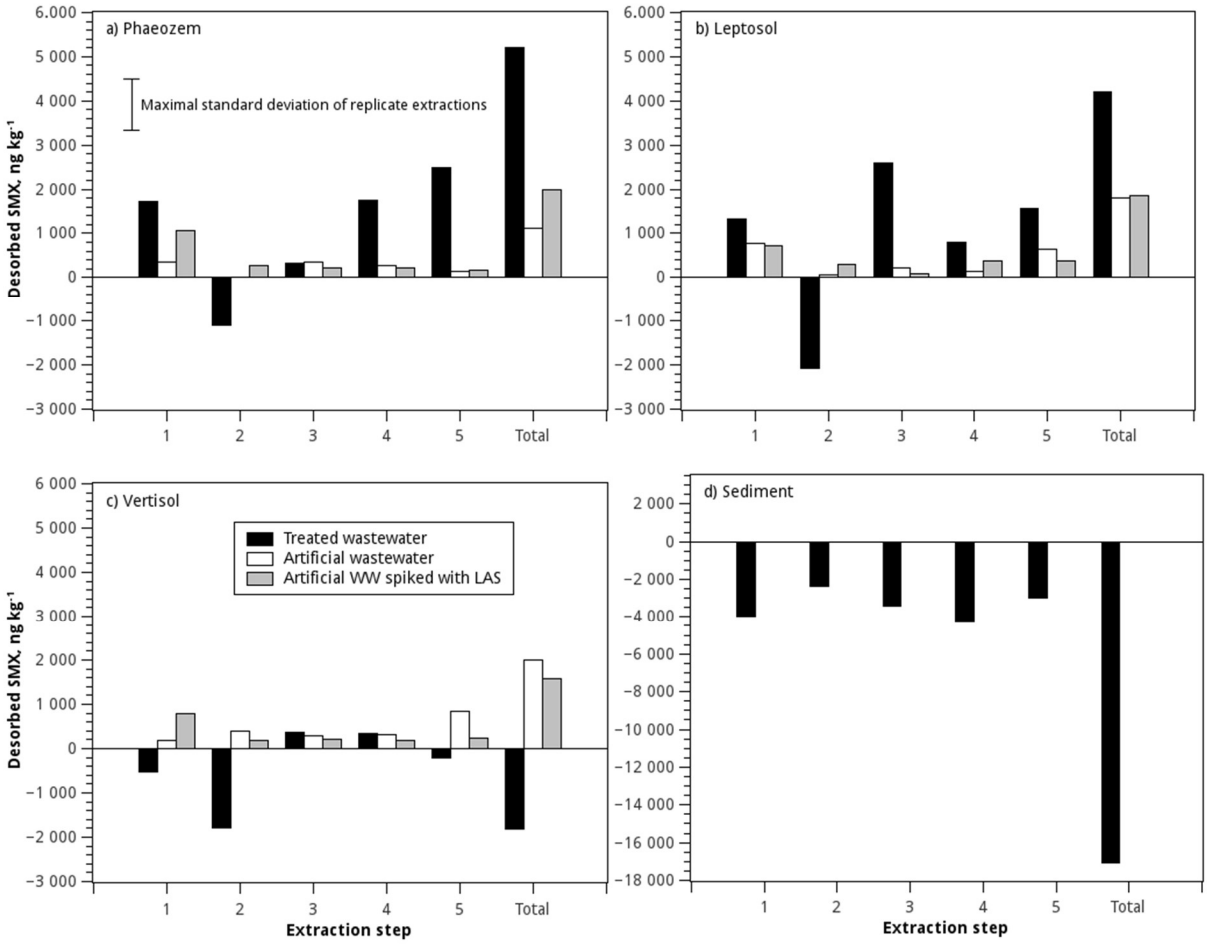


Figure V-1. Desorption of sulfamethoxazole at each extraction step and total extracted amount from (a) Phaeozem, (b) Leptosol, (c) Vertisol and (d) sediment. Negative desorption values correspond to a net sorption

In the two cases for which we observed a net desorption of SMX from the soil with treated wastewater (Phaeozem and Leptosol), this liquid phase extracted around two times more SMX than artificial wastewater, regardless of the presence of the surfactant. Interestingly, the total amount of SMX desorbed from these two soils with treated wastewater after the five desorption steps corresponds to more than 90% of the tightly bound fraction, determined previously (Dalkmann et al. 2012) by accelerated solvent extraction (Table V-1).

3.2 CIP desorption as affected by water quality

Only small amounts of CIP were desorbed from soils or sediment with artificial wastewater, regardless of the presence or absence of the anionic surfactant, although previous studies demonstrated the presence of sorbed CIP on these soils (Table V-1; Dalkmann et al. 2012). Therefore, the bars corresponding to these two extractants are virtually absent in Fig. V-2. When using treated wastewater with a CIP concentration of 3.475 µg L^{-1} for the extractions, we found for all samples even an almost complete sorption of CIP. However, with each additional extraction step, the sorbed amount of CIP decreased slightly.

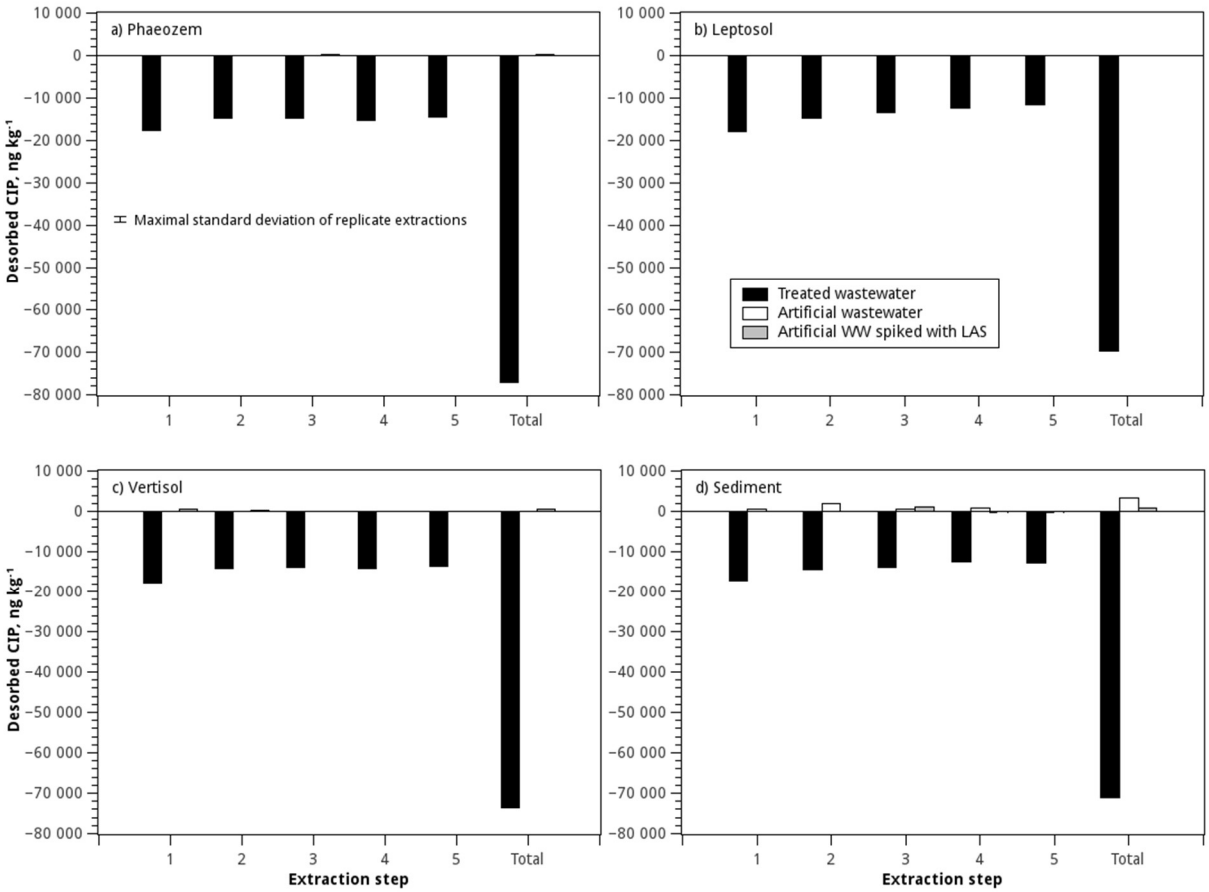


Figure V-2. Desorption of ciprofloxacin at each extraction step and total extracted amount from (a) Phaeozem, (b) Leptosol, (c) Vertisol and (d) sediment. Negative desorption values correspond to a net sorption

3.3 Desorption kinetics

We used Eq. (V-1) to describe the desorption kinetics of the pharmaceuticals from soil and sediments, but this was not feasible for some cases. As CIP was not significantly desorbed from the soils but quantitatively sorbed to the sediment, an analysis of its desorption kinetics was not possible. An analysis of the SMX desorption kinetics from the sediment sample was also not possible as no SMX was present in the sediment. The net sorption of SMX from treated wastewater hampered the interpretation of the desorption kinetics in contact with this extractant. Nevertheless, Fig. V-3 nicely illustrated the transient reduction of SMX desorption. Desorption of SMX into artificial wastewater with or without surfactant could be well described with the biphasic desorption model (Eq. V-1, Fig. V-3).

Table V-3. Kinetic parameters for sulfamethoxazole desorption from the studied soils

Parameter	Desorption solution	Phaeozem	Vertisol	Leptosol
Y_o	Artificial WW	0.0056 ± 0.2372	n.d.	0.6886 ± 0.0891
µg kg^{-1}	LAS-spiked artificial WW	0.6754 ± 0.0753	0.5362 ± 0.0801	0.5007 ± 0.0949
Y_e	Artificial WW	1.1611 ± 0.1548	2.4365 ± 0.5211	1.8952 ± 9.8703
µg kg^{-1}	LAS-spiked artificial WW	1.9798 ± 0.0312	1.6013 ± 0.0499	1.9398 ± 0.1013
k	Artificial WW	0.0111 ± 0.0056	0.0050 ± 0.0027	0.0008 ± 0.0023
h^{-1}	LAS-spiked artificial WW	0.0150 ± 0.0017	0.0115 ± 0.0021	0.0082 ± 0.0018

n.d. not detected

The instantaneous SMX desorption from the Phaeozem and Vertisol sample into artificial wastewater without surfactant was close to zero (Table V-3). Regarding to the effect of the anionic surfactant on this first instantaneous desorption phase, we found a greater desorption of SMX from Phaeozem and Vertisol compared with the extraction without surfactant (Fig. V-3). Rate constants for the kinetic desorption of SMX decreased in the order Phaeozem > Vertisol > Leptosol, regardless of the presence of surfactant. Remarkably, the desorption rate constant we estimated for the extraction with surfactant was always higher than the rate constant for the extraction without surfactant.

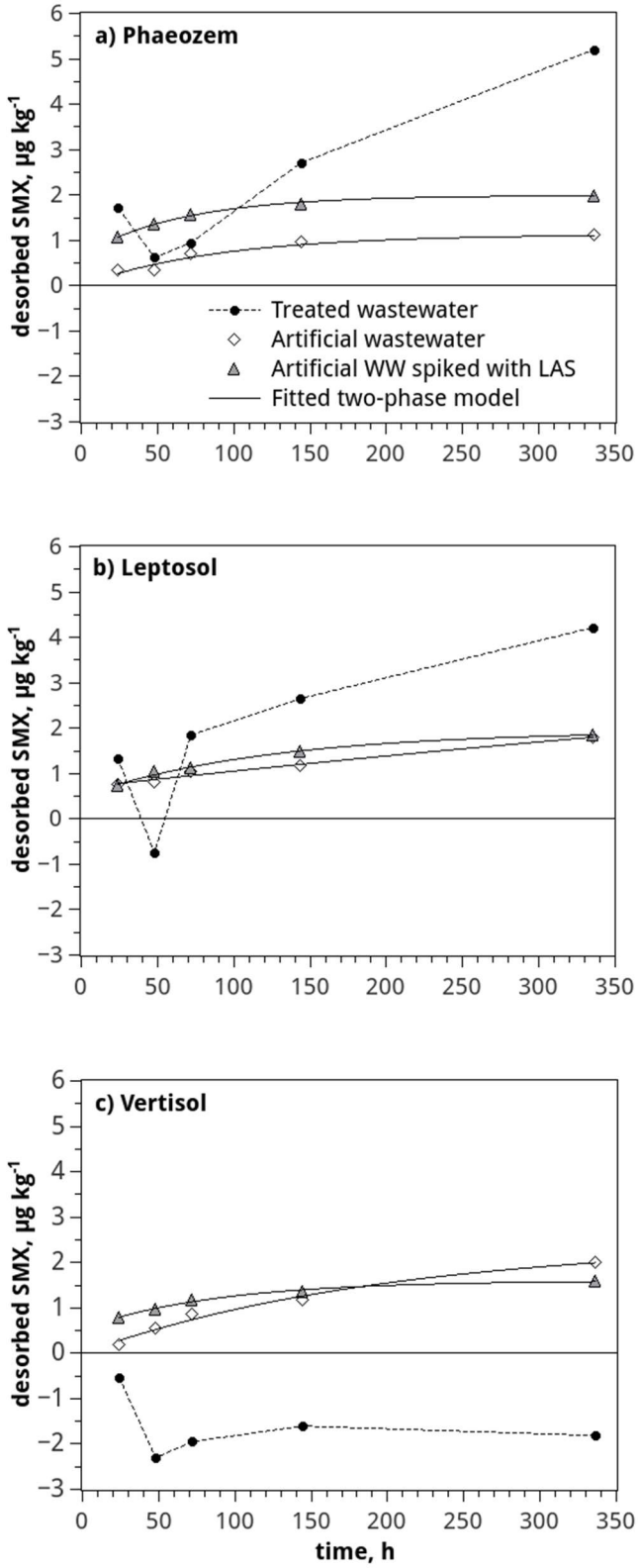


Figure V-3. Cumulative desorbed sulfamethoxazole as a function of time. The solid lines represent the fit of the experimental data to the bi-phasic desorption model described by Equation V-1

4. Discussion

4.1 SMX desorption as affected by water quality

Despite long-term exposure to wastewater, we did not detect any SMX in sediment even with an accelerated solvent extraction, which accesses the tightly bound fraction. This was possibly due to the biodegradation of SMX by facultative anaerobic bacteria in lake sediment, as reported by Zhang et al. (2013). Therefore, no SMX was desorbed from sediment with artificial wastewater, either with or without surfactant. The treated wastewater used in our experiments contained 1.045 µg L^{-1} SMX and 3.475 µg L^{-1} CIP. During conventional wastewater treatment, many organic compounds are degraded but some emerging contaminants like pharmaceuticals can persist (Hirsch et al. 1999). Considerable concentrations of sulfamethoxazole (Carballa et al. 2004) and ciprofloxacin (Lindberg et al. 2006) in the effluent of wastewater treatment plants after activated sludge treatment have also been reported in other studies; hence, there is doubt that the wastewater treatment in the Mezquital Valley will succeed in eliminating pharmaceutical loads completely. This is the reason why we observed a "negative desorption" when we used this extractant (Fig. V-1). Although pharmaceuticals have accumulated in soils in Mezquital Valley due to long-term wastewater irrigation (Dalkmann et al. 2012), they can still sorb SMX and CIP as Dalkmann et al. (2014b) observed in sorption batch experiments. The sorption degree of SMX was different in the soils and sediments, but at the second desorption step, we observed a net sorption to all the three soils (Fig. V-1a–c). This might be explained by a breakdown of soil aggregates during the first and second extraction steps, exposing new surfaces and sorption sites that were previously unavailable to the SMX-containing extractant. The sediment showed a very different behavior than the soils because (i) the sediment did not contain originally any SMX, as discussed above, and (ii) the sediment had a high OC content (Table V-1), promoting SMX sorption by hydrophobic interactions as suggested for SMX and other sulphonamides although the predominant SMX species at the pH of the experiments is the anionic form (Sukul et al. 2008; Zhang et al. 2010; Leal et al. 2013; Zheng et al. 2013). The neutral and cationic species of SMX did not play a significant role in our experiments as the pH of the soils and the sediment were always above the pKa_2

(Table V-2). Also, SMX sorption to the Vertisol was likely promoted by larger clay content and—in tendency—also higher organic matter content compared with the Leptosol and Phaeozem (Table V-1). Overall, the amount of desorbed or sorbed SMX was negatively related to the organic matter content of the soils and the sediment (Pearson $r=-0.96$, $p<0.05$), highlighting the importance of maintaining or even raising organic matter contents of irrigated soils in the Mezquital Valley after the implementation of wastewater treatment. A main difference between treated and artificial wastewater was the dissolved organic carbon concentration. While artificial wastewater was prepared only with inorganic salts and, in the case of the LAS-spiked solution, a low concentration of anionic surfactant (100 µg L^{-1} LAS; ~0.06 mg L^{-1} DOC), we measured a DOC concentration of 9.5 mg L^{-1} for the treated wastewater. Haham et al. (2012) reported a reduced sorption of the sulfonamide sulfapyridine to soils with low organic carbon contents when the liquid phase was enriched with dissolved organic carbon. They concluded that this effect might be caused by competition between sulfapyridine and dissolved organic carbon for binding sites or through direct interactions between the organic compound and the dissolved organic carbon. Additionally, Chefetz et al. (2008) suggested a competition of the anionic form of naproxen with dissolved organic matter for binding sites in the soil organic matter to explain the higher mobility of the pharmaceutical in topsoil from column experiments. A reduced sorption of sulphonamides was also observed when manure was applied to soil as it increased the DOM concentration (Thiele-Bruhn and Aust 2004). Based on these independent observations, we suggest that the combined effect of the competition between dissolved organic matter in treated wastewater and sulfamethoxazole for sorption sites, and the sorption of the sulphonamide by DOM reducing its activity and increasing its concentration in the liquid phase, promoted the desorption of sulfamethoxazole from the Phaeozem and Leptosol with lower clay and Fe oxide contents than the Vertisol and lower organic matter contents than the sediment in our experiments. This explains why treated wastewater extracted around two times more SMX than artificial wastewater, regardless of the presence of the surfactant.

4.2 CIP desorption as affected by water quality

Due to the strong sorption of CIP in soils (Dalkmann et al. 2014b), we observed only small amounts of desorbed CIP with artificial wastewater, with or without surfactant. As artificial wastewater did not contain any CIP, no sorption from these solutions was possible. This high affinity of CIP for soils also led to an almost complete sorption on the solid phases from treated wastewater. Given the CIP concentration in wastewater and the volume used in the experiments, a maximum of approximately 75 000 ng kg^{-1} of CIP could be sorbed after the five extraction steps (assuming a complete sorption). Figure 2 shows that all samples sorbed approximately 70 000 ng kg^{-1} of CIP, reflecting the strong binding of CIP to soils and sediments. According to a kinetic study (Dalkmann et al. 2014b), CIP is sorbed mainly to negatively charged clay minerals via a cation exchange mechanism in soils with pH values in the range of 7.1–7.5. This process could be enhanced at smaller pH values, as CIP would be present mainly as cation, like Vasudevan et al. (2009) observed in Vertisols with a lower pH (3.0–5.5); nevertheless, the soils we tested have a pH between 6.76 and 7.48, so CIP was present mainly as zwitterion (Table V-2). Anyhow, we observed a high affinity of CIP for all the soils and the sediment tested.

4.3 Desorption kinetics

Desorption of SMX from the three soils with artificial wastewater could be well described by Eq. (V-1) (Fig. V-3). The model encompasses an instantaneous desorption of the SMX sorbed to easily accessible sorption sites on the surface of soil and sediment particles and a slower rate-limited desorption process, e.g., from the micropores of the solid, that is characterized by a rate constant k (h^{-1}). According to this theory, most of the desorbed SMX extracted from these soils was located in poorly accessible sites, because of the very small values of the instantaneous SMX desorption from the Phaeozem and Vertisol sample into artificial wastewater without surfactant (Table V-3). This is probably due to the long-term accumulation of this compound in the crop fields in the Mezquital Valley, allowing diffusion to poorly accessible pores and binding sites upon aging (e.g., Rosendahl et

al. 2011). Instantaneous desorption from the Leptosol into artificial wastewater was likely facilitated by its small contents of soil organic matter and clay (Table V-1) as well as iron oxides (0.68 mg g^{-1} oxalate-extractable iron; Siebe 1994). Therefore, the soil with the lowest OC, Fe oxide, and clay contents released SMX at the highest rate, regardless of the presence of surfactant (Table V-3). The greater instant desorption of SMX from Phaeozem and Vertisol with artificial wastewater with surfactant compared with the extraction without surfactant (Fig. V-3) suggests a promoting effect of even a concentration of 100 µg L^{-1} of anionic LAS on the rapid desorption of anionic SMX that can be explained by (an)ion exchange reactions at soil organic matter or iron oxide surfaces. Thiele-Bruhn et al. (2004) suggested that beside the soil organic matter, pedogenic oxides are relevant for sulfonamide sorption. In addition, Förster (2011) described the contribution of iron oxides to the process of intraparticle diffusion of sulfadiazine. Thus, weak sorption of SMX in the Leptosol poorest in iron oxide, clay, and organic matter probably prevented a promoting effect of LAS on the rapid desorption of SMX in this soil. This and the larger desorption rate constants for the extractions with surfactant compared to those without surfactant for the three soils, reflect again the competitive sorption of both compounds and perhaps also an effect of the surfactant on soil organic matter conformation (and "rigidity") or its dispersing effect on aggregates (Schaumann and Thiele-Bruhn 2011), which could both accelerate the release of SMX from poorly accessible binding sites.

5. Conclusions

Strong sorption likely prevents desorption and release of CIP from the Mezquital Valley soils and sediments after the implementation of wastewater treatment. However, Leptosols and Phaeozems with particularly lower contents in clay and organic matter can turn into net sources of SMX when they are irrigated with treated wastewater in the future. SMX release from sediments is limited by their small SMX contents.

The desorption of SMX from soils in contact with artificial wastewater can be subdivided into an instantaneous desorption and a slower rate-limited desorption, and it has been the latter step that controlled the ongoing release of the sulfonamide by surfactants and treated wastewater from the soils.

VI. Summary and synthesis

In order to cope with the challenges that water scarcity represents, the reuse of wastewater plays a major role. One way to do this is to irrigate crop fields with treated or untreated municipal wastewater. This has been an ancient practice in many regions worldwide and is still a common practice in many countries nowadays due to the accelerated growth of world´s population. In this way, wastewater can be used to produce crops with the additional value that it contains quite a range of nutrients. At the same time, the disposal of wastewater is achieved. The technique implies, however, that the irrigated soils and crops also receive pollutants and pathogens carried by wastewater. The fate of contaminants in the soils relies on the physicochemical properties of wastewater, on soil properties, and the compounds themselves. This work focused on the behaviour of pharmaceuticals transported by untreated wastewater from Mexico City to the largest irrigated area worldwide: Mezquital Valley, in the state of Hidalgo, Mexico. Soils from Mezquital Valley have received untreated wastewater since more than a century. This practice has changed the properties of the soils (Siebe and Cifuentes, 1995; Dalkmann et al., 2012), with consequences for the retention capacity of pollutants (Dalkmann et al., 2014a). Pharmaceuticals in the environment have been studied intensively in recent times, but there are still open questions in relation to sorption competition with LAS and other compounds in the wastewater.

Dalkmann et al. (2012) observed that the soils of the Mezquital Valley tend to retain and accumulate some pharmaceuticals along time by means of sorption processes. These processes may thus explain why water quality has remained acceptable in some recent springs in the region (Siemens et al., 2008; Chavez et al., 2011). Besides, these sorption processes reflect the potential of the soils to reduce the total load of pollutants from wastewater before it reaches the aquifers. The sorption capacity is however limited and might be affected by other dissolved compounds present in wastewater, like organic matter or surfactants. Having an historical record of the input of pollutants can be useful to get a better estimation of the risk and prevent groundwater contamination. This record could be stored in sediments of the Enhó reservoir, where the untreated wastewater from Mexico City has been

collected since the 70s before being distributed to the crop fields. Sediments are typically considered a sink of pollutants (Acuña et al., 2015; Arias-Andrés et al., 2014; Hu et al., 2012), so this reservoir may act as primary treatment where suspended particles settle and a fraction of the dissolved pollutants are removed by sorption to those particles. A considerable change in wastewater quality might also affect the sorption-desorption equilibria of pharmaceuticals, which can lead to a net desorption of the accumulated compounds. This would make sediments and soils a potential source of pharmaceuticals rather than a sink. This work focused on factors that can influence the sorption-desorption equilibria of pharmaceuticals on sediments and soils from the Mezquital Valley, Mexico exposed to wastewater for several decades.

Summary of the results

i) Surfactants may have an influence on the sorption of antibiotics, hindering the sorption of sulfamethoxazole by competition, but not of ciprofloxacin due to the strong sorption of the fluoroquinolone.

Sorption batch experiments of these two antibiotics were performed in the presence of linear alkylbenzene sulfonates using wastewater-irrigated soils and soils from rain fed agriculture to compare the effect of the long-term wastewater irrigation. LAS sorption was non-linear in the presence of the antibiotics, and as general trend, it increased with rising OM content of soils. Free LAS was also removed from solution by complexation with Ca^{2+}. Dissolved organic compounds released from soils with OM contents ≥ 18.4 g kg^{-1} further reduced LAS sorption. Sorption of sulfamethoxazole was reduced by LAS sorption only in one soil with a small OM content of 9.5 g kg^{-1}. I concluded that the strong sorption of ciprofloxacin is not affected by LAS. Sulfamethoxazole sorption only competes with LAS sorption in organic matter-poor soils. Accumulation of organic matter in soils, for example due to long-term wastewater irrigation, provides extra sorption capacity for LAS and sulfamethoxazole so that competition for sorption sites is reduced.

ii) Antibiotics present in wastewater from Mexico City sorb to suspended particles, so sediments from the Endhó reservoir contain an historical record of the input of those pollutants into the crop fields in Mezquital Valley.

In this reservoir untreated wastewater from Mexico City is collected before its distribution to the crop fields. A sediment core from the reservoir was analysed for radionuclides to achieve a dating along the layers of sediments, and for antibiotics to reconstruct the historical input of pharmaceuticals to the fields. Although the uncertainties of the radionuclide measurements where large due to atypical large background activities of ^{226}Ra, a dating of the sediment core was achieved applying the constant flux constant sedimentation rate model, obtaining a sedimentation rate of 2.19 cm year^{-1}. Generally speaking, pharmaceuticals were found in higher concentrations compared to those found in soils that receive the wastewater from the Endhó reservoir, having diclofenac and bezafibrate the highest differences. Apparently degradation processes of some pharmaceuticals like sulphonamides under the anaerobic conditions in sediments take place, as several of them were not detected at any depth while other were found in the upper layers of the sediment column (recent sediments) at relative high concentrations, with a trend to decrease at increasing depths (older sediments). These pharmaceuticals comprised for example ciprofloxacin, bezafibrate and trimethoprim, and their persistence implies that at least for these compounds I may confirm the hypothesis that the sediments are an important sink of pharmaceuticals, which are associated to suspended particles.

iii) **Treatment of the wastewater before reaching the crop fields would lead to new conditions that promote the desorption of antibiotics from wastewater-irrigated soils, a process also enhanced by anionic surfactants that compete directly for sorption sites with sulfamethoxazole.**

In order to elucidate whether and to which degree irrigation with treated wastewater might cause desorption of antibiotics from three soil types (Leptosol, Phaeozem, Vertisol) and one sediment (Endhó reservoir) from the Mezquital Valley, Mexico, that were exposed to untreated wastewater in the past,

sequential batch desorption experiments with treated wastewater, artificial wastewater with anionic surfactants, and artificial wastewater without surfactants were performed.

The results showed no desorption, but net sorption of ciprofloxacin in contact with treated wastewater containing 3.475 µg L^{-1} of ciprofloxacin. Sulfamethoxazole was desorbed from the Leptosol, the Phaeozem, and the Vertisol in contact with artificial wastewater in a similar degree with and without surfactant, but not from sediment, where no sulfamethoxazole was detected. In contact with treated wastewater containing 1.045 µg L^{-1} of sulfamethoxazole, the compound was desorbed from the Leptosol and the Phaeozem with low clay, Fe oxide, and organic matter contents, whereas the Vertisol and sediment showed a net sulfamethoxazole sorption. Desorption could be described with a biphasic kinetic desorption model, with most sulfamethoxazole being desorbed via a rate-limited process from poorly accessible binding sites, where it had been accumulated during the long-term irrigation in the past. The study showed that a potential release of pharmaceuticals as a result from changes in wastewater irrigation is soil specific: Leptosols and Phaeozems of the Mezquital Valley might act as long-term sources of the sulfonamide sulfamethoxazole, though not of the fluoroquinolone ciprofloxacin.

Synthesis

This work explored the potential of soils and sediments that have been exposed to untreated wastewater for several decades to become a net source of pharmaceuticals. The soils from Mezquital Valley have accumulated heavy metals (Siebe and Fischer, 1996) and pharmaceuticals (Dalkmann et al., 2012) along decades by sorption processes. These processes, however, can be affected by the influence of other agents present in untreated wastewater or by a change in the chemical properties of the medium, i.e. the water quality, as it would occur after a wastewater treatment. In the comparable case of the sewage farms (*Rieselfelder*) in Berlin, where soils accumulated pollutants from wastewater for more than hundred years, the potential of those soils to become a net source of organic

pollutants has been demonstrated, where agents like enzymes enhance the desorption processes (Becker, 2006; Wicke 2008). In the Mezquital Valley soils I observed a reduced sorption of the antibiotic sulfamethoxazole by the influence of linear alkylbenzene sulfonate, presumably by a competition between both compounds for sorption sites. This effect however, was not observed for the antibiotic ciprofloxacin, as it is sorbed strongly mainly by a cation exchange mechanism (Wu et al. 2013), compared to the weaker sorption of the sulfonamide sulfamethoxazole, which sorbs mainly by hydrophobic forces. The data point to the relevance of the chemical behaviour and sorption mechanism of each pharmaceutical when considering the potential competition with other dissolved substances. Linear alkylbenzene sulfonamides are the most widely used surfactants in household products and therefore I performed the corresponding experiments with this kind of surfactants. Nevertheless, the presence of non-ionic and cationic surfactants in wastewater from Mexico City might not be overlooked. Those surfactants display a different chemical behaviour and might exert different influence on the sorption of pharmaceuticals. Cationic surfactants could compete with positive charged pharmaceuticals like fluoroquinolones that sorb mainly by a cation exchange mechanism, but the corresponding experiments should be performed to confirm this.

In our experiments, the competition between the antibiotic and the surfactant took place only when the organic matter content of the soil was low. I conclude that only when the sorption sites are scarce, the effect of the competition is noticeable, therefore, the properties of the soils are also an important factor regarding the influence of other dissolved compounds on the sorption and desorption of pharmaceuticals. Again, the main sorption mechanism(s) would define which soil property has a greater influence, like the type and content of clay, the dominating exchangeable cations, the quantity and quality of organic matter for example.

The local environment also plays an important role in the fate and dissipation of pharmaceuticals, as was observed in the sediments of the Endhó reservoir, where apparently the degradation or transformation of some pharmaceuticals took place under the reducing environment at the bottom of the water column. This underlines the important role of the properties of the medium, i.e. the water

quality and is of particular interest because the wastewater from Mexico City will be treated at the *Atotonilco* WWTP before reaching the Endhó reservoir and the fields. The conventional treatment of the municipal wastewater removes a considerable fraction of pollutants, but some pharmaceuticals might still be present after the treatment, as found in the effluent of the WWTP "*Cerro de la Estrella*" in Mexico City. The dissolved organic carbon was also relative high in the same effluent, and it has an effect on the sorption-desorption processes of pharmaceuticals in soils, promoting the desorption of sulfamethoxazole from some soils. Unquestionably the treatment of wastewater is a desirable practice to reduce the risk of contamination and health problems, but this might exert an influence on the sorption-desorption equilibria of pharmaceuticals in soils and sediments. As the *Atotonilco* WWTP started operations recently, it is not clear how this would affect the sorption and desorption of pharmaceuticals in the Mezquital Valley.

A reconstruction of the historical input of pharmaceuticals from Mexico City might help to have an insight on the pharmaceuticals' accumulation capacity of soils and sediment in Mezquital Valley. Although this reconstruction using a sediment core of the Endhó was not possible due to the apparent dissipation of pharmaceuticals, valuable information could be retrieved. It is known that sediments in rivers and lakes act commonly as a sink of pharmaceuticals, but the concentrations I found in sediments were much higher compared to those in wastewater-irrigated soils. The Endhó reservoir serves unintended as a cleaning step that "protects" the fields and crops from receiving a larger load of pharmaceuticals.

The results of this work show that although sediments and soils have been a sink for pharmaceuticals for several decades, attention is required as they have a limited retention capacity and there are several factors besides that can turn them into net sources of pharmaceuticals. Accumulated organic pollutants in soils of the Berlin´s sewage farms were mobilized in column experiments as a consequence of the mineralization of soil organic matter triggered by a change towards a treated-wastewater irrigation regime (Savric et al. 1998). A similar scenario is to be expected when soils of Mezquital Valley start receiving treated wastewater from the Atotonilco wastewater treatment plant

in the next future. Therefore, similar experiments using soils from the Mezquital Valley would be very useful as a complement of the present work to achieve a better understanding of the dynamics of pharmaceuticals affected by wastewater quality.

A permanent monitoring system of the waste and ground water is desirable to detect as soon as possible any occasional leaching/migration of pharmaceuticals or other contaminants into the aquifer and prevent the exposition of people and ecosystems to those chemicals.

VII. References

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VIII. Appendix A

Details of experimental methods

Table A-1. Conditions of the two-step extraction of soil and sediment samples by accelerated solvent extraction (ASE)

Parameter	Step 1 [a]	Step 2 [b]
Solvent	methanol : Millipore-water (1:1) (v/v)	50 mM aqueous H_3PO_4 : acetonitrile (1:1) (v/v)
Pressure [bar]	100	100
Temperature [°C]	100	100
Heating time [min]	5	5
Static extraction [min]	5	10
Extraction cycles	2	3
Flush volume [%]	60	90
Flush with N_2 [sec]	60	180

[a] after Gobel et al., 2005
[b] after Golet et al., 2002

Table A-2. Extraction recoveries of pharmaceuticals from solid matrices by accelerated solvent extraction (ASE) and from the solid phase extraction (SPE) cartridges (data from Dalkmann et al., 2012)

Compound	Recovery, %		
	ASE	SAX cartridge (Chromabond SB)	HLB cartridge (OASIS)
Ciprofloxacin	89	100	74
Enrofloxacin	78	100	76
Sulfamethoxazole	54	100	84
Trimethoprim	83	99.6	32
Clarithromycin	93	100	99
Carbamazepine	77	99.8	97
Naproxen	95	100	90
Diclofenac	85	100	72
Bezafibrate	96	100	105

Table A-3. Mass and collision energy of the detected fragments of pharmaceuticals by tandem mass spectrometry

Analyte	Precursor ion ($m\ z^{-1}$)	Fragment ions ($m\ z^{-1}$)	Collision energy (eV)
Ciprofloxacin	332.09	245.06	24
		288.11	17
Enrofloxacin	360.12	245.06	26
		316.16	18
Sulfamethoxazole	254.02	108.03	23
		155.97	15
Trimethoprim	291.10	123.06	32
		230.09	23
Clarithromycin	748.43	158.00	28
		590.23	18
Carbamazepine	237.08	179.08	34
		194.10	20
Naproxen	231.08	170.08	26
		185.10	12
Diclofenac	296.00	214.02	35
		250.02	13
Bezafibrate	362.08	121.06	29
		138.97	26

Table A-4. Composition and properties of the treated and artificial wastewater used for the desorption experiments compared to those of untreated wastewater from Mezquital Valley

Property	Treated WW used in this study	Artificial WW used in this study	CNA et al. [1][a]	Dalkmann et al. [2][b]
NH_4^+-N (mg L^{-1})	–	12.5	8.5 - 18.5	3.6 - 4.0
ortho-P (mg L^{-1})	–	1.7	1.6 - 1.7	–
Ca^{2+} (mg L^{-1})	–	45.5	–	33 - 47
Mg^{2+} (mg L^{-1})	–	21.5	–	15 - 30
K^+ (mg L^{-1})	–	22.1	18 - 37	21 - 37
Na^+ (mg L^{-1})	–	123.2	78 - 337	101 - 203
Cl^- (mg L^{-1})	–	163.2	77 - 243	81 - 162
HCO_3^- (mg L^{-1})	–	243.0	233 - 597	400 - 720
SO_4^{2-} (mg L^{-1})	–	103.8	187 - 346	31 - 103
LAS C_{10}-C_{13} (µg L^{-1})	n.d.	100.0‡	–	–
Non-purgeable organic C (mg L^{-1})	9.54	n.d.	–	–
Total N (mg L^{-1})	10.81	12.5	23 - 23	31 - 40
pH	8.93*	8.10*	6.97 - 7.64	7.26 - 8.07
Electrical conductivity (µS cm^{-1})	563*	1131*	1114 - 1673	1013 - 1559

n.d. : not detected
‡ Present only in the LAS-spiked solution
* at 25 °C
[a] Data from 1993
[b] Data from 2011-2012

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IX. Appendix B

Details of the results

Table B-1. Loss of dissolved LAS as complexes with the divalent cation Ca^{2+} used as background electrolyte. Values were obtained with controls without soil

Initial LAS concentration (mg/L)	**Fraction of surfactant lost as LAS- Ca^{2+} complexes**	
	In presence of ciprofloxacin (soil to solution ratio 1:50)	In presence of sulfamethoxazole (soil to solution ratio 1:5)
5	0.55 ± 0.02	0.53 ± 0.01
10	0.47 ± 0.01	0.39 ± 0.00
30	0.49 ± 0.01	0.27 ± 0.00

Table B-2. Content of pharmaceuticals in the sediment core from the Endhó reservoir

Depth (cm)	Content in sediment (µg kg^{-1}, dry mass)								
	BEZ	**CAR**	**CIP**	**CLA**	**DIC**	**ENR**	**NAP**	**SMX**	**TRI**
2	68.24	5.66	22.72	n.d.	4.61	1.75	n.d.	n.d.	24.80
10	79.48	7.95	12.54	n.d.	252.18	2.93	n.d.	n.d.	23.76
20	48.20	9.03	5.97	n.d.	158.89	1.24	n.d.	n.d.	65.33
26	24.26	6.35	5.49	n.d.	103.66	4.34	n.d.	n.d.	12.23
29	30.31	7.23	3.97	n.d.	3.29	0.98	n.d.	n.d.	10.54
36	26.09	6.31	2.27	n.d.	84.37	1.34	n.d.	n.d.	3.71
41	27.52	6.92	0.97	n.d.	100.45	1.47	n.d.	n.d.	3.11
46	19.74	5.71	1.15	n.d.	61.21	1.78	n.d.	n.d.	3.35
53	14.85	4.51	1.42	n.d.	1.12	0.66	n.d.	n.d.	3.88
56	29.57	7.17	n.d.	n.d.	89.54	2.01	n.d.	n.d.	6.06
60	17.06	5.51	1.11	n.d.	40.02	2.00	n.d.	n.d.	5.39
65	13.30	4.59	1.31	n.d.	32.83	2.19	n.d.	n.d.	5.98
69	9.71	3.11	2.46	n.d.	31.58	1.58	n.d.	n.d.	2.02
75	7.48	2.57	n.d.	n.d.	124.93	1.47	n.d.	n.d.	4.86
80	9.22	3.87	3.00	n.d.	24.29	1.52	n.d.	2.57	3.38
83	15.03	4.79	1.35	n.d.	21.09	1.62	n.d.	n.d.	5.95
86	9.36	1.55	2.17	n.d.	n.d.	0.86	n.d.	n.d.	n.d.

n.d.: not detected

BEZ – bezafibrate; CAR – carbamazepine; CIP – ciprofloxacin; CLA – clarithromycin; DIC – diclofenac; ENR – enrofloxacin; NAP – naproxen; SMX – sulfamethoxazole; TRI – trimethoprim