Science of the Total Environment 538 (2015) 350–362

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Environmental fate of naproxen, carbamazepine and triclosan in wastewater, surface water and wastewater irrigated soil — Results of laboratory scale experiments

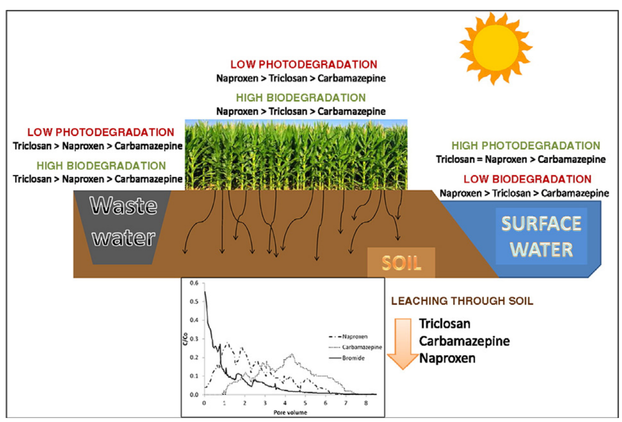
J.C. Durán-Álvarez [a], B. Prado [b], D. González [c], Y. Sánchez [c], B. Jiménez-Cisneros [d,*]

[a] Centro de Ciencias Aplicadas y Desarrollo Tecnológico, Universidad Nacional Autónoma de México, Mexico
[b] Instituto de Geología, Universidad Nacional Autónoma de México, Mexico
[c] Instituto de Ingeniería, Universidad Nacional Autónoma de México, Mexico
[d] International Hydrological Programme (IHP), UNESCO, France

HIGHLIGHTS

- Degradation and transport of pharmaceuticals studied in a wastewater irrigated area
- Naproxen and triclosan readily photo and biodegraded, carbamazepine was recalcitrant
- Biodegradation inhibited at high spiking concentrations for the tested matrices
- Transport of triclosan and carbamazepine was delayed by soil chemical components
- Naproxen can easily reach aquifer in case of low degradation in the soil

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 20 May 2015
Received in revised form 15 July 2015
Accepted 7 August 2015
Available online xxxx

Editor: Kevin V Thomas

Keywords:
Adsorption
Biodegradation

ABSTRACT

Lab-scale photolysis, biodegradation and transport experiments were carried out for naproxen, carbamazepine and triclosan in soil, wastewater and surface water from a region where untreated wastewater is used for agricultural irrigation. Results showed that both photolysis and biodegradation occurred for the three emerging pollutants in the tested matrices as follows: triclosan > naproxen > carbamazepine. The highest photolysis rate for the three pollutants was obtained in experiments using surface water, while biodegradation rates were higher in wastewater and soil than in surface water. Carbamazepine showed to be recalcitrant to biodegradation both in soil and water; although photolysis occurred at a higher level than biodegradation, this compound was poorly degraded by natural processes. Transport experiments showed that naproxen was the most mobile compound through the first 30 cm of the soil profile; conversely, the mobility of carbamazepine and triclosan through the soil was delayed. Biodegradation of target pollutants occurred within soil columns during transport experiments. Triclosan was not detected either in leachates or the soil in columns, suggesting its complete biodegradation.

* Corresponding author at: 1 rue Miollis, 75732 Paris Cedex 15, France.
E-mail address: bjimenezc@iingen.unam.mx (B. Jiménez-Cisneros).

http://dx.doi.org/10.1016/j.scitotenv.2015.08.028

Transport
Pharmaceutical compounds
Photolysis

Data of these experiments can be used to develop more reliable fate-on-the-field and environmental risk assessment studies.

1. Introduction

Reuse of treated and untreated wastewater for agricultural irrigation is a widespread practice in arid and semiarid areas (Raschid-Sally and Jayakody, 2008). Despite the benefits of reusing wastewater (Adrover et al., 2012; Raschid-Sally and Jayakody, 2008; Toze, 2006; Jiménez, 1995), the potential of spoiling soil, water sources and crops with a wide variety of contaminants, notably emerging pollutants, is a source of concern. Previous studies have reported the occurrence of several emerging pollutants in urban wastewater in developing countries, such as Mexico, South Africa, Brazil, Tunisia, Vietnam and other tropical Asian countries, at levels of ng/L–μg/L, and even at mg/L for some phthalate esters (Shimizu et al., 2013; Olujimi et al., 2012; Mnif et al., 2010; Moreira et al., 2009; Duong et al., 2008; Gibson et al., 2007). On the other hand, in rural areas or small towns, even when the load of most of emerging pollutants in wastewater is lower than that observed in big cities (Vystavna et al., 2012), the presence of antibiotics at levels of ng/L to μg/L has been systematically observed and attributed to human and livestock medications as well as to aquaculture (Zou et al., 2011; Cabello, 2006; Sarmah et al., 2006). Considering the aforementioned, the use of wastewater for agricultural irrigation in both urban and rural areas should be carried out with caution, and knowing as much as possible the effects and fate of the pollutants that are discharged into the environment. The harmful effects that emerging pollutants may cause to aquatic and soil organisms are as the matter of facts still poorly understood. Toxicity studies are mostly focused on acute damages to aquatic organisms. In the case of soil, some studies on the impact of emerging pollutants to plants, soil microfauna and accumulation in worms have been performed. Moreover, the information on the chronic effects of complex mixtures of emerging pollutants at trace levels, which are the most realistic conditions, is very scarce (see Cleuvers, 2004 as a good example of this). Extensive reviews on the effects that emerging pollutants cause to aquatic and soil organisms can be found in literature (Durán-Álvarez and Jiménez-Cisneros, 2014; Stuart et al., 2012; Pal et al., 2010; Farré et al., 2008).

The study of the environmental fate of emerging pollutants has been performed mostly on wastewater and drinking water treatment systems (see reviews in Verlicchi et al., 2013 and Huerta-Fontela et al., 2011); thus the study of the potential degradation, mobility and accumulation of these chemicals in soil and natural waters, and assimilation by crops is necessary, particularly in regions where large volumes of wastewater are used for irrigation.

In the environment, a succession of natural processes leading to the dissipation and/or the mobility of pollutants in soil and water are continuously occurring. Biodegradation, photolysis, hydrolysis, adsorption and leaching through soil have been previously reported for specific emerging pollutants in natural systems (Yamamoto et al., 2009; Farré et al., 2008). Some studies have conjunctively addressed the degradation and partition of specific pharmaceuticals in freshwater/sediments systems at laboratory scale (Yamamoto et al., 2009). From these studies, it is known that some pharmaceuticals, such as diclofenac, naproxen and sulfamethoxazole, are readily photodegradable in fresh water (Bahnmüller et al., 2014; Zhang et al., 2011; Isidori et al., 2005), whereas other compounds, such as anti-epileptic and β-blocker drugs, are recalcitrant to natural photolysis (Acuña et al., 2015; Dong et al., 2015; Kunkel and Radke, 2012). However, it is noteworthy that most of the reported studies addressing natural photolysis of emerging pollutants in water have been carried out in regions above 40° North latitude (Boreen et al., 2003), thus it is necessary to elucidate the potential of natural photolysis, not only in water but in soil, using sunlight irradiation conditions that are found near the tropics, where many developing countries are found.

Biodegradation of emerging pollutants has been extensively studied in wastewater treatment systems (Verlicchi et al., 2013; Salgado et al., 2012); although, biodegradation in agricultural soils and fresh water has been less explored. From what has been reported so far, it is known that some microorganisms capable of degrading highly recalcitrant chemicals, such as carbamazepine and polybrominated flame retardants, can be isolated from soils (Jelic et al., 2012; Rodríguez-Rodríguez et al., 2012). High biodegradation rates may be expected in wastewater and soils due to the high content of both organic matter and degrading microorganisms (Ma et al., 2015). Moreover, higher biodegradation rates may be expected in long-term wastewater irrigated soils than in rainfed or groundwater irrigated agricultural soils. This is because of the high and varied microorganism populations, the excess of nutrients in soil and the high acclimatization of the native microfauna to degrade toxic and recalcitrant chemicals (Ma et al., 2015; Müller et al., 2007).

When wastewater is used to irrigate crop fields, it is naturally treated by infiltration through soil. Whether biodegradation occurs or not, the mobility of dissolved contaminants within the soil is influenced by the physical and chemical properties of the solid matrix (e.g., texture, porosity, pH, salinity and organic matter content) and the properties of the contaminants (such as pK_a, log D, chemical structure and vapor pressure) (Wehrer and Totsche, 2008). Since soil properties are indeed modified by wastewater irrigation (Durán-Álvarez and Jiménez-Cisneros, 2014), it is necessary to study the mobility of emerging pollutants in soils that have been irrigated using wastewater for long periods of time.

The aim of this work was to determine the environmental fate of three emerging pollutants, namely naproxen, carbamazepine and triclosan, in wastewater, surface water and wastewater irrigated soils using samples coming from an agricultural irrigation district where untreated wastewater has been applied to soil for more than a century.

These pollutants were selected for this study given that: a) they have been consistently found in different environmental compartments of the Tula Valley irrigation area (i.e., waste and surface waters and soil); and, b) these compounds display differences in their physical and chemical properties, which may result in differences in the environmental fate.

2. Materials and methods

2.1. Chemicals

All reagents used in the experiments were analytical grade. The standards naproxen, carbamazepine and triclosan; the surrogate standards 3,4-dichlorophenoxyacetic acid (3,4-D), [$^2H_4$] 4-n-nonylphenol and [$^2H_{16}$] bisphenol-A; the internal standards clofibric acid, 4-n-nonylphenol and 10,11-dihydrocarbamazepine; the reagents sodium bicarbonate, sodium sulfate, calcium chloride, diatomaceous earth and acetic acid; as well as the derivatizing agents N-*tert*-butyldimethylsilyl-N-methyltrifluoroacetamide (MTBSTFA) with 1% of *tert*-butyldimethylsilylchlorane and N,O-bis(trimethylsilyl) trifluoroacetamide (BSTFA) with 1% of trimethylsilylchlorane were obtained from Sigma-Aldrich (St. Louis, MO, USA). All the solvents and pure water were HPLC grade, purchased from Burdick and Jackson (Morristown, NJ, USA). Oasis HLB extraction cartridges (200 mg, 60 cm^3) were bought from Waters (Milford, MA, USA). The relevant