Science of the Total Environment 473–474 (2014) 125–131

Contents lists available at ScienceDirect

Science of the Total Environment

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

Impact of materials used in lab and field experiments on the recovery of organic micropollutants

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HIGHLIGHTS

- Influences of materials on organic micropollutants during storage and filtering
- First study: A mixture of 43 organic compounds was stored in batches.
- Second study: Mixture was filtered with filter materials and fractions were sampled.
- The softer the material was, the more influence on the mass recoveries was observed.

ARTICLE INFO

Article history:
Received 28 August 2013
Received in revised form 2 December 2013
Accepted 2 December 2013
Available online 21 December 2013

Keywords:
Emerging pollutants
Laboratory experiments
Fluoxetine
Teflon
Tygon
Effect of filtration

ABSTRACT

Organic micropollutants are frequently detected in the aquatic environment. Therefore, a large number of field and laboratory studies have been conducted in order to study their fate in the environment. Due to the diversity of chemical properties among these compounds some of them may interact with materials commonly used in field and laboratory studies like tubes, filters, or sample bottles. The aim of our experiment was to study the interaction between those materials and an aqueous solution of 43 widely detected basic, neutral, and acidic organic micropollutants hereby covering a broad range of polarities. Experiments with materials were conducted as a batch study using spiked tap water and for different syringe filters by filtration with subsequent fraction collection. The best recoveries over a wide range of organic compounds were observed for batches in contact with the following materials (in descending order) acryl glass, PTFE, HDPE, and PP. The use of Pharmed©, silicone, NBR70, Tygon©, and LDPE should be avoided. Flexible tubing materials especially influence many of the investigated compounds here. Filtration with most of the tested filter types leads to no significant loss of almost all of the investigated micropollutants. Nonetheless, significant mass losses of some compounds (loratadine, fluoxetine, sertraline, and diuron) were observed during the first mL of the filtration process. No systematic correlation between compound properties, tested materials, and observed mass losses could be identified in this study. The behavior of each compound is specific and thus, not predictable. It is therefore suggested to study the interaction of compounds with filters and material prior to the actual experiment or include blank studies.

1. Introduction

Micropollutants such as pharmaceuticals, pesticides, stimulants, and corrosion inhibitors are frequently detected in the water cycle including surface water, sea water, groundwater, and tap water (Heberer, 2002a, b; Ternes, 2007; Nödler et al., 2011, 2013a; Reh et al., 2013; Hillebrand et al., 2012). Transport and attenuation behavior of micropollutants in the aqueous environment are often studied in laboratory experiments such as water/sediment-batch tests (including microcosm studies) and soil column experiments (Banzhaf et al., 2012; Barbieri et al., 2012; Caracciolo et al., 2013; Drillia et al., 2005; Maeng et al., 2011; Mersmann et al., 2002; Mohatt et al., 2011; Müller et al., 2013; Scheytt et al., 2005, 2006; Yao et al., 2012). However, the materials and devices (e.g., tubes, filters etc.) used in these experiments and during sample pre-treatment prior to analysis may have significant impact on the measured concentrations. These effects (e.g., sorption) may need to be considered in data interpretation. Accordingly, the OECD guidelines for testing of chemicals request "suitably inert material (e.g., glass, stainless steel, aluminum, Teflon© and PVC)" in the construction of leaching columns (OECD, 2004). However, besides the octanol/water distribution coefficient (K_{OW}) organic compounds such as pharmaceuticals

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http://dx.doi.org/10.1016/j.scitotenv.2013.12.004

Table 1
Investigated compounds and their application/origin.

Application/origin	Compound	Application/origin	Compound
Analgesics/anti-inflammatories	Diclofenac	Lipid regulators	Bezafibrate
	Ibuprofen		Clofibric acid
	Naproxen		Gemfibrozil
	Paracetamol	Anticonvulsants/sedatives	Carbamazepine
	Phenazone		Diazepam
Stimulants	Caffeine		Primidone
Antihypertensives (and one metabolite)	Atenolol		Tetrazepam
	Metoprolol	Antidepressants (SSRIs)	Citalopram
	Sotalol		Fluoxetine
	Valsartan acid		Sertraline
Iodinated contrast media	Iohexol	Herbicides/herbicide metabolites	Atrazine
	Iomeprol		Desethylatrazine
	Iopamidol		Desisopropylatrazine
	Iopromide		Diuron
Antibiotics (and metabolites)	Clarithromycin		Isoproturon
	Erythromycin		Mecoprop
	Roxithromycin		Metazachlor
	Sulfamethoxazole		Terbuthylazine
	Desamino-SMX	Corrosion inhibitors	1H-benzotriazole
	4-Nitro-SMX		Tolyltriazole
	Trimethoprim		
Antiallergics	Cetirizine		
	Loratadine		

and pesticides bear a large variety of characteristics and functional groups, which may lead to specific interactions (Schaffer et al., 2012a, b). Therefore, the suitability of typically applied materials was tested with the aim of evaluating their applicability in laboratory and field experiments.

The goal of these experiments was not to provide absolute numbers of mass loss, because these are not transferable to other experiments due to the wide range of material properties within identical product batches. Our aim was to raise the awareness for potential mass loss effects (here defined as a concentration decrease in the water phase for investigated compounds) in experimental studies, which may be caused by interactions of the solutes with the used materials (tubes, sample bottles, filters, etc.). Many experimental studies are not aware of this problem and therefore, details about their laboratory materials are often not known or published (e.g., Chen et al., 2011; Gibson et al., 2010; Rauch-Williams et al., 2010; Ternes et al., 2002). In some experimental setups, like column studies, it is even impossible to conduct blank tests for excluding material–solute interactions. Most critical is that commonly compound loss is solely related to the tested substrate. An additional mass loss of the compounds of interest to the materials used in the setup of such studies is rarely considered. To address these concerns, a benchmark study with 43 basic, neutral, and acidic organic micropollutants covering a broad polarity range (log K_{OW} < 0–5.1) was conducted using two experimental setups: (i) a temporally resolved batch study (1–28 days) in which the compounds were exposed to typical experimental components such as bottles, tubes, and O-rings, and (ii) a volumetrically resolved filtration study, where three 5 mL aliquots of a standard solution were subsequently filtered with frequently used filters and analyzed individually.

2. Material and methods

2.1. Studied organic micropollutants

The investigated compounds (Table 1) were selected based on their wide distribution and application as well as their frequent detection in the environment. They cover a broad polarity range (log K_{OW} < 0–5.1) and include numerous functional groups.

The transformation products 4-nitro-sulfamethoxazole (4-nitro-SMX), desamino-SMX, and valsartan acid were synthesized according to Nödler et al. (2012, 2013b). Terbuthylazine was purchased from Dr. Ehrenstorfer (Augsburg, Germany). The suppliers of all other used reference standards and chemicals can be found in Nödler et al. (2010). A mix of 17 internal standards (IS) was prepared in acetonitrile. A detailed information on the IS and their assigned compounds is provided in the Supplementary material (S1).

2.2. Water

A spiked solution of 50 μg mL^{-1} of each individual micropollutant in 50:50 (v/v) methanol:water was prepared. For the test solution, tap water from Berlin was mixed with the spike solution. Individual compound concentrations of 100 μg L^{-1} and 83 μg L^{-1} were used in the batch and filtration experiments, respectively. Prior to spiking, the tap water was stirred overnight in contact with the atmosphere allowing the water to equilibrate with air. Therefore, significant changes of boundary conditions (decrease of the pH value by dissolution of CO_2) during the experiment could be avoided. The resulting methanol concentration in the test solution was ≤0.1% (v/v), which is expected to have no significant effect on the sorption process (Nkedi-Kizza et al., 1987). The applied micropollutant concentrations were chosen for analytical reasons (injection without preconcentration). Furthermore, soil column experiments are often conducted at this concentration level (e.g., Banzhaf et al., 2012; Schaffer et al., 2012a,b). Both tests were started immediately after the preparation of the two test solutions. In Table 2 the chemical composition and the physicochemical properties of both test solutions are shown.

2.3. Tested materials

Several widely used materials (sampling, storage, column experiment, and filter materials) were tested in the batch study. They include low-density polyethylene (LDPE) sample bottles, polypropylene (PP) sample bottles, Teflon© tubing (polytetrafluoroethene, PTFE), Pharmed© tubing, Tygon© tubing (all from Carl Roth GmbH + Co. KG, Karlsruhe, Germany), nitrile rubber NBR70 O-rings (HUG Industrietechnik und Arbeitssicherheit GmbH, Ergolding, Germany), high-density polyethylene Nalgene® (HDPE-Nalgene) and VWR Series 310 (HDPE-310) sample bottles (all from VWR International GmbH, Darmstadt, Germany), acryl glass panel (Plexiglas© XT, Evonik Industries AG, Darmstadt, Germany), and silicone tubing (Th. Geyer GmbH & Co. KG, Renningen, Germany). Batch experiments were conducted in amber glass sample bottles as containers (neoLab Migge Laborbedarf-Vertriebs GmbH, Heidelberg, Germany).

The materials evaluated in the filtration test were cellulose-acetate (CA) filter paper, polycarbonate (PC) filter paper, fiber glass filter

Table 2
Compositions of the test solutions.

	pH	EC [μS cm^{-1}]	T [°C]	Ca^{2+} [mg L^{-1}]	K^{+} [mg L^{-1}]	Na^{+} [mg L^{-1}]	Mg^{2+} [mg L^{-1}]	Fe_{ges} [mg L^{-1}]	Mn_{ges} [mg L^{-1}]	Cl^{-} [mg L^{-1}]	NO_3^{2-} [mg L^{-1}]	SO_4^{2-} [mg L^{-1}]	Spiked compounds [μg L^{-1}]
Batch test	8.5	671	22.7	110	6.3	37	10	0.009	0.002	50	3.9	95	Each 100
Filter test	8.2	682	21.6	109	6.0	40	10	0.003	0.001	67	3.5	93	Each 83