Water Research 101 (2016) 292–299

Contents lists available at ScienceDirect

Water Research

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

Halogenated methanesulfonic acids: A new class of organic micropollutants in the water cycle

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ARTICLE INFO

Article history:
Received 18 March 2016
Received in revised form
24 May 2016
Accepted 25 May 2016
Available online 2 June 2016

Keywords:
Non-target screening
HILIC
Drinking water
Organic micropollutants
Halogenated disinfection by-products

ABSTRACT

Mobile and persistent organic micropollutants may impact raw and drinking waters and are thus of concern for human health. To identify such possible substances of concern nineteen water samples from five European countries (France, Switzerland, The Netherlands, Spain and Germany) and different compartments of the water cycle (urban effluent, surface water, ground water and drinking water) were enriched with mixed-mode solid phase extraction. Hydrophilic interaction liquid chromatography - high resolution mass spectrometry non-target screening of these samples led to the detection and structural elucidation of seven novel organic micropollutants. One structure could already be confirmed by a reference standard (trifluoromethanesulfonic acid) and six were tentatively identified based on experimental evidence (chloromethanesulfonic acid, dichloromethanesulfonic acid, trichloromethanesulfonic acid, bromomethanesulfonic acid, dibromomethanesulfonic acid and bromochloromethanesulfonic acid). Approximated concentrations for these substances show that trifluoromethanesulfonic acid, a chemical registered under the European Union regulation REACH with a production volume of more than 100 t/a, is able to spread along the water cycle and may be present in concentrations up to the µg/L range. Chlorinated and brominated methanesulfonic acids were predominantly detected together which indicates a common source and first experimental evidence points towards water disinfection as a potential origin. Halogenated methanesulfonic acids were detected in drinking waters and thus may be new substances of concern.

1. Introduction

The contamination of water resources with numerous anthropogenic chemicals of which only a fraction is known and even less are regularly monitored or regulated is a major challenge in water management today (Daughton, 2004; Schwarzenbach et al., 2006). Many studies were dedicated to the monitoring of all kinds of chemicals in different compartments of the water cycle (Loos et al., 2009; Rodil et al., 2005; Ternes et al., 2001; Wode et al., 2015) and it was observed that persistent and polar substances are more likely to spread along the water cycle than their nonpolar counterparts (Reemtsma et al., 2006). Target screening studies, however, are limited to well-known substances which are available as reference substances.

Suspect screening campaigns (Krauss et al., 2010) on the other hand are largely independent from reference compounds and only require them for definite confirmation of detected substances, and thus such screening campaigns may encompass more substances than traditional target screenings (Chiaia-Hernandez et al., 2013; Segura et al., 2011). In addition, suspect screenings may include transformation products of which no reference compounds are available. Truly unknown compounds, however, are not amenable by suspect screening since pre-existing knowledge is required for suspect selection.

Non-target screening (Krauss et al., 2010) is largely independent of pre-existing knowledge since it covers all analytes amenable to the selected analytical technique. Thus, it is the least biased, but also most laborious screening approach where identification of detected substances is not guaranteed (Schymanski et al., 2015), and gets increasingly difficult fur substances that are not present in spectra databases or not even described in literature. Non-target screening is the least frequently deployed of the three screening approaches. The most common instrumentation for non-target screening is reversed-phase high performance liquid chromatography - high resolution mass spectrometry (RP-HPLC-HRMS),

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http://dx.doi.org/10.1016/j.watres.2016.05.082
0043-1354/

which facilitates the analysis of substances of intermediate to low polarity (Hogenboom et al., 2009; Hug et al., 2014; Schymanski et al., 2014b). Despite the increasing attention on very polar substances in modern analytics, which is governed by both, a high interest in polar substances (e.g. benzotriazoles (Reemtsma et al., 2010), artificial sweeteners (Scheurer et al., 2009) and chelating agents (Knepper et al., 2005) and technical developments facilitating their analysis (Alpert, 1990), the use of hydrophilic interaction liquid chromatography (HILIC) as chromatographic technique in non-target screening, and thus the study of very polar substances, is still rare (Gago-Ferrero et al., 2015). This might be caused by the worse retention time stability of HILIC in comparison to RP-HPLC which complicates peak list alignment and thus the study of multiple samples and effective blank subtraction, the lack of a universally applicable column chemistry and difficulties in the enrichment of very polar substances from aqueous matrices.

In this study mixed-mode solid phase extraction (SPE) enrichment in combination with HILIC-HRMS non-target screening was deployed to analyse nineteen water samples form five European countries and different compartments of the water cycle. The focus of this work was the identification of mobile and persistent contaminants that may impact raw and drinking waters and are thus of concern for human health.

2. Material and methods

2.1. Chemicals and reagents

Oasis WAX (30 μm) and Oasis WCX (30 μm) bulk materials were purchased from Waters (Milford, USA). Supelclean ENVI-Carb 120/400 was purchased from Supelco (Bellefonte, USA). Potassium methanesulfonate (≥98.0%), ammonium formate (≥99.0%), potassium bromide (≥99%) and aqueous sodium hypochlorite solution (10–15% available chlorine) were purchased form Sigma-Aldrich (Schnelldorf, Germany). Trifluoromethanesulfonic acid (99%) was purchased from Carbolution (Saarbrücken, Germany) while formic acid (98–100%) was supplied by Merck (Darmstadt, Germany). Acetonitrile, methanol (both LC-MS Ultra Grade), dichloromethane (≥99%, not stabilized) and ammonium hydroxide (30%) were purchased from Carl Roth GmbH (Karlsruhe, Germany). Pierce ESI Negative Ion Calibration Solution and Pierce LTQ Velos ESI Positive Ion Calibration Solution were purchased from Thermo Scientific (Bremen, Germany). Ultrapure water (18 MΩcm) was supplied by a Simplicity UV water purification system (Merck, Darmstadt, Germany).

2.2. Water samples

Nineteen water samples were collected from five European countries (France, the Netherlands, Switzerland, Germany and Spain) and different compartments of the water cycle (urban effluent (UE), surface water (SW), ground water (GW) and drinking water (DW)) in the time period from spring to summer 2015 and anonymized. Samples were named with a two letter code indicating the sample type and a consecutive number. All samples were grab samples and not treated in any way before enrichment. Detailed information about the samples cannot be given due to confidentiality reasons. Two sampling points (one surface water and one drinking water sampling point, used as quality control) were sampled again in February 2016, and a sampling blank consisting of mineral water was prepared in parallel to these samples. The drinking water sample DW-19 was also taken in February.

2.3. Solid phase extraction

SPE was performed by filling 3 mL CHROMABOND polypropylene cartridges (Macherey-Nagel, Düren, Germany) with 60 mg of graphitized carbon black (GCB, ENVI-Carb), polymeric weak anion exchanger (Oasis WAX) and polymeric weak cation exchanger (Oasis WCX) each. The different SPE materials were separated by CHROMABOND polyethylene filters (Macherey-Nagel, Düren, Germany). After washing and conditioning of the cartridges (1 mL methanol with 5% ammonium hydroxide, 1 mL methanol with 2% formic acid and 1 mL methanol with 20% dichloromethane, and 3 mL H_2O), 200 mL sample (pH adjusted to 5.5 ± 0.1 with formic acid or ammonium hydroxide) was passed through the cartridge. The cartridge was eluted in several steps with methanol containing different additives in the following order: 5% ammonium hydroxide (2×1 mL), 2% formic acid (2×1 mL) and 20% dichloromethane (1×1 mL). All elution steps were combined and after evaporation to dryness at 50 °C under a gentle stream of nitrogen, the residue was reconstituted with 1 mL acetonitrile/water 95:5 (v:v) and filtered through a syringe filter (regenerated cellulose, pore size 0.45 μm, Whatman, Little Chalfont, UK). The filtrate was used for subsequent analysis. A separate laboratory blank, derived from the enrichment of 200 mL ultrapure water, was prepared in parallel at every day sample enrichment was performed.

2.4. LC-MS method

Analysis of samples was performed with a HILIC-HRMS non-target screening method utilizing a Nucleodur HILIC column (150 × 2.1 mm; 5 μm) and a Nucleodur HILIC guard column (5 μm, both Macherey-Nagel, Düren, Germany) and a Surveyor LC system consisting of a quaternary pump (‘MS Pump), an auto sampler and a photodiode array detector (‘PDA Plus’) interfaced with an LTQ Orbitrap Velos Pro with ‘Heated Electrospray Ionization’ (H-ESI II, all Thermo Scientific, Bremen, Germany).

HILIC was carried out at pH 3.0 with an acetonitrile-water gradient containing 5 mM ammonium formate at any time. After a 5 min isocratic step at 95% acetonitrile, the water content of the mobile phase was raised to 60% within 22 min and held constant for 8 min before reequilibration of the column. During the initial isocratic step, 2.5% water was replaced with methanol to increase the retention of early eluting compounds. The flow rate was set to 200 μL/min and increased to 500 μL/min during reequilibration, the injection volume was 20 μL. ESI(−) was performed with a spray voltage of 3.5 kV, a source heater temperature of 300 °C, sheath and auxiliary gas flow rates of 40 and 20 arbitrary units, respectively, and a capillary temperature of 325 °C. For HRMS measurements, a nominal resolution of 60.000 (at m/z 400) was set. Trifluoroacetate, a common background ion often persistent in LC-MS systems, was used as lock mass to increase mass accuracy.

2.5. Chlorination experiment

Chlorination of methanesulfonic acid (MSA) was performed by preparing four solutions containing bromide (10 mM) and hypochlorite (20 mM, solution I), MSA (5 mM, solution II), MSA (5 mM) and hypochlorite (20 mM, solution III) or MSA (5 mM), bromide (10 mM) and hypochlorite (20 mM, solution IV). All solutions were prepared in ultrapure water. The pH was not controlled during chlorination, but expected to be 7 since all reactants were added as neutral salts. Aliquots were taken after 3 h, 1 day and 6 days and diluted 1:20 with acetonitrile for subsequent analysis.