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Baseline

Methods comparison, transport and distribution of polar herbicides in the Baltic Sea

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ABSTRACT

Two LC-MS/MS methods including different sample preparation and quantitative processes showed a good agreement for analysis of the herbicides MCPA, mecoprop, isoproturon, bentazon and chloridazon, and the metabolite chloridazon-methyl-desphenyl (CMD) in estuarine waters. Due to different sensitivity of the methods only one could be used to analyze marine samples. The transport of these compounds to the Baltic Sea via ten German estuaries and their distribution between coastal water and sediments was studied. The results showed that all selected compounds can be transported to the Baltic Sea (0.9–747 ng/L). Chloridazon, bentazon, isoproturon and CMD were detected (0.9–8.9 ng/L) in the coastal waters and chloridazon and isorproturon in the sediments (5–136 pg/g d.w.). Levels of contaminants in the sediments could be influenced by the total organic carbon content. Concentrations observed in the Baltic Sea are most likely not high enough to cause acute effects, but long term effect studies are strongly recommended.

The Baltic Sea is a shallow inland sea with a population over 85 million inhabitants in its catchment area (Dailidiene and Davuliene, 2008; Håkanson et al., 2003). It has been subjected to many problems including eutrophication, overfishing, introduction of alien species and pollution which caused a negative effect on its biological diversity (Walday and Kroglund, 2002). Water residence time in the Baltic Sea was estimated to be about 25 years with a restricted exchange with the North Sea via the Danish straits. Therefore, pollutants can remain in the Baltic Sea for a long time making it one of the most polluted seas in the world (Håkanson et al., 2003; HELCOM, 2003). In the last decades, the contamination of the aqueous environment by anthropogenic trace pollutants has clearly changed from hydrophobic pollutants (i.e. persistent, volatile, toxic and accumulative in sediment and food chains) to hydrophilic pollutants (e.g. polar pollutants) (Fobbe et al., 2006). Even though most conducted studies and monitoring programs on the pollution of the Baltic Sea and its estuaries have focused on persistent organic pollutants (POPs) (Falandysz et al., 2004; HELCOM, 2010).

The German Baltic catchment area consists of 72% agricultural areas and 15% woodland and forms almost 4% (28,600 km^2) of the total Baltic catchment area (HELCOM, 2004). The area of federal state of Mecklenburg-Vorpommern (M-V) is the largest catchment area of the German Baltic Sea, with the coastline of 340 km (Brügmann and Bachor, 1990; BUND, 2012).

Germany is the second largest consumer of pesticides in Europe (Zhang et al., 2011). Almost half of pesticides used in Germany are herbicides (BVL, 2013). MCPA ((4-chloro-2-methyl-phenoxy) acetic acid), mecoprop, isoproturon, bentazon and chloridazon are polar herbicides used in amounts ranging from 25 t to 2500 t in 2012 (BVL, 2013). Chloridazon-methyl-desphenyl (CMD) is a degradation product of the herbicide chloridazon observed in the environment (Buttiglieri et al., 2009). These compounds were detected in ground and fresh surface water of M-V federal state (Bachor et al., 2008).

Rivers are the predominant pathway for herbicides transportation to the marine environment (Albanis et al., 1995; Olsson et al., 2012). Herbicides can enter the surface water by either a point source input, such as spillage, fault equipment, waste disposal, tank filling and washing, or by non-point emissions resulting from leaching, spry-drift and surface runoff (Carter, 2000; Dabrowski et al., 2002). In general, polar herbicides can easily enter the aquatic environment due to their high water solubility and low adsorption to soils (RED, 1994, 2004, 2007). Once herbicides reach the river streams, they are transported to the marine environment.

Estuaries are transition zones between rivers and open seas which play an important role for both biodiversity and human existence. They are frequently subjected to anthropogenic contamination resulting from agriculture, domestic and industrial activities presenting a threat to the aquatic ecosystem (CIESM, 2004; Shimmield, 2011). Even though of many estuarine and marine organisms maybe negatively affected when exposed to polar herbicides (Kirby and Sheahan, 1994; Sjollema et al., 2014), information about their occurrence and transport to the Baltic Sea via its estuaries is still scarce.

For polar herbicide residue analysis, liquid chromatography tandem mass spectrometry (LC-MS/MS) via electrospray ionization (ESI) interface has proven to have a high sensitivity and selectivity when operating in the selected reaction monitoring (SRM) mode (Giordano et al.,

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2009; Steen et al., 1999). Nonetheless, the determination of organic contaminants in environmental samples requires accurate methods. In fact, several reasons such as incorrect sampling, losses of analytes during sample storage, error during sample preparation, sample contamination, uncertain identification of the target analytes can cause inaccurate results. Moreover, matrix effect through other unwanted components presented in environmental samples is a major problem that occurs when the technique is used. This problem can lead to a suppression or enhancement of the analyte signals (Patel, 2011), consequently to incorrect quantitative results.

The objectives of the present study were: (I) to compare between two LC-MS/MS analytical methods including different sample preparation methodologies and quantitative methods for determination of the herbicides MCPA, mecoprop, isoproturon, bentazon and chloridazon, and the metabolite CMD in the Baltic estuarine water samples; (II) to study transport of the mentioned substances to the Baltic Sea via some of its estuaries; (III) to study their distribution between Baltic Sea coastal waters and sediments.

The water samples from the estuaries and marine stations were collected in order to determine an occurrence and distribution of five polar herbicides in the German Baltic coast. In addition to the water samples, sediment samples were collected from the Baltic coastal stations (Fig. 1).

Two analytical approaches were used in the analysis of the water samples. The first approach is based on a standard addition method (SAM), without pre-concentration or cleanup step. In the second approach the samples were pre-concentrated and the internal standard method (ISM) was used for quantification. For the SAM samples, 1 L of estuarine surface water samples were collected in amber glass bottles, in spring and summer 2012 (May, June, August and September) and in June 2014. The samples reached the laboratory a few hours after sampling and were stored in the dark at 5 °C prior analysis. A volume of 40 mL of each sample was filtered using 0.45 μm RC syringe filters (Phenomenex, Germany). The filtered 40 mL sample was split into four 10 mL fractions. Three increasing concentrations of the mixed standard solution of all analytes (MCPA ((4-chloro-2-methyl-phenoxy) acetic acid), mecoprop (methyl chlorophenoxypropionic acid), isoproturon (3-(4-isopropyl- pheneyl)-1,1-dimethylurea), bentazon (3-isopropyl-1H-2,1,3-benzothiadiazin-4(3H)-one2,2-dioxide), chloridazon (5-amino-4-chloro-2-phenyl-3(2H)-pyridazinone), chloridazon-methyl-desphenyl (5-amino-4-chloro-2methyl-3(2H)-pyridazinone) - Dr. Ehrenstorfer GmbH, Germany) were added. 1 mL of fortified samples was transferred into 1.5 mL glass vials. A volume of 50 μL was injected into the LC-MS/MS system and measured according to the developed method. The quantitative analysis of the environmental samples was carried out based on four calibration points, each in triplicate injections.

For the ISM samples, 2 L estuarine water samples were collected in May and June 2014. The samples in June were simultaneously taken with the SAM samples. The samples were stored in darkness, in pre-rinsed amber bottles, at 5 °C. Further treatment was done within 48 h. In addition to estuarine samples, sea water was collected during three cruises in February (cruise AL430), May (cruise EMB69) and June (cruise EMB76) 2014. The detailed description of the sampling and the analysis of these samples can be found in Orlikowska et al. (2015). In brief, the samples were divided into two 1 L subsamples. Each sample was spiked with 1 mL of 5 ng/mL internal standard mixture (mecoprop-D_6, isoproturon-D_6, bentazon-D_6 and chloridazon-D_5 - Dr. Ehrenstorfer GmbH, Germany) and the pH was adjusted to 2 with 5 M HCl (Merck KGaA, Germany). A Chromabond Easy (3 mL, 200 mg; Marchery-Nagel GmbH, Germany) cartridge was used for extraction. Pesticides were eluted with 4 mL of HPLC grade acetone/methanol (v/v, 1/1) and 6 mL methanol/13% $NH_{3(aq)}$ (v/v, 97/3). The extract was evaporated to dryness, re-dissolved in 1 mL water/methanol (v/v, 1/1) and measured according to the developed LC-MS/MS method. An injected sample volume was 10 μL.

The sediment samples were collected during the cruise EMB76 in June 2014 from 5 stations (11, 13–16, Fig. 1) using a multiple corer (MUC). The uppermost sediment samples were sealed in glass jars and stored at −20 °C until freeze-drying. Five grams of the homogenized sediments weighted into the glass vials were saturated with LC-

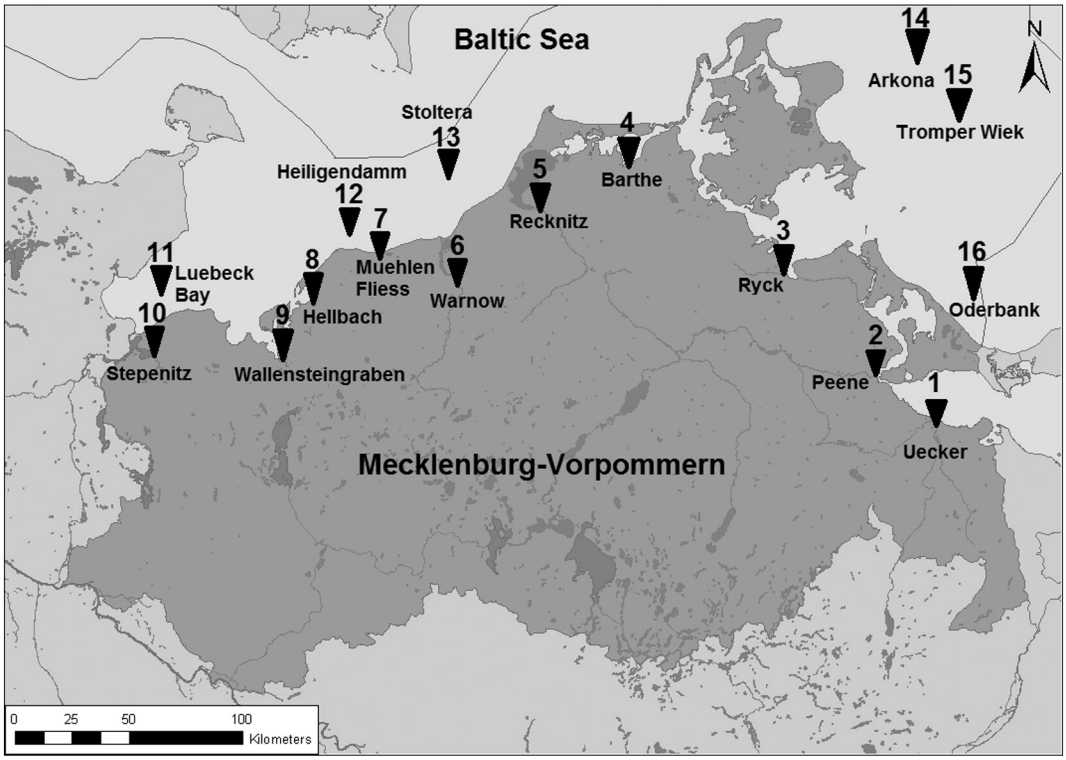

Fig. 1. Sampling locations in the German Baltic coast and estuaries in Mecklenburg-Vorpommern in 2012 and 2014.

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