



Spatial, seasonal and vertical distributions of currently-used pesticides in the marine boundary layer of the North Sea



Carolin Mai^a, Norbert Theobald^{a,*}, Gerhard Lammel^{b,c}, Heinrich Hühnerfuss^d

^a Federal Maritime and Hydrographic Agency (BSH), Bernhard-Nocht-Straße 78, 20359 Hamburg, Germany

^b Max Planck Institute for Chemistry, Hahn-Meitner-Weg 1, 55128 Mainz, Germany

^c Masaryk University, Research Centre for Toxic Compounds in the Environment, Kamenice 5, 62500 Brno, Czech Republic

^d University of Hamburg, Department of Chemistry, Martin-Luther-King-Platz 6, 20146 Hamburg, Germany

HIGHLIGHTS

- 23 pesticides were analysed in the marine boundary layer of the North Sea.
- Simultaneously, these pesticides were quantified in the surface seawater.
- Concentrations were seasonally highly variable.
- Deposition of contaminated air from land contributes to seawater contamination.
- Deposition was most significant for the distribution of pendimethalin and trifluralin.

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ABSTRACT

Pesticides are transported beyond source regions and reach coastal waters and shelf seas. 23 representatives of six chemical classes of currently-used pesticides (CUPs) were simultaneously quantified in the marine boundary layer and the surface seawater of the German Bight and the central North Sea in 2009 and 2010. Terbutylazine, metolachlor, metazachlor, pendimethalin and trifluralin exhibited the highest concentrations, seasonally highly variable. Advection of contaminated air from land and subsequent atmospheric deposition was shown to contribute to surface seawater contamination significantly, in particular in regions beyond riverine input and during the main seasons of application in agriculture. Deposition was most significant for the seasonal and spatial distributions of pendimethalin and trifluralin. Atrazine and simazine levels in the air are lower than 1–2 decades ago.

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1. Introduction

Knowledge about atmospheric concentrations and pathways of organic contaminants is essential for the establishment of effective national and international environmental regulations and politics. Currently-used pesticides (CUPs), mostly polar organics of diverse chemical nature, poses a hazard for the environment, humans and wildlife due to their occurrence in surface and ground water (Kiefer and Sturm, 2008). They are among the list of ‘emerging pollutants’. Despite the intention of the criteria applied to the registration of pesticides on the markets, which aim to prevent from long-range atmospheric transport, there is ample evidence that CUPs (and other biocides) used in agriculture and forestry are not only transported regionally within the source regions (Goolsby et al.,

1997; van Pul et al., 1999; Duyzer and Vonk, 2001; Asman et al., 2005; Scheyer et al., 2007; Yao et al., 2008), but do reach coastal waters and shelf seas (e.g., Bester and Hühnerfuss, 1993; Law et al., 1994; Alegria and Shaw, 1999) and even remote environments including the Arctic (Chernyak et al., 1996; Muir et al., 2004; Hoferkamp et al., 2010; Zhong et al., 2012). Both riverine and atmospheric deposition have been identified as sources in shelf seas, including in the North Sea (Hühnerfuss et al., 1997; Alegria and Shaw, 1999; BLMP, 2005).

In agricultural areas (Asman et al., 2005; Scheyer et al., 2007; Yao et al., 2008) strong seasonalities of atmospheric levels as well as in precipitation related to CUPs’ application were observed. However, the atmospheric cycling of CUPs is far from understood: The vapour pressures of active ingredients of pesticides on the market classify the substances as semivolatiles ($p_{\text{sat}} = 10^{-6}$ – 10^{-2} Pa at 298 K; Franklin et al., 2000) and besides volatilisation additional ways of mass transfer into air, such as re-suspension of dust (e.g., Cessna

* Corresponding author. Tel.: +49 40 3190 3300; fax: +49 40 3190 5033.
E-mail address: norbert.theobald@bsh.de (N. Theobald).

et al., 2006) and mobilisation with sea spray (e.g., Albert et al., 2012) may be significant. On the other hand, wet deposition as a consequence of polarity, and to some extent photochemistry (Palm et al., 1998; Atkinson et al., 1999; Pflieger et al., 2011) should provide effective sinks limiting long-range atmospheric transport and accumulation in remote environments. Accumulation in the marine environment must be expected at least for some CUPs, e.g. the triazines, which resist degradation and reach long lifetimes (months, Widmer et al., 1993). Corresponding to limited knowledge, modelling of CUPs' multicompartamental fate was so far confined to atrazine (Cooter and Hutzell, 2002; Lammel et al., 2007) and lags behind progress made with regard to less polar semivolatiles.

Studies investigating CUPs' concentration levels and spatial and temporal distributions in the marine atmosphere are scarce, even for European seas. The aim of this study was the determination of the atmospheric levels of CUPs in the marine boundary layer (MBL) of the North Sea with emphasis on the contribution of atmospheric deposition to the surface seawater contamination. Except for triazines and organophosphates no data on CUPs levels were available one decade ago (Weigel, 2001) and very few data have been added since. 23 representatives of six pollutant classes of CUPs (in central and western Europe) were targeted in this study: nine triazine herbicides (ametryn, atrazine, hexazinone, irgarol, prometryn, propazin, simazin, terbuthylazine, terbutryn) and the metabolite desethylatrazine, six organophosphate insecticides (chlorfenvinphos, malathion, azinphos-ethyl, azinphos-methyl, diazinone, dimethoate), the thiadiazine insecticide bentazon, two carbamate pesticides (carbendazim, pirimicarb), two chloroacetanilide herbicides (metazachlor, metolachlor) and two dinitroaniline herbicides (trifluralin, pendimethalin). Atrazine and simazine are not any longer registered pesticides in Germany, the Netherlands, Denmark and the United Kingdom. The selection was directed by the results of seawater monitoring of the Federal Maritime and Hydrographic Agency of Germany (BSH; BLMP, 2005; Theobald, 2011). Seasonal, vertical and spatial distribution patterns of CUPs in the MBL of the North Sea in 2009 and 2010 will be presented and discussed along with the results of seawater monitoring.

2. Experimental

2.1. Air sampling

High volume air samplers (HVS, Digital DHM-60, Riemer, Hausen, Germany) were used for the volumetric quantification of atmospheric trace concentrations of the targeted CUPs allowing the investigation of their spatial distribution at definite times. They were placed at the topdeck of research vessels during two sampling campaigns in the German Bight (May–June 2009 and May 2010) and one in the central North Sea (August/September 2009). Contamination by ship exhausts was carefully avoided by interrupting sampling whenever relative winds arriving from the rear of the ship. In addition, bad weather conditions forced a sampling stop. Therefore, sampling duration and sample volume varied from sample to sample. On average approximately 260 m³ (106–518 m³) of ambient air was sampled within 4–21 h. Glass fibre filters (GFFs, MN85/90BF of 15 cm diameter, Macherey-Nagel, Düren, Germany) and adsorber cartridges (ORBO 2500 PUF/XAD-2/PUF cartridges, Supelco, Sigma–Aldrich, Taufkirchen, Germany) consisting of a sandwich of polyurethane foam (PUF) and XAD-2 were applied to the separate collection of the particle associated and the gaseous mass fraction of CUPs. In addition, gauze-insertions were developed, which were inserted into the adsorber cartridge in order to prevent the loss and contamination of the air sampler by XAD-2 particles.

Seasonal and vertical fluctuations of CUPs in ambient air were monitored by time integrating (28–50 days) passive air sampling studies. PUF disk passive air samples (PAS) were collected at a residential land based sampling site, Hamburg-Sülldorf, and at a rural coastal sampling site Tinnum on the island Sylt, between October 2009 and December 2010, respectively. Three passive air sampling campaigns were conducted on the research platforms FINO1 and FINO3 in the German Bight. The samplers were simultaneously exposed in 60 m, 80 m and 100 m height above sea level. The first two sampling campaigns were performed almost in parallel (time delay of 7 days) at FINO1 located at Borkum Riffgrund (40 km distance to the coast) and at FINO3 west of the island Sylt (70 km distance to the coast) during 50 d in August/September 2010. The third sampling campaign was performed at FINO1 during 34 d in September/October 2010. This study applied PUF disks of 14 cm diameter, 1.4 cm thickness and 0.0213 g cm⁻³ density, which were placed in a protective chamber during exposure (Harner et al., 2004; Klánová et al., 2006). The unmodified design of the protection chamber was used for the campaigns in Hamburg-Sülldorf and Tinnum, but it was found to be deformed at high wind speeds (>7 m s⁻¹). It was improved by connecting the bowls with a hinge-joint providing a more effective fixation of the bowls and a simplified exchange of PUF disks at places difficult to operate at, e.g., on masts. Seasonal and vertical trend investigations were carried out based on the total amount of CUPs accumulated on the PUF disks. The following principles were applied: The PUF disks in Hamburg-Sülldorf and Tinnum were simultaneously exchanged in fixed time intervals of 28 days. Sampling rates were controlled by the recoveries of performance reference compounds (PRCs) spiked prior to exposure (Section 2.2). Additional information to the air sampling methodologies is given in the [Supplementary Material \(SM\), S1.1](#).

2.2. Preparation for the sample collection

PUF plugs, PUF disks and XAD-2 were rinsed with tap water and underwent Soxhlet-extraction with acetone, hexane and methanol for 12 h. The pre-cleaned adsorber materials were dried in a vacuum dessicator for 24–48 h. Thereafter, the PUF plugs and PUF disks were wrapped twofold in aluminium foil, sealed in zip-lock plastic bags and stored in a freezer (–20 °C) until use. The XAD-2 resin was transferred to a pre-cleaned glass jar with screw cap and kept frozen (–20 °C). Adsorber cartridges were assembled at the clean bench. PUF/XAD-2/PUF adsorber cartridges were equipped with pre-cleaned gauze insertions. A smaller PUF plug (250 mm × 550 mm) was placed above the insertion to prevent clogging of the gauze pores by the XAD-2 resin. Thereafter, 10 g of XAD-2 and a second PUF plug (500 mm × 550 mm) were placed inside the cartridge. The assembled adsorber cartridges were wrapped in aluminium foil, sealed in plastic bags and stored in the freezer (–20 °C) until deployment. Glass fibre filters were baked at 500 °C in a muffle furnace for 24 h. Subsequently GFFs were separately placed in pre-cleaned petri dishes, which were sealed with parafilm[®], wrapped in aluminium foil and stored at –20 °C.

Prior to exposure the GFFs, adsorber cartridges, PUF disks and their respective field blanks were defrosted. Thereafter, the adsorber cartridges, PUF disks and their field blanks were spiked with PRCs (for details see [SM S1.2](#)), respectively. GFF and adsorber cartridge were inserted in their respective solvent-rinsed sampler holders prior to their installation into the HVS. Field blanks were packed and stored in the freezer until extraction in parallel to the samples.

2.3. Air sample preparation

Experimental details are presented in [SM, S1.3](#) and in [Mai \(2012\)](#). In short: All air samples were defrosted prior to extraction, spiked

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