Journal of Marine Systems 162 (2016) 47–56

Contents lists available at ScienceDirect

Journal of Marine Systems

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

Exploring the occurrence and distribution of contaminants of emerging concern through unmanned sampling from ships of opportunity in the North Sea

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ARTICLE INFO

Article history:
Received 29 July 2015
Received in revised form 14 December 2015
Accepted 7 March 2016
Available online 9 March 2016

Keywords:
Pollution monitoring
Mobile platforms
Monitoring systems
Marine environment
North Sea
Drugs
Pesticides
Organic compounds

ABSTRACT

Chemical pollution is of concern for the marine environment. New European regulation demands exposure and impact assessment to be conducted in coastal environments in order to define and ensure fulfillment of environmental quality standards. A cost-effective approach for monitoring the over 100,000 km of European coasts is necessary. This proof-of-concept study focuses on the use of unmanned water sampling from a commercial ship of opportunity to implement monitoring of marine contaminants of emerging concern. Marine areas that are not directly affected by river plumes or other direct sources were covered in order to provide information on background pollution. 14 currently used pesticides, 11 pharmaceuticals and personal care products and 3 food additives were detected in water samples through targeted analysis at sub-ng to tenths of ng/L levels in both coastal and offshore areas of the North Sea. Among contaminants, 6 pesticides (dimethoate, fenpropimorph, pendimethalin, propiconazole, tebuconazole and temephos), 3 pharmaceuticals (acetaminophen, naproxen and ketoprofen) and 2 food additives (acesulfame and saccharine) have never been detected before in offshore areas. 4 pesticides (diuron, isoproturon, metazachlor and terbuthylazine), 4 pharmaceuticals (carbamazepine, atenolol, ibuprofen and ketoprofen) and 2 food additives (sucralose and acesulfame) were detected in over 90% of the samples. The antibiotic sulfamethoxazole was detected in 50% of the samples at tenths of pg/L levels, including some offshore areas. Our study highlights that the use of ships of opportunity can provide a key support for the development and cost-effective implementation of marine monitoring of chemical pollutants in Europe and elsewhere.

1. Introduction

Synthetic organic chemicals have become central to medicine, personal and house care, food production, and virtually any type of industrial process. Several million substances have been traded, used and potentially emitted to the environment (CAS, 2015a). 350,000 of them are somehow regulated in the international markets (CAS, 2015b), while more than 140 000 chemicals are currently produced at industrial scale and traded globally at environmentally relevant volumes (ECHA, 2015). Among these, about 5000 are listed as high production volume chemicals by the OECD (OECD, 2009). In contrast to these numbers available data on substances' safety and occurrence in the environment are still very limited.

Marine coastal waters are receptors of thousands of chemical pollutants (Dachs and Méjanelle, 2010) emitted through waste water, deposited from the atmosphere or released directly to the sea from vessels or other coastal or offshore infrastructures during both professional and recreational activities. Several anthropogenic chemicals are detected in surface water even in remote oceanic regions (Echeveste et al., 2010; Lohmann et al., 2007; Yamashita et al., 2005). A number of international treaties and conventions aim at regulating some classes of prioritized substances of particular concern. Priority lists, however, are generally limited to a few dozens of chemicals with well-studied toxic properties. Unregulated chemicals, referred to as Contaminants of Emerging Concern (CECs) by EPA (EPA, 2015) and by the EU NORMAN network (NORMAN, 2015) are defined as those substances frequently detected in environmental samples. These include several classes of chemicals encompassing both high- and low- production volume substances (Loos et al., 2013; Munschy et al., 2013; Picot Groz et al., 2014; Weigel et al., 2002). Loos et al. reported the results of a seminal screening of CECs in European marine waters (Loos et al., 2013). Analyzed CECs include antifouling pesticides, industrial additives (e.g. plasticizers, anticorrosive agents, surfactants and

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http://dx.doi.org/10.1016/j.jmarsys.2016.03.004
0924-7963/

flame retardants), several pharmaceuticals and personal care products (PPCPs), herbicides and a food additive (namely, sucralose). During a large scale screening performed in different coastal systems, Nödler et al. also reported the detection of 37 substances including pharmaceuticals, pesticides and corrosion inhibitors (Nödler et al., 2014). Zhong et al. (2012) reported occurrence of 6 currently used pesticides (CUPs) in open ocean waters at pg/L levels. These CECs are prevalently hydrophilic substances with lower partitioning onto sediments and suspended particles. Marine water is therefore a final receptor for most of these substances.

Traditionally, resistance against degradation in the environment (i.e. "persistence") has been described as a crucial factor driving to long range transport of pollutants towards areas far from sources (as in the case of offshore areas) (Scheringer, 2002). Several of the substances reported in these seminal studies (such as several pharmaceuticals and CUPs) are not intrinsically persistent. The drivers and mechanisms controlling their presence in transitional and coastal waters and their transport to the open sea require therefore further elucidation.

Running exploratory studies to target CECs in marine waters is necessary for an effective development and implementation of marine protection actions. There obviously are several practical challenges, in particular: i) cost-effective monitoring strategies are mandatory due to the geographical extension of coastal and offshore areas. Organizing dedicated scientific cruises may not prove feasible for long-term intensive monitoring. ii) State-of-the-art sampling and analytical techniques are necessary to monitor seawater contamination due to the very high dilution level. iii) There is a need for testing and proofing suitability of established analytical chemistry tools initially conceived for application in fresh water environments.

A possible strategy for cost-effective monitoring considers the use of unmanned sampling devices on ships and marine platforms of opportunity. These ships and platforms are extensively available from commercial fleet and coastal infrastructures (Allan and Harman, 2011). In addition, the number of multi-purpose marine observing systems is constantly increasing around European coasts and the level of harmonization/standardization of installed sensors/sampling devices and accessibility to international stakeholders is rapidly improving thanks to initiatives such as the EC Framework Programme 7 — JERICO project (Jerico, 2015).

In this paper we present a study aimed at demonstrating the possible effective use of existing robotic sampling devices installed on the European FerryBox fleet (a set of commercial vessels serving on European routes and hosting scientific instrumentation operated by several institutes) (Petersen, 2014) in combination with state of the art mass spectrometry to detect a broad range of CECs in marine coastal and offshore waters.

2. Materials and methods

2.1. Ship of opportunity and sampling instrumentation

As a proof of concept we used a cargo/container ship (Lysbris, DFDS Seaways, Copenhagen, Denmark) in service in the North Sea equipped with an in-line multi-sensor device for water quality assessment and remote communication instruments for forecasting/receiving data to/from land. Such a system has characteristics similar to several other units currently installed in the European FerryBox fleet including also an automatic device for the collection and preservation of bulk water samples.

The Lysbris regularly cruises from Moss/Halden (Norway) across the southern part of the North Sea along the offshore of Germany and the Netherlands to Ghent/Zeebrügge (Belgium). It then crosses the eastern end of the English Channel to head westerly during its approach to Immingham (UK). Finally the ship returns to Norway across the central part of the North Sea (Fig. S1). Altogether, each cruise takes between 6 and 7 days.

The sampling focused on collecting seawater in five areas both in coastal locations (i.e. several km from shore) as well as in offshore areas (i.e. up to 200 km from shore). All selected areas were chosen to be not directly affected by river plumes (Fig. S1). The rationale for this was to stress sensitivity of analytical methods and obtain information on background pollution in the North Sea.

The FerryBox system deployed on Lysbris is operated by the Helmholtz–Zentrum Geesthacht (Germany). As other FerryBox units it is equipped with sensors for temperature, salinity, and many other optical and chemical parameters (Petersen, 2014). An inline automated refrigerated (4 °C) water sampler (6712FR, Teledyne Isco, Lincoln, NE, USA) is interfaced to the communication unit of the FerryBox with a capacity of 24 one-liter bottles made of high-density polyethylene. The dedicated water intake is installed at the hull of the ship at a depth of 3–4 m depending on the load of the vessel. Sampling in an individual bottle takes place in less than one minute (i.e. the ship sails several hundred of meters during one-bottle sample collection). No pre-filtration unit is used. Water sample collection events were remotely preprogrammed using mobile phone network connection. A set of geographical coordinates' ranges defining sampling locations was input to trigger automatic sample collection in individual bottles (i.e. the system collects one sample when the ship intercepts one of the preselected areas).

2.2. Sampling

Aggregated samples from five different areas (Figs. 1 and S1) (area 1: Skagerrak-North Sea confluence, area 2: Vesterhavet, area 3: Dutch coast, area 4: English Channel mouth and area 5: East Britain/central North Sea) were collected. This was repeated during three consecutive cruises in October 2014. Each aggregated sample comprised four individual samples collected along routes approximately 120 to 200 km long within each of the selected areas. The overview of individual sampling sites and the total volume sampled per location during individual cruises can be found in the supplementary information (Fig. S1, Table S1).

The sampler bottles were pre-cleaned using Decon 90 (Decon Laboratories Limited, Hove, UK), Milli-Q water and rinsed with methanol at least three times. Residual methanol was allowed to evaporate for at least one hour under the fume hood before sealing the bottles and transporting them to the ship. Before and after the collection of the water samples the bottles remained unsealed (albeit contained in the closed dark cabinet of the automatic sampler) during the full duration of the cruise.

The sampling train integrated into the automatic sampler included coupled metal and polytetrafluoroethylene (PTFE) tubing, PTFE coated rubber gaskets, and a peristaltic pump where all wet parts were in PTFE or polypropylene. At the end of each cruise the samples were transferred (on board) to pre-cleaned amber glass bottles sealed and shipped to the laboratory where concentrated hydrochloric acid was added to set the samples to pH 2. Before analysis the samples were stored in a dark refrigerated room at 4 °C until further processing. Storage time ranged between 1 and 3 weeks.

2.3. Targeted substances

The target analytes included 3 artificial sweeteners (acesulfame, saccharine, sucralose), 11 pharmaceuticals (atenolol, acetaminophen, caffeine, carbamazepine, clofibric acid, diclofenac, hydrochlorothiazide, ibuprofen, ketoprofen, naproxen, and sulfamethoxazole), 3 personal care products (DEET, triclocarban, triclosan) and 40 pesticides (Table S2). Information on analytical standards and reagents is included in Supplementary information (Text S1).