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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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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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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 pre-programmed 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).

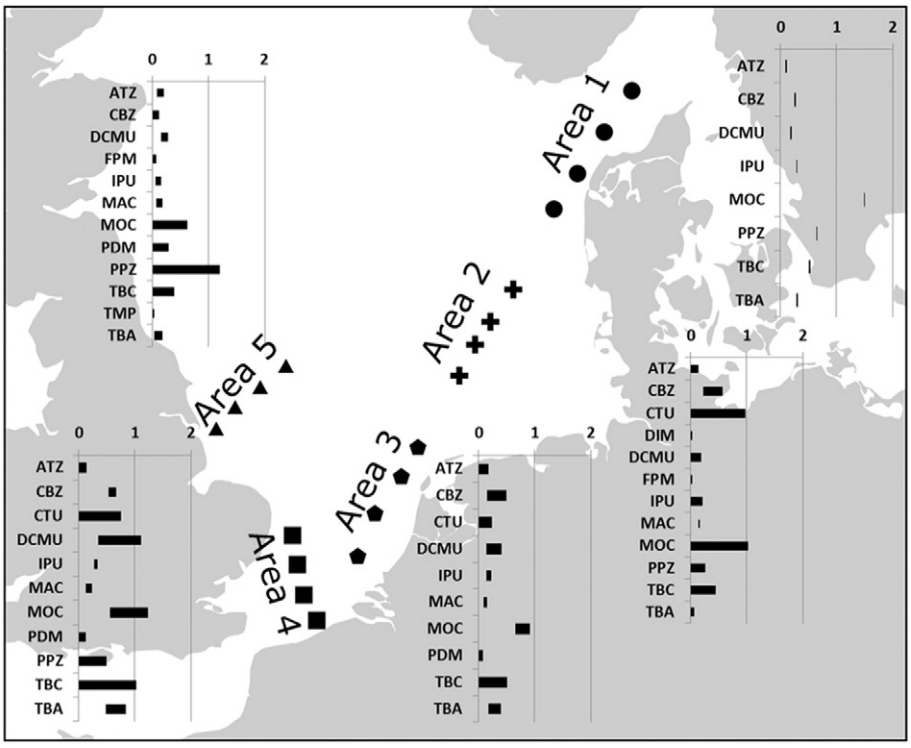

Fig. 1. Ranges of detected concentrations of currently used pesticides found in the North Sea in ng/L (October 2014). Only detected compounds are presented: ATZ — atrazine; CBZ — carbendazim; CTU — chlortoluron; DIM — dimethoate; DCMU — diuron; FPM — fenpropimorph; IPU — isoproturon; MAC — metazachlor; MOC — metolachlor; PDM — pendimethalin; PPZ — propiconazole; TBC — tebuconazole; TMP — temephos; TBA — terbuthylazine. In area 1, samples were collected only during cruise 3; therefore, ranges could not be determined.

2.4. Sample extraction

Solid phase extraction was conducted using Waters® Oasis hydrophilic–lipophilic blend (HLB, 1 g) columns. No pre-filtration of samples was necessary owing to the low particle concentrations. Before extraction, the column was conditioned with 10 mL of methanol and then equilibrated with 10 mL of Milli-Q water adjusted to pH 2. The water sample was passed through the cartridge using PTFE tube connected to the sample bottle at an approximate flow rate of 10 mL/min generated by negative pressure. After extraction, the columns were rinsed with 20 mL Milli-Q water adjusted to pH 2 in order to remove sea salt residues and dried for 15 min under vacuum. To remove residual water, columns were placed in polypropylene centrifuge tubes precleaned with methanol at least three times and spun on a centrifuge 5810 R (Eppendorf, Hamburg, Germany) at 3250 g for 2 min. Elution was performed with 15 mL of methanol and then 15 mL of acetone (no vacuum applied). The extract was subsequently evaporated to near dryness under a gentle stream of nitrogen at a temperature of 40 °C using nitrogen evaporator EVATERM (LABICOM, Olomouc, Czech Republic). Samples were reconstituted in 0.5 mL methanol and completed to an exact final volume of 1 mL by the addition of HPLC water. For the analysis of artificial sweeteners and the first fraction of PPCPs, a part of the sample (40 μL) was further diluted using HPLC water by a factor of 5 to obtain a final content of methanol 10%.

2.5. UPLC–MS/MS and HPLC–MS/MS analysis

Four methods with different mobile phase composition described below were used for the analysis of different groups of substances. Separation and detection of pharmaceuticals, personal care products and sweeteners were performed using different methods (Table S3) by a ultra-performance liquid chromatograph (UPLC Acquity, Waters, Milford, MA, USA) coupled to a mass spectrometer Xevo TQS (Waters, Milford, MA, USA). The systems were interfaced with an electrospray ionization source Z-spray® (Waters, Milford, MA, USA). Quantitative LC-MS/MS analysis was performed for all target compounds in the multiple reaction monitoring (MRM) mode. The most intense MRM transition was employed for quantification and the second one for confirmation. Quantification of target analytes was done using an external calibration curve of freshly prepared standards with a range of 0.01–100 ng/mL (9 points). Both calibration standards and analysed samples were spiked into the final extract prior to analysis with mass-labelled internal standards (acetaminophen-d4 and ibuprofen-d3) to control possible matrix effect.

Artificial sweeteners were separated using an ACQUITY UPLC BEH C18 column (100 × 2.1 mm, 1.7 μm, 130 Å) column (Waters, Milford, MA, USA). Both water and methanol used as mobile phases contained 0.1% formic acid. Gradient elution with initial content of 10% of methanol was applied and final content of methanol (90%) was reached in 5 min. The flow rate of mobile phase was 0.4 mL/min. The injection volume was 10 μL per individual sample. Before next separation, the column was equilibrated using initial composition of mobile phase for 3 min. The mass spectrometer was operated in negative ion mode (ESI-).

For the analysis of the first fraction of the PPCPs, the same column used for the artificial sweeteners was used with methanol and water as mobile phase, both containing 0.01% formic acid and 0.1 M ammonium acetate. The separation gradient, flow rate of mobile phase and injected volume were similar to those previously described. The mass spectrometer was operated in positive ion mode (ESI+).

The second fraction of PPCPs was separated using Xterra C18 (100 × 2.1 mm, 3.5 μm) column (Waters, Milford, MA, USA). Water containing 0.1% acetic acid and 0.1% ammonium acetate and mixture of methanol and acetonitrile (50:50) were used as mobile phases. The initial gradient was set at 40:60 organic:water, in ten minutes the content of organic mixture increased up to 100% (hold for 2 min). The flow rate of mobile phase was 0.2 mL/min. The injection volume was

10 μL per individual sample. Before the next run, the column was equilibrated using the initial composition of mobile phase for 4 min. The mass spectrometer was operated in negative mode (ESI-).

Separation and detection of CUPs in marine water samples were performed using an Agilent 1290 series HPLC (Agilent Technologies, Waldbronn, Germany) coupled to a mass spectrometer AB Sciex Qtrap 5500 (AB Sciex, Concord, ON, Canada). Mass spectrometer parameters for all individual compounds are listed in the supplementary information (Table S4). CUPs were separated using Phenomenex Synergi Fusion C-18 endcapped (4 μm) 100 × 2 mm i.d. column (Phenomenex, Torrance, CA, USA). The mobile phase consisted of 5 mM ammonium acetate in water and 5 mM ammonium acetate in methanol. Mobile phase gradient was as follows: increase of methanol from 20% to 80% during the first minute, then to 90% at minute 5 (hold for 3 min). The flow rate of mobile phase was 0.25 mL/min. The injection volume was 10 μL per individual sample. Prior to next analysis, 5 min of initial conditions were applied on the column. The mass spectrometer was operated in positive ion mode (ESI+). Quantification of analytes was based on mass-labelled internal standards (Alachlor-D13, Acetochlor-D11, Chlorpyrifos-D10, Desisopropylatrazine-D5, Dimethoate-D6, Diuron-D6, Fenitrothion-D6, Isoproturon-D3, Simazine-D10 and Terbuthylazine-D5). Calibration curve was made using freshly prepared standards with a range of 0.03–300 ng/mL (9 points).

2.6. Quality assurance and control (QA/QC)

Procedural blanks (n = 3) as well as field blanks (6 one-liter sampling bottles aggregated by 3 for analysis) and tap water blanks (n = 3) were used to control potential contamination during sampling, transport, sample extraction and analysis. Procedural blanks consisted of SPE cartridges without any loaded water sample, and were handled and extracted identically as the marine water samples and field blanks. Aggregated field blanks consisted of a total of 2.70 L tap water deployed (unsealed) during the whole cruise inside the automatic sampler cabinet. Similarly to field blanks, tap water blanks were refrigerated (4 °C) and stored under dark conditions in the laboratory. Tap water blanks were analyzed and results compared with those from the field blanks in order to assess whether the contamination in the field blanks originated from the bottles or during sampling and handling of samples, or, alternatively if it was present in origin in the tap water used as blank matrix. The determination of the method detection limits (MDLs) followed three different approaches. First, in case the analytes were detected in the field blanks at levels significantly higher than those measured in the tap water blank (meaning contamination of field blank occurred during the sampling campaign), MDLs were calculated for each individual compounds as the average value in field blanks plus 3 times their standard deviation (SD). Second, in case the analytes were detected at similar levels in the tap water and the field blanks (meaning that the tap water used as matrix for the field blank was contaminated in origin), MDLs were calculated as the average of procedural blanks plus 3 times their standard deviation. Similarly, situations in which one or more field or tap blanks had levels significantly higher than those measured in the field samples where interpreted as evidence that contamination was already present in the tap water before it was shipped to the ship to be used as a field blank matrix. Third, in case no signal of the analytes was detected in any blanks, MDLs were calculated as a concentration producing a signal-to-noise ratio equal to 3.

A set of 10 recovery tests was performed using spiked artificial seawater with addition of target compounds at levels 20–200 ng/L (Table 1). Artificial seawater was prepared according to the ASTM standard D1141–98(2013) without the addition of trace metal salts (Stock Solution No. 3) (ASTM International, 2013). 100 mL of spiked artificial seawater were extracted and analyzed using procedures adopted for the field samples. During the recovery test, as a further quality assurance measure, the analysis of 5 procedural blanks consisting of 100 mL of artificial seawater was conducted. Concentration data from marine water samples were not corrected for recovery.

3. Results and discussion

3.1. Results for QA/QC

MDLs ranged 0.01–1.18 ng/L (Tables S3 and S4). The highest MDLs were observed for caffeine (1.18 ng/L), saccharine (0.95 ng/L) and triclosan (0.29 ng/L) possibly due to contamination from the laboratory and/or tap water used as blank matrix. Several compounds were detected in procedural blanks with highest concentration observed for caffeine, triclosan and saccharine (Table S5). A number of analytes were occasionally detected in the field blanks and tap water blanks, too. The comparison between tap water blanks and field blanks is summarized in supplementary information (Table S6). Compounds with concentrations in the field blanks higher than in the tap water blanks included saccharine, acetaminophen, caffeine, ibuprofen and chlortoluron pointing to a possible on board contamination or contamination during handling of sampling materials for these substances. However, a consistent pattern for the occurrence of these substances in field blanks and tap water blanks was not identified. Often, in fact, the signal of blank contamination was present in individual replicates of field or tap water blanks. Several compounds (e.g. ketoprofen and pendimethalin) were even detected in tap water blanks in higher levels than in the field blanks. Surprisingly, higher concentration of acetaminophen was observed in a single event in one field blank compared to all field samples. For the large majority of the substances detected in the blanks we observed a high variability in the measured levels. We could exclude that the source of the contamination was from individual "dirty" sampling bottles. The bottles were in fact previously used only to sample marine waters and routinely cleaned (in batches) between every usage. They therefore never

Table 1
Recovery test results for PPCPs, artificial sweeteners and selected pesticides in artificial seawater.

Compound	% recovery ± RSD	Spiking level (ng/L)
Pharmaceuticals		
Acetaminophen	92 ± 12	200
Atenolol	75 ± 8	200
Caffeine	101 ± 6	200
Carbamazepine	62 ± 13	20
Clofibric acid	125 ± 11	200
Diclofenac	56 ± 13	200
Hydrochlorothiazide	99 ± 13	200
Ibuprofen	95 ± 6	200
Ketoprofen	116 ± 17	200
Naproxen	86 ± 7	200
Sulfamethoxazole	54 ± 11	200
Personal care products		
DEET	110 ± 12	200
Triclocarban	113 ± 6	200
Triclosan	120 ± 19	200
Artificial sweeteners		
Acesulfame K	17 ± 1	200
Saccharine	52 ± 5	200
Sucralose	48 ± 7	200
Selected currently used pesticides		
Acetochlor	76 ± 10	200
Carbaryl	90 ± 8	200
Carbendazim	75 ± 11	200
Chlorsulfuron	76 ± 9	200
Isoproturon	88 ± 12	200
Metribuzin	78 ± 7	200
Pirimicarb	98 ± 13	200
Pyrazon	77 ± 2	200
Simazime	76 ± 6	20

entered into contact with waste water or another potentially highly contaminated matrix. The origin of contamination in field blanks and tap water blank must therefore be attributed to the contamination of the tap water used as blank matrix. The fact that in some cases the analytes were found at higher levels in the blanks than in the field samples supports such a conclusion. The accentuated variability may also be dependent to the time of collection of the tap water or the point in the tap water distribution network. Fortunately, the low levels of the analytes in the blanks did not invalidate the analysis for most of the target substances.

When dealing with the analysis of contaminants at trace levels (typical for marine water samples) it is crucial to correctly select the matrix used as field blank. Our results showed that the use of tap water might be critical, nevertheless the simultaneous analysis of tap water blanks helped (to a certain extent) to infer on the origin of contamination in the field blanks. Tap water contamination may vary depending on the time of collection and the specific location in the water distribution network. In order to improve the resolution of such an approach it is important to prepare field blanks and corresponding tap water blanks from a single well-mixed stock of tap water to guarantee consistency in the results.

The use of purified tap water is also a possibility useful alternative. This includes distillation or ultrafiltration processes. Contamination may however occur also in the laboratory during the purification treatment. A possible useful approach for the definition of field blank matrix is to utilize a water phase (possibly sea water) which has been pre-extracted with the same method used for the extraction of the target compounds from the field samples. Although this approach would guarantee removal of target compounds traces, it may also interfere with the composition of the water matrix by removing some natural organic constituents which may result in a different matrix effect during chromatographic and spectrometric analysis. Seawater may yet prove more accurate than tap water for the use as a field blank due to more similar characteristics to the sample matrix. Different salt concentration may cause differences in the leaching rate of contaminants from the sampling devices and absorption from the surrounding air.

Another crucial aspect concerned with the analysis of polar compounds in marine waters is the possible interference of sea salt during extraction. The recovery test performed here provided satisfactory results. Recoveries of most compounds ranged from 50% to 125% except for acesulfame (17%) (Table 1). Relative standard deviations among replicated ($n = 5$) recovery tests was <20%. Despite poor acesulfame recovery, recovery values were highly consistent (i.e. RSD = 1%).

Previous studies on recovery performance for water samples provided very different results (Klosterhaus et al., 2013; Loos et al., 2013; Nödler et al., 2014; Weigel et al., 2001). This is likely due to the different methods adopted, including different characteristic of seawater (e.g. different salinity and different organic content), different extraction phases and different extraction conditions. Similarly to what has been done in the present and previous studies, it is therefore recommended as a good practice to complement the quantitative analysis with a detailed analysis of recovery performance for individual target compounds using for example a spiked matrix as similar as possible to the field seawater samples.

When using automatic water samplers installed in FerryBox devices it is crucial to take into account possible losses of analytes by volatilization from unsealed sampler bottles. Compounds targeted in the present study have very low Henry's law constants, therefore very little volatilization is expected to occur in the refrigerated cabinet. For the analysis of more volatile compounds, however, a volatilization test is necessary in order to track potential losses (e.g. by adding spiked samples on board for the full duration of the cruise). Another issue when sampling volatile compounds is an increased risk of cross-contamination among samples.

3.2. Currently used pesticides

Pesticides are one of the most monitored classes of chemicals. These substances are used in very large amounts while they are designed to be toxic to organisms at low levels. Of the compounds investigated in this study, alachlor, atrazine, chlorpyrifos, diuron and isoproturon are included on the list of priority substances of the Water Framework Directive (European Comission, 2013). Despite the large monitoring effort in fresh water environments, data of CUPs in marine water are very scarce (Loos et al., 2013; Weigel et al., 2005; Zhong et al., 2012) as well as information on their impacts on marine biota.

Overall, 14 out of the 40 pesticides screened in this study were detected (at least once) in the North Sea. Fig. 1 depicts a summary of the results. Table 2 summarizes detection frequency in marine water samples. Diuron, isoproturon, metazachlor and terbuthylazine were the most abundant and frequently detected currently used pesticides (present in 92% samples). Carbendazim and metolachlor were detected in 83% of the samples. Despite its ban in the EU in 2004, atrazine reached high detection frequency, being present in 75% of the samples. Metolachlor was detected at the highest concentration (1.49 ng/L) in the Skagerrak-North Sea confluence area. Chlortoluron, dimethoate, fenpropimorph, propiconazole and temephos were detected only in few locations. The sum of the concentrations of the currently used pesticides detected, $\sum CUPs$, varied between 0.73 and 5.13 ng/L among different locations and sampling campaigns. $\sum CUPs$ was found maximum in the mouth of the English Channel although levels did not vary very much across different locations. Detailed results are reported in Table S7. It is surprising that pesticides were detected at such a high frequency in marine waters and offshore areas in autumn when their use in Europe is expected to peak in spring–summer.

Lower salinity observed in some samples from the English Channel (area 4) and the Skagerrak-North Sea confluence (area 1) indicates mixing with freshwater. River estuaries serve as main sources of pesticides to the marine coastal environment. Salinity was generally homogeneous across all other sampling areas reflecting sampling locations not directly affected by river plumes. A significant relationship between $\sum CUPs$ levels and pooled sample salinity (average of salinity levels in individual spot samples (Table S1) was not found, possibly due to the limited variability on both pesticides and salinity levels observed in the selected areas. Despite this, $\sum CUPs$ had a maximum in the area of local minimum of salinity (e.g. area 4, English Channel).

Several pesticides have been routinely detected in near-shore and estuarine areas (Booij et al., 2015; Munaron et al., 2012; Nödler et al., 2014). One study also reported the presence of 6 pesticides in open oceanic water (Zhong et al., 2012). Among the pesticides detected in the present study, dimethoate, fenpropimorph, pendimethalin, propiconazole, tebuconazole and temephos were, to our knowledge, never analyzed/detected before in offshore marine waters. The presence of diuron in the North Sea coastal water (used as a substitute for organotin antifouling paints) was already reported at similar levels (0.401–1.957 ng/L) in the offshore water 16 km from Venice coasts (Loos et al., 2013). The levels of isoproturon observed in the present study in the North Sea (<MDL-0.34 ng/L) were one order of magnitude higher than in the aforementioned study conducted in the northern Adriatic Sea. In contrast, concentration of terbuthylazine (<MDL-0.84 ng/L) was one order of magnitude lower, which is consistent with previous studies performed in the North Sea by Weigel et al. (Weigel et al., 2005, 2001). The measured levels of metolachlor and carbendazim were also in agreement with previous reports (Loos et al., 2013; Weigel et al., 2001; Weigel et al., 2005).

The pesticides detected here in marine water are used in Europe following strictly disciplined practices to reduce off-site detrimental exposure. Following European regulation they should be conceived to minimize their environmental half-life and their potential for leaching and run-off from the treated fields (European Comission, 2009). We detected here several CUPs in offshore marine waters at sub-ng

Table 2
Detection frequencies.

Currently used pesticides		Pharmaceuticals and personal care products		Artificial sweeteners	
	% detection		% detection		% detection
Atrazine	75				
Carbendazim	83	Acetaminophen	75		
Chlortoluron	33	Atenolol	92		
Dimethoate	8	Caffeine	83		
Diuron	92	Carbamazepine	100	Acesulfame	100
Fenpropimorph	17	Clofibric acid	33	Saccharine	58
Isoproturon	92	DEET	83	Sucralose	100
Metazachlor	92	Ibuprofen	100		
Metolachlor	83	Ketoprofen	92		
Pendimethalin	42	Naproxen	83		
Propiconazole	33	Sulfamethoxazole	50		
Tebuconazole	58	Triclocarban	8		
Temephos	8				
Terbuthylazine	92				

to ng/L levels in a season that did not match the period of their maximum usage. These findings highlight the need of elucidating the drivers controlling transport and persistence of CUPs in the marine environment. In particular large uncertainty exists on the persistence of these substances in marine waters and sediments. Some of these substances may have environmental half-lives in marine environment longer than anticipated. Reiterated seasonal applications may also determine a continuous replenishment of losses due to degradation in the sea. Such a pseudo-persistent behavior (Daughton, 2003) may result in broadening their spatial range.

3.3. Pharmaceuticals and personal care products

There is relatively little information on the fate and occurrence of pharmaceuticals and personal care products in marine waters. Similarly to pesticides, pharmaceuticals in the environments are of concern since they are synthesized to be biologically active at very low concentrations.

Nine out of 11 pharmaceuticals investigated were detected in one or more areas of the North Sea. These were: three anti-inflammatory drugs (ibuprofen, ketoprofen, and naproxen), one antipyretic (acetaminophen), one stimulant (caffeine), one anticonvulsant (carbamazepine), one lipid-lowering agent (clofibric acid), one β-blocker (atenolol) and one antibiotic (sulfamethoxazole). Detected compounds with corresponding concentration levels are depicted in Fig. 2. Carbamazepine and ibuprofen were detected in 100% of the samples (Table 2). Atenolol and ketoprofen were detected in 92% and caffeine and naproxen in 83% of the samples, respectively. Diclofenac and hydrochlorothiazide were present below the detection limit in all samples. Detailed results are shown in Table S7.

Two out of three personal care products investigated were also detected in the North Sea. Insect repellent DEET was found in 83% of the samples in the range < MDL–0.47 ng/L which is consistent with data reported by Weigel et al. (Weigel et al., 2002, 2001). Triclocarban was detected only in one sample in concentration of 0.07 ng/L. To our knowledge this is the first time this antimicrobial is detected in offshore areas. The antibacterial agent triclosan was not detected in this study, however its occurrence has been previously reported in the North Sea by Xie et al. (Xie et al., 2008). This is probably due to the lower MDLs reached by Xie et al. (0.5–15 pg/L) compared to our method.

The overall sum of the concentrations of the detected pharmaceuticals and personal care products ($\sum PPCPs$) varied between 3.00 and 37 ng/L among different locations and sampling campaigns. $\sum PPCPs$ was found maximum in the Vesterhavet area (area 2) although higher variability was observed within an individual sampling area (e.g. during different cruises) than between them. No significant relationship between $\sum PPCPs$ levels and pooled sample salinity (i.e. average of salinity levels in individual spot samples (Table S1)) was found.

Occurrence of pharmaceuticals in marine waters was already investigated in several coastal studies (Borecka et al., 2015; Gros et al., 2012; Klosterhaus et al., 2013; Magnér et al., 2010; Munaron et al., 2012; Nödler et al., 2014; Vidal-Dorsch et al., 2012; Weigel et al., 2004). These compounds were often detected in coastal and estuarine regions; however, data on their levels in offshore are very limited. During a study performed 16 km offshore from Venice, Loos et al. also detected several of the compounds investigated in the present study (Loos et al., 2013). Nevertheless, the Adriatic Sea is a relatively small and enclosed marine area and the sampling location is influenced by the plume of the major Italian river (Po) draining one of the most densely populated areas of Europe. The presence of caffeine (Weigel et al., 2002, 2001), clofibric acid (Buser et al., 1998; Weigel et al., 2002) and carbamazepine (Weigel et al., 2001) has been reported before for truly offshore areas in the North Sea. To the author's knowledge, acetaminophen, naproxen and ketoprofen were detected for the first time in offshore.

Ibuprofen was the most abundant of the PPCPs ranging 0.57–22 ng/L which is one order of magnitude higher than values observed in the northern Adriatic Sea (<0.049–1.146 ng/L) (Loos et al., 2013). The highest value was measured in the Vesterhavet location (area 2). Caffeine is ubiquitous in water environment essentially due to coffee consumption and has been previously detected in the North Sea (Weigel et al., 2002, 2001) and the northern Adriatic Sea (Loos et al., 2013). In this study, caffeine was measured in the range < MDL-3.92 ng/L which is in good agreement with previous studies (Weigel et al., 2002, 2001). Carbamazepine concentrations ranged 0.08–0.44 ng/L which is one order of magnitude lower than value previously reported in the North Sea by Weigel et al. (Weigel et al., 2001) and consistent with values measured in the northern Adriatic Sea (Loos et al., 2013). Also atenolol (<MDL − 0.35 ng/L) was found in this study at levels similar to those from the northern Adriatic Sea (Loos et al., 2013). The concentration of clofibric acid ranged between <MDL–0.20 ng/L which is in good agreement with values reported by Weigel et al. (Weigel et al., 2002) and one order of magnitude lower than values reported by Buser et al. in the North Sea (Buser et al., 1998). Ketoprofen was previously reported to be below a detection limit of 33 pg/L in the North Sea (Weigel et al., 2002). In our case ketoprofen was present in all field and tap water blanks. This condition drove to the definition of MDL for ketoprofen based on procedural blanks levels since it is clear that field blanks were contaminated at the origin and not during the cruise. Ketoprofen was found to be ubiquitous in the investigated areas of the North Sea at concentrations ranging 0.25–9.7 ng/L.

The presence of the antibiotic sulfamethoxazole was confirmed in half of the samples, including samples from offshore areas. Sulfamethoxazole has been previously detected in marine near-shore waters (Borecka et al., 2015; Nödler et al., 2014; Shimizu et al., 2013; Zhang et al., 2013a) as well as 16 km offshore Venice in the Adriatic Sea (Loos et al., 2013). One previous report has documented the occurrence

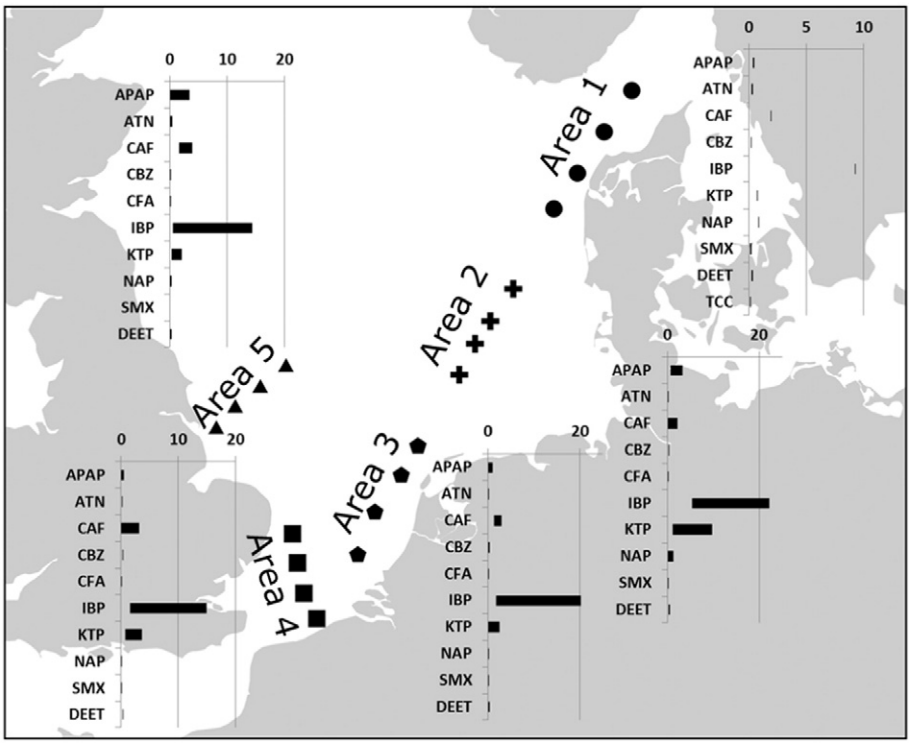

Fig. 2. Ranges of detected concentrations of pharmaceuticals and personal care products found in the North Sea in ng/L (October 2014). Only detected compounds are presented: APAP — acetaminophen; ATN — atenolol; CAF — caffeine; CBZ — carbamazepine; CFA — clofibric acid; IBP — ibuprofen; KTP — ketoprofen; NAP — naproxen; SMX — sulfamethoxazole; DEET — diethyltoluamide; TCC — triclocarban. In area 1, samples were collected only during cruise 3; therefore, ranges could not be determined.

of antibiotics in offshore areas of the Yellow Sea (Zhang et al., 2013b). Antibiotics are particularly toxic to microorganisms and may harm the marine ecosystem. Their continuous presence in marine environment at low concentrations is of particular concern since it may induce the selection of antibiotic-resistant strains. Studies have already documented the presence of antibiotic (including sulfonamide antibiotics) resistant strains in some coastal environment (Rahman et al., 2008; Suzuki et al., 2013).

3.4. Artificial sweeteners

The use of artificial sweeteners has become increasingly widespread in recent years (MECAS, 2012). These are used as food additives to replace sugar in diet products and to enhance the taste of some personal care products, e.g., pharmaceuticals and toothpaste. The most commonly used artificial sweeteners are not readily metabolized in the human body and are excreted largely unaltered. During the wastewater treatment, only 40% of acesulfame and less than 20% of sucralose are degraded/retained. In contrast, about 90% of saccharine undergoes degradation in waste water treatment plant (Scheurer et al., 2009).

All the three studied artificial sweeteners were detected in the North Sea. Sucralose and acesulfame had 100% detection frequency (Table 2). The measured concentrations of artificial sweeteners are depicted in Fig. 3. Detailed analytical results are shown in Table S7. Sucralose was the most abundant artificial sweetener in the North Sea ranging 6.41–32.3 ng/L and the most abundant contaminant measured in the present study.

The sum of the concentrations of the artificial sweeteners detected, $\sum As$, varied between 8.65 and 36.5 ng/L among different locations and sampling campaigns, with the maximum recorded in area 4 (English channel). So far, sucralose has been detected in a marine offshore area only once during a campaign in the Gulf Stream in a concentration ranging from below the detection limit to 68 ng/L (Mead et al., 2009). It was also reported in the offshore of Venice at similar levels as in our study (Loos et al., 2013). In other few studies sucralose has been detected in coastal/estuarine areas in proximity to highly populated cities (Gan et al., 2013; Green et al., 2008; Mead et al., 2009; Sang et al., 2014). Saccharine and acesulfame were detected in the previous studies only in close-to-shore waters in estuarine areas close to municipal drains (Gan et al., 2013; Sang et al., 2014).

Saccharine is the oldest and most diffuse artificial sweetener in the markets (MECAS, 2012). Saccharine was detected in about half of the collected samples and was the less abundant among the three analyzed artificial sweeteners with concentrations ranging <MDL–3.01 ng/L. This may reflect lower emissions associated to efficient removal of this AS during waste water treatment (Scheurer et al., 2009). Similarly to sucralose, acesulfame was ubiquitous in the North Sea with concentrations ranging 0.94–9.7 ng/L. Considering the low recoveries obtained for this analyte, the reported concentrations may underestimate the real environmental concentrations up to a factor of 5–6.

Despite the common source and emission pathway there was no evidence of spatial correlation among artificial sweetener concentrations. Similarly to what observed for pesticides, there was not a significant relationship between salinity and concentrations. It has however to be acknowledged that the present dataset may lack the spatial resolution necessary to successfully conduct such a correlative analysis. This is essentially due to the large geographic areas considered when aggregating samples for analysis. An in-depth assessment of contaminant origin and distribution in marine waters was in fact beyond the scope of this proof of concept study.

Sucralose, acesulfame and saccharine were among the most abundant chemical contaminants detected in the North Sea during the campaigns. While the safety of artificial sweeteners for both human consumption and the environment has been extensively analyzed showing low risk levels (against, at least, the hazard endpoints considered by the international regulatory risk assessment frame), their accumulation in the marine environment should raise some ethical concern. Sucralose in particular is a very persistent substance that will keep accumulating in marine surface water following increasing global emissions (Tollefsen et al., 2012). This will be the case of other contaminants

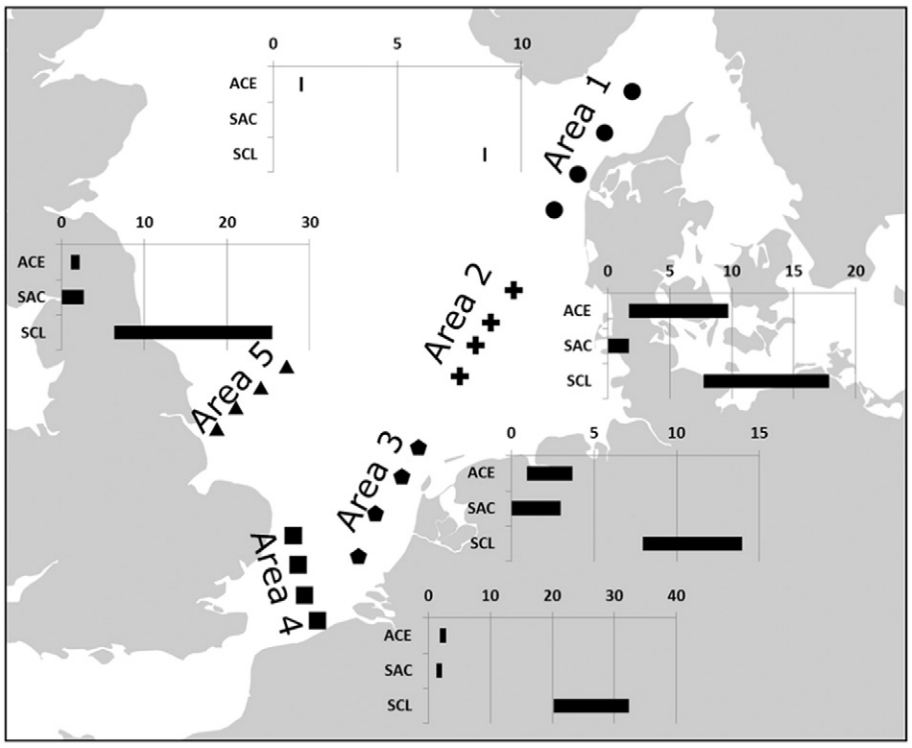

Fig. 3. Ranges of detected concentrations of three artificial sweeteners found in the North Sea in ng/L (October 2014). ACE — acesulfame; SAC — saccharine; SCL — sucralose. In area 1, samples were collected only during cruise 3; therefore, ranges could not be determined.

exhibiting low toxicity and high persistence in the environment. Standing the current criteria, these substances will never be included into priority lists for regulation and management. Nevertheless, the problem of the presence of hydrophilic substances recalcitrant to degradation in the marine environment has many similarities with the problem of microplastics in the Ocean. In both situations in fact, the problem relate to uncontrolled disposal and accumulation of waste products in the environment. While waste disposal in the sea was banned by the London Convention several decades ago, the discharge of solid waste in the sea from land-based sources has continued. In recent years, there has been a tremendous increase in scientific and public interest in pollution from plastics leading to consideration within the European marine protection regulation (MFSD, descriptor 10). Similarly, an argument for the revision of prioritization criteria for chemical substances to deal with low-toxicity highly-persistent pollutants can also be brought upon, considering the result of the present and previous monitoring results.

3.5. Evaluation of effectiveness of unmanned sampling

Occasionally, the unmanned sampling system failed in collecting individual samples. In these cases aggregated samples encompassed only the content of the sampling bottles that were successfully filled in the selected area. In one case (area 1: Skagerrak-North Sea confluence, Fig. S1) none of the individual grab samples could be collected during the first and second cruises (Table S1). During cruise 3, after performing an adjustment of the triggering geographical coordinate ranges, all samples were successfully collected.

Officers on board of cargo ship may opt for last-minute changes on routes because of contingent conditions (e.g. optimization of navigation in relation to wind and marine currents or other unforeseen events). Sampling failures during cruise 1 and 2 depended on the fact that the ship did not pass through the programmed range of geographical coordinates set to trigger the sampling. The ship had in fact followed a more westerly heading after leaving Oslo Fjord to maintain a route which was closer to the southern Norwegian coasts than anticipated. The problem was solved by simply prompting the system with broader triggering coordinate ranges.

Several FerryBox systems installed on other ships of opportunity in Europe are equipped with instrumentation supporting satellite-assisted communication protocols. In this case, a land-based operator can communicate with the FerryBox in nearly real time during the full duration of the cruise. This empowers the possibility of manual-remote triggering of the automatic sampler, an option that guarantees full control on the sampling campaign. Remotely assisted manual operations may however increase sampling costs since they will require land-based operators being active around the clock.

4. Conclusion

The suitability of existing mobile research infrastructures of opportunity for carrying out both routine and exploratory monitoring of contaminants in marine waters has been demonstrated in this study. The sampling approach allowed the detection of several contaminants of emerging concern at trace levels, including several pesticides, pharmaceuticals, personal care products and synthetic food additives. During this proof-of-concept study, 6 pesticides, 3 pharmaceuticals and 2 artificial sweeteners, were detected for the first time in offshore marine waters. The main endpoint of the study was the trace-level detection of CECs, however, focused experiments on the stability of the analytes in the samples during collection and on-board storage should be considered as a further step for a more quantitative analysis. Taking into consideration this confounding factor it can be hypothesized that data presented in this paper may underestimate to a certain extent the real concentrations in marine water.

The European FerryBox fleet currently encompasses 33 commercial ships regularly operating on routes in the North Sea, Baltic Sea, Norwegian Sea, North Atlantic and the Mediterranean, offering a very broad (although still incomplete) coverage of European Coastal waters

("FerryBox,", 2015). Only in Europe, the fleet of commercial ships on regular line service encompasses thousands of units, many of them in service over short regional routes. We envisage a synergic effort of researchers/environmental managers and maritime companies that can produce enormous benefits for the implementation of regulation and the protection of marine environment from chemical pollution.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.jmarsys.2016.03.004.

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