# Line ferries and cargo ships for the monitoring of marine contaminants of emerging concern: application along a Europe-Arctic transect

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# Abstract

Contaminants of emerging concern (CEC) are a focus in marine protection. Several CECs are released with wastewater effluents to coastal environments and their offshore occurrence has been recently documented. Routine monitoring is key for implementing marine protection acts, however infrastructural, financial, and technical limitations hinder this task along broad spatial transects. Here we show the efficacy of a new infrastructure enabling unmanned sampling of surface water from ships of opportunity in providing reliable and cost-effective routine monitoring of CECs along a Europe-Arctic transect. The distribution and long-range transport of several pharmaceuticals and personal care products, artificial food additives, and stimulants were assessed. Validation of operations through strict procedural and analytical quality criteria is presented. A framework to estimate a compound-specific Spatial Range (SR) index of marine long-range transport based on monitoring results and information on source spatial distribution, is introduced. Estimated SR values ranged 50-300 km depending on compound, yielding a ranking of long-range transport potential which reflected expectations based on degradation half-lives. SR values were used to calculate prior maps of detection probability that can be used to plan future routine monitoring in the region.



# Keywords

Marine environments, Marine Long-Range Transport; Pharmaceuticals; Artificial Sweeteners; Personal care products; Carbamazepine; Sucralose


# 1. Introduction

Several studies have documented the widespread occurrence of synthetic organic contaminants from municipal wastewater effluents in freshwater and coastal environments (e.g., (aus der Beek et al., 2016; Dachs and Méjanelle, 2010; Loos et al., 2013a; Montes-Grajales et al., 2017; Noguera-Oviedo and Aga, 2016; Sousa et al., 2018; Venkatesan and Halden, 2014a; Verlicchi et al., 2012). These are

45 referred to as “contaminants of emerging concern” (CECs)(EPA, 2019) and include, among others,
46 pharmaceuticals for human and veterinary use, personal care products, artificial food additives and
47 stimulants. Due to their moderately hydrophobic or hydrophilic character and resistance to microbial
48 degradation, the removal of these CECs by conventional wastewater treatment plants (WWTP) is
49 incomplete, resulting in their release with effluents (Jelic et al., 2011). Furthermore, owing to their
50 moderate to high persistence, water solubility, and low vapor pressure, CECs can reach marine
51 environments through riverine transport and potentially be advected to offshore areas (Hughes et al.,
52 2013; Li, 2014; Murray et al., 2010).

53 Knowledge of the occurrence, behaviour, and long-range transport in marine coastal and open waters
54 is limited and mostly based on the results of sporadic scientific campaigns (rather than systematic
55 monitoring) (Arpin-Pont et al., 2016; Gaw et al., 2014). Data of CEC levels in seawater are available
56 from America, Europe and Asia (Ali et al., 2017; Arpin-Pont et al., 2016; Björlenius et al., 2018;
57 Brumovský et al., 2017; Brumovsky et al., 2016; Fisch et al., 2017; Hernandez et al., 2019; Huber et al.,
58 2016; Krogh et al., 2017; Kroon et al., 2020; Sousa et al., 2020; Yang et al., 2020) with a large majority
59 covering coastal or marginal seas (Lopez-Pacheco et al., 2019). A recent study qualitatively elucidated
60 the complexity of the mix of wastewater-derived CECs in marine waters (Lara-Martín et al., 2020). The
61 most frequently investigated and detected pharmaceuticals are antibiotics (e.g., erythromycin,
62 sulfamethoxazole and trimethoprim), the antiepileptic carbamazepine, the stimulant caffeine, non-
63 steroidal anti-inflammatory drugs (NSAIDs), and the antipyretic paracetamol (Alygizakis et al., 2016;
64 Björlenius et al., 2018; Borecka et al., 2015; Brumovský et al., 2017, 2016; Jiang et al., 2014; Klosterhaus
65 et al., 2013; Loos et al., 2013b; Nödler et al., 2014; Togola and Budzinski, 2008; Weigel et al., 2005,
66 2004, 2002; Zhang et al., 2013b, 2013a). Artificial sweeteners acesulfame and sucralose have been also
67 detected in coastal and open seawater at relatively high levels (Brumovský et al., 2017, 2016; Lara-
68 Martín et al., 2020). While coastal contamination by CECs in the Arctic was previously discussed in
69 relation to local human settlements (Kallenborn et al., 2018), the bulk of CEC discharges occurs at low
70 and mid latitudes where sources are concentrated (AMAP, 2017).

Concerning offshore environments, the presence of highly persistent water-soluble contaminants emitted mostly at low latitudes (such as various perfluoroalkyl substances) is well documented (Armitage et al., 2009; Wania, 2007). Wastewater-derived CECs found in offshore, however, also include compounds with intermediate or relatively short environmental half-lives (Bu et al., 2016) (such as many pharmaceuticals and personal care products (PPCPs)). High emission rates and the efficiency of marine advection are responsible for such a broad distribution. To enable exposure and risk assessments of wastewater-derived CECs in marine environments at regional or continental scales, an understanding of their distribution and potential for long-range transport is needed. At present, this is hindered by limited availability of CEC data in the marine environment, still fragmented knowledge on CEC environmental degradation rates (Björlenius et al., 2018; Bu et al., 2016), and the poorly characterized transport pathways linking coastal sources to remote marine regions.

Considering these knowledge gaps, monitoring of CECs in the marine environment plays a crucial role informing environmental policies and protection. Branchet et al., 2020 have recently reviewed the current practices and challenges in monitoring strategies of pharmaceuticals in marine matrices and provided insights for the future of this field. Monitoring infrastructures suitable for routine and cost-effective operations along broad marine transects represent an important, yet unavailable, asset. In addition, monitoring should be informed based on sampling strategies that can effectively capture spatio-temporal trends of contamination in relation to source distribution and other geographic and hydrophysical factors. This is not a trivial task, especially when considering transects stretching thousands of kilometres, requiring carefully optimized monitoring designs that can yield useful information while keeping costs under control. Elaborating priors for the probability of detecting CECs in marine areas is a necessary step to define sound and cost-effective sampling strategies (Branchet et al., 2020). To this end, a purely model-based approach, while likely useful, would require use of integrated coastal-open sea high-resolution hydrophysical models of CEC marine transport. These models still lack full validation for most CECs and are still affected by large uncertainties, especially on compound chemical-physical properties and behaviour. To date, empirical and heuristic approaches

are most frequently used to define marine monitoring of chemical pollution. To this end, elaboration of prior distribution of detection probability estimates can be an important aid to monitoring design.

This paper describes a proof-of-concept study addressing these infrastructural and knowledge demands. The aims of the study were:

- to show (through a series of stringent quality assurance criteria) the efficacy of unmanned sampling from a novel marine monitoring infrastructure based on a fleet of ships-of-opportunity to reliably, quantitatively, and cost-effectively elucidate distribution of CECs in surface seawater along a Europe-Arctic marine transect.
- to utilize results from the pilot study in connection with a spatial analysis of wastewater source distributions to elaborate a heuristic framework for the calculation of a compound-specific long-range transport potential index (hereafter defined as Spatial Range (SR)), and derive a series of prior maps of probability of detection for a group of tracer compounds.

# 2. Experimental section

## 2.1 The Marine monitoring infrastructure

Sampling of sea surface water was performed along a continental transect (Central Europe to European Arctic) exploiting a fleet of commercial ships of opportunity equipped with automatic water samplers. Sampling campaigns were conducted as part of the JERICO-Next project (Farcy et al., 2019). The ships of opportunity used here are among those included in the NorSOOP research infrastructure (www.norsoop.com) coordinated by the Norwegian Institute for Water Research (Table S1) and part of the European FerryBox network initiative (Petersen, 2014). FerryBox is an international research joint venture involving several line ferry and cargo ship operators in Europe. The NorSOOP fleet currently includes five vessels covering the Eastern North Sea, two Eastern North Atlantic transects, the Norwegian Sea, and the transect between continental Norway and the Svalbard archipelagos in the Arctic (Figure S1a). The complete FerryBox network currently includes 17 ships of opportunity

extending the spatial coverage to the Baltic sea, most of the North Sea, and part of the Eastern Mediterranean (altogether over 50% of European coastal waters). Ships enrolled in these infrastructures are equipped with a suite of standard instruments, including an in-line automated refrigerated water sampler (6712FR, Teledyne Isco, Lincoln, NE, USA) interfaced to the communication unit of the multisensory system (FerryBox). The multisensory system record and forecast in real time several biophysical and chemical parameters of surface sea water (such as temperature, turbidity, and fluorescence).

## 2.2 Monitoring transect

The present pilot study utilized three ships of opportunity included in the NorSOOP infrastructure: the M/S Color Fantasy (Color Line, operating between Oslo, Norway and Kiel,Germany), the M/S Trollfjord (Hurtigruten, operating between Bergen – Kirkenes, Norway), and the M/S Norbjørn (Bring AS/Marine Supply, operating between Tromsø, Norway and Longyearbyen, Svalbard). Using these ships, surface water samples were collected along a transect covering the eastern North Sea (specifically: the Little Belt (Danish Strait), Kattegat and Skagerrak Sea (hereon jointly referred to as the Baltic Outflow (BO)), the western and northern coasts of Norway (hereon referred to as the Norwegian West Coast (NWC)), and the transect between northern Norway and the Svalbard archipelagos including the western boundary of the Barents Sea (BS) and the southern boundary of the Arctic Ocean (AO) (Figure S1b). The transect is intersected by the Norwegian Coastal Current, a surface current conveying North Sea and Baltic waters northward to the BS and the AO. The Baltic (and consequently the BO) is the dominant wastewater recipient from, Sweden, Finland, and many central European countries. Similarly, water masses originating from the southern North Sea and conveyed by the Norwegian Coastal Current to the southern part of the NWC, were shown to be recipients of CECs emitted from central Europe (Borecka et al., 2015; Brumovský et al., 2016). Norway coastal areas, with a total draining population of about 2 million spread over 2500 km, can be described as low-impact

with respect to residential wastewater pollution. The northern part of the transect (BS and AO) is assumed to be a remote, pristine area.

Along the transect, monitoring activities included sampling in proximity of major river estuaries (i.e., Göta älv, Sweden and Glomma, Norway), major harbours and cities (Kiel, Odense, Gothenburg, Oslo, Bergen, Trondheim, and Tromsø), and smaller settlements (such as, Longyearbyen, in the Arctic) that can represent local sources, as well as off-shore and open ocean locations.

## 2.3 Sampling

The 6712FR automatic sampler (Teledyne Isco, Lincoln, NE, USA) with a capacity of 24 one-litre bottles was installed on all ships. The dedicated water intake was installed at the hull of the ships at a depth of 3–4 m (depending on the ship and the load of the cargo vessel). The sampling device includes coupled metal and polytetrafluoroethylene (PTFE) tubing, PTFE-coated rubber gaskets, and a peristaltic pump where all wet parts are made of PTFE, polypropylene or metal. No sample pre-filtration was performed during collection owing to low particulate matter content. The seawater intake line of the automatic sampler was constantly flushed while ships were moving. When triggered, the sampler filled one individual bottle in about 1 minute. The sampling location could be selected based on geographic coordinates, time, or seawater conditions. In this study, sampling was mostly automatically trigged using predefined GPS positions from the FerryBox system or remotely triggered from satellite or mobile phone assisted internet communication from a desktop positioned at NIVA headquarters in Oslo. For half of the transect covered by the M/S Trollfjord sampling was manually triggered by an operator present on board for routine instrument maintenance.

A total of 50 individual samples were collected during three campaigns: 17 samples in the BO area, 13 samples in the NWC area, and 20 samples in the BS and AO areas (Figure S1b). Exact coordinates, sampled volumes, temperature, and salinity of individual sampling sites are provided in the SI (SI) (Table S2). Samples were collected into one-litre high density polyethylene bottles inside the

refrigerated (4 °C) chamber of the automatic sampler. Bottles were pre-cleaned using Decon 90 (Decon Laboratories Limited, Hove, UK), Milli-Q water, and rinsed with methanol at least three times before they were deployed in the automatic sampler carousel. After sample collection, the bottles remained unsealed (albeit contained in the closed cabinet) during the full duration of the cruise (i.e., 3-5 days). At least 2 field blanks were included in each sampling campaign (described in detail in the Quality Assurance and Control section below). At the end of each cruise, samples were sealed and transported to NIVA laboratory in Oslo where they were stored in a freezer at –20 °C until further processing. Storage time ranged between 1 and 3 weeks.

## 2.4 Target substances

The target analytes included 11 pharmaceuticals (atenolol, caffeine, carbamazepine, clofibric acid, diclofenac, hydrochlorothiazide, ibuprofen, ketoprofen, naproxen, paracetamol, and sulfamethoxazole), three personal care products (DEET, triclocarban, and triclosan) and three artificial sweeteners (acesulfame, saccharin, and sucralose). The choice of analytes was based on a literature search of their detection frequency and occurrence in the freshwater environment and on limited literature on CECs available for the marine environment. Information on analytical standards and reagents is provided in the Supporting Information (SI) (Text S1).

## 2.5 Sample extraction

Extraction and analytical methods used in this pilot study were optimized for marine waters and validated in two previous studies of our group (Brumovský et al., 2017, 2016). Samples were slowly thawed in a fridge (4 °C). The exact mass and volume of each sample were recorded. Samples were subsequently acidified to a pH of 2 by adding concentrated hydrochloric acid. Solid phase extraction (SPE) was conducted using Waters® Oasis HLB columns (200 mg, 6 $cm^3$, 30 µm) (Waters Corp., Milford, MA, USA) at NIVA laboratory in Oslo, Norway. No sample pre-filtration was performed owing to the

low particulate matter concentrations. The SPE columns were conditioned with 5 mL of methanol and then equilibrated with 5 mL of Milli-Q water adjusted to pH 2 using concentrated hydrochloric acid. The water sample was loaded onto the cartridge using PTFE tube connected to the sample bottle at a flow rate of approximately 2 mL/min. In order to remove residual seawater, cartridges were rinsed with 10 ml of Milli-Q water adjusted to pH 2 after extraction and dried for 15 min under vacuum. The residual water was removed from the cartridges by centrifugation. This was done by placing the cartridges into polypropylene centrifuge tubes pre-cleaned with methanol at least three times and spun at 3250 g for 2 min on a centrifuge 5810 R (Eppendorf, Hamburg, Germany). The SPE cartridges were subsequently frozen and shipped on ice to RECETOX laboratory in Brno, Czech Republic, where elution and CEC instrumental analysis were performed within 48 hours after delivery. Specifically, 5 mL of methanol were used as eluent, followed by 5 mL of methanol:acetone 1:1 (no vacuum applied). The eluates were combined and reduced to near dryness under a gentle stream of purified 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 grade water. For the analysis of the first fraction of PPCPs and food additives, 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%. 200 µL aliquots were analyzed using UPLC-MS/MS.

## 2.6 UPLC-MS/MS analysis

A detailed description of the instrumental analysis is provided elsewhere (Brumovský et al., 2016). Briefly, the separation and detection of pharmaceuticals, personal care products, and food additives were performed using three complementary methods by an 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). Food additives and the first fraction of the PPCPs were separated using an ACQUITY UPLC BEH C18 column (100x 2.1 mm, 1.7 µm, 130 Å) column (Waters, Milford, MA, USA), the second fraction of PPCPs was separated using Xterra C18 (100 x 2.1 mm, 3.5µm) column (Waters, Milford, MA,

USA). Further details on mass spectrometry analysis are reported in the SI (Tables S3 and S4). Quantitative LC-MS/MS analysis was performed in multiple reaction monitoring (MRM) mode. The most intense MRM transition was employed for quantification and the second one for confirmation. Quantification of target substances (except sucralose) was done using an external calibration curve of freshly prepared standards with a range of 0.01–100 ng/mL (9 points). Mass-labelled internal standards were spiked in all blanks, field samples and calibration standards prior instrumental analysis to control possible matrix effect. Sucralose was quantified using the internal standard method with sucralose-d6 to adequately compensate for matrix effects.

## 2.7 Quality assurance and control (QA/QC)

Laboratory procedural blanks: The analysis included a set of procedural laboratory blanks (n=7) to check for potential contamination during sample extraction and analysis. Procedural blanks consisted of an SPE cartridge without any loaded samples and were processed in the laboratory identically to those used for the extraction of field samples and field blanks.

Field blanks: At least two field blanks were included in each cruise (seven throughout the study) to check for contamination during sampling, on-board storage, and transport. Each field blank consisted of 1 L of natural seawater collected from the intake of NIVA marine field station at Solbergstrand at a depth of 60 m in Oslo Fjørd (59.615 N, 10.649 E). This water was pre-extracted using the same method described above to remove traces of the target contaminants, transferred into plastic sampling bottle identical to the ones used for sample collection and positioned unsealed inside the cabinet of the automatic sampler for the whole cruise duration. .

A matrix blank (i.e., the same water as used for field blanks but without prior pre-extraction) was also analyzed to check background contamination and efficacy of the pre-extraction of the matrix used for certain QA/QC samples including field blanks.

Recovery tests: Recovery tests (n=3) were obtained by spiking approx. 1 L (exactly measured) of the pre-extracted seawater with analytical standards at 10 ng/L. The recovery tests were then extracted using the same procedure as used for field samples.

Stability tests: The stability tests assessed any loss of the target compounds during the on-board storage and sample transport. One litre of the pre-extracted seawater matrix was spiked with 10 ng of all analytical standards prior to one of the cruises (Color Fantasy) in triplicates, transferred into empty polypropylene sampling bottles and placed unsealed in the cabinet of the automatic sampler for the duration of the cruise (4 days) under the same conditions as for real field samples. These stability test samples were then analyzed in the same way as field samples. To infer possible losses, recovered masses were compared with the results of recovery tests..

Method detection Limits: The determination of the method detection limits (MDL) was based on the results of field blanks and laboratory procedural blanks analysis through the following algorithm: i) in case the analytes were detected in the field blanks (after correcting for matrix background contamination) at levels significantly higher than those found in the procedural blanks (meaning contamination of field blank occurred during storage on board or transport), MDL were calculated for each individual compound as 3 times the standard deviation (SD) of the field blanks; ii) in case the analytes were detected at similar levels in the procedural and field blanks, MDL were calculated as 3 times the SD of the procedural and field blanks; iii) if no signal of the analytes was detected in blanks, MDL were calculated as the concentration producing a signal-to-noise ratio equal to 3. All results were blank-corrected with the average concentration in the field blanks after correcting for matrix background contamination in case i), and the average concentration in the procedural and field blanks in case ii). Reported marine concentration data were not corrected for recovery and stability.

Instrumental quality assurance: To control LC-MS instrument sensitivity, QA/QC standards prepared by dilution of calibration standards in the mobile phase were analyzed after each batch of 10 samples. As an additional QA/QC measure, the overall performance of the analytical procedure was monitored

per individual samples by looking at the recovery of two internal labelled standards (paracetamol-d4 and caffeine-$^{13}C_3$) added to all samples, blanks, matrix spike tests, and stability tests prior to extraction.

## 2.8 Statistical treatment

Non-parametric correlations (Spearman's $r_s$) were calculated between the detected levels of individual analytes and several other parameters (i.e., latitude, salinity and distance from the coast), as well as the relationships between the levels of individual compounds. Only compounds with detection frequency >50% were used for the calculation to minimize uncertainty.

## 2.9 Calculation of priors of spatial distribution and detection probability

### 2.9.1 Definition of Spatial Range (SR)

A framework is introduced here describing how results from the pilot monitoring campaign were used to estimate compound-specific SR and calculate priors approximating the probability of detection of tracer compounds along the transect. The framework introduces a minimalist model generating first-tier estimates of a compound detection probability spatial distribution (accounting for coastal sources' distribution and estimated strength), optimizes it by comparing estimated trends delivered by the minimalistic model with observed trends of contaminant concentrations in seawater, and heuristically validates it through statistical correlation. There is no claim here that the SR framework represents a predictive model of marine exposure to CEC. It is rather conceived as a framework that assimilates preliminary monitoring data to generate useful priors of the distribution of probability detection that can be then used to optimize future monitoring activities.

In more detail, SR (in km) is defined as the mean radius of the circular area around a point source (e.g., a coastal discharge point) within which a given substance has a detectable concentration in marine surface waters. Obviously, in the environment many point sources with different strengths

simultaneously release CECs to the sea. Hence a framework that aggregates the influence of all sources is necessary. This was resolved through the following algorithm:

i) Locate all coastal sources in a spatial domain that exceed the largest expected values of SR and attribute to each source a scalar proportional to the source strength;

ii) Select the form of a probabilistic function $\Phi_{x_i,s_i,r}$ defining the likelihood of detecting a given substance at a distance x from a given source point *i*, whereby *s* is a function defining the characteristic of source *i* accounting for the release rate approximated by the size of human population draining into point *i* and the characteristics of the coastline (See Text S2 in the SI for details), while *r* is the search radius (km) parameter, proportional to the variance of the probability function $\Phi$ (e.g. through representing the distance from the source at which the probability of detecting a given substance become negligible).

iii) Define the aggregated probability function for each sampling point along the monitored transect as:

$$\overline{\Phi}_r = \sum_{i=1}^{n} \Phi_{x_i,s_i,r} \qquad \text{Equation 1)}$$

$\overline{\Phi}_r$ is given by the sum of $\Phi$ calculated for each of the *n* point sources relevant for the monitored transect.

iv) Find the value of *r* that minimizes the sum of the squared differences between $\overline{\Phi}_r$ calculated for each sampling point and the concentration of a given substance measured at the respective points. Such a value represents the SR.

A schematic example of the framework to calculate SR is presented in Text S2, SI.

Such a heuristic framework offers the advantage of requiring little data, realizing the complexity of describing marine advection at the necessary high resolution (e.g., when dealing with coastal areas along large transects) and the difficulties of detailing processes governing fate of chemical pollutants

317 at sea. Another benefit is that it enables a rigorous extrapolation of a continuous (in space)
318 probabilistic function starting from discrete, low resolution, observations of compound
319 concentrations.

320 **2.9.2 Assumptions adopted for the implementation of the SR calculation frame**

321 As stated above, the scope of the SR calculation framework was to provide a heuristic estimation of
322 the detection probability distribution by introducing a minimalistic model heuristically validated with
323 results from the pilot monitoring. It should not be considered as a predictive model of marine exposure
324 to CECs. Its main output is the SR value of tracer compounds. SR can also be used to prepare prior
325 maps of probability distributions. These, in turn, describe the spatial patterns the probability of
326 detection of compounds with different value of SR expectedly has in a given marine region. A first
327 simplification is that only wastewater source points located along coastal or inland Europe are
328 considered. In case of inland sources, the emission point to the sea is considered to be the estuary
329 point of the catchment where the source is present. Other type of CEC marine sources (e.g., fish farms
330 or discharges by ships), are neglected for the sake of minimalism. While untreated veterinary
331 wastewater effluents directly releasing to the sea are possible, it is considered (in first approximation)
332 that in Central and Northern Europe, most large animal factories are connected to WWTPs on the coast
333 or inland and share the same emission points as municipal wastewater.

334 The SR framework assumes that the temporal variability of concentration of a given compound at each
335 sampling point is negligible compared to the spatial variability along the transect. Temporal
336 fluctuations may occur due to fluctuating sources or variability in marine advection. It is argued that
337 these assumptions can be considered valid in a first approximation, given the scale of the monitored
338 transect. Even though the release rate of CECs from wastewater source points are known to vary
339 considerably on a daily or weekly basis, the spatial distribution of wastewater discharge points
340 simultaneously feeding any given sampling location at sea can vary from few to hundreds of km (e.g.,
341 when considering inland source points). This means that the time needed for a compound to be

advected to a given sampling location varies considerably among different source points. Such a variability buffers the temporal variation at the sampling points. However, we acknowledge that seasonal variability in the use of PPCPs or marine advection could be reflected in seasonal shifts in marine concentrations. Hence the results of the framework provided here are valid for the season of the monitoring campaign (i.e. winter for the BO transect where most of the data used for the SR assessment were generated).

In order to locate discharge points and weight their strength, a Geographic Information System (GIS) dataset of population distribution in Europe was used as one of key model inputs along with a dataset of river discharge points and catchment area throughout central and northern Europe. Emissions of CECs are expected to be proportional to the size of human population in the drained catchment of each discharge point. Population counts were aggregated to river basins and river discharge points were then considered as locations of inland sources of CECs to the seawater.

A two-dimensional kernel density function was used to approximate $\phi_{x_i,s_i,r}$ from each source point. According to the framework described in Section 2.9.1, this function assumes half-normal distribution in all directions from the source point. The topography of the coastline near the point source is considered to have an influence on the source strength. For example, loads of contaminants discharged in points enclosed by land (e.g., narrow bays or fjords) will likely experience a lower dilution in proximity of the point source. Hence, given equal size of the served population, such a source will provide a stronger signal near the discharge point compared to one discharging in a more open costal area. A framework to account for this effect was introduced when defining the source characteristic function *s*. That is:

$$s_i = p_i * \left[\frac{(lcov_i+10)}{110} * 5\right]^c \qquad \text{Equation 2)}$$

where $p_i$ is the population attributed to a watershed to a given discharge point *i*, *lcov* is the percentage of land within 50 km radius from the source point (accounting therefore for the topology of the

366 coastline in the surrounding of the source point), and *c* is a variable numerical coefficient. The influence
367 of $s_i$ on the SR results was assessed through varying coefficient *c* as explained later.

368

369 **2.9.3 Heuristic validation of the framework**

370 Considering the heuristic nature of this framework, the estimates of SR and prior maps of probability
371 detection are considered valid if:

372 i) the correlation between $\overline{\Phi}_{SR}$ calculated in each sampling point and monitoring data is
373 statistically significant;
374 ii) the coefficient of determination $R^2$ of the relation is high (i.e., > 0.7);
375 iii) the quality of the correlation has limited sensitivity to uncertainties in source strength (i.e.,
376 variations of function *s*); and
377 iv) the quality of the correlation is sensitive to variations of parameter *r.*

378

379 **2.9.4 Calculation of priors of detection probability**

380 Priors describing the probability of detecting a substance in any point of the transects were finally
381 calculated by integrating equation 1 throughout the full marine spatial domain of interest using the
382 calibrated value of SR as input for parameter *r.* Results for selected compounds (e.g., those for which
383 SR calculation was heuristically validated) were presented in maps. Note that prior maps defined
384 through the SR framework are more general than those that could be obtained through pure
385 geostatistical methods. Producing distribution maps through the SR framework is substantially less
386 data-intensive. In addition, by attributing a similar value of SR to compounds with similar physical
387 chemical properties and source distribution as the tracer compounds, one could generate prior maps
388 for broader families of substances (even including compounds for which marine monitoring data are

not yet available or possible). This could be done for example by multiplying parameter *s* (Equation 1) by the mean concentration ratio between a selected compound and an adequate tracer compound measured at the source points.

# 3. Results

## 3.1 Results of quality assurance and control

MDLs for individual analytes ranged 0.005-0.32 ng/L (Table S4) except for caffeine (17.5 ng/L), where elevated concentrations were found in the field blanks (Table S5). Several analytes, including caffeine, diclofenac, paracetamol, DEET, and acesulfame, were detected in field blanks at higher levels compared to laboratory procedural blanks. The higher contamination of field blanks can be, in most cases, attributed to the presence of analyte residues in matrix blank (Table S5), indicating the extraction procedure did not completely remove the residuals of the target compounds in the blank matrix. Nevertheless, evidence of ship-born contamination or contamination during handling of samples or sampling materials were observed for caffeine, paracetamol, and acesulfame as indicated by their significantly higher levels observed in field blanks compared to the pre-extracted matrix blank (Table S5). The levels of the analytes measured in the field blanks were generally substantially lower than in the field samples (Table S5).

The recovery test provided satisfactory results. Recoveries of all compounds were in the range 50–110% (Table S6), except for acesulfame which reached lower values (34±8%). The stability test indicated that the recovery of most target substances in the spiked sample was >65% (Table S7), except for saccharin (34%), triclosan (44%), triclocarban (48%), and caffeine (54%). These results provide a "worst case" estimate of the analytes' stability since the spiked matrixes for stability tests were kept in the sampler cabinets for the full duration of the cruise (i.e., for a longer period than most of the real samples). The recoveries of paracetamol-d4 and caffeine-$^{13}C_3$ added to all samples, blanks and spike tests before extraction were generally between 60-120% (Table S8).

413 The positive results obtained for blanks, stability tests, and recovery tests demonstrate that the use of
414 field infrastructure based on ships of opportunity in combination with the analytical procedures and
415 methods described above, yielded meaningful results of the distribution of the target CECs along this
416 marine transect and can represent a valid support for conducting routine observation (even for
417 compounds at trace levels) in the context of national or regional marine pollution management and
418 policy.

## 419 3.2 Distribution of CECs along the Europe-Arctic transect

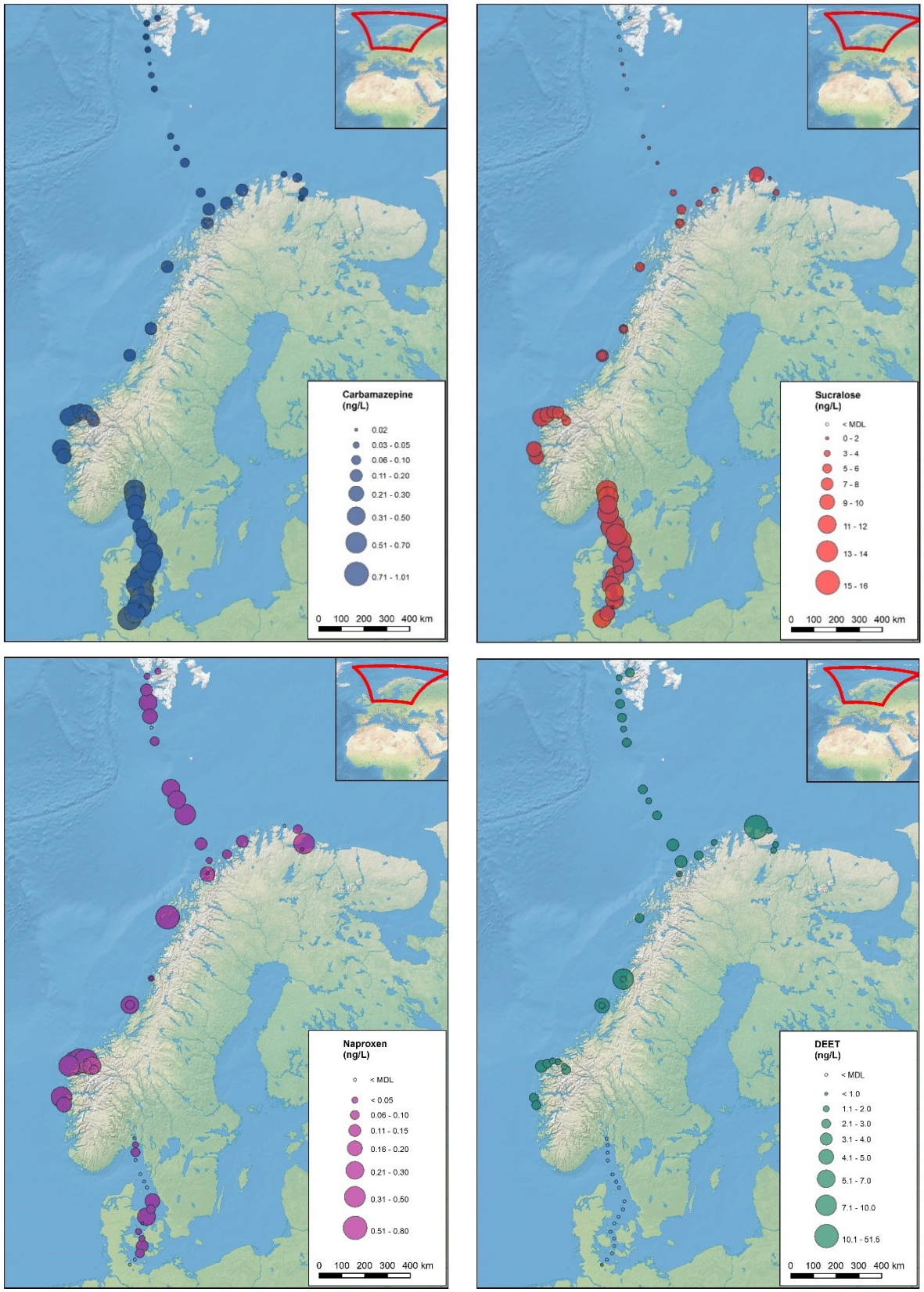
420 Fourteen out of 17 targeted CECs were detected at least once in Northern European and Arctic sea
421 waters (Tables S9-S11 in the SI), five of them with an overall mean detection frequency >50% (Table
422 1).

423 **Table 1** Detection frequencies of targeted chemicals

| | Detection frequency (%) and (range of concentrations) (min-max, ng/L) | | | |
|---|---|---|---|---|
| | **Overall detection frequency** | **Baltic outflow (BO)** | **Norwegian West Coast (NWC)** | **Arctic Ocean (AO)** |
| ***Pharmaceuticals*** | | | | |
| Atenolol | 12 | 35 (0.07-0.12) | 0 (<0.01) | 0 (<0.01) |
| Caffeine | 14 | 18 (<5.03-71.8) | 15 (<5.03-24.9) | 10 (<5.03-36.6) |
| Carbamazepine | 100 | 100 (0.23-1-01) | 100 (0.05-0.33) | 100 (0.02-0.16) |
| Clofibric acid | 0 | 0 (<0.01) | 0 (<0.01) | 0 (<0.01) |
| Diclofenac | 4 | 6 (<0.09-0.64) | 0 (<0.09) | 5 (<0.09-0.3) |
| Hydrochlorothiazide | 0 | 0 (<0.05) | 0 (<0.05) | 0 (<0.05) |
| Ibuprofen | 12 | 18 (<0.15-0.36) | 15 (<0.15-0.27) | 5 (<0.15-0.26) |
| Ketoprofen | 18 | 53 (<0.1-0.95) | 0 (<0.1) | 0 (<0.1) |
| Naproxen | 74 | 53 (<0.02-0.24) | 92 (<0.02-0.78) | 80 (<0.02-0.35) |
| Paracetamol | 34 | 29 (<0.16-11.8) | 62 (<0.16-46.0) | 20 (<0.16-16.3) |
| Sulfamethoxazole | 56 | 100 (0.17-0.45) | 62 (<0.03-0.31) | 15 (<0.03-0.12) |
| ***Personal care prod.*** | | | | |
| DEET | 68 | 6 (<0.26-0.63) | 100 (1.52-9.56) | 100 (0.75-51.5) |
| Triclocarban | 0 | 0 (<0.005) | 0 (<0.005) | 0 (<0.005) |
| Triclosan | 4 | 0 (<0.02) | 0 (<0.02) | 10 (<0.02-0.67) |
| ***Food Additives*** | | | | |
| Acesulfame | 28 | 82 (<0.19-1.94) | 0 (<0.19) | 0 (<0.19) |
| Saccharin | 34 | 100 (3.01-285) | 0 (<0.1) | 0 (<0.1) |
| Sucralose | 86 | 94 (<0.1-14.1) | 100 (2.19-10.4) | 70 (<0.1-9.77) |

424

These include: carbamazepine, naproxen, sulfamethoxazole, DEET, and sucralose (Figures 1 and S2). Carbamazepine was detected in 100% of all samples in the range 0.02–1.01 ng/L. The second most frequently detected contaminant was sucralose, found at 86% sites at levels 0.82–15.3 ng/L. Naproxen, DEET, and sulfamethoxazole were found at 74%, 68%, and 56% sites at levels 0.03–0.78, 0.63–51.5, and 0.11–0.45 ng/L, respectively. The analgesic paracetamol and the artificial sweetener saccharin were found >MDL at 34% sampling sites at levels up to 46.1 and 285 ng/L.


Carbamazepine
(ng/L)
0.02
0.03 - 0.05
0.06 - 0.10
0.11 - 0.20
0.21 - 0.30
0.31 - 0.50
0.51 - 0.70
0.71 - 1.01
0 100 200 300 400 km
Sucralose
(ng/L)
< MDL
0 - 2
3 - 4
5 - 6
7 - 8
9 - 10
11 - 12
13 - 14
15 - 16
0 100 200 300 400 km
Naproxen
(ng/L)
< MDL
< 0.05
0.06 - 0.10
0.11 - 0.15
0.16 - 0.20
0.21 - 0.30
0.31 - 0.50
0.51 - 0.80
0 100 200 300 400 km
DEET
(ng/L)
< MDL
< 1.0
1.1 - 2.0
2.1 - 3.0
3.1 - 4.0
4.1 - 5.0
5.1 - 7.0
7.1 - 10.0
10.1 - 51.5
0 100 200 300 400 km

431

432

**Figure 1** Levels of carbamazepine,sucralose, naproxen, and DEET. Measured concentrations are depicted as circles at individual sampling sites. Maps for other compounds are reported in the Figure S2, .

For most of the target CECs, detection frequency was highest in the BO area which is the closest to coasts impacted by human activities and wastewater discharges. The detection frequency declined from south to north, reflecting the postulated distribution of sources. Maximum levels of contaminants were mostly measured in the BO (e.g., in case of carbamazepine, saccharin, sucralose, and sulfamethoxazole). Saccharin was detected in this area at high concentrations ranging 3.01–285 ng/L. Maximum detected caffeine concentration was also found in the BO (71.8 ng/L). In contrast, maximal DEET and paracetamol levels were surprisingly measured in the BS area (51.5 and 46.1 ng/L, respectively). Maximal concentrations measured for other contaminants ranged typically 0.1–1 ng/L.

Significant positive correlations were noted among the spatial distribution of several frequently detected CECs (i.e., carbamazepine, sucralose, and sulfamethoxazole) (Table 2). In contrast to this general pattern, DEET showed an inverse correlation with the distribution of most other frequently detected CECs.

**Table 2** Spearman's correlation between the levels of detected compounds and salinity. Only compounds with overall detection frequency >50% are reported. Coefficients marked with * indicate significnt correlations ($p<0.05$).

| Variable | Spearman's Rank Order Correlations<br>Marked correlations are significant at p <.05000 | | | | | |
|---|---|---|---|---|---|---|
| | Carbamazepine | Naproxen | Sulfamethoxazole | DEET | Sucralose | Salinity |
| Carbamazepine | 1 | -0.080 | 0.881* | -0.581* | 0.778* | -0.746* |
| Naproxen | -0.080 | 1 | -0.130 | 0.368* | -0.255 | 0.014 |
| Sulfamethoxazole | 0.881* | -0.130 | 1 | -0.548* | 0.746* | -0.579* |
| DEET | -0.581* | 0.368* | -0.548* | 1 | -0.489* | 0.408* |
| Sucralose | 0.778* | -0.255 | 0.746* | -0.489* | 1 | -0.488* |

## 3.3 Results for SR estimations

The framework for estimating SR and priors for CEC detection probability through the results of the pilot monitoring was assessed for the seven compounds with overall detection frequency higher than 30% (carbamazepine, naproxen, paracetamol, sulfamethoxazole, saccharin, DEET, and sucralose). Eleven remote sites (sampling points 3-13) were excluded from the analysis as salinity and temperature measured at these sites indicate a clear open Atlantic origin of the water, infringing the inherent condition of the framework based on postulated spatial autocorrelation of CEC levels (i.e., such as that expected when water soluble compounds analysed along a transect derive from the same coastal source points). Including these remote observations in the SR calculation would have probably yielded less accurate results of SR estimates. To assess the sensitivity of the framework on variations of the search radius and eventually search for the SR value, the variable *r* was varied by discrete steps of 50 km (50, 100, 150, 200, 250, 300 and 350 km). Results of the SR correlation with spatial distribution of compounds were sensitive to variation of the search radius *r* (Figure 2 and Table S15)). This is a necessary condition for the meaningfulness of the proposed framework.

Results of Spearman's correlation are shown in Figure 2 and Table S12. A significant positive correlation between $\overline{\Phi}_r$ outputs and measured concentration data was observed for five out of seven compounds with a coordination coefficient $R^2$>0.7, fulfilling key quality criteria for the calculation SR results and heuristically validating the framework for these groups of tracer compounds. In the following sub-section results of SR for different compounds and their sensitivity on the parameterization of the calculation framework are presented.

### 3.3.1 SR variability across different compounds

The positive correlation between $\overline{\Phi}_{SR}$ calculated in each sampling point and monitoring data was verified for carbamazepine, sulfamethoxazole, saccharin, and sucralose, while DEET showed a negative

correlation (driven by its inverse correlation with latitude described above likely driven by seasonality of the use of this compound). Naproxen concentrations did not exhibit any significant correlation with $\overline{\Phi}_{SR}$ for any applied values of *r*, hence for this frequently detected compound SR could not be calculated.

Useful SR results were obtained for carbamazepine, sulfamethoxazole, saccharin, and sucralose (Figure 2, Table 3). For carbamazepine, the best fit was observed using *r*=350 km ($R^2$=0.906). For sulfamethoxazole and sucralose, the best fit was achieved using *r*=150 km ($R^2$=0.798 and 0.745 respectively). Saccharin showed the best fit at the second lowest value, with *r*= 100 km ($R^2$=0.858) and paracetamol showed a statistically significant correlation only at *r*=50 km (although with a low correlation coefficient: $R^2$=0.391).

### 3.3.2 SR sensitivity on scaling factor *c*

The sensitivity of SR results on uncertainties in the source characteristic (defined here by the function $s_i$) was studied by varying the parameter *c* in Equation 2 (See also text S2). The following three scenarios were considered: i) *c*=0, population counts in drained watersheds are the only determinant of $s_i$; ii) *c*=1, moderate influence of coastal topology parameter *lcov*; and iii) *c*=2 extreme influence of *lcov* on $s_i$ value. Results show that variations of the coefficient *c* had negligible influence on SR results. (Table S15).

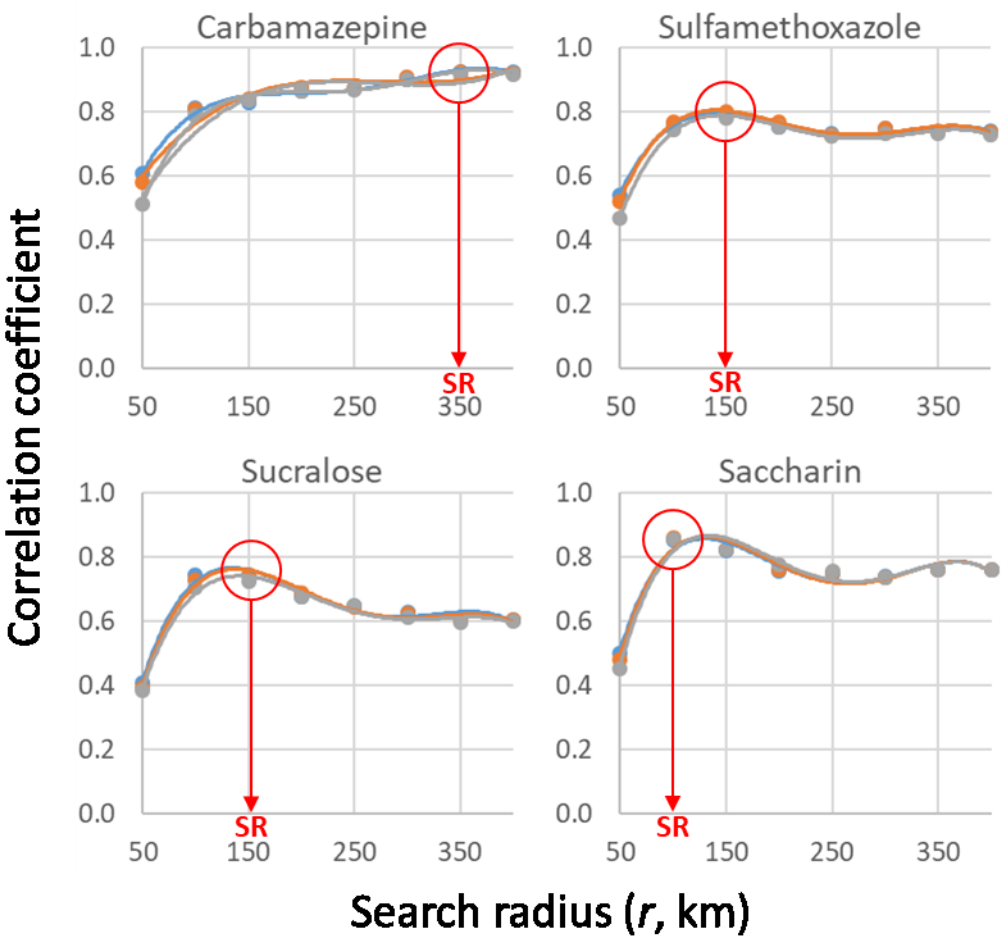



**Figure 2** Correlation coefficients at varying search radius *r* (50-350 km). All correlation analysis represented were statistically significant ($p<0.05$). Points are fitted with fourth order polynomial curves. Colors represent calculations with different values of parameter *c* (blue *c*=0, orange *c*=1, grey: *c*=2). SR represent the value of *r* corresponding to the maximum correlation coefficient. Only compounds yielding statistically positive correlations (i.e., fulfilling quality criteria for SR calculation frame) are reported. Results for other compounds are presented in the Supporting Information.

**Table 3** Characteristics of carbamazepine, saccharin, sucralose, and sulfamethoxazole relevant for their use as markers of wastewater pollution

| Compound | Carbamazepine | Sucralose | Sulfamethoxazole | Saccharin |
|---|---|---|---|---|
| CAS | 298-46-4 | 56038-13-2 | 723-46-6 | 81-07-2 |
| Use | Anticonvulsant | Artificial sweetener | Antibiotic | Artificial sweetener |
| Sources | Human excretion, manufacture, disposal | Human excretion, manufacture, disposal | Human excretion, manufacture, disposal | Human excretion, manufacture, disposal, agriculture |
| Solubility in water[a] | 112 mg $L^{-1}$ (25 °C) | 2.275 × $10^4$ mg $L^{-1}$ (25 °C) | 379 mg $L^{-1}$ (25 °C) | 4000 mg $L^{-1}$ (25 °C) |
| Log $K_{OW}$[a] | 2.45 | -1.00 | 0.89 | 0.91 |
| Henry's Law Constant[a] | 1.09 x $10^{-5}$ Pa $m^3$ $mol^{-1}$ (25 °C) | 4.04 x $10^{-14}$ Pa $m^3$ $mol^{-1}$ (25 °C) | 9.67 x $10^{-8}$ Pa $m^3$ $mol^{-1}$ (25 °C) | 1.25 x $10^{-4}$ Pa $m^3$ $mol^{-1}$ (25 °C) |
| WWTP removal | Negligible (Clara et al., 2004; Gurke et al., 2015) | negligible (Subedi and Kannan, 2014) | 42.4% (Gurke et al., 2015) | 90.3% (Subedi and Kannan, 2014) |
| Predicted Biodeg. Half-Life (OPERA Model) | 6.5 days | 4.4 days | 3.3 days | 4.2 days |
| Half-life in surface waters | 63 days (Tixier et al., 2003)-3.5 years (Benotti and Brownawell, 2009; Björlenius et al., 2018) | Years (Grice and Goldsmith, 2000) | 13 -100 days (Baena-Nogueras et al., 2017; Benotti and Brownawell, 2009; Radke et al., 2009) | 7-28 days (Howard, 2013) |
| Detected levels in marine waters[b] | 0.02–1.01 ng $L^{-1}$ | 0.82–15.29 ng $L^{-1}$ | 0.11–0.45 ng $L^{-1}$ | 3.01–285.15 ng $L^{-1}$ |
| Detection limit[c] | 0.005 ng $L^{-1}$ | 0.50 ng $L^{-1}$ | 0.1 ng $L^{-1}$ | 0.50 ng $L^{-1}$ |
| **Estimated SR** | **350 km** | **150 km** | **150 km** | **100 km** |

[a] Retrieved from EPI Suite

[b] Levels detected in this study

[c] The detection limits depend on the volume of collected water sample. Here values from the present study are shown (sample volume ca. 1 L).

# 4. Discussion

## 4.1 CEC marine concentrations and comparison with previous observations

Many earlier studies documented the occurrence and fate of CECs in freshwater, while their occurrence and behaviour in marine waters is far less studied (Branchet et al., 2020). These earlier reports, however, generally investigated CECs in coastal settings and estuaries (Biel-Maeso et al., 2018; 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). A recent study deployed state of the art non-target analysis for the detection of waterborne CECs in transitional, coastal, and marine waters providing important qualitative information on the complexity of this pollution (Lara-Martín et

al., 2020). However, quantitative data of CECs in offshore and open ocean waters remain rare, highlighting the relevance of the present study. A comprehensive overview of the occurrence of pharmaceuticals in the marine environment was published recently (Branchet et al., 2020). Such an analysis highlighted the anticonvulsant drug carbamazepine being ubiquitous in freshwater and coastal environments. It has also been detected at low levels (sub-ng/L up to 12.2 ng/L) in offshore European marine waters (Alygizakis et al., 2016; Biel-Maeso et al., 2018; Björlenius et al., 2018; Brumovský et al., 2017, 2016; Loos et al., 2013b; Vanryckeghem et al., 2019; Weigel et al., 2001). Our results confirm this scenario.

The antibiotic sulfamethoxazole has also been frequently observed in marine waters, both in coastal (Alygizakis et al., 2016; Borecka et al., 2015; Klosterhaus et al., 2013; Nödler et al., 2014; Shimizu et al., 2013; Zhang et al., 2013a) and in the open sea areas (at sub-ng/L to 7.70 ng/L) (Alygizakis et al., 2016; Björlenius et al., 2018; Brumovský et al., 2017, 2016; Loos et al., 2013b; Vanryckeghem et al., 2019; Zhang et al., 2013b). The levels measured in the present study are in the lower range of those previously reported in other marine areas.

Similarly, NSAIDs such as ibuprofen or naproxen are some of the most monitored and detected CECs in marine areas (Branchet et al., 2020). Naproxen was one of the most abundant pharmaceuticals detected in this study at similar levels as previously recorded in the North Sea and the Mediterranean Sea (Alygizakis et al., 2016; Brumovský et al., 2017, 2016). The observed concentrations of ibuprofen were also in the same order of magnitude as those previously reported in the Mediterranean (Brumovský et al., 2017; Loos et al., 2013b). Higher ibuprofen levels were previously detected in coastal areas (up to 1219 ng/L) (Ali et al., 2017; Biel-Maeso et al., 2018; Klosterhaus et al., 2013; María Baena-Nogueras et al., 2016; Nödler et al., 2014), in the open North Sea (22.0 ng/L) (Brumovský et al., 2016) and in the offshore seawater from the Gulf of Cadiz (32.3 ng/L) (Biel-Maeso et al., 2018). Diclofenac was found in this study only at two sampling sites at concentrations 0.30 and 0.64 ng/L which is lower compared to earlier data from coastal (Afsa et al., 2020; Alygizakis et al., 2016; Biel-Maeso et al., 2018;

546 María Baena-Nogueras et al., 2016; McEneff et al., 2014; Nödler et al., 2014; Vanryckeghem et al.,
547 2019) and offshore (Alygizakis et al., 2016; Biel-Maeso et al., 2018; Björlenius et al., 2018;
548 Vanryckeghem et al., 2019) locations.

549 Concerning antipyretics, paracetamol (acetaminophen) has been previously detected at similar levels
550 as in the present study in the North Sea, Baltic Sea, Adriatic Sea, offshore areas in the Gulf of Cadiz,
551 Mediterranean coast and Svalbard coast (Alygizakis et al., 2016; Biel-Maeso et al., 2018; Björlenius et
552 al., 2018; Brumovský et al., 2016; Choi et al., 2020; Nödler et al., 2014). Higher levels of paracetamol
553 were previously measured in the offshore areas of the Eastern Mediterranean Sea (Alygizakis et al.,
554 2016) and in the Belgian area of the North Sea (Vanryckeghem et al., 2019), while in the offshore areas
555 of the Western Mediterranean Sea paracetamol occurred at one order of magnitude lower
556 concentrations than measured here in the BO in the present and an earlier study (Brumovský et al.,
557 2017). Such a difference is likely due to the higher dilution factor and the presence of deep water
558 formation zones in the Western Mediterranean Sea that drive contaminants loading in surface waters
559 to the depth.

560 Caffeine has been frequently detected in coastal and offshore waters (Alygizakis et al., 2016; Biel-
561 Maeso et al., 2018; Brumovský et al., 2017, 2016; Choi et al., 2020; Klosterhaus et al., 2013; Loos et al.,
562 2013b; María Baena-Nogueras et al., 2016; Munaron et al., 2012; Nödler et al., 2014; Vanryckeghem
563 et al., 2019; Weigel et al., 2002, 2001). The levels measured in the present study (18.62-71.81 ng/L)
564 are in agreement with other European offshore data (Alygizakis et al., 2016; Biel-Maeso et al., 2018;
565 Choi et al., 2020), although slightly higher than concentrations detected in the open North Sea in our
566 previous study (Brumovský et al., 2016). Wastewater inputs to the Baltic reflecting the very high per
567 capita coffee consumption in the Northern Europe can justify this difference. The detection frequency
568 of caffeine in the present study was lower compared to the cited studies due to high MDL (17.5 ng/L)
569 caused by field blank contamination.The insect repellent DEET was typically detected at slightly higher
570 levels (by a factor of 3) to levels previously found in the North Sea (Brumovský et al., 2016; Weigel et

al., 2002, 2001) and the Mediterranean Sea (Brumovský et al., 2017; Loos et al., 2013b). However, similar or even higher levels of DEET (up to 50 ng/L) were recently measured along the shoreline near Ny-Ålesund in Svalbard (Choi et al., 2020).

The antimicrobial triclosan has been detected in this study only at two sampling sites near Tromsø (at 0.35-0.67 ng/L). Previously, triclosan was measured in the German Bight at concentrations ranging 0.0008–6.870 ng/L (Xie et al., 2008) and in the offshore Mediterranean Sea ranging 0.008-0.305 ng/L (Brumovský et al., 2017).

Several artificial sweeteners were detected in coastal/estuarine areas near highly populated cities (Baena-Nogueras et al., 2018; Gan et al., 2013; Mead et al., 2009; Sang et al., 2014). All three artificial sweeteners investigated in the present study were also previously detected in the offshore North Sea (Brumovský et al., 2016). Acesulfame and sucralose were found at levels similar to those reported here. Sucralose was the most abundant artificial sweetener whereas the levels of saccharin were notably lower (<0.95–3.01 ng/L). Sucralose has been reported in the open Atlantic ocean waters (Mead et al., 2009) and offshore of Venice at similar levels to this study (Loos et al., 2013b)..

## 4.2 Distribution patterns of CECs along the Europe-Arctic transect

The observed significant positive spatial correlations among carbamazepine, sucralose, and sulfamethoxazole (Table 2), reflect the dominant influences of their common sources and similar processes controlling their marine transport and distribution. The influence of wastewater sources (especially those whose signal is conveyed to the sea by riverine transport) in this area was also confirmed by: i) the significant inverse correlation between salinity and the concentration of several compounds, and ii) the inverse correlation with latitude (driven by lower anthropic presence at higher latitudes (Tables 2 and S14, respectively). The BO was obviously the most exposed area. The Danish straits and the Kattegat area are receptors of the BO conveying freshwater from rivers draining densely

595 populated regions in Central and Northern Europe. Beyond land-based sources, the intense passenger
596 marine traffic may also represent a significant input of PPCPs and food additives in this region (Vicente-
597 Cera et al., 2019).

598 Unlike most compounds, DEET concentrations were inversely correlated with salinity and directly
599 correlated with latitude (Tables 2 and S14 in the SI). This is likely because the BO was sampled in winter
600 when the use of insect repellents is minimal, while sampling in the Barents Sea was carried out in
601 summer. The influence of seasonality on spatio-temporal trends of marine contamination has been
602 addressed recently (Cui et al., 2019; McEneff et al., 2014; Merel et al., 2015), including specifically for
603 DEET (Marques dos Santos et al., 2019). The use of carbamazepine, sucralose, and sulfamethoxazole
604 is rather uniform throughout the year and, therefore, less dependent on sampling season, but clearly
605 dependent on source spatial distribution. A different trend was observed for naproxen, the occurrence
606 of which was not correlated to salinity nor latitude (Tables 2and S14). This pattern could be explained
607 as an evidence of different regional uses of this compound.

608 The ubiquitous distribution of several CECs observed along this latitudinal transect, also noted for
609 relatively short-lived compounds can be ascribed to: i) pseudo-persistent behavior (Daughton, 2004)
610 (i.e., losses of compounds from the system due degradation are offset by constant replenishment from
611 sources), ii) environmental conditions hindering their degradation (Bu et al., 2016), and iii) efficient
612 marine advection in this area. Data on environmental half-lives of these compounds in marine water
613 are scarce (Baena-Nogueras et al., 2017; Björlenius et al., 2018) (see also Table 3 for a summary). The
614 effectiveness of northward transport in this region stems from a well-known system of marine
615 currents. The BO conveys the bulk of CECs released to the sea from central and Northern Europe to
616 the North Sea and the Norwegian Coastal Currents. This, in turn, is an advective system streaming
617 northward at an average velocity of 1-2 knots. The travel time of passive tracers from southern Norway
618 to the Arctic (i.e. Longyearbyen) is therefore expected to be in the order of 1 or 2 months.

Several sampling locations in the AO region (e.g., sampling points 3-12) were characterized by water masses with a temperature and salinity signature consistent with that of North Atlantic waters. Despite the remote origins of these water masses, samples collected here contained measurable levels of some CECs, including in carbamazepine, naproxen, DEET, and sucralose. Contaminants detected here may therefore not be related to the same sources feeding the Norwegian coastal current described above. Instead, results point at their remote origin and indicate these substances are very persistent in these conditions.

The surprisingly high concentrations of saccharin measured in the Baltic/Kattegat area is linked to proximity of sources including riverine transport of municipal wastewaters, direct discharges from ships (Vicente-Cera et al., 2019), agricultural runoff, or photo-transformation of some sulfonylurea herbicides (Bottaro et al., 2008; Buerge et al., 2011; Paul and Singh, 2008). Saccharin is normally efficiently degraded in the WWTP processes (Gan et al., 2013; Scheurer et al., 2009; Subedi and Kannan, 2014) and undergoes degradation in seawater (Baena-Nogueras et al., 2017). However, low temperature and reduced solar irradiation during winter season may have contributed to its less effective attenuation (Sang et al., 2014). According to a recent industrial report (MECAS, 2014) saccharin is the artificial sweetener with the highest production volume. Saccharin is also authorized in the EU for use as an additive in animal feed for piglets, pigs, bovines and calves and it is largely excreted after feeding to manure that can be applied to agricultural areas (Buerge et al., 2011). During intensive rainfall, saccharin may mobilize from applied manure and be transported via runoff to coastal waters.

## 4.3 Critical appraisal of the SR calculation frame

The high-quality significant correlation obtained between the calculated value of $\overline{\Phi}_{SR}$ and observed concentration data for the four compounds identified as tracers for compounds with different environmental degradability (carbamazepine, naproxen, sucralose, and saccharin) fulfilled the first two criteria set for the heuristic validation of the calculation framework described in section 2.9 and Text

S2. The SR framework was developed as a minimalistic tool to estimate potential for long-range marine transport of selected tracer compounds. As such it included several major simplifying assumptions on the homogeneous marine advection and by excluding from the calculation the potential influence of some sources of the selected CECs (e.g., fish-farms, discharges from ships, etc.). Despite these approximations, it yielded a distribution of detection potential that was significantly correlated with the observed distribution of contaminants, by means of optimizing a single variable (e.g., *r*). It has to be acknowledged, however, that the validation was carried out using a dataset collected during a specific season (in this case winter in the BO). Seasonality in environmental conditions and source strength could yield a different distribution pattern in another period of the year. Hence these results are not in principle extendible throughout the year. Reiteration of this optimization exercise across monitoring campaigns conducted in different periods of the year, would be necessary to assess the general validity of the assessment.

The variability of SR results reflected compound persistence. Carbamazapine showed the highest SR. This compound is resistant to photodegradation (Kim and Tanaka, 2009) and it is commonly described as a persistent environmental contaminant (US EPA, 2020). A lower SR value indicates instead families of water-soluble compounds with relatively lower environmental persistence and long-range transport potential (the concentration of which are therefore expected to drop rapidly with the distance from the source). This was the case of saccharin, the most reactive among the frequently detected compounds included in the SR calculations (see Table 3). The two compounds scoring intermediate SR values (sulfamethoxazole and sucralose) have estimated half-life in surface waters in the order of months or years (Table 3).

Lack of sensitivity of the SR results on the parameterization of function $s_i$ (equation S2) indicates that major uncertainties over the characterization of source point emission rates and uncertainties on marine water circulation and renewal in proximity of source points did not significantly affect SR estimations, corroborating trust in this simplistic framework.

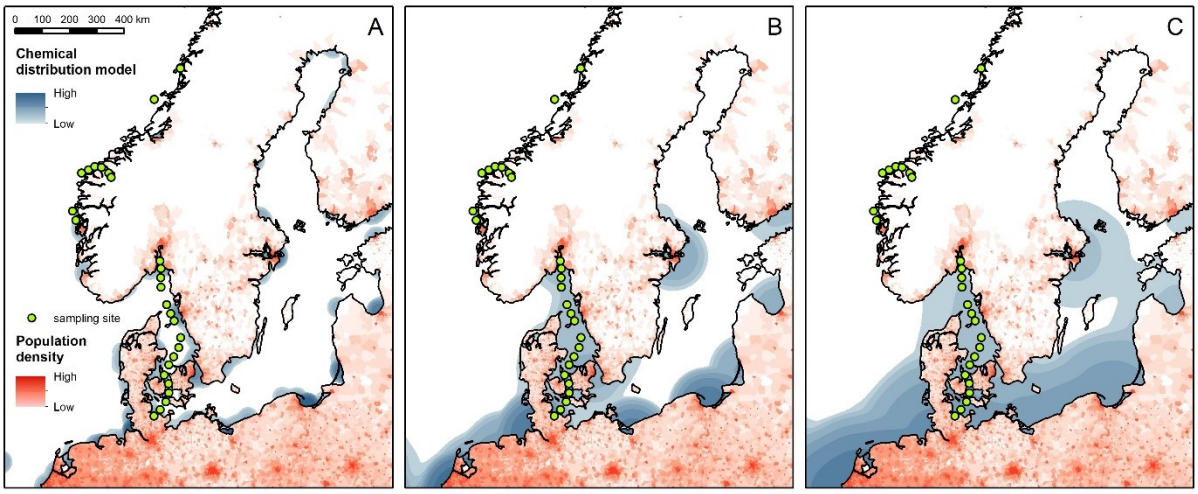
## 4.4 Prior maps of detection probability, applicability and limitations

Owing to the high correlation between $\overline{\Phi}_{SR}$ and monitoring data, SR results could be used to elaborate prior maps of tracer compound spatial distributions along the studied transect. Prior maps for virtual compounds with different SR values are presented in Figure 3 (Layers for the GIS necessary to reproduce these maps are given in the in the SI attached to this paper). These maps describe heuristically validated expectations of spatial distribution patterns (and inherently of the probability of their detection) for compounds originated from coastal and riverine wastewater sources to the sea and with solubilities and degradation half-lives in the range of those of the respective tracer compounds used for validation. By assimilating information on source distribution and observed compound distribution, these prior maps can serve as first tier guidance for designing monitoring campaigns for a broader range of compounds co-emitted from wastewater sources in the region.

Importantly, spatial distribution priors formulated through equation 1 are dependent on the quality of the method used to generate concentration data. For example, if a method with a higher detection limit was chosen, most likely smaller SR values would have been obtained. The method applied here utilized the currently highest level of quality assurance and end-of-line high resolution-/high sensitivity analytical instrumentation for targeted quantitative analysis. Results provided here can therefore be considered as a reference for describing priors of spatial distribution in future campaigns, including in cases where methods with lower analytical sensitivity will be deployed. If technological advances enable a substantial lowering of detection limits, prior maps will require revision and a new validation.

The need of defining priors of spatial trends of contamination in relation to marine hydrographic and distribution of sources has been highlighted as a pivotal element for effective marine monitoring (Branchet et al., 2020). To this end, a fully analytical and deterministic approach based on physically modelling transport of contaminants from well characterized coastal sources would be the ideal

693 approach. This however is hindered by several practical limitations. First, this approach requires data-
694 intensive high-resolution hydrophysical models of contaminant marine transport which still lack
695 sufficient accuracy. Furthermore, operating these models would require specialized human and
696 computational resources which may currently not be systematically available to support marine
697 pollution monitoring. While in future reliable mechanistic fate and distribution models will probably
698 represent better tools for monitoring planning, it is argued that minimalistic approaches represent a
699 valid alternative for the present. The SR framework introduced here embodies an example of such an
700 alternative. Furthermore (similarly to deterministic fate models), the heuristic model proposed here
701 can be reiteratively improved as more monitoring data become available, leading to a higher
702 predictivity of the spatial and temporal distribution of CECs.




703

704 **Figure 3** Modelled distribution of detection probability of a hypothetical chemical depending on
705 varying search radius *r* of the kernel density function: A) *r* = 50 km, B) *r* = 150 km, C) r=300 km. Blue
706 shade in marine area estimates the detection probability for compounds with different SR. SR
707 presented here were calculated setting parameter *c*=1. Data for GIS to reproduce these maps are given
708 in the in the Supplementary materials attached to this paper.

# Conclusions

We demonstrated the effective combined use of a multi-purpose marine research infrastructure based on a fleet of ships of opportunity and state-of-the-art analytical chemistry methods for reliable and cost-effective monitoring of marine chemical pollution. In a broad coastal-open sea transect stretching from central Europe to the European Arctic, 50 samples were collected and analysed for the levels of several PPCPs and artificial food additives. The use of infrastructure and methodology described here has the potential to considerably improve knowledge on the occurrence of CECs in marine areas , by enabling routine and cost-effective observations. As part of this proof-of-concept study, the potential for marine long-range transport for several frequently detected contaminants was empirically assessed through an original index of marine SR. Such an index was useful to produce prior maps of spatial distribution estimating detection probability for a range of compounds identified as “tracers” (such as carbamazepine, sucralose, sulfamethoxazole, and saccharine). Priors obtained from these tracers could be used as a proxy for defining distribution priors for a broader range of compounds co-emitted with wastewater into the sea. These in turn will serve as useful tools for planning effective monitoring in the area and, together with the infrastructure and methodology presented here, provide crucial support for European and international policies on marine pollution.

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Supporting Information

# Line ferries and cargo ships for monitoring marine contaminants of emerging concern: application along a Europe-Arctic transect.

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**Table S1** Information on individual FerryBox cruises along the Baltic outflow-Barents Sea transect.

| Transect region | Cruise route | Sampling period | Ship name/type* | Ship owner |
|---|---|---|---|---|
| Baltic outflow | Kiel-Oslo | 24.–25. 1. 2017 | MS Color Fantasy/P | Color Line |
| Norwegian West Coast | Bergen-Kirkeness | 8.–25. 8. 2016 | MS Vesterålen/P | Hurtigruten Group |
| Arctic Ocean | Tromsø-Longyearbyen | 21.–23. 6. 2016 | MS Nordbjorn/C | Nb Norbjorn as |

*C - cargoship, P – passenger ship


**Figure S1a. The NorSOOP fleet of ships of opportunity.**

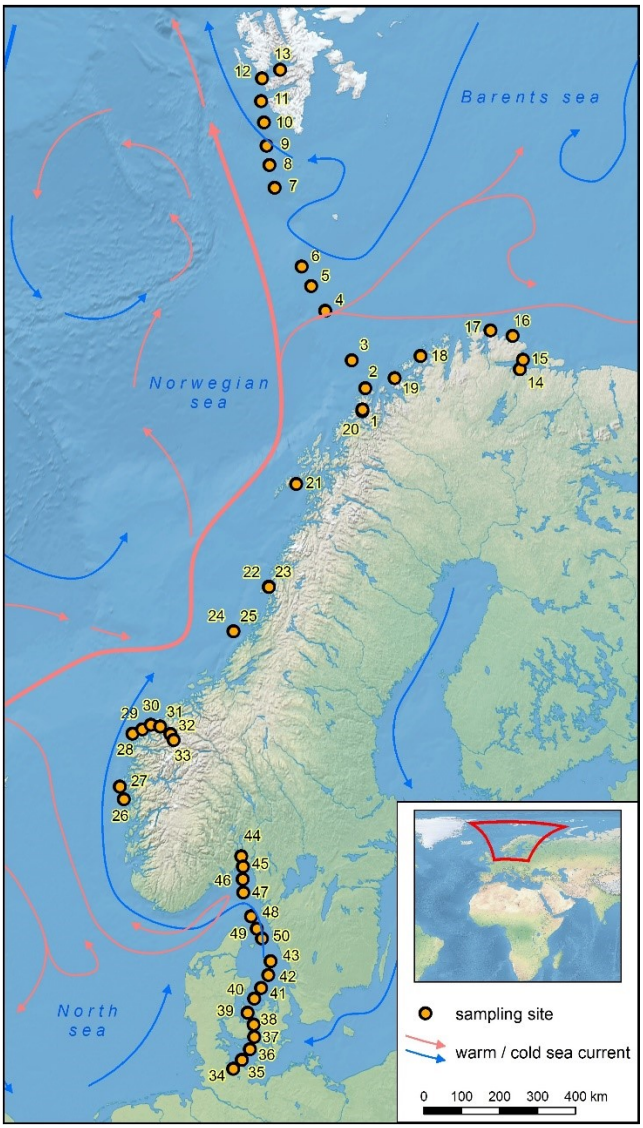


**Figure S1b** Map of sampling sites (June and August 2016, January 2017). Arrows in the map display surface currents. The transect can be divided into three sections: a) Arctic Ocean (sites 1-20), b) Norwegian west coast (sites 21-33) and c) Baltic outflow (sites 34-50).

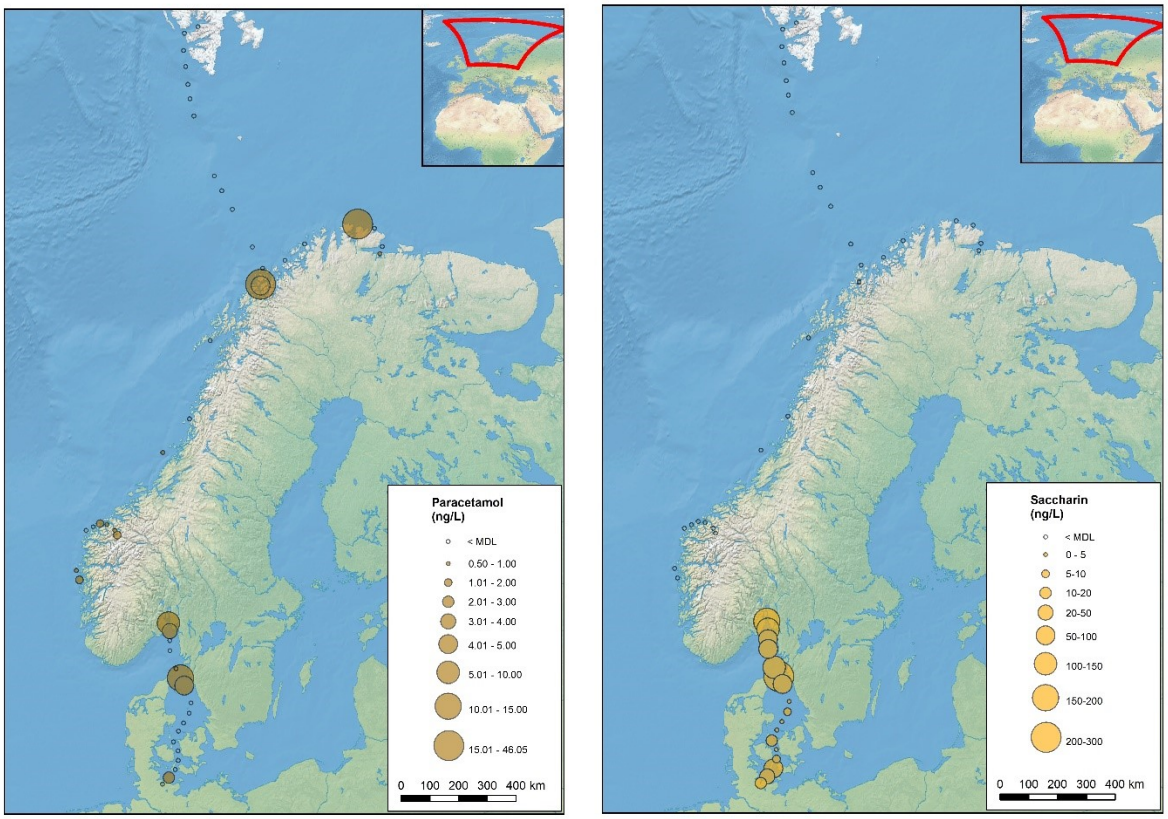


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**Figure S2** Levels of paracetamol, saccharin and sulfamethoxazole. Detected concentrations are depicted as circles at individual sampling sites.

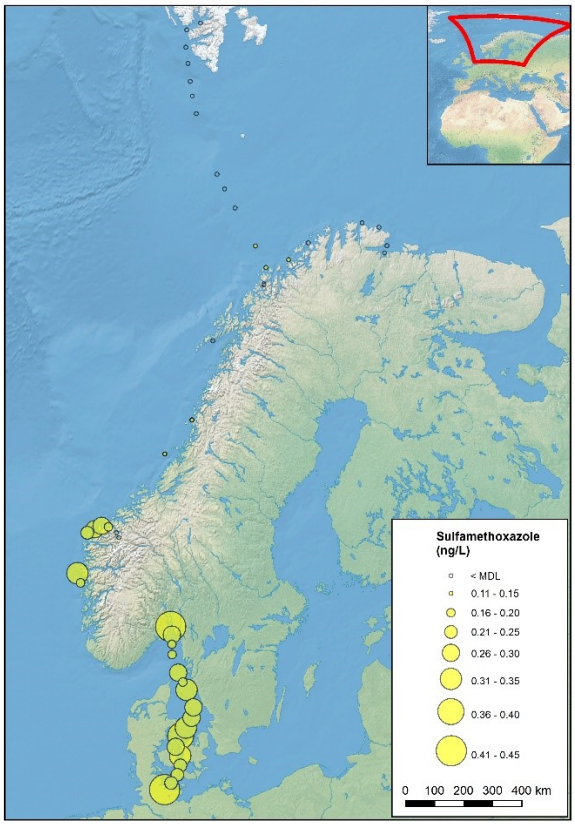


**Figure S2** Continued.

**Table S2** Coordinates of collected samples, volume, sampling date, salinity and temperature data.

| Sample No. | Latitude (N) | Longitude (E) | Collected volume (mL) | Date | Salinity (PSU)* | Temperature (°C) |
|---|---|---|---|---|---|---|
| 1 | 69.71 | 19.05 | 995 | 21.6.2016 | 32.48 | 8.85 |
| 2 | 70.24 | 19.46 | 911 | 21.6.2016 | 33.34 | 8.77 |
| 3 | 70.95 | 18.80 | 985 | 21.6.2016 | 34.49 | 8.55 |
| 4 | 72.21 | 17.33 | 880 | 22.6.2016 | 34.91 | 8.93 |
| 5 | 72.84 | 16.45 | 956 | 22.6.2016 | 34.99 | 8.57 |
| 6 | 73.33 | 15.83 | 934 | 22.6.2016 | 34.98 | 8.79 |
| 7 | 75.31 | 14.07 | 848 | 22.6.2016 | 35.04 | 7.85 |
| 8 | 75.88 | 13.73 | 862 | 23.6.2016 | 35.03 | 7.62 |
| 9 | 76.36 | 13.57 | 899 | 23.6.2016 | 35.02 | 7.14 |
| 10 | 76.95 | 13.42 | 882 | 23.6.2016 | 34.74 | 5.63 |
| 11 | 77.49 | 13.25 | 845 | 23.6.2016 | 34.49 | 4.78 |
| 12 | 78.07 | 13.48 | 928 | 23.6.2016 | 34.43 | 4.57 |
| 13 | 78.26 | 15.43 | 872 | 23.6.2016 | 33.96 | 5.54 |
| 14 | 69.846 | 30.099 | 893 | 8.8.2016 | 12.68 | 13.48 |
| 15 | 70.039 | 30.5 | 985 | 8.8.2016 | 32.83 | 12.17 |
| 16 | 70.66 | 30.33 | 977 | 8.8.2016 | 33.9 | 9.68 |
| 17 | 70.9452 | 28.9608 | 630 | 8.8.2016 | 32.91 | 10.18 |
| 18 | 70.7638 | 23.6696 | 969 | 9.8.2016 | 33.78 | 8.99 |
| 19 | 70.3677 | 21.5914 | 951 | 9.8.2016 | 32.9 | 10.59 |
| 20 | 69.7519 | 19.069 | 517 | 9.8.2016 | 33.21 | 8.96 |
| 21 | 68.147 | 14.2525 | 966 | 10.8.2016 | 32.29 | 13.61 |
| 22 | 65.7467 | 12.3004 | 1000 | 11.8.2016 | 31.8 | 13.26 |
| 23 | 65.7395 | 12.29948 | 1006 | 11.8.2016 | 31.74 | 13.25 |
| 24 | 64.7089 | 10.2489 | 1010 | 11.8.2016 | 32.07 | 14.41 |
| 25 | 64.7089 | 10.2489 | 999 | 11.8.2016 | 32.13 | 14.39 |
| 26 | 60.6411 | 4.9200 | 983 | 24.8.2016 | 21.635 | 15.56 |
| 27 | 60.9339 | 4.6695 | 967 | 24.8.2016 | 28.96 | 15.13 |
| 28 | 62.2030 | 5.0950 | 990 | 25.8.2016 | 28.41 | 15.42 |
| 29 | 62.3198 | 5.5723 | 994 | 25.8.2016 | 30.26 | 15.69 |
| 30 | 62.44 | 6.0016 | 998 | 25.8.2016 | 29.05 | 15.62 |
| 31 | 62.416 | 6.4736 | 1012 | 25.8.2016 | 25.72 | 16.29 |
| 32 | 62.2532 | 7.0188 | 984 | 25.8.2016 | 20.35 | 16.77 |
| 33 | 62.1073 | 7.1896 | 999 | 25.8.2016 | 16.82 | 16.68 |
| 34 | 54.3387 | 10.1714 | 884 | 25.1.2017 | n.a. | 3.89 |
| 35 | 54.5496 | 10.5233 | 871 | 25.1.2017 | n.a. | 2.58 |
| 36 | 54.8028 | 10.852 | 841 | 25.1.2017 | 12.2 | 2.59 |
| 37 | 55.0903 | 11.0338 | 852 | 25.1.2017 | 13.62 | 2.72 |
| 38 | 55.3869 | 11.0213 | 885 | 25.1.2017 | 14.8 | 2.82 |
| 39 | 55.674 | 10.7793 | 843 | 25.1.2017 | 16.82 | 2.92 |
| 40 | 56.0046 | 11.0587 | 847 | 25.1.2017 | 19.12 | 3.13 |

*psu = practical salinity unit; n.a. = not available

**Table S2** Continued.

| Sample No. | Latitude (N) | Longitude (E) | Collected volume (mL) | Date | Salinity (PSU)* | Temperature (°C) |
|---|---|---|---|---|---|---|
| 41 | 56.2555 | 11.361 | 877 | 25.1.2017 | 22.83 | 3.05 |
| 42 | 56.558 | 11.6781 | 881 | 25.1.2017 | 27.44 | 3.75 |
| 43 | 56.8847 | 11.8024 | 846 | 25.1.2017 | 25.81 | 3.17 |
| 44 | 59.387 | 10.5746 | 853 | 24.1.2017 | 26.17 | 2.53 |
| 45 | 59.141 | 10.6404 | 858 | 24.1.2017 | 27.98 | 3.24 |
| 46 | 58.8396 | 10.6295 | 733 | 24.1.2017 | 26.44 | 3.43 |
| 47 | 58.5279 | 10.6412 | 822 | 24.1.2017 | 33.48 | 5.93 |
| 48 | 57.9625 | 10.9758 | 865 | 24.1.2017 | 33.72 | 6.24 |
| 49 | 57.6666 | 11.2297 | 816 | 24.1.2017 | 33.10 | 5.38 |
| 50 | 57.4281 | 11.4415 | 841 | 24.1.2017 | 31.67 | 5.83 |

*psu = practical salinity unit; n.a. = not available

## Text S1 Reagents and Standards

The following isotopically labeled internal surrogate standards were used for quantification of the water samples: ibuprofen-d3, paracetamol-d4, $^{13}C_6$-sucralose, sulfamethoxazole-d4 and $^{13}C_6$-triclosan. Analytical standards (both native and isotopically labelled) were purchased from Sigma-Aldrich (St. Louis, MO, USA), LGC (Teddington, UK), Absolute Standards Inc. (Hamden, CT, USA), AccuStandard (New Haven, CT, USA), Chem Service Inc. (West Chester, PA, USA) and Dr. Ehrenstorfer (Augsburg, Germany). The standards were supplied in the form of methanolic solutions. Working solutions at different concentrations were prepared by appropriate dilution of these solutions in methanol and HPLC grade water. LC-MS grade methanol used in this work was purchased from Biosolve b. v. (Valkenswaard, The Netherland). LC/MS grade acetone was obtained from Lab Scan analytical sciences (POCH S.A., Gliwice, Poland). HPLC grade water was obtained from Fisher Scientific (Loughborough, UK). Ammonium acetate and formic acid used as addition to mobile phase (p. a. grade; ≥98.0%) were obtained from Fluka (FlukaChemie GmbH, Buchs, Germany). Hydrochloric acid (37% in water, p. a. grade) used for adjusting sample pH was purchased from Fluka (FlukaChemie GmbH, Buchs, Germany). Water was purified in the laboratory using Milli-Q Water System (Millipore Corp., Bedford, MA, USA). Seawater pre-extracted using the same procedure as adopted for the extraction of field samples was used as a matrix for field blanks, recovery and stability test.

**Text SI2. Further explanation of the SR frame**

Figure 1 schematically illustrates this approach considering (for the sake of simplification) a unidimensional spatial transect. During application the method was obviously applied to the two-dimensional field of environmental concentrations in surface marine waters along the geographic transect.

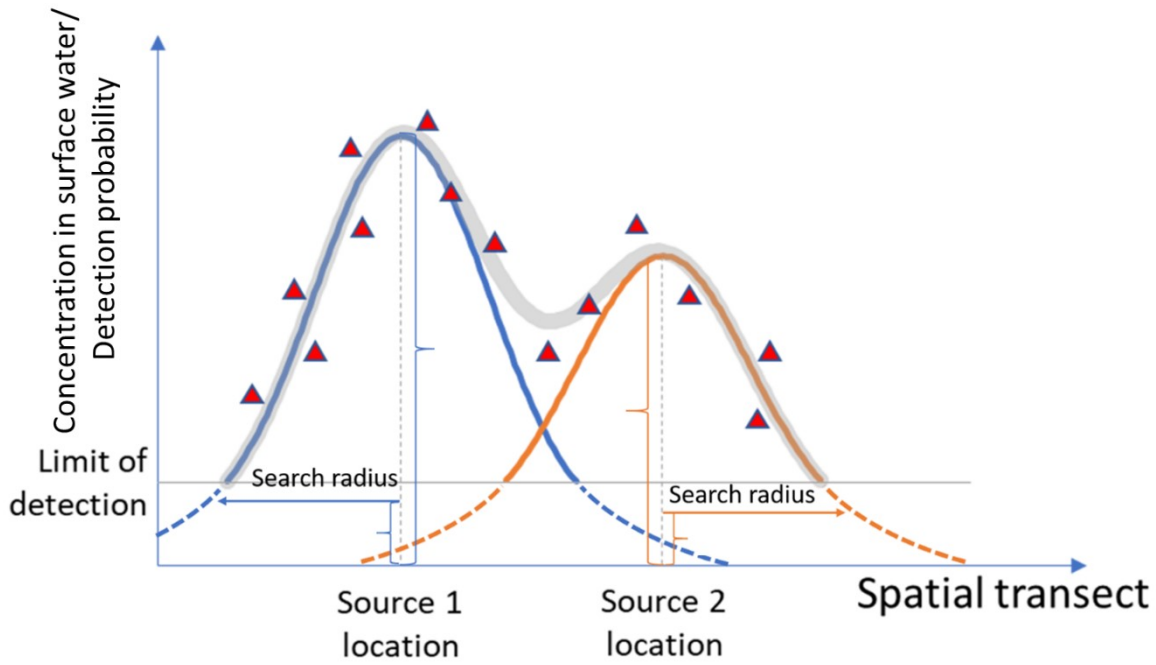


**Figure S2.1 Schematic representation of the approach for estimating the spatial range of a given contaminant. The figure depicts two source points located at different places along the spatial transect (i.e., the coastline) with different strength. Red triangles represent hypothetical observations from monitoring along the transect. The blue and orange curve represent $\Phi_{x_i,s_i,r}$ calculated for Source 1 and Source 2, respectively. The grey line is $\overline{\Phi}_{SR}$. SR is the value of the search radius that optimize $\overline{\Phi}_{SR}$ to the monitoring results.**

Based on the example in the figure, consider a hypothetic substance emitted in two locations along a coastline. The mean emission rate (i.e., source strength) is different at the two sites as, for example, a larger human population drains into Source 1 compared to Source 2. This is reflected by the higher concentration peak expected near Source 1. While, the concentration near the point source can be also mediated by several other processes (e.g., the local rate of renewal of marine water driven by currents),

here the focus is in defining a minimalistic model for estimating SR. The most simplistic assumption is that dilution and transport in different directions of the transect are similar in average. A normal distribution function with a maximum at the source point is therefore chosen to embody this minimal assumption and shape $\phi_{x_i,s_i,r}$ (Figure 1). Multiple sources will contribute simultaneously to the concentration field of a compound over a marine area. The aggregated probability of detecting a substance simultaneously emitted by multiple sources is given by $\bar{\phi}_r$ (Equation 1). This is depicted by the grey line in Figure 1. Note that based on this frame, once the location and characteristics of all relevant coastal sources are known in a given transect, $\bar{\phi}$ is solely a function of *r*. Next, it can be demonstrated that the probability of detecting a substance at a given distance from a point source is proportional to the concentration of the substance at that same point. SR can therefore be assessed as the value of *r* for which $\bar{\phi}_r$ values calculated at all the sampling points best fit monitoring results (e.g by minimizing the sum of squared errors between $\bar{\phi}_r$ values at the sampling points and monitoring results).

**Table S3** ESI-MS/MS parameters for pharmaceuticals, personal care products and food additives.

| Parameter | ESI- | ESI+ |
|---|---|---|
| Capillary (kV) | 2.5 | 2.5 |
| Source Temperature (°C) | 150 | 150 |
| Desolvation Temperature (°C) | 350 | 350 |
| Cone Gas Flow (L/hr) | 150 | 150 |
| Desolvation Gas Flow (L/hr) | 700 | 800 |
| Collision Gas Flow (mL/min) | 0.14 | 0.15 |
| Nebuliser Gas Flow (bar) | 7 | 7 |

**Table S4** ESI-MS/MS MRM analysis parameters for pharmaceuticals, personal care products and food additives targeted in this study.

| Analyte | Ionization mode | Precursor ion (m/z) | Cone voltage (V) | Product ions (m/z) | Collision energy (eV) | MDL (ng/L) |
|---|---|---|---|---|---|---|
| ***Pharmaceuticals*** | | | | | | |
| Atenolol | ESI+ | 267 | 30 | 190, 145 | 20, 30 | 0.05 |
| Caffeine | ESI+ | 195 | 30 | 182, - | 15, - | 17.5 |
| Caffeine-$^{13}C_3$ | ESI+ | 198 | 30 | 140, 112 | 17, 20 | |
| Carbamazepine | ESI+ | 237 | 30 | 194, 179 | 20, 35 | 0.005 |
| Clofibric acid | ESI- | 213 | 20 | 127, 85 | 17, 10 | 0.01 |
| Diclofenac | ESI+ | 296 | 20 | 214, - | 32, - | 0.20 |
| Hydrochlorothiazide | ESI- | 296 | 10 | 205, 269 | 20, 20 | 0.05 |
| Ibuprofen | ESI- | 205 | 30 | 159, 161 | 10, 10 | 0.15 |
| Ibuprofen-d3 | ESI- | 208 | 10 | 164 | 5 | |
| Ketoprofen | ESI- | 253 | 30 | 209, - | 5, - | 0.10 |
| Naproxen | ESI- | 229 | 20 | 170, 185 | 10, 10 | 0.02 |
| Paracetamol | ESI+ | 152 | 30 | 110, 93 | 15, 25 | 0.50 |
| Paracetamol-d4 | ESI+ | 156 | 30 | 114, 97 | 15, 25 | |
| Sulfamethoxazole | ESI+ | 254 | 30 | 156, 92 | 16, 26 | 0.1 |
| Sulfamethoxazole-d4 | ESI+ | 258 | 30 | 112, 96 | 25, 25 | |
| ***Personal care products*** | | | | | | |
| DEET | ESI+ | 192 | 20 | 119, - | 10, - | 0.50 |
| Triclocarban | ESI- | 313 | 20 | 160, - | 10, - | 0.005 |
| Triclosan | ESI- | 287 | 10 | 35, - | 5, - | 0.1 |
| Triclosan-$^{13}C_6$ | ESI- | 293 | 10, 20 | 35, 97 | 7, 7 | |
| ***Food additives*** | | | | | | |
| Acesulfame | ESI- | 162 | 34 | 78, 82 | 22, 15 | 0.32 |
| Saccharin | ESI- | 182 | 34 | 92, 106 | 20, 17 | 0.50 |
| Sucralose | ESI+ | 419 | 34 | 239, 221 | 17, 20 | 0.50 |
| Sucralose-d6 | ESI+ | 425 | 34 | 243, 225 | 15, 20 | |

**Table S5** Concentration of target compounds in procedural blanks (n=7), matrix blank and field blanks (n=7) in ng/mL of final extract.

| Analyte | IDL* | Procedural blanks | | | | | | | MB** | Field blanks | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 1 | 2 | 3 | 4 | 5 | 6 | 7 | | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
| ***Pharmaceuticals*** | | | | | | | | | | | | | | | | |
| Atenolol | 0.01 | <IDL | <IDL | <IDL | <IDL | <IDL | <IDL | <IDL | <IDL | <IDL | <IDL | <IDL | <IDL | <IDL | <IDL | <IDL |
| Caffeine | 0.01 | 0.128 | 0.236 | <IDL | <IDL | <IDL | <IDL | <IDL | 1.343 | 1.031 | 1.202 | 4.186 | 3.201 | 2.137 | 1.746 | 1.438 |
| Carbamazepine | 0.001 | <IDL | <IDL | <IDL | <IDL | <IDL | <IDL | <IDL | <IDL | <IDL | <IDL | <IDL | <IDL | <IDL | <IDL | <IDL |
| Clofibric acid | 0.01 | <IDL | <IDL | <IDL | <IDL | <IDL | <IDL | <IDL | <IDL | <IDL | <IDL | <IDL | <IDL | <IDL | <IDL | <IDL |
| Diclofenac | 0.005 | 0.034 | 0.037 | 0.039 | 0.034 | 0.036 | 0.031 | 0.035 | 0.044 | 0.046 | 0.07 | 0.057 | 0.041 | 0.035 | 0.069 | 0.033 |
| Hydrochlorothiazide | 0.05 | <IDL | <IDL | <IDL | <IDL | <IDL | <IDL | <IDL | <IDL | <IDL | <IDL | <IDL | <IDL | <IDL | <IDL | <IDL |
| Ibuprofen | 0.15 | <IDL | <IDL | <IDL | <IDL | <IDL | <IDL | <IDL | <IDL | <IDL | <IDL | <IDL | <IDL | <IDL | <IDL | <IDL |
| Ketoprofen | 0.10 | <IDL | <IDL | <IDL | <IDL | <IDL | <IDL | <IDL | <IDL | <IDL | <IDL | <IDL | <IDL | <IDL | <IDL | <IDL |
| Naproxen | 0.02 | <IDL | <IDL | <IDL | <IDL | <IDL | <IDL | <IDL | <IDL | <IDL | <IDL | <IDL | <IDL | <IDL | <IDL | <IDL |
| Paracetamol | 0.01 | <IDL | <IDL | <IDL | <IDL | <IDL | <IDL | <IDL | 0.015 | 0.049 | 0.068 | 0.085 | 0.099 | 0.135 | 0.057 | 0.051 |
| Sulfamethoxazole | 0.003 | <IDL | <IDL | <IDL | 0.015 | 0.015 | 0.014 | <IDL | <IDL | <IDL | 0.017 | 0.016 | <IDL | 0.022 | 0.019 | 0.021 |
| ***Personal care products*** | | | | | | | | | | | | | | | | |
| DEET | 0.02 | 0.155 | 0.138 | 0.097 | 0.101 | 0.062 | 0.097 | 0.089 | 0.192 | 0.212 | 0.17 | 0.218 | 0.149 | 0.227 | 0.184 | 0.19 |
| Triclocarban | 0.005 | <IDL | <IDL | <IDL | <IDL | <IDL | <IDL | <IDL | <IDL | <IDL | <IDL | <IDL | <IDL | <IDL | <IDL | <IDL |
| Triclosan | 0.02 | <IDL | <IDL | <IDL | <IDL | <IDL | <IDL | <IDL | <IDL | <IDL | <IDL | 0.117 | <IDL | <IDL | <IDL | <IDL |
| ***Food additives*** | | | | | | | | | | | | | | | | |
| Acesulfame | 0.03 | <IDL | <IDL | <IDL | <IDL | 0.065 | <IDL | 0.063 | <IDL | 0.104 | 0.14 | 0.118 | 0.126 | 0.13 | 0.153 | 0.162 |
| Saccharin | 0.10 | <IDL | <IDL | <IDL | <IDL | <IDL | <IDL | <IDL | <IDL | <IDL | <IDL | <IDL | <IDL | <IDL | <IDL | <IDL |
| Sucralose | 0.01 | 0.01 | 0.084 | 0.091 | 0.029 | <IDL | 0.033 | <IDL | <IDL | <IDL | 0.079 | 0.07 | 0.071 | 0.048 | 0.048 | 0.034 |

*IDL – instrumental detection limit in ng/mL of final sample

**MB – matrix blank

**Table S6** Recovery test results for targeted analytes. Recovery test (n=3) was performed using 1 L of pre-extracted seawater spiked with a mixture containing individual analytes to a final level 10 ng/L.

| Analyte | % recovery ± RSD (10 ng/L) |
|---|---|
| ***Pharmaceuticals*** | |
| Atenolol | 110±10 |
| Caffeine | 95±19 |
| Carbamazepine | 87±8 |
| Clofibric acid | 99±16 |
| Diclofenac | 61±3 |
| Hydrochlorothiazide | 95±3 |
| Ibuprofen | 57±9 |
| Ketoprofen | 64±15 |
| Naproxen | 99±9 |
| Paracetamol | 96±3 |
| Sulfamethoxazole | 58±3 |
| ***Personal care products*** | |
| DEET | 84±12 |
| Triclocarban | 94±12 |
| Triclosan | 107±6 |
| ***Food additives*** | |
| Acesulfame K | 34±8 |
| Saccharin | 74±7 |
| Sucralose | 80±6 |

**Table S7** Stability test results for targeted analytes. Stability test (n=3) was performed using 1 L of pre-extracted seawater spiked with a mixture containing individual analytes to a final level of 10 ng/L and deployed for the full duration of a cruise in the water sampler installed on board. Reported data represent the ratio between the detected levels of individual analytes after the end of the cruise divided by their recovery at the same nominal concentration (10 ng/L, see Table S5).

| Analyte | Stability during sampling cruise |
|---|---|
| ***Pharmaceuticals*** | |
| Atenolol | 100% |
| Caffeine | 54% |
| Carbamazepine | 94% |
| Clofibric acid | 82% |
| Diclofenac | 87% |
| Hydrochlorothiazide | 65% |
| Ibuprofen | 100% |
| Ketoprofen | 100% |
| Naproxen | 75% |
| Paracetamol | 86% |
| Sulfamethoxazole | 85% |
| ***Personal care products*** | |
| DEET | 94% |
| Triclocarban | 48% |
| Triclosan | 44% |
| ***Food additives*** | |
| Acesulfame K | 99% |
| Saccharin | 34% |
| Sucralose | 97% |

**Table S8** Recovery of surrogate standards. Mass-labelled caffeine-$^{13}C_3$ and paracetamol-d4 were added as internal standards to all samples, blanks, matrix spike tests and stability tests at a level of 100 ng/L prior to extraction to control the overall performance of the analytical method.

| Sample No. | % recovery | |
|---|---|---|
| | Caffeine-$^{13}C_3$ | Paracetamol-d4 |
| 1 | 78 | 71 |
| 2 | 56 | 75 |
| 3 | 93 | 69 |
| 4 | 109 | 72 |
| 5 | 62 | 68 |
| 6 | 50 | 70 |
| 7 | 50 | 76 |
| 8 | 73 | 69 |
| 9 | 54 | 63 |
| 10 | 93 | 71 |
| 11 | 122 | 72 |
| 12 | 82 | 61 |
| 13 | 119 | 67 |
| 14 | 45 | 56 |
| 15 | 78 | 66 |
| 16 | 61 | 75 |
| 17 | 67 | 87 |
| 18 | 101 | 64 |
| 19 | 46 | 65 |
| 20 | 80 | 95 |
| 21 | 46 | 64 |
| 22 | 94 | 124 |
| 23 | 47 | 127 |
| 24 | 56 | 119 |
| 25 | 57 | 118 |
| 26 | 54 | 93 |
| 27 | 102 | 104 |
| 28 | 41 | 100 |
| 29 | 45 | 98 |
| 30 | 139 | 114 |
| 31 | 76 | 114 |
| 32 | 56 | 117 |
| 33 | 128 | 115 |
| 34 | 50 | 44 |
| 35 | 64 | 45 |
| 36 | 60 | 39 |
| 37 | 70 | 40 |
| 38 | 58 | 39 |
| 39 | 80 | 43 |
| 40 | 93 | 44 |

**Table S8** Continued.

| Sample No. | % recovery | |
|---|---|---|
| | Caffeine-$^{13}C_3$ | Paracetamol-d4 |
| 41 | 60 | 45 |
| 42 | 51 | 54 |
| 43 | 57 | 52 |
| 44 | 88 | 56 |
| 45 | 85 | 52 |
| 46 | 54 | 59 |
| 47 | 134 | 65 |
| 48 | 72 | 53 |
| 49 | 101 | 74 |
| 50 | 51 | 54 |
| Matrix blank | 70 | 57 |
| Procedural blank 1 | 59 | 69 |
| Procedural blank 2 | 124 | 113 |
| Procedural blank 3 | 71 | 108 |
| Procedural blank 4 | 99 | 90 |
| Procedural blank 5 | 84 | 80 |
| Procedural blank 6 | 82 | 110 |
| Procedural blank 7 | 88 | 112 |
| Field blank 1 | 85 | 65 |
| Field blank 2 | 47 | 76 |
| Field blank 3 | 125 | 112 |
| Field blank 4 | 93 | 98 |
| Field blank 5 | 55 | 104 |
| Field blank 6 | 124 | 102 |
| Field blank 7 | 130 | 111 |
| Matrix spike 1 ng/L 1 | 64 | 63 |
| Matrix spike 1 ng/L 2 | 116 | 115 |
| Matrix spike 1 ng/L 3 | 97 | 121 |
| Matrix spike 1 ng/L 4 | 124 | 109 |
| Matrix spike 10 ng/L 1 | 70 | 59 |
| Matrix spike 10 ng/L 2 | 54 | 125 |
| Matrix spike 10 ng/L 3 | 61 | 127 |
| Stability test 1 | 103 | 126 |
| Stability test 2 | 57 | 120 |
| Stability test 3 | 91 | 128 |

**Table S9** Detailed analytical results of the occurrence of pharmaceuticals (part A) in the northern European sea waters; data are shown in ng/L.

| Sample No. | Atenolol | Caffeine | Carbamazepine | Clofibric acid | Diclofenac | Hydrochlorothiazide |
|---|---|---|---|---|---|---|
| 1 | <MDL | 36.27 | 0.16 | <MDL | <MDL | <MDL |
| 2 | <MDL | <MDL | 0.14 | <MDL | <MDL | <MDL |
| 3 | <MDL | <MDL | 0.09 | <MDL | <MDL | <MDL |
| 4 | <MDL | <MDL | 0.05 | <MDL | <MDL | <MDL |
| 5 | <MDL | <MDL | 0.03 | <MDL | 0.30 | <MDL |
| 6 | <MDL | <MDL | 0.04 | <MDL | <MDL | <MDL |
| 7 | <MDL | <MDL | 0.03 | <MDL | <MDL | <MDL |
| 8 | <MDL | <MDL | 0.02 | <MDL | <MDL | <MDL |
| 9 | <MDL | <MDL | 0.02 | <MDL | <MDL | <MDL |
| 10 | <MDL | <MDL | 0.03 | <MDL | <MDL | <MDL |
| 11 | <MDL | <MDL | 0.02 | <MDL | <MDL | <MDL |
| 12 | <MDL | <MDL | 0.03 | <MDL | <MDL | <MDL |
| 13 | <MDL | <MDL | 0.03 | <MDL | <MDL | <MDL |
| 14 | <MDL | <MDL | 0.02 | <MDL | <MDL | <MDL |
| 15 | <MDL | <MDL | 0.08 | <MDL | <MDL | <MDL |
| 16 | <MDL | <MDL | 0.08 | <MDL | <MDL | <MDL |
| 17 | <MDL | 36.63 | 0.05 | <MDL | <MDL | <MDL |
| 18 | <MDL | <MDL | 0.11 | <MDL | <MDL | <MDL |
| 19 | <MDL | <MDL | 0.13 | <MDL | <MDL | <MDL |
| 20 | <MDL | <MDL | 0.05 | <MDL | <MDL | <MDL |
| 21 | <MDL | <MDL | 0.14 | <MDL | <MDL | <MDL |
| 22 | <MDL | <MDL | 0.12 | <MDL | <MDL | <MDL |
| 23 | <MDL | <MDL | 0.12 | <MDL | <MDL | <MDL |
| 24 | <MDL | <MDL | 0.16 | <MDL | <MDL | <MDL |
| 25 | <MDL | <MDL | 0.17 | <MDL | <MDL | <MDL |
| 26 | <MDL | 18.62 | 0.23 | <MDL | <MDL | <MDL |
| 27 | <MDL | <MDL | 0.33 | <MDL | <MDL | <MDL |
| 28 | <MDL | <MDL | 0.30 | <MDL | <MDL | <MDL |
| 29 | <MDL | <MDL | 0.32 | <MDL | <MDL | <MDL |
| 30 | <MDL | <MDL | 0.30 | <MDL | <MDL | <MDL |
| 31 | <MDL | <MDL | 0.25 | <MDL | <MDL | <MDL |
| 32 | <MDL | <MDL | 0.14 | <MDL | <MDL | <MDL |
| 33 | <MDL | 24.92 | 0.15 | <MDL | <MDL | <MDL |
| 34 | <MDL | <MDL | 1.01 | <MDL | 0.64 | <MDL |
| 35 | <MDL | <MDL | 0.65 | <MDL | <MDL | <MDL |
| 36 | 0.12 | <MDL | 0.71 | <MDL | <MDL | <MDL |
| 37 | 0.13 | <MDL | 0.73 | <MDL | <MDL | <MDL |
| 38 | 0.12 | <MDL | 0.84 | <MDL | <MDL | <MDL |
| 39 | 0.10 | <MDL | 0.75 | <MDL | <MDL | <MDL |
| 40 | 0.10 | <MDL | 0.75 | <MDL | <MDL | <MDL |

**Table S9** Continued.

| Sample No. | Atenolol | Caffeine | Carbamazepine | Clofibric acid | Diclofenac | Hydrochlorothiazide |
|---|---|---|---|---|---|---|
| 41 | 0.07 | <MDL | 0.64 | <MDL | <MDL | <MDL |
| 42 | <MDL | <MDL | 0.52 | <MDL | <MDL | <MDL |
| 43 | <MDL | <MDL | 0.57 | <MDL | <MDL | <MDL |
| 44 | <MDL | 49.46 | 0.55 | <MDL | <MDL | <MDL |
| 45 | <MDL | <MDL | 0.50 | <MDL | <MDL | <MDL |
| 46 | <MDL | <MDL | 0.45 | <MDL | <MDL | <MDL |
| 47 | <MDL | <MDL | 0.23 | <MDL | <MDL | <MDL |
| 48 | <MDL | <MDL | 0.29 | <MDL | <MDL | <MDL |
| 49 | <MDL | 71.81 | 0.26 | <MDL | <MDL | <MDL |
| 50 | <MDL | 43.34 | 0.59 | <MDL | <MDL | <MDL |

**Table S10** Detailed analytical results of the occurrence of pharmaceuticals (part B) in the northern European sea waters; data are shown in ng/L.

| Sample No. | Ibuprofen | Ketoprofen | Naproxen | Paracetamol | Sulfamethoxazole |
|---|---|---|---|---|---|
| 1 | <MDL | <MDL | 0.17 | 4.23 | <MDL |
| 2 | <MDL | <MDL | 0.04 | <MDL | 0.12 |
| 3 | <MDL | <MDL | 0.12 | <MDL | 0.12 |
| 4 | <MDL | <MDL | 0.35 | <MDL | <MDL |
| 5 | <MDL | <MDL | 0.25 | <MDL | <MDL |
| 6 | <MDL | <MDL | 0.26 | <MDL | <MDL |
| 7 | 0.26 | <MDL | 0.06 | <MDL | <MDL |
| 8 | <MDL | <MDL | <MDL | <MDL | <MDL |
| 9 | <MDL | <MDL | 0.16 | <MDL | <MDL |
| 10 | <MDL | <MDL | 0.24 | <MDL | <MDL |
| 11 | <MDL | <MDL | 0.10 | <MDL | <MDL |
| 12 | <MDL | <MDL | 0.04 | <MDL | <MDL |
| 13 | <MDL | <MDL | 0.03 | <MDL | <MDL |
| 14 | <MDL | <MDL | <MDL | 0.86 | <MDL |
| 15 | <MDL | <MDL | 0.34 | <MDL | <MDL |
| 16 | <MDL | <MDL | 0.05 | <MDL | <MDL |
| 17 | <MDL | <MDL | <MDL | 16.34 | <MDL |
| 18 | <MDL | <MDL | 0.13 | <MDL | <MDL |
| 19 | <MDL | <MDL | 0.09 | <MDL | 0.11 |
| 20 | <MDL | <MDL | <MDL | 46.05 | <MDL |
| 21 | <MDL | <MDL | 0.78 | <MDL | <MDL |
| 22 | <MDL | <MDL | <MDL | <MDL | <MDL |
| 23 | 0.25 | <MDL | 0.03 | <MDL | 0.11 |
| 24 | <MDL | <MDL | 0.22 | 0.55 | <MDL |
| 25 | <MDL | <MDL | 0.06 | 0.71 | 0.12 |
| 26 | <MDL | <MDL | 0.16 | 1.92 | 0.20 |
| 27 | <MDL | <MDL | 0.32 | 0.92 | 0.31 |
| 28 | 0.27 | <MDL | 0.37 | <MDL | 0.24 |
| 29 | <MDL | <MDL | 0.71 | <MDL | 0.30 |
| 30 | <MDL | <MDL | 0.65 | 1.09 | 0.29 |
| 31 | <MDL | <MDL | 0.52 | 0.72 | 0.19 |
| 32 | <MDL | <MDL | 0.23 | 0.51 | 0.00 |
| 33 | <MDL | <MDL | 0.05 | 1.80 | 0.00 |
| 34 | 0.27 | <MDL | <MDL | <MDL | 0.45 |
| 35 | <MDL | 0.38 | <MDL | 2.44 | 0.21 |
| 36 | <MDL | <MDL | 0.08 | <MDL | 0.22 |
| 37 | <MDL | 0.95 | 0.13 | <MDL | 0.22 |
| 38 | <MDL | <MDL | 0.04 | <MDL | 0.32 |
| 39 | <MDL | 0.24 | 0.05 | <MDL | 0.27 |
| 40 | 0.31 | <MDL | <MDL | <MDL | 0.38 |

**Table S10** Continued.

| Sample No. | Ibuprofen | Ketoprofen | Naproxen | Paracetamol | Sulfamethoxazole |
|---|---|---|---|---|---|
| 41 | <MDL | 0.14 | 0.24 | <MDL | 0.31 |
| 42 | <MDL | 0.25 | 0.08 | <MDL | 0.27 |
| 43 | 0.36 | 0.83 | 0.19 | <MDL | 0.27 |
| 44 | <MDL | 0.29 | <MDL | 9.28 | 0.43 |
| 45 | <MDL | <MDL | 0.04 | 3.18 | 0.30 |
| 46 | <MDL | 0.50 | 0.08 | <MDL | 0.17 |
| 47 | <MDL | 0.57 | <MDL | <MDL | 0.17 |
| 48 | <MDL | <MDL | <MDL | <MDL | 0.29 |
| 49 | <MDL | <MDL | <MDL | 11.83 | 0.17 |
| 50 | <MDL | <MDL | <MDL | 4.03 | 0.34 |

**Table S11** Detailed analytical results of the occurrence of personal care products and food additives in the northern European sea waters; data are shown in ng/L.

| Sample No. | DEET | Triclocarban | Triclosan | Acesulfame | Saccharin | Sucralose |
|---|---|---|---|---|---|---|
| 1 | 0.75 | <MDL | <MDL | <MDL | <MDL | 5.30 |
| 2 | 3.25 | <MDL | 0.35 | <MDL | <MDL | 4.41 |
| 3 | 3.17 | <MDL | 0.67 | <MDL | <MDL | 2.38 |
| 4 | 2.49 | <MDL | <MDL | <MDL | <MDL | 1.31 |
| 5 | 1.81 | <MDL | <MDL | <MDL | <MDL | 0.82 |
| 6 | 2.70 | <MDL | <MDL | <MDL | <MDL | 1.57 |
| 7 | 2.66 | <MDL | <MDL | <MDL | <MDL | <MDL |
| 8 | 1.77 | <MDL | <MDL | <MDL | <MDL | 0.83 |
| 9 | 2.01 | <MDL | <MDL | <MDL | <MDL | 1.18 |
| 10 | 2.32 | <MDL | <MDL | <MDL | <MDL | <MDL |
| 11 | 1.65 | <MDL | <MDL | <MDL | <MDL | <MDL |
| 12 | 1.81 | <MDL | <MDL | <MDL | <MDL | <MDL |
| 13 | 2.31 | <MDL | <MDL | <MDL | <MDL | <MDL |
| 14 | 1.22 | <MDL | <MDL | <MDL | <MDL | <MDL |
| 15 | 1.61 | <MDL | <MDL | <MDL | <MDL | 2.90 |
| 16 | 1.32 | <MDL | <MDL | <MDL | <MDL | 1.86 |
| 17 | 51.54 | <MDL | <MDL | <MDL | <MDL | 9.77 |
| 18 | 1.73 | <MDL | <MDL | <MDL | <MDL | 3.49 |
| 19 | 2.72 | <MDL | <MDL | <MDL | <MDL | 2.38 |
| 20 | 1.49 | <MDL | <MDL | <MDL | <MDL | 2.19 |
| 21 | 2.84 | <MDL | <MDL | <MDL | <MDL | 4.48 |
| 22 | 9.56 | <MDL | <MDL | <MDL | <MDL | 3.22 |
| 23 | 1.99 | <MDL | <MDL | <MDL | <MDL | 4.02 |
| 24 | 4.46 | <MDL | <MDL | <MDL | <MDL | 4.79 |
| 25 | 1.52 | <MDL | <MDL | <MDL | <MDL | 6.95 |
| 26 | 2.09 | <MDL | <MDL | <MDL | <MDL | 8.43 |
| 27 | 2.77 | <MDL | <MDL | <MDL | <MDL | 8.36 |
| 28 | 3.02 | <MDL | <MDL | <MDL | <MDL | 10.42 |
| 29 | 2.18 | <MDL | <MDL | <MDL | <MDL | 9.03 |
| 30 | 1.56 | <MDL | <MDL | <MDL | <MDL | 7.92 |
| 31 | 1.87 | <MDL | <MDL | <MDL | <MDL | 6.38 |
| 32 | 1.93 | <MDL | <MDL | <MDL | <MDL | 3.55 |
| 33 | 2.35 | <MDL | <MDL | <MDL | <MDL | 4.97 |
| 34 | 0.63 | <MDL | <MDL | 1.35 | 14.53 | 11.46 |
| 35 | <MDL | <MDL | <MDL | 1.27 | 23.13 | 9.61 |
| 36 | <MDL | <MDL | <MDL | 1.22 | 69.42 | <MDL |
| 37 | <MDL | <MDL | <MDL | 1.17 | 5.23 | 11.05 |
| 38 | <MDL | <MDL | <MDL | 1.38 | 3.01 | 10.58 |
| 39 | <MDL | <MDL | <MDL | 1.32 | 10.08 | 11.68 |
| 40 | <MDL | <MDL | <MDL | 1.14 | 3.06 | 11.73 |

**Table S11** Continued.

| Sample No. | DEET | Triclocarban | Triclosan | Acesulfame | Saccharin | Sucralose |
|---|---|---|---|---|---|---|
| 41 | <MDL | <MDL | <MDL | 0.83 | 4.28 | 4.38 |
| 42 | <MDL | <MDL | <MDL | 0.57 | 6.15 | 12.59 |
| 43 | <MDL | <MDL | <MDL | 1.02 | 3.95 | 8.54 |
| 44 | <MDL | <MDL | <MDL | 1.94 | 174.96 | 13.57 |
| 45 | <MDL | <MDL | <MDL | 1.08 | 127.53 | 12.39 |
| 46 | <MDL | <MDL | <MDL | 0.84 | 92.95 | 11.60 |
| 47 | <MDL | <MDL | <MDL | <MDL | 79.73 | 12.93 |
| 48 | <MDL | <MDL | <MDL | <MDL | 113.70 | 14.12 |
| 49 | <MDL | <MDL | <MDL | <MDL | 285.15 | 12.61 |
| 50 | <MDL | <MDL | <MDL | 0.94 | 69.22 | 15.29 |

**Table S12** Spearman's correlation between the levels of detected compounds. Only compounds with overall detection frequency >50% were considered in this analysis.

| Variable | Spearman's Rank Order Correlations<br>Marked correlations are significant at p <.05000 | | | | |
|---|---|---|---|---|---|
| | Carbamazepine | Naproxen | Sulfamethoxazole | DEET | Sucralose |
| Carbamazepine | 1.000000 | -0.080466 | 0.881182 | -0.581335 | 0.778334 |
| Naproxen | -0.080466 | 1.000000 | -0.130008 | 0.367592 | -0.255501 |
| Sulfamethoxazole | 0.881182 | -0.130008 | 1.000000 | -0.547726 | 0.745588 |
| DEET | -0.581335 | 0.367592 | -0.547726 | 1.000000 | -0.488740 |
| Sucralose | 0.778334 | -0.255501 | 0.745588 | -0.488740 | 1.000000 |

**Table S13** Spearman's correlation between the concentration of detected compounds and salinity. Only compounds with overall detection frequency >50% were considered in this analysis.

| Pair of Variables | Spearman's Rank Order Correlations<br>Marked correlations are significant at p <.05000 | | | |
|---|---|---|---|---|
| | Valid | Spearman | t(N-2) | p-value |
| Carbamazepine & Salinity (PSU) | 48 | -0.745678 | -7.59025 | 0.000000 |
| Naproxen & Salinity (PSU) | 48 | 0.014034 | 0.09519 | 0.924577 |
| Sulfamethoxazole & Salinity (PSU) | 48 | -0.579053 | -4.81710 | 0.000016 |
| DEET & Salinity (PSU) | 48 | 0.408239 | 3.03306 | 0.003971 |
| Sucralose & Salinity (PSU) | 48 | -0.487620 | -3.78807 | 0.000439 |

**Table S14** Spearman's correlation between the levels of detected compounds and latitude. Only compounds with overall detection frequency >50% were considered in this analysis.

| Pair of Variables | Spearman's Rank Order Correlations<br>Marked correlations are significant at p <.05000 | | | |
|---|---|---|---|---|
| | Valid | Spearman | t(N-2) | p-value |
| Carbamazepine & Latitude | 50 | -0.942736 | -19.5822 | 0.000000 |
| Naproxen & Latitude | 50 | 0.204973 | 1.4509 | 0.153311 |
| Sulfamethoxazole & Latitude | 50 | -0.801959 | -9.3008 | 0.000000 |
| DEET & Latitude | 50 | 0.657807 | 6.0509 | 0.000000 |
| Sucralose & Latitude | 50 | -0.767293 | -8.2894 | 0.000000 |

**Table S15** Spearman's correlation coefficients of selected compounds and distribution model of varying search radius and source scaling factor *r*. Statistically significant values ($p<0.05$) are in red.

| | | search radius | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | i | 50 | 100 | 150 | 200 | 250 | 300 | 350 | 400 |
| Carbamazepine | 0 | 0,607 | 0,811 | 0,830 | 0,864 | 0,871 | 0,899 | 0,926 | 0,923 |
| | 1 | 0,580 | 0,808 | 0,842 | 0,876 | 0,872 | 0,906 | 0,923 | 0,921 |
| | 2 | 0,513 | 0,787 | 0,834 | 0,863 | 0,869 | 0,902 | 0,916 | 0,917 |
| Naproxen | 0 | -0,117 | -0,285 | -0,243 | -0,121 | -0,116 | -0,121 | -0,176 | -0,194 |
| | 1 | -0,152 | -0,304 | -0,221 | -0,129 | -0,122 | -0,133 | -0,194 | -0,197 |
| | 2 | -0,195 | -0,340 | -0,237 | -0,147 | -0,129 | -0,164 | -0,210 | -0,200 |
| Paracetamol | 0 | 0,350 | 0,115 | 0,044 | -0,111 | -0,122 | -0,134 | -0,114 | -0,137 |
| | 1 | 0,391 | 0,118 | 0,059 | -0,081 | -0,115 | -0,129 | -0,137 | -0,136 |
| | 2 | 0,423 | 0,143 | 0,049 | -0,065 | -0,108 | -0,129 | -0,119 | -0,138 |
| Sulfamethoxazole | 0 | 0,542 | 0,765 | 0,790 | 0,751 | 0,733 | 0,746 | 0,737 | 0,742 |
| | 1 | 0,521 | 0,770 | 0,798 | 0,767 | 0,727 | 0,750 | 0,742 | 0,737 |
| | 2 | 0,469 | 0,746 | 0,780 | 0,751 | 0,725 | 0,731 | 0,731 | 0,728 |
| Saccharin | 0 | 0,500 | 0,852 | 0,820 | 0,756 | 0,749 | 0,740 | 0,759 | 0,759 |
| | 1 | 0,479 | 0,858 | 0,822 | 0,760 | 0,751 | 0,736 | 0,759 | 0,759 |
| | 2 | 0,450 | 0,855 | 0,823 | 0,774 | 0,757 | 0,737 | 0,759 | 0,759 |
| DEET | 0 | -0,489 | -0,766 | -0,766 | -0,771 | -0,764 | -0,752 | -0,734 | -0,723 |
| | 1 | -0,481 | -0,762 | -0,768 | -0,767 | -0,769 | -0,756 | -0,723 | -0,723 |
| | 2 | -0,451 | -0,765 | -0,773 | -0,769 | -0,765 | -0,755 | -0,731 | -0,724 |
| Sucralose | 0 | 0,406 | 0,745 | 0,743 | 0,676 | 0,648 | 0,629 | 0,606 | 0,603 |
| | 1 | 0,393 | 0,729 | 0,745 | 0,689 | 0,644 | 0,622 | 0,603 | 0,602 |
| | 2 | 0,384 | 0,706 | 0,725 | 0,675 | 0,648 | 0,612 | 0,597 | 0,598 |