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Chemical monitoring of Swedish coastal waters indicates common exceedances of environmental thresholds, both for individual substances as well as their mixtures

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ABSTRACT

Chemical pollution was monitored and assessed along the Swedish west coast. 62 of 172 analyzed organic chemicals were detected in the water phase of at least one of five monitored sites. A Concentration Addition based screening-level risk assessment indicates that all sites are put at risk from chemical contamination, with total risk quotients between 2 and 9. Only at one site did none of the individual chemicals exceeded its corresponding environmental threshold (PNEC, EQS). The monitoring data thus demonstrate a widespread blanket of diffuse pollution, with no clear trends among sites. Further issues critical for the environmental chemical risk assessment include the challenges to achieve sufficiently low levels of detection, especially for hormones and cypermethrin (a pyrethroid insecticide), the appropriate consideration of non-detects and the limited availability of reliable PNECs and EQS values.

1. Introduction

Chemical pollutants in the marine environment stem from sources such as atmospheric deposition, river runoff and direct immissions, together creating a complex exposure pattern (Roose et al., 2011). Within the European Union the marine strategy framework directive (MSFD) requires that "concentrations of contaminants are at levels not giving rise to pollution effects" (Directive 2008/56/EC, Annex I) (OJEU, 2008). This requirement relates to the priority pollutants defined in Directive 2013/39/EU, the water framework directive (WFD), (OJEU, 2013; OJEC, 2000), as well as to chemicals which "may entail significant risks to the marine environment from past and present pollution in the marine region" (2010/477/EU), (OJEU, 2010). Chemical monitoring is one of the management tools used to fulfill this requirement (Quevauviller, 2016).

Due to the dilution in the marine environment, water concentrations in areas not directly affected by point sources are typically low. It is therefore often easier to analyze bioaccumulative chemicals in tissue samples (Quevauviller, 2011). However, as data linking tissue concentrations to ecotoxicological effects are sparse, it is often hard to assess the risk of chemical body residues. In most cases it is necessary to recalculate tissue concentrations to the corresponding water concentrations (Dyer et al., 2011). However, such back-calculations introduce a degree of uncertainty into the concentration estimates, direct analyses of water-concentrations are therefore often preferable.

When performing chemical risk assessments, measured or predicted environmental concentrations are typically compared to environmental thresholds, i.e. concentrations which should not be exceeded in order to avoid adverse effects. Within the European Union environmental thresholds are set in accordance with different regulatory frameworks and specific guidelines exist for e.g. industrial chemicals, biocides, human and veterinary pharmaceuticals, plant protection products and WFD priority pollutants. Although the same principle is used across regulatory frameworks, the details of how environmental thresholds are estimated differ across regulations and the final environmental threshold are labelled differently (e.g. Environmental Quality Standards (EQS) for the WFD-priority pollutants or Predicted No Effect Concentrations (PNEC) for industrial chemicals under REACH, see methods section for details). With the exception of products that are in themselves chemical mixtures, hazard assessments are typically carried out only for individual substances.

Several studies have demonstrated that effects from chemical

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mixtures are larger than those from any individual contributor (e.g. Belden et al., 2007; Faust et al., 2003; Rodney et al., 2013). This is true even if all compounds in the mixture are present at concentrations below their individual no observed effect concentrations (NOEC) (Faust et al., 2001; Silva et al., 2002) or their individual EQS (Carvalho et al., 2014). Nevertheless, mixture effects are currently only implicitly considered in the WFD and the MSFD (Kienzler et al., 2014).

The risk posed by chemical mixtures may be assessed using the concept of concentration addition (CA), (Kortenkamp et al., 2009). Despite that the concept originally assumes that all mixture components share a similar mode of action, it has been successfully used as conservative approach also for mixtures containing compounds with heterogeneous modes of action (Bopp et al., 2015; Kortenkamp et al., 2009; Verbruggen and van den Brink, 2010).

Non-detected compounds pose a specific problem for the assessment of mixture risks. Non-detects may be present at any concentration between zero and the limit of detection (LOD) and depending on how this uncertainty is accounted for, final risk estimates vary. Options on how to treat non-detects include the substitution of non-detects with a priori set concentration-values between zero and the LOD, and various statistical methods for estimating the expected risk contribution of non-detected compounds (Helsel, 2012), see discussion in Gustavsson et al. (2017).

In this study we determined the concentrations of 172 organic compounds from 16 different classes in marine water at five sites along the Swedish west coast and estimated their joint risks for exposed biota. The sampling sites were chosen to represent five different exposure patterns with integrated samples taken over five consecutive days. The study i) provides a snapshot of the chemical pollution along the Swedish west coast in spring 2012, ii) estimates the environmental risks posed by the detected compounds by comparing their concentrations to their individual environmental thresholds, iii) quantifies the combined risk from the chemical mixtures found at each of the sampling sites, and iv) discusses how the treatment of non-detects influence the final risk estimate.

2. Material and methods

2.1. Sampling

2.1.1. Sampling sites

Sampling was performed at five sites along the generally northbound Baltic current. The first sample was taken 30 km south of Gothenburg, the last one was taken 80 km north of the city (Table 1 and Fig. 1).

Lerkil, located south of Gothenburg, was selected as a reference site and was assumed to be representative for background levels of anthropogenic pollutants present in the marine environment along the Swedish west coast. The site *Skalkorgarna* is situated close to Gothenburg harbour and is expected to contain chemicals associated with traffic from cargo ships and shipping-related industries. Additionally the area is exposed downstream from Gothenburg's sewage treatment plant (STP) Ryaverken, which treats waste water from approximately 700,000 people. *Instö ränna* lies immediately north of Gothenburg and is located upstream the estuaries of the river Göta älv and the river Nordre älv along the Baltic current. *Stenungsund* is located further north of Gothenburg and the area is the major hub for chemical industries in Sweden and important local emission sources are the industries and harbours found in the area. Finally, *Fiskebäckskil* is a shallow marina used for smaller boat and located at the northern end of the sampling region. The site's main emissions are assumed to be chemical discharges from recreational boating activities.

Table 1
Coordinates and characteristics of the selected sampling sites.

	Coordinates (WGS84 dec)		Salinity (average)	
Sampling site	North	East	g/L	Characteristics
Lerkil	57.460243°	11.907620°	19.7	Upstream Gothenburg
Skalkorgarna	57.679133°	11.763917°	13.5	Gothenburg harbour
Instö ränna	57.890050°	11.665550°	17.1	Downstream Gothenburg
Stenungsund	58.103090°	11.806200°	21.8	Industrial site
Fiskebäckskil	58.243440°	11.462030°	23.3	Small boats marina

2.1.2. Sampling period

Water was sampled from the five sites between the 4th and 8th of June 2012. 6 × 1 L of subsurface water were collected at each site at each day. Each liter of water was acidified to a pH < 2 with 1.5 mL orthophosphate buffer (6 mol/L) to prevent degradation of organic chemicals. Finally, the water from each site was pooled to generate a time integrated sample. One sixth of the sample from each site was stored in a 6 L glass bottle and the reminder stored in the dark at 4 °C in two 13 L teflon-coated containers.

2.1.3. Selection of analyzed chemicals

In total 16 classes of anthropogenic organic compounds were investigated (Table 2), comprising a total of 172 individual organic chemicals. The initial selection of organic chemicals of importance for the marine environment was based on existing screening results obtained from the Swedish Environmental Research Institute (IVL, 2016) plus 31 of the organic WFD priority pollutants, listed in 2008/105/EC (OJEU., 2008).

2.1.4. Compilation of environmental thresholds

No single data-source listed environmental thresholds for all analyzed compounds. A broad range of different databases was therefore used to compile the environmental thresholds for each chemical included in the monitoring (details in the supplementary information (S.I.)). If data were available from several sources, the threshold used in the present study was gathered using the following priority order: WFD background documents (CIRCABC, 2016), REACH dossiers (ECHA, 2014a), EFSA conclusions on pesticides (EFSA, 2016), ECHA biocide background documents (ECHA, 2016), Norwegian pharmaceutical risk ranking report (Grung et al., 2007), other documents (See S.I.), US EPA ECOTOX database (US EPA, 2016), and ECOSAR v1.11 (ECOSAR, 2016).

Any freshwater-specific threshold was adjusted for the marine environment by dividing it with a factor of 10. This is in accordance to the Reach Guidance Document on chemical risk assessment and compensates for the greater biodiversity in the marine environment (ECHA, 2008).

2.1.4.1. WFD background documents. Environmental quality standards (EQS) for WFD priority pollutants can be found in the EQS Directive 2013/39/EU (OJEU, 2013). Data for the compounds flagged as “priority substances in the field of water policy” were collected from the respective background document (CIRCABC, 2016) and the specific quality standards for the marine pelagic environment were extracted. No background documents were available for DDT and its breakdown-products, nor for aldrin and endrin. The EQS was used for these compounds, rather than the quality standard for the marine pelagic compartment. Environmental thresholds for 48 compounds were compiled from these documents.

2.1.4.2. REACH dossiers. The European Chemicals Agency (ECHA) hosts a database comprising the dossiers from the REACH registration process (ECHA, 2014a), including ecotoxicological data. Marine PNEC values for 37 compounds were collected from this source in March