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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 individual environmental threshold (PNEC, EQS). The monitoring data thus demonstrate a widespread blanket of diffuse pollution, with no clear trends amongst sites. Further issues critical for the environmental chemical risk assessment include the challenges to achieve sufficiently low levels of detection especially for hormones and cybermethrin (a pyrethroid insecticide), the appropriate consideration of non-detects and the limited availability of reliable PNECs and EQS values.

Keywords: Chemical mixture, Risk assessment, Non-target screening, Multi-residue screening, Triclosan, Quality standards.

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), 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 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, 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 & 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.

Material and Methods

Sampling

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 Figure 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.

Sampling period

Water was sampled from the five sites between the 4th and 8th of June 2012. 6 x 1 liters 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 liter glass bottle and the reminder stored in the dark at 4 °C in two 13 liter teflon-coated containers.

Selection of analysed 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. 2008b). 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).

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.

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 2014.

EFSA conclusions on pesticides. Data for 10 compounds were gathered in April 2016 by analyzing the "conclusions on pesticides" reports published by the European Food Safety Authority (EFSA, 2016). Only data for active ingredients were considered. NOEC data were given precedence over EC50 data for aquatic invertebrates and fish, if both types were available. For algae and higher plants/macrophytes EC50 values were used. This is in line with the risk assessment scheme as presented within the guidance document for plant protection products (EFSA, 2013). Data from species sensitivity distributions or mesocosm experiments were used if the species group suspected to be the most sensitive was included. The EC50 or NOEC, from the most sensitive bioassay was divided with the corresponding trigger value suggested in the conclusion reports (10 for algal and plant EC50 data, 100 for fish and aquatic invertebrates EC50 data, 10 for fish and aquatic invertebrates NOEC data).

ECHA biocide background documents. Data was gathered from (ECHA, 2016), retrieving data for all approved substances in June 2016. The environmental threshold of 2 compounds come from this source.

Norwegian pharmaceutical risk ranking report. Hazard data for pharmaceutical and personal care products (PCP) were gathered from a report on risks from human and veterinary pharmaceuticals published by the Norwegian Pollution Control Authority (Grung et al., 2007). PNECs based on experimental ecotoxicity data were given priority over PNECs based on modeled ecotoxicological data. Environmental threshold values of 21 compounds were retrieved from this source.

Other sources See S.I. table 2 for specific details. A total of 39 environmental thresholds were gathered from other sources.

US EPA ECOTOX database. The US EPA database ECOTOX (US EPA, 2016) was queried for all compounds for which no environmental thresholds (PNECs, EQS, etc.) were found in the previous sources. A provisional marine PNEC was derived from these data for 9 compounds, following the REACH guidance document on chemical risk assessment (ECHA, 2008). See S.I. table 2 for details.

ECOSAR v1.11. Finally, ECOSAR, a collection of QSAR models (ECOSAR, 2016), was used for 6 compounds, for which neither published environmental thresholds nor experimental ecotoxicological data were available. An assessment factor was applied to the modeled ecotoxicological data, following the REACH guidance document on chemical risk assessment (ECHA, 2008). See supporting information for details.

Risk Estimation

The risk quotient (RQ) of each compound was estimated by comparing the measured environmental concentration (MEC) with the corresponding environmental threshold:

$$RQ_{individual} = \frac{MEC}{Environmental\ Threshold} \qquad \text{eq:1}$$

The total risk from all compounds was then determined as the sum of all RQ values:

$$RQ_{total} = \sum_{i=1}^{n} RQ_i = \sum_{i=1}^{n} \frac{MEC_i}{Environmental\ Threshold_i} \qquad \text{eq:2}$$

where n is the total number of compounds. This approach was suggested as a first tier assessment by (Backhaus and Faust, 2012). The conceptual idea is rooted in CA, a concept which is also recommended as a conservative approach for setting EQS values of mixtures within the WFD (EC, 2011) as well as for assessing pesticide and biocide mixtures (EFSA, 2013; ECHA 2014b).

The Maximum Cumulative Ratio

The ratio between the sum of all individual risk quotients and the maximum individual risk quotient has been termed the maximum cumulative ratio (MCR, Price 2011).

$$MCR = \frac{RQ_{total}}{\max\limits_{i=1\ldots n}\left(MEC_i / Threshold_i\right)} \qquad \text{eq:3}$$

When all compounds contribute equally to the RQ_{total} the MCR reaches its theoretical maximum, which equals the number of compounds in the mixture (n). If the risk is dominated by a single compound the MCR approaches 1. The MCR has therefore been suggested as a measure of the value of performing mixture toxicity assessments (Price, 2011). The MCR is also the maximum ratio between the mixture risk as estimated by CA and the concept of Independent Action (IA, also termed Response Addition) (Junghans et al, 2006).

Treatment of Non-detects

Three different approaches were used to estimate the potential risk contribution of chemicals whose concentrations were below their level of detection (LOD). In the first approach, all non-detects were assumed to be present at their LOD, a worst case scenario. In the second approach, non-detects were assumed to be present at a concentration of zero, a best case scenario (minimum risk). In the third approach, risk estimation was carried out using the Kaplan-Meier (KM) method. KM is non-parametric method which estimates the risk including non-detects (Bolks et al., 2014; Helsel, 2010; Helsel, 2012). Applying the KM-method yields an intermediate mixture risk estimate between the best and worst-case estimates, see discussion in Gustavsson et al., 2017. As the underlying distribution of concentrations is impossible to estimate, given the available data, regression based approaches (Helsel, 2012), were not further explored in this paper.

Results and Discussion

In the following section we first report the results from the sampling campaign and discuss the risks of the individual chemicals and their mixtures at each sampled site. We then discuss the consequences of the three different approaches for including non-detects in assessing chemical risks for the environment.

Detected concentrations

62 of the 172 analysed compounds were detected in at least one sample (

Table **2**). The number of detects per sample varied between 30 (*Lerkil*) and 41 (*Fiskebäckskil*). Concentrations and occurrences are dominated by anionic surfactants (between 53 ng/L and 927 ng/L), phthalate esters (between 16 ng/L and 611 ng/L), chlorinated volatile organic compounds (VOC) (between 79 ng/L and 148 ng/L) and petroleum residues (between 72 ng/L 564 and ng/L) (Table 2).

The comparatively high surfactant concentrations at *Skalkorgarna* (927 ng/L) and Stenungsund (366 ng/L) are due to their proximity to STP wastewater discharges while elevated surfactant concentrations at *Fiskebäckskil* (443 ng/L) are likely caused by boat cleaning, an activity that peaks just prior to the sampling campaign. In comparison, the surfactant concentrations at *Instö ränna* and *Lerkil* were only 53 and 56 ng/L.

The phthalate group also displayed a highly localized concentration pattern, found at 412 and 611 ng/L at *Fiskebäckskil* and *Stenungsund*, while only being detected at 16 and 20 ng/L at *Instö ränna* and *Skalkorgarna*. An intermediate concentration of 145 ng/L was detected as *Lerkil*. These detections are likely due to the phthalates use as plasticizers, for instance used in hulls of pleasure crafts in the shallow marina *Fiskebäckskil* and potentially also being released at *Stenungsund* due to the local production of plastics.

The petroleum residue group and chlorinated volatile organic carbons (VOCs) are also associated with boat traffic. Petroleum residues originate from gasoline, while chlorinated VOCs are used in the production of plastics and in various paints. At *Fiskebäckskil* the highest concentration of petroleum residues (564 ng/L) were found, as well as the second highest concentration of VOCs (124 ng/L). Surprisingly, *Skalkorgarna* had a comparatively low concentration of petroleum residues (249 ng/L), although the location is located close to the harbour of Gothenburg. Slightly higher VOC concentrations were found at *Slakorgarna* (148 ng/L) than at *Fiskebäckskil*.

At least one pharmaceutical was detected at each site, totaling between 13.05 ng/L at *Fiskebäckskil* and 88.58 ng/L at *Skalkorgarna*. *Skalkorgarna* also stands out with a total of 13 different pharmaceuticals detected while at *Instö ränna,* the location with the second most detections of pharmaceuticals, only 5 pharmaceuticals were detected. The detected pharmaceuticals are primarily painkillers, blood pressure lowering agents and antidepressants, but also an anti-mycotic and an anti-epileptic pharmaceutical was detected. These detections are in line with *Skalkorgarna* being downstream of the major STP in Gothenburg.

Triclosan, a common antimicrobial, was detected at concentrations ranging between 7.2 and 9.8 ng/L (below detection limit only at *Skalkorgarna*). That triclosan was below the detection limit only

downstream of the Gothenburg STP implies that it is either currently emitted from sources other than personal care products, or that the detected concentrations are from legacy pollution. Triclosan has previously been detected in the marine environment outside Stenungsund at concentrations of up to 160 ng/L in deep water, while it was not detected in surface water (Remberger et al., 2002). It was also detected in the German Bight at concentrations of up to 7 ng/L (Xie et al., 2008). Furthermore, triclosan has also been found in several European lakes and rivers (Bester, 2005; Lindström et al., 2002; Singer et al., 2002; Tixier et al., 2002; Van Wezel & Jager, 2002; von der Ohne et al., 2012), with typical concentrations ranging from one to tens of ng/L.

Risk from individual compounds

Triclosan, irgarol and TBT are the only compounds for which the detected concentrations exceeded their individual environmental thresholds (figure 2). Triclosan exceeded its environmental threshold of 6.9 ng/L (retrieved from the corresponding REACH dossier) at all locations (detections between 7.2 and 9.8 ng/L) with the exception of *Skalkorgarna*. Also irgarol was detected at all sites (between 0.22 and 8 ng/L) except at *Skalkorgarna,* but only exceeded its individual threshold of 2.5 ng/L (retrieved from EFSA's conclusions on pesticides) at *Fiskebäckskil*. TBT was only detected at *Fiskebäckskil* at concentrations 3.6 times higher than the environmental threshold (0.2 ng/L, retrieved from a WFD background document)

The REACH registration dossier of triclosan does not provide information on which tested species group that is most sensitive, and therefore does not allow identification the species on which the PNEC is based. However, the reported PNEC value is consistent with the data from one of the biotests documented in the dossier, a growth inhibition study with the algae *Desmodesmus subspicatus*. The documented NOEC of 690 ng/L from this assay, taken together with an assessment factor of 100, would yield the reported PNEC of 6.9 ng/L. Also the respective Biocide Assessment Report (2015a) and von der Ohne et al. (2012) report freshwater PNEC's derived from tests with algae, indicating that this group is the most sensitive out of the three species groups normally used to determine a PNEC (algae, aquatic invertebrates and fish). In contrast, an EC50 of 11 mg/L for activated sludge is used to derive a PNEC of 110 000 ng/L for microorganisms in an STP (Biocide Assessment Report. 2015a) while tests performed on Vibrio Fischeri has reported EC50s between 53 000 and 520 000 ng/L (Bedoux et al., 2012). This demonstrates that, despite triclosan's primary use as a bactericide, it is far more toxic to microalgae than to bacteria.

Triclosan also has been suggested as a candidate for regulatory monitoring and a freshwater PNEC of 4.7 ng/L was then suggested (von der Ohe et al., 2012). Additionally triclosan was recently evaluated by the EU Biocidal Products Committee, whose assessment report suggests a freshwater PNEC of 50 ng/L (Biocide Assessment Report, 2015a). The two freshwater PNEC's would translate into marine PNECs of 0.47 ng/L and 5 ng/L respectively, if the approaches of the REACH guidance were followed (using an additional assessment factor of 10 in order to account for the greater biodiversity in the marine environment (ECHA, 2008)).

Even lower PNECs are estimated if data on effects on community structure is included. A freshwater NOEC of 15 ng/L was determined when measuring the structure of freshwater algal communities for the genera *Chroococcus*, *Chlamydomonas* and *Synedra* (Wilson et al., 2003). The sampling site of the study was in that case chosen so that "no known industrial or major agricultural sources were

present in the upstream portion of the stream" (Wilson et al., 2003). Assuming that NOEC data is also available for aquatic invertebrates and fish the REACH guidance suggest using an AF of 100 (ECHA, 2008), resulting in a PNEC of 0.15 ng/L. In contrast, two studies from the Swedish west coast, testing marine periphytic algal assemblages from a site close to Fiskebäckskil, have demonstrated a lower sensitivity towards triclosan, recording an EC10 of 4100 ng/l (Johansson et al., 2014) and a NOEC of 9100 ng/l (Eriksson et al., 2015). This lower sensitivity is likely a results of the tested marine algal assemblages being dominated by diatoms and cyanobacteria (Porsbring et al., 2007), while green algae have been shown to be most sensitive species group (Orvos, 2002). A local PNEC for the Swedish west coast based on the NOEC values from the communities sampled there, again using an AF of 100 (ECHA, 2008), would thus be 91 ng/L (as compared to the detected concentrations between 7.2 and 9.8 ng/L).

It should be noted that in 2015, three years after the sampling performed within this study, the EU Biocidal Products Committee stated that triclosan should not be approved in biocidal products used for human hygiene (ECHA, 2015a) and in 2014 triclosan was not approved for use in disinfectants or film preservative or preservative of fibre, leather, rubber and ploymerized materials (OJEU, 2014a). Thus, within the EU triclosan is currently not authorized for use in biocidal products. Over time this reduction in potential use should lead to lowered environmental exposure. However, triclosan is still allowed for use in cosmetic products (OJEU, 2014b).

Irgarol, also known as cybutryne, is a photosystem-II inhibitor which has previously been used as an algicide in antifouling paints (Konstantinou & Albanis, 2004). The compound was found at all sampling location besides *Skalkorgarna* but only at *Fiskebäckskil* did the detected concentrations (8 ng/L) exceed its environmental threshold of 2.5 ng/L. The threshold was retrieved from the WFD background document and is based on a species sensitivity distribution using NOECs and an assessment factor of 3 (CIRCABC, 2016).

Irgarol has been tested with algal assemblages sampled close to *Fiskebäckskil*, where an EC50 of 4100 ng/L for algal photosynthesis was recorded (Eriksson et al., 2009). Meanwhile algal assemblages from less polluted sites along the Swedish West Coast had EC50 values of 890 ng/l (Blanck et al., 2009). These differences in sensitivity have been suggested to stem from a selection pressure for a less sensitive photosystem as an effect of long-term irgarol exposure (Eriksson et al., 2009). Meanwhile, the last antifouling paint containing irgarol as an active ingredient was removed from the Swedish market in the end of 2010 (KEMI, 2016), and the compound is currently not registered for any other biocidal use in the EU (ECHA, 2015b). As the half-life of the compound in seawater is 56 days (Irgarol SDS, 2011) these concentrations likely demonstrate leeching from visiting crafts, illegal use of banned products, leeching from the soil in boatyards either due to legacy contamination or releases during maintenance (Eklund 2014), or any combination thereof.

Tributyl-tin (TBT) was detected in *Fiskebäckskil* at 360% of its environmental threshold value of 0.2 ng/L (retrieved from the WFD background document). As both TBT and irgarol have been used as biocides in antifouling paints, the detection of the compounds at *Fiskebäckskil* is not entirely surprising. However, it should be noted that no paint containing TBT has been allowed for use on recreational crafts in Sweden since 1989 (KEMI, 2016), and the compound is currently banned world-wide under the International Convention on the Control of Harmful Anti-fouling Systems on Ships which entered into force in 2008 (IMOO, 2001). Albeit tin-containing layers of paint can still be

detected on crafts in the area, the tin-containing paint is typically covered with several layers of other coating (Ytreberg, 2016) and the majority of environmental exposure is thought to occur during maintenance (Eklund, 2014).

Among the top ten contributors of risk are also the phthalates DINP, DIDP, DEHP and DBP. For DINP, DIDP and DEHT sources have provided conflicting information on what a suitable environmental threshold should be. In the EU risk assessment reports DIDP and DINP was tentatively concluded to not cause adverse chemical effects towards the aquatic ecosystem (ECB, 2003a, ECB, 2003b) while no aquatic PNEC could be derived for DEHP (apart from for fish-feed where a PNEC of 16 mg/kg was estimated, ECB 2008). However, for the DEHP the WFD background data for water-concentrations for the endpoint secondary poisoning was used (1.3 µg/L), as no pelagic QS was derived (S.I. table 2), while for DINP and DIDP NOEC data from Daphnia magna was used to derive the environmental thresholds of 0.34 µg/L and 0.3 µg/L (AF = 100, data collected from Staples et al. 1997, S.I. table 2). These DIDP and DINP data used was also noted in the risk assessment reports, but were disregarded as the likely effect was entrapment, and not an actual toxic effect (ECB, 2003a, ECB, 2003b). The logic behind this choice is reasonably that the entrapment effect will be rapidly lost as concentrations are lowered and that the normal AF method is therefore unsuited for deriving environmental thresholds. Thus, the phthalate estimates presented could be viewed as worst case risk estimates for the endpoints currently used in the environmental risk assessment process.

Finally, *Skalkorgarna* was the only location where no individual compound exceeded its environmental threshold; the largest individual contributor was naproxen (RQ=0.49, figure 2). Naproxen is a nonsteroidal anti-inflammatory and pain-relieving drug (NSAID), only detected at *Skalkorgarna,* with the likely source being the STP in Gothenburg.

Compounds with environmental thresholds below the level of detection

A few of the detected compounds have environmental thresholds which are below their respective LOD. These compounds might cause environmental risks even at concentrations which cannot be detected with the employed analytical methods. Most prominently among those compounds is cypermethrin which has a ratio of LOD to its environmental threshold of 97 000 (S.I. table 1). Also the LOD to threshold ratio of diphenyltin (402), monophenyltin (120), ethinylestradiol (71), estriol (56), estrone (13), trifluralin (4.5), dibenzo(ah)anthracene (3.6), estradiol (2.5) and tricresylphosphate (1.9) indicate insufficient LODs. The environmental risk of those compounds can only be estimated by exposure modelling, based on emission values and environmental fate data. In the long run, analytical methods with lower detection limits are needed, in order to allow a better assessment of environmental risks.

Risk from mixtures

After summing up all the individual risk quotients, RQ_{total} exceeds 1 at all locations, independent of how non-detects were considered (table 4). Approach 1 assumes that all non-detects are present at their individual LOD and therefore results in the highest of the three risk estimates (see above), with RQ values between 97 612 and 97 617. These values are driven by the insufficient LOD of cypermethrin (see above). Approach 2 assumes that all non-detects are actually not present (i.e. that their concentration at the sampling site is zero). The resulting RQ_{total} therefore reflects a best-case scenario, with final values varying between 1.7 (*Instö ränna*) and 9.0 (*Fiskebäckskil*), (table 4).

Estimating the risk from the non-detects using the KM-method (approach 3) leads to risk estimates which are close to those calculated by approach 2, with a maximum difference in estimated risks of 7% (table 4). This shows that the LODs of the non-detects are sufficiently close to the corresponding environmental thresholds, so that the gaps bridged by the KM method are of little relevance. However, it should be emphasized that the KM method simply ignores all potential risk contributions from non-detects whose LOD/environmental threshold ratio exceeds the highest risk quotient of a detected compound (Helsel, 2010), e.g. cypermethrin.

The MCR is below 2 at 2 out of 5 sites. This demonstrates that the total risk is largely dominated by the one compound with the highest individual risk quotient (primarily triclosan, see figure 2). Under these conditions, the particular mixture risk assessment method used (CA or IA) is of little relevance (Backhaus & Faust 2012). The higher MCR at Fiskbäckskil indicates that that an assessment using IA would likely lower the absolute risk, but as three compounds independently exceed their environmental threshold the situation will still be perceived as at risk. In contrast, the exposure situation at *Skalkorgarna* would warrant further exploration. In particular, a trophic-level specific risk assessment is called for as the next step (Backhaus & Faust 2012). Such a step would avoid over-estimating the risk by using environmental thresholds based on different organism groups for individual compounds.

Summary and Conclusions

All locations were at risk from the detected chemical mixtures, and at four out of five sites the environmental thresholds were exceeded also by individual compounds. Triclosan is the compound with the largest contribution to the overall risk, with risk quotients between 1 and 1.4. Irgarol and TBT are the only other compounds which exceeds their individual environmental threshold, but only at one location. Both triclosan and irgarol are currently in the process of being removed from the EU market, at least as biocides, and the use of TBT is banned worldwide. Detections of these compounds therefore indicate either a substantial environmental persistence, or that some emission sources still remain, for example from triclosan-treated long-lived consumer products such as plastics or textiles.

Four groups of compounds have to be considered when assessing the environmental risks based on the results of a chemical monitoring campaign:

1. Compounds which were found at quantifiable concentrations. For those we can directly determine their individual risk in the form of a risk quotient, i.e. their ratio of the measured environmental concentration to an environmental threshold, and, consequently, their contribution to the mixture risk.
2. Compounds that were included in the monitoring, but were not found at concentrations exceeding the chemical-analytical LOD, and whose maximum potential risk quotient, i.e. LOD/environmental threshold, is smaller than the maximum actual risk quotient of the mixture components present at quantifiable concentrations. The contribution of those compounds to the overall risk quotient can be estimated using the KM approximation, or related parametric methods. In the current study those compounds had only had a minor impact, the risk estimates between approaches 2 and 3 differed only by 4 to 7 %, or in absolute units between 0.1 and 0.2 RQ.

3. Compounds that were included in the monitoring, but were not found at concentrations exceeding the chemical-analytical LOD, and whose maximum potential risk quotient exceeds the maximum actual risk quotient of the mixture components present at quantifiable concentrations. The potential contribution of those non-detects cannot even be approximated by the KM method (or any other estimation technique). Consequently, those compounds have to be ignored when estimating the mixture risk. As a result, the mixture risk estimate is most likely an underestimation. In the present study the contributions especially of cypermethrin, but also of diphenyltin, monophenyltin, estrone, estriol and ethinylestradiol could not be adequately quantified.
4. Chemicals that were not included in the monitoring campaign, and for which hence no risk-related conclusions can be drawn.

An assessment based on chemical monitoring data therefore provides only the lower boundary of the chemical risk potentially present at a site. As such it motivates targeted and more demanding follow-up monitoring activities, directly taking biological responses into account. The potential of such effect-based monitoring strategies is currently explored in a series of projects (Brack et al., 2015; Brack et al., 2016; Hylland et al., 2017). However, the fact that chemical contamination was at unacceptable levels at all sites, with no clear trend along the Baltic current, represents a major challenge to any biological or ecological approaches. Due to the lack of pristine control sites, such a widespread “blanket of pollution” will make it difficult, if not impossible, to quantify ecotoxicological effects *in situ*.

Assuming that the joint risks of a chemical mixture can be approximated by the summation of individual risk quotients, it becomes clear that monitoring efforts cannot be limited to specific substances or even groups of substances. This holds especially true in situations in which the assessment of each individual substance would lead to the erroneous conclusion that the risk at a site might be acceptable, a situation that is demonstrated for the site *Skalkorgarna* in the present study. Biological tools for assessment the ecotoxicological consequences of such complex exposure situations are currently under development (Altenburger et al., 2015).

The presented results are consistent with a similar study conducted by Ghekiere et al. (2013), who also found a widespread exceedance of environmental thresholds in a monitoring study of the Belgian coastal zone. However, more worrisome than the determined total risk quotients of 9.3 or less (if only the quantifiable risk quotients are considered) is the fact that for several highly potent environmental chemicals, such as phenyltins, estrogens and pesticides, current routine analytical methods are not powerful enough to determine whether the corresponding environmental threshold concentrations are exceeded, or whether there is a certain margin of safety. This renders a realistic environmental risk assessment of these chemicals, and mixtures potentially containing them, impossible at the moment. Additionally, only limited ecotoxicological data are available for several of the monitored chemicals, even for well-known environmental chemicals. In particular, data for marine species and marine specific species-groups are too often missing and the resulting necessity to extrapolate from freshwater data is certainly less than optimal.

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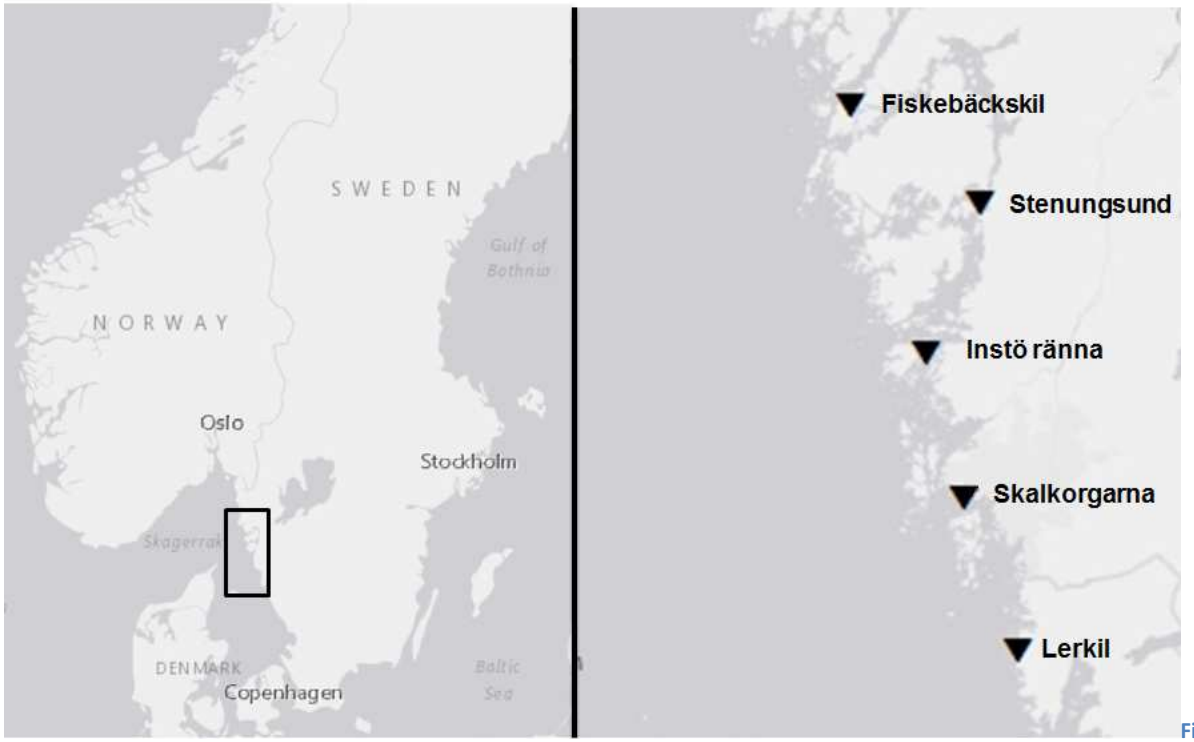

Figure 1: The 5 sampling-sites along the Swedish west coast. The sampling site Fiskebäckskil is close to a shallow marina. At Stenungsund chemical industry and associated harbours are the main sources of pollution in the area. Instö ränna lies north of the city of Gothenburg along the Baltic current. Skalkorgarna is located at the mouth of Gothenburg harbour and is also located downstream the municipality STP (serving appx. 700 000 people). Lerkil was selected as a reference site with no clear sources of pollution close by.

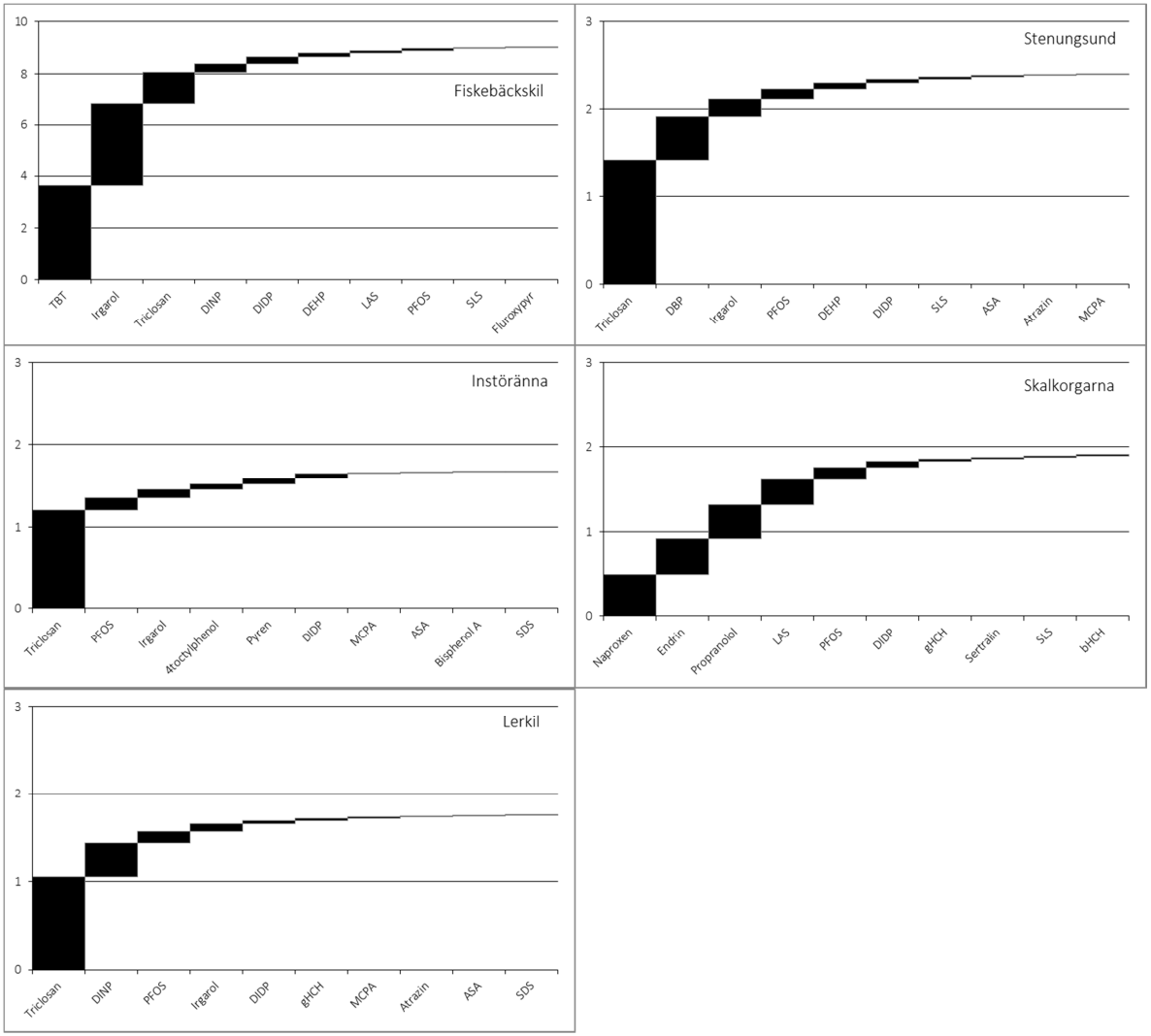

Figure 2: Cumulative sum of risk quotients of the 10 largest risk-contributors per site. Top left, Fiskebäckskil. Top right , Stenungsund. Mid left, Instö ränna. Mid right, Skalkorgarna. Bottom Left, Lerkil. The y-axis displays the sum of the individual risk quotients, RQ_{total}. A value of RQ_{total} above 1 indicates potential risk. Note that the y-axis of Fiskebäckskil (top left) has a different scaling.

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

Table 2: Analytical methods used for the different chemical groups. Table abbreviations: PAH= Polycyclic aromatic hydrocarbons, DCM = Dichlormethane, ECD = Electron capture detector, EDTA = Ethylenediaminetetraacetic acid, FID = Flame ionisation detector, FLD = Fluorescence detectors, GC = Gas-chromatography, HPLC =High-performance liquid chromatography, H2SO4 = Sulphuric acid, KOH = Potassium hydroxide, LLE = Liquid-liquid extraction, MeOH = Methanol, MS/MS = Triple quadrupole mass spectrometry, MTBE = Methyl-tert-butyl ether, SPE = Solid-phase extraction, TMAOH = Tetramethylammonium hydroxide, VOCs = Volatile organic compunds.

Substance class	Sample volume	pH adjustment of sample	Extraction method	Eluents	Additives	Derivatization agent	Post-extraction/ clean up	Analytical instrument	Extraction method modified based on:	Clean-up/derivatization modified based on:
Biocides	2000 ml	Neutralized with KOH	SPE, Oasis HLB	MeOH followed by Acetone	-	-	-	HPLC-MS/MS	Gros et al., 2006	-
Chlorinated pesticides	2000 ml	-	SPE, C18	Acetone	-	-	1. LLE of eluate with water, pentane and diethyl ether 2. Treated with H_2SO_4 3. Fractionation on an Alox-column	GC-ECD	Erger et al., 2012	Karlsson and Viktor, 2013
Hormones	2000 ml	Neutralized with KOH	SPE, C18	Acetone	-	2.3-Pyridinedicarboxylic anhydride (Post-extraction)	-	HPLC-MS/MS	Erger et al., 2012	Licea-Perez et al., 2008
Organophosphate esters	2000 ml	-	SPE, Oasis HLB	MeOH followed by Acetone	-	-	LLE of eluate with water	GC-MS/MS	Gros et al., 2006	Remberger et al., 2013
Perfluorinated compounds	1000 ml	-	SPE, Oasis WAX	MeOH followed by 0,1% ammonium/MeOH	-	-	-	HPLC-MS/MS	ISO 25101:2009	-
Petroleum residues	100 ml	-	Purge and trap, Tenax TA	-	-	-	-	GC-FID	Potter et al., 2009	-
Chlorinated VOCs	20 ml		Purge and trap,	-	-	-		GC-ECD	Potter et al., 2009	-

			Tenax TA							
Pharmaceuticals	2000 ml	Neutralized with KOH	SPE, Oasis HLB	MeOH followed by Acetone	EDTA-Na_2 (Pre-extraction)	-	-	HPLC-MS/MS	Gros et al., 2006	-
Phenolic compounds	2000 ml	-	SPE, ENV+	Acetone and Hexane:MTBE	-	Acetic anhydride (Post-extraction)	LLE of eluate with water and Hexane: MTBE	GC-MS/MS	Remberger et al., 2003	-
Phthalate esters	2000 ml	-	SPE, C18	Methanol:MTBE: hexane	-	-	LLE of eluate with water	GC-MS/MS	Remberger et al., 2013	-
Polybrominated flame retardents	2000 ml	-	SPE, C18	Acetone	-	-	1. LLE of eluate with water, pentane and diethyl ether 2. Treated with H_2SO_4 3. Fractionation on an Alox-column	GC-ECD	Erger et al., 2012	Karlsson and Viktor, 2013
Polychlorinated biphenyls	2000 ml	-	SPE, C18	Acetone	-	-	1. LLE of eluate with water, pentane and diethyl ether 2. Treated with H_2SO_4 3. Fractionation on an Alox-	GC-ECD	Erger et al., 2012	Karlsson and Viktor, 2013

							column			
Polycyclic aromatic hydrocarbons	2000 ml	-	SPE, C18	Acetone	-	-	1. LLE of eluate with water, pentane and diethyl ether 2. Fractionation on a Silica-column	HPLC-FLD	Erger et al., 2012	Karlsson and Viktor, 2013
Surfactants	2000 ml	-	SPE, ENVI-Carb	10mM TMAOH in DCM:MeOH	-	-	-	HPLC-MS/MS	CEN, 2007	-
Tin organic compounds	800 ml	To pH 5 with KOH and acetic acid	LLE with hexane	-	-	Sodium tetraethylborate (Pre-extraction)	-	GC-MS/MS	ISO 17353:2005	-
Vulcanizing residues	2000 ml	Neutralized with KOH	SPE, C18	Acetone	-	-	-	HPLC-MS/MS	Brorström-Lundén et al., 2011	-

Table 3: Environmental concentrations in Swedish coastal waters, and the corresponding level of detection (LOD), note that only compounds which were detected in the monitoring is included in the table. For a table including all analyzed compounds see S.I. table 1.

Substance	Lerkil ng/L	Skalkorgarna ng/L	Instö ränna ng/L	Stenungsund ng/L	Fiskebäckskil ng/L	LOD (S/N=3) ng/L
Biocides						
Atrazine	5.6	<3.4	<3.4	6.2	<3.4	<3.4
Fluroxypyr	<2.0	<2.0	<2.0	<2.0	6.8	<2.0
Irgarol	0.22	<0.2	0.25	0.49	8.0	<0.2
Propiconazole	<0.5	<0.5	<0.5	0.71	0.73	<0.5
MCPA	1.3	1.2	1.6	1.3	1.4	<0.3
Chlorinated pesticides						
b-HCH (Hexachlorocyclohexane)	<0.10	0.14	<0.10	<0.10	0.11	<0.10
g-HCH (Hexachlorocyclohexane)*	0.06	0.06	<0.05	<0.05	<0.05	<0.05
Pentachlorophenol	<0.05	0.08	<0.05	0.07	<0.05	0.05
Endrin	<0.45	2.16	<0.45	<0.45	<0.45	<0.45
Organophosphate esters						
Tributyl phosphate (TBP)	29	47	27	45	<23	<23
Perfluorinated compounds						
Perfluorooctanesulfonic acid (PFOS)	2.9	3.4	3.3	2.6	2.0	<1.8
Perfluorooctanoic acid (PFOA)	1.3	3.8	3.6	1.5	1.7	<0.7
Perfluorohexanesulfonic acid (PFHxS)	0.56	1.5	1.0	0.84	0.65	<0.1
Perfluorohexoic acid (PFHxA)	1.4	2.0	1.8	1.8	1.4	<0.4
Petroleum residues						
Methyl tert-butyl ether (MTBE)	370	150	85	<61	130	<61
Ethyl tert-butyl ether (ETBE)	18	16	18	19	<14	<14
Benzene	<10	<10	<10	<13	19	<10
Toluene	100	46	38	32	110	<19
Ethylbenzene	<10	<10	<10	<10	16	<10
m+p-Xylene	31	36	13	21	120	<13
o-Xylene	<50	<50	<50	<50	82	<50
1,3,5-Trimethylbenzene	<13	<13	<13	<13	18	<13
1,2,4-Trimethylbenzene	<30	<30	<30	<30	46	<30
1,2,3-Trimethylbenzene	<13	<13	<13	<13	23	<13
Chlorinated VOCs						
1,2-dichloroethane	21	<20	<20	24	<20	<20
Chloroform	60	110	44	38	72	<21
1,1,1-Trichloroethane	1.3	<1.0	1.4	<1.0	2.9	<1.0
Carbon-tetrachloride	4.5	4.4	5.6	3.3	6.3	<2.3
1,1,2-Trichloroethene	34	30	27	16	41	<8.3
Tetrachloroethene	1.3	3.9	1.0	1.4	2.6	<1.0
Pharmaceuticals						
Hydrochlorothiazide	<0.04	1.4	<0.04	<0.04	<0.04	<0.04
Ibuprofen	<0.2	2.2	0.42	<0.2	<0.2	<0.2
Naproxen	<0.8	31	<0.8	<0.8	<0.8	<0.8
Metoprolol	<0.1	3.5	0.23	0.44	0.2	<0.1

Oxazepam	<0.1	0.14	<0.1	<0.1	<0.1	<0.1
Carbamazepine	0.4	1.2	0.45	0.49	0.45	<0.1
Ketoprofen	<0.8	2.7	<0.8	<0.8	<0.8	<0.8
Propranolol	<0.1	0.2	<0.1	<0.1	<0.1	<0.1
Citalopram	<0.1	0.91	<0.1	<0.1	<0.1	<0.1
Sertralin	<0.1	0.11	<0.1	<0.1	<0.1	<0.1
Ketoconazole	<0.1	0.22	<0.1	<0.1	<0.1	<0.1
Acetylsalicylic acid (ASA)	13	17	11	28	12	<3.2
Salicylic acid	26	28	22	32	<19	<19
Phenolic compounds						
4-t-octylphenol	<0.4	<0.4	0.89	<0.4	<0.4	<0.4
Triclosan	7.2	<6.8	8.3	9.8	8.5	<6.8
Bisphenol A	<52	<52	68	<52	<52	<52
Phtalate esters						
Di-n-butylphthalate (DBP)	<188	<188	<188	498	<188	<188
Butylbenzylphthalate (BBP)	<1.2	<1.2	<1.2	1.7	3.5	<1.2
Di(2-ethylhexyl)phthalate (DEHP)	<68	<68	<68	94	223	<68
Diisononylphthalate (DINP)	134	<50	<50	<50	110	<50
Diisodecylphthalate (DIDP)	11	20	16	18	75	<5.3
Polycyclic aromatic hydrocarbons						
Fluorene	0.20	0.19	0.19	0.29	0.29	<0.15
Phenanthrene	1.0	0.80	0.58	<0.50	0.71	<0.50
Anthracene	<0.010	0.025	0.016	0.010	0.012	<0.010
Fluoranthrene	0.22	0.18	0.34	0.064	0.34	<0.18
Pyrene	<0.25	<0.25	0.31	<0.25	<0.25	<0.25
Surfactants						
Sodium dodecyl sulfate (SDS)	56	55	53	95	55	<14
Sodium laureth sulfate (SLS)	<180	250	<180	271	203	<180
Linear alkylbenzene sulfonate (LAS)	<150	622	<150	<150	185	<150
Tin organic compounds						
Dibutyltin	<0.5	<0.5	<0.5	<0.5	0.59	<0.5
Tributyltin	<0.5	<0.5	<0.5	<0.5	0.73	<0.5
Vulcanizing residues						
N,N-dicyclohexylbenzothiazole-2-sulphenamide	0.22	0.20	0.43	0.30	0.43	<0.2

Table 4: The estimated risk using three different approaches for compounds which were below their individual LOD. In the first column all compounds below the LOD has been assumed to be present at their individual LOD (worst case). In the second column all compounds below their individual LOD has been assumed not to be present (best case). In the third column the RQ has been determined using the KM method to estimate the risk contribution of non-detects. The MCR is calculated for each approach in accordance to equation 3.

	Approach 1	Approach 2	Approach 3	MCR Approach 1	MCR Approach 2	MCR Approach 3
Fiskebäckskil	97613	9.1	9.3	1.0	2.5	2.6
Stenungsund	97611	2.4	2.6	1.0	1.7	1.8
Instö ränna	97610	1.7	1.8	1.0	1.4	1.5
Skalkorgarna	97611	2.0	2.1	1.0	4.1	4.3
Lerkil	97610	1.8	1.9	1.0	1.7	1.8