Determination of 54 contaminants of emerging concern in surface river- and seawater samples from Sør-Trøndelag, Norway

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Abstract

Bisphenols, benzophenones, benzothiazoles, benzotriazoles, parabens, triclocarban and polyfluorinated contaminants present endocrine disrupting potential and are considered environmental contaminants of emerging concern. A solid phase extraction (SPE) protocol was applied for the simultaneous extraction of 54 of these emerging contaminants from surface seawater and freshwater. Analysis of the samples was performed by four rapid (≤5 min) multi-residue UPLC-MS/MS methods, all using the same SPE extract. Overall, 33 water samples were collected from 15 different locations in and near Trondheim, Sør-Trøndelag, Norway (63°25'49.76"N, 10°23'42.22"E.). Of the 54 contaminants analyzed, 30 were detected with each analyte group represented. The sum concentrations of parabens and their transformation products (∑(8)Parab) ranged from 68.4 to 511 (median 166) ng/L. The sum concentrations of benzothiazoles (∑(9)BTHs) and benzotriazoles (∑(7)BTRs) ranged from 0.78 to 70.1 (median 9.09) and from 6.49 to 880 (median 5.07) ng/L, respectively. The sum concentrations of bisphenols (∑(9)Bisph) and benzophenones (∑(5)BzPs) ranged from 1.59 to 60.5 (median 11.3) and from 1.32 to 28.0 (median 5.45) ng/L, respectively. The sum concentrations of the polyfluorinated compounds (∑(15)PFAS) ranged from 1.21 to 648 (median 88.4) ng/L, while triclocarban ranged from 0.97 to 195 (median 2.00) ng/L. 27 compounds demonstrated reproducibility (relative standard deviation; RSD %) ranging from 2.31 to 9.89 %, 14 compounds ranged from 12.0 to 19.2 % (RSD %), while the remaining 11 compounds ranged from 20.1 to 34.3 %. The method lower limit of quantification (MLLOQ) ranged from 0.06 to 8.85 ng/L for 35 compounds, 11.6 to 99.0 ng/L for 14 compounds, and 139 to 576 ng/L for the remaining 4 compounds. 34 chemicals demonstrated absolute recoveries ranging from 81.5 to 105 %, 13 compounds ranged from 40.5 to 77.0 %, and 8 compounds ranged < 34 %. From the water samples, the most detected analytes were benzophenone 2 (BzP-2), bisphenol S (BPS), vanillic acid (OH-MeP) and benzotriazole (BTR) at 97.0%, 90.9 %, 84.8 %, and 78.8 % detection rate, respectively. ∑PFAS were detected in 87.9 % of the samples, but no single PFAS was detected in more than 39.4 % of the samples (e.g., perfluorooctanesulfonic acid; PFOS). Contamination loads were spaced evenly throughout samples, with no areas showing significantly higher or lower contamination loads.

Conclusions

- Benzophenone-2, bisphenol S, vanillic acid and benzotriazole were the most detected analytes (present in over 78 % of the samples) from the area in and around Trondheim.
- Perfluorinated compounds as a group were ubiquitous and detected in over 87 % of the samples, but no single PFAS was detected in more than 39 % of the samples.
- The most highly populated areas were dominated by perfluorinated compound contamination (∑PFAS) and parabens/paraben metabolites (∑Parabens).
- Benzotriazoles dominated in an area known for industrial activity (location 5).
- A method for the extraction and analysis of 54 different target analytes of emerging concern has been successfully developed.
- Four different UPLC-MS/MS methods were developed for the analysis, all ≤ 5 minutes and using the same extract.
- The method works for both saltwater and freshwater.

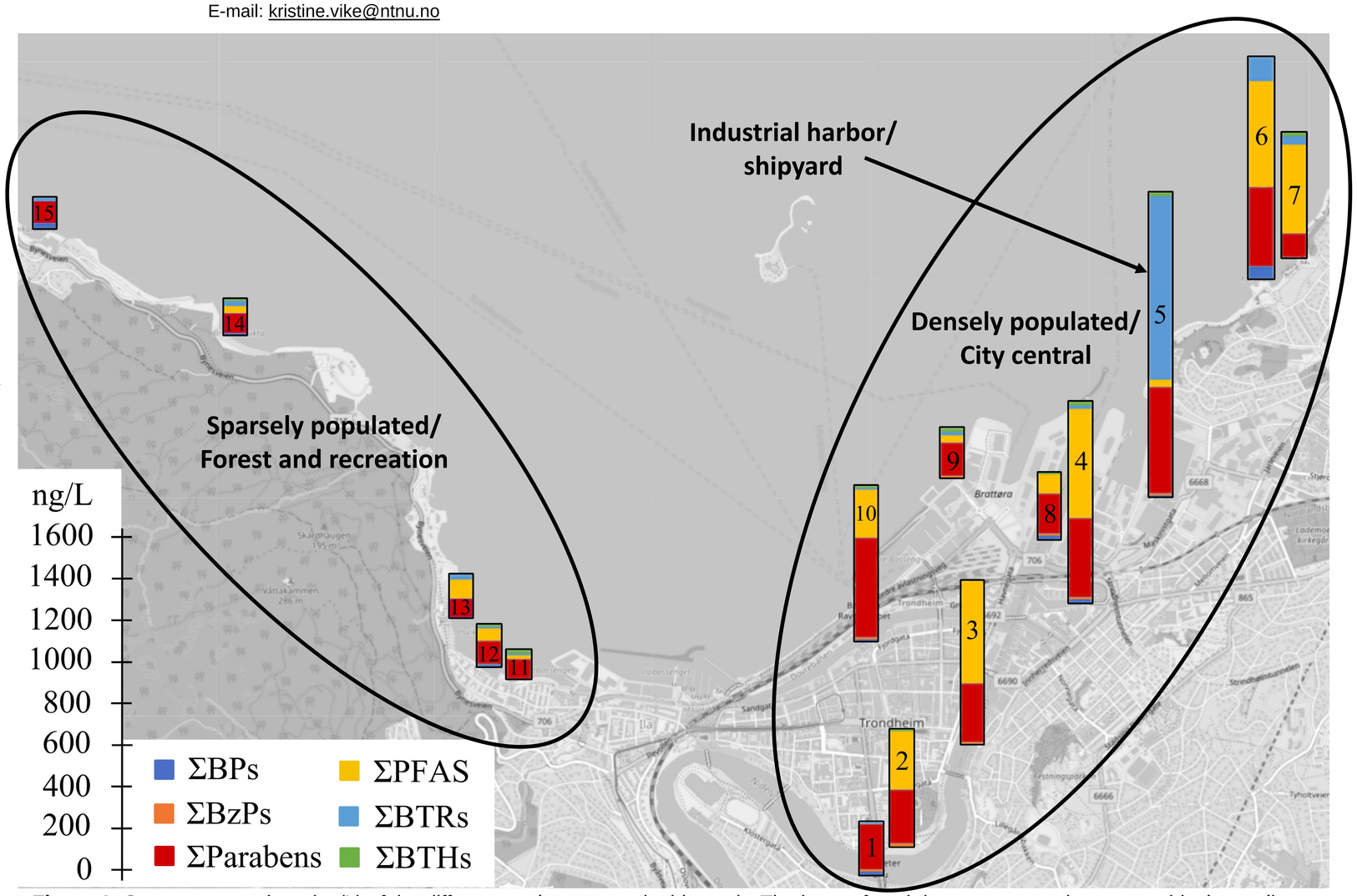

Figure 1: Sum concentrations (ng/L) of the different analyte groups in this study. The base of each bar represents the geographical sampling point in and around Trondheim.

Extraction protocol

1. 50 mL samples were acidified to pH<3 using 3M HCl. 10 µL of a 1 ppm IS mixture was added, for a total of 10 ng.

2. Strata X-RP cartridges (33 µL, polymeric reversed phase, 200 mg/3 cm^3) were conditioned with 10 mL MeOH. and equilibrated with 10 mL acidified H_2O (pH<3 w/HCl).

3. Acidified samples were passed through under vacuum.

4. The SPE cartridges were washed with 10 mL acidified H_2O (pH<3 w/HCl) and dried under vacuum for 30-40 min.

5. Samples were eluted with 10 mL MeOH:ACN (1:1 v/v).

6. Samples were dried under a gentle stream of nitrogen in a water bath at 35°C until near dryness (~250 µL).

7. Samples were transferred to LC-vials and diluted up to a total volume of ~1 mL with a mixture of MeOH:H_2O w/0.1 % ammonium hydroxide (1:1 v/v) for UPLC-MS/MS analysis.

Target analytes

Bisphenols (∑(9)BPs): Bisphenol S (BPS), bisphenol F (BPF), bisphenol A (BPA), bisphenol AF (BPAF), bisphenol B (BPB), bisphenol Z (BPZ), bisphenol AP (BPAP), bisphenol M (BPM), bisphenol P (BPP)

Benzophenones (∑(5)BzPs): Benzophenone 2 (BzP2), 4-hydroxy benzophenone (4-OH-BzP), benzophenone 1 (BzP1), benzophenone 8 (BzP8), benzophenone 3 (BzP3).

Parabens and paraben metabolites (∑(8)Parabens): Methyl paraben (MeP), ethyl paraben (EtP), propyl paraben (PrP), butyl paraben (BuP), benzyl paraben (BezP), heptyl paraben (HeP), methyl protocatechuic acid (OH-MeP), ethyl protocatechuic acid (OH-EtP)

Antimicrobials: Triclocarban (TCC)

Benzothiazoles (∑(9)BTHs): Benzothiazole (BTH), 2-Aminobenzothiazole (2-NH2-BTH), 2-Mercaptobenzothiazole (2-S-BTH), 2-(Methylthio)benzothiazole (2-Me-S-BTH), 2-Hydroxybenzothiazole (2-OH-BTH), 2-Morpholin-4-yl-benzothiazole (2-M-BTH), 2-Chlorobenzothiazole (2-Cl-BTH), 2-Thiocyano-methylthio-benzothiazole (2-SCNMeS-BTH), 2-Methylbenzothiazole (2-Me-BTH)

Benzotriazoles (∑(7)BTRs): Benzotriazole (BTR), 4-Methyl-1H-benzotriazole (TTR), 5,6-Dimethyl-1H-benzotriazole (XTR), 1-Hydroxybenzotriazole (1-OH BTR), Benzotriazole-5-carboxylic acid (BTR COOH), 5-Amino-1H-benzotriazole (5-Amino BTR), 5-Chlorobenzotriazole (5-Cl-BTR).

Perfluorinated compounds (∑(15)PFAS): Tetrabutylammoniumnonafluorobutane sulfonate (PFBS), perfluorotetradecanoic acid (PFTeDA), perfluorotridecanoic acid (PFTrDA), perfluorononanoic acid (PFNA), tricoafluorododecanoic acid (PFDoDA), perfluoroheptanoic acid (PFHpA), undecafluorohexanoic acid (PFHxA), perfluoropentanoic acid (PFPeA), perfluoroundecanoic acid (PFUnDA), perfluorooctanoic acid (PFOA), perfluorodecanoic acid (PFDA), tridecafluorohexane-1-sulfonic acid potassium salt (PFHxS), sulfluramid (sulf), perfluorooctane sulfonate (PFOS), perfluorooctane sulfonamide (PFOSA).

Internal standards (IS) Benzotriazole-d4 (BTR-d4), benzothiazole-d4 (BTH-d4), 5-Methyl-1H-1,2,3-Benzotriazole d6 (5-Me-BTR-d6), bisphenol A-13C12 (BPA-C13), bisphenol F-13C6 (BPF-C13), bisphenol B-13C6 (BPB-C13), bisphenol S-13C6 (BPS-C13), bisphenol F-13C12 (BPAF-C13), methyl paraben-13C6 (MeP-C13), ethyl paraben-13C6 (EtP-C13), propyl paraben-13C6 (PrP-C13), butyl paraben-13C6 (BuP-C13), perfluorooctanoic acid-13C8 (PFOA-13C), perfluorooctane sulfonate-13C8 (PFOS-13C).