SINTEF

Report

Arctic Ecosense – PAH-analysis

Water samples from Arctic Ecosense

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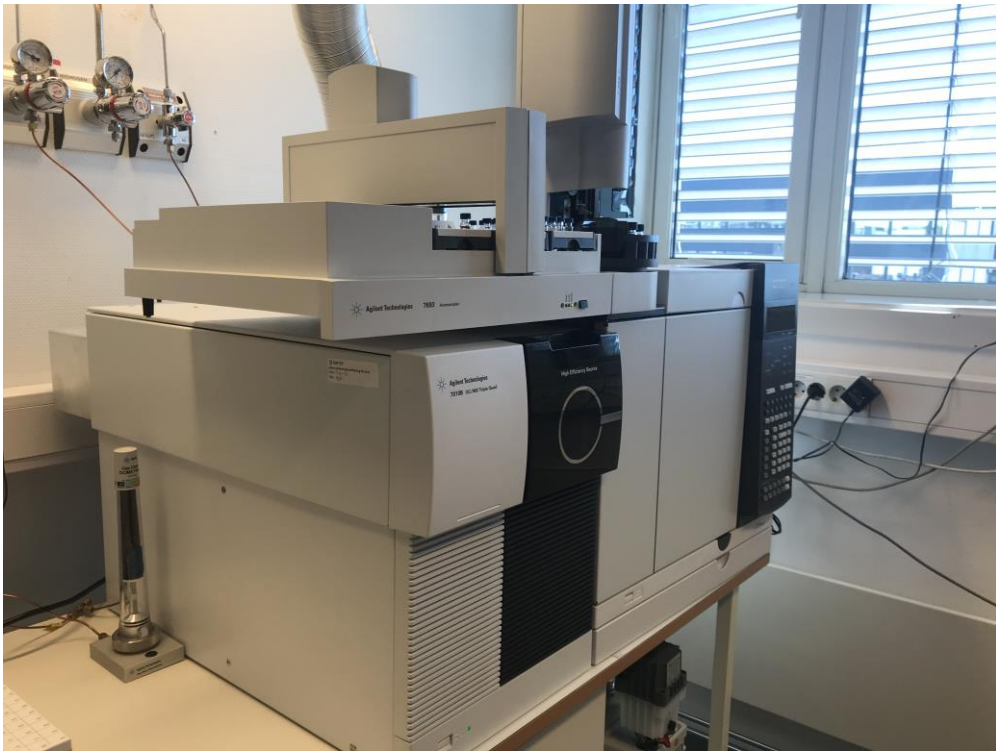

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Report

Arctic Ecosense – PAH-analysis

Samples from polar cod experiments at University of Tromsø winter 2018-2019

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ABSTRACT
For the NFR Arctic Ecosense project, SINTEF Ocean has provided sample extraction and analysis of an extended suite of PAHs and alkyl PAHs in a set of water samples. This report details the analysis and results.

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APPENDICES

1 Background

For the NFR Arctic Ecosense project, SINTEF Ocean has provided sample extraction and analysis of an extended suite of PAHs and alkyl PAHs in a set of water samples. This report details the analysis and results.

2 Samples

2.1 Water samples

Water samples were received acidified in 1L glass bottles. Upon receipt at SINTEF Ocean Sealab in Trondheim, the samples were checked and registered with a unique SINTEF-ID. Samples were stored dark and cool (4 °C) until extraction. A total of 20 samples were analysed. An overview of the samples analysed are given in Table 1. Figure 1 shows the samples after registration at SINTEF.

Table 1 Water samples

SINTEF-ID	Day of exposure	Treatment
2019-8923	0	Control
2019-8928	4	Control
2019-8933	10	Control
2019-8938	18	Control
2019-8924	0	Low
2019-8929	4	Low
2019-8934	10	Low
2019-8939	18	Low
2019-8925	0	Medium
2019-8930	4	Medium
2019-8935	10	Medium
2019-8940	18	Medium
2019-8926	0	High
2019-8931	4	High
2019-8936	10	High
2019-8941	18	High
2019-8927	0	Very high
2019-8932	4	Very high
2019-8937	10	Very high
2019-8942	18	Very high

Figure 1 Samples after registration at SINTEF Ocean.

3 Methods

3.1 Extraction of water samples

On the day of extraction, the water samples were allowed to adjust to room temperature and the pH verified (<2). After transfer of the entire sample to separatory funnels, the sample bottles were rinsed with three portions of dichloromethane (DCM), a total of 30 (0.5 L samples) or 60 (0.8 L samples) mL, which was subsequently transferred to the separatory funnel and used for the first extraction. Surrogate internal standards (SIS, 25.08 ng naphthalene-*d*8, 5.00 ng phenanthrene-*d*10, 4.86 ng chrysene-*d*12 and 5.08 ng perylene-*d*12) were added to each sample. The samples were shaken manually for 3 minutes and the phases allowed to separate before transferring the organic phase to a flask with sodium sulfate (Na_2SO_4). The extraction was repeated two more times, with two portions of 15 (0.5 L samples) or 30 mL (0.8 L samples) DCM, and shaken for 2 minutes. The combined organic phases were concentrated to approximately 1 mL using a TurboVap® evaporator. Recovery internal standards (RIS, 9.84 ng fluorene-*d*10 and 10.64 ng acenapthene-*d*10) were added to the samples immediately prior to analysis. A laboratory blank (800 mL MilliQ water) was included with each sample set.

3.2 Chemical analysis

Samples were analysed by an Agilent 7890 gas chromatograph coupled with an Agilent 7010B triple quadrupole mass spectrometer fitted with an EI source and collision cell was used (Agilent Technologies,

Santa Clara, CA, USA). Two Agilent J&W HP-5MS UI GC-columns (30 m × 0.25 mm x 0.25 µm) were coupled in series through a purged ultimate union (PUU). The carrier gas was high purity helium at constant flow (1.2 mL/min). Samples (1µL) were injected at 310 °C splitless. The oven temperature was kept at 40 °C for 1 min, then ramped to 110 °C by 40 °C/min, to 220 °C by 6 °C/min and finally to 325 °C by 4 °C/min. The temperature was then held at 330 °C for 5 minutes, while the first column was back-flushed. The transfer line temperature was 300 °C, the ion source temperature was 230 °C and the quadrupole temperatures were 150 °C. The EI source was operated at 70 eV. N_2 was used as collision gas at a flow of 1.5 mL/min and helium was used as a quench gas at a flow of 2.25 mL/min. Target PAH analytes were identified by two unique MRM transitions and quantified by the most intense peak (Sørensen et al., 2016b). Alkyl PAH clusters were determined by MRM using transitions from the molecular ion, as described previously in Sørensen et al. (2016a). Standards were run throughout the sample sequence to monitor system performance and a variation of no more than 25 % was accepted.

Parent PAH compounds were quantified by quadratic regression of a 12-level calibration curve (0.01-250 ng/mL), while alkyl PAH homologue groups were quantified by the response factor calculated for a methyl-substituted PAH reference compound.

4 Results

Results are appended in spreadsheets. Water sample concentrations are given in ng PAH/L sample.

4.1 Quality assurance

Laboratory blank samples were extracted with each sample set and the levels of contamination were checked against sample concentrations. Limits of detection established based on historical blank samples for each method are reported with the data set. Calibration was verified throughout sample sequences and no deviation above 25 % was accepted. Extractions and GC-MS/MS analysis were executed according to SINTEF internal standard operating procedures, by trained personnel. Manual integration of peaks, transfer of raw data from laboratory journals, and spreadsheet formulas and calculations has been verified by an internal 'quality assuror'. Additionally, a standard sample with known concentration is analysed and goes through the calculation procedure to verify the accuracy and flawlessness of the analysis and calculation methods.

5 References

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Sørensen, L., Silva, M.S., Booth, A.M., Meier, S., 2016b. Optimization and comparison of miniaturized extraction techniques for PAHs from crude oil exposed Atlantic cod and haddock eggs. Anal. Bioanal. Chem. 408, 1023-1032.