

DETERMINATION OF AIRBORNE POLYFLUORINATED ORGANIC COMPOUNDS IN NORTHERN GERMANY

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Abstract

This work describes the determination of volatile polyfluorinated organic compounds (PFCs) in air samples taken in metropolitan Hamburg as well as at a rural site in Northern Germany. The method developed by Martin et al. [1] and Stock et al. [2] for high-volume air samples has been modified. Special attention has been paid to the application of adequate internal standards (IS).

Introduction

PFCs have been produced since the early 1950ies and are used in various consumer products, including food wraps, spray-on treatments for clothing, leather, carpets and upholstery, non-stick cooking pans, and cosmetics. **Scotchgard**[®] and **Teflon**[®] are only two examples of product lines that contain PFCs. Millions of kilograms of PFCs are produced worldwide annually. Many PFCs combine **persistence**, **bioaccumulation** and **toxicity** to an extraordinary degree. Concern about PFCs has risen due to their **global distribution** (see Fig. 1). Perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) are the PFCs which have been studied the most so far.

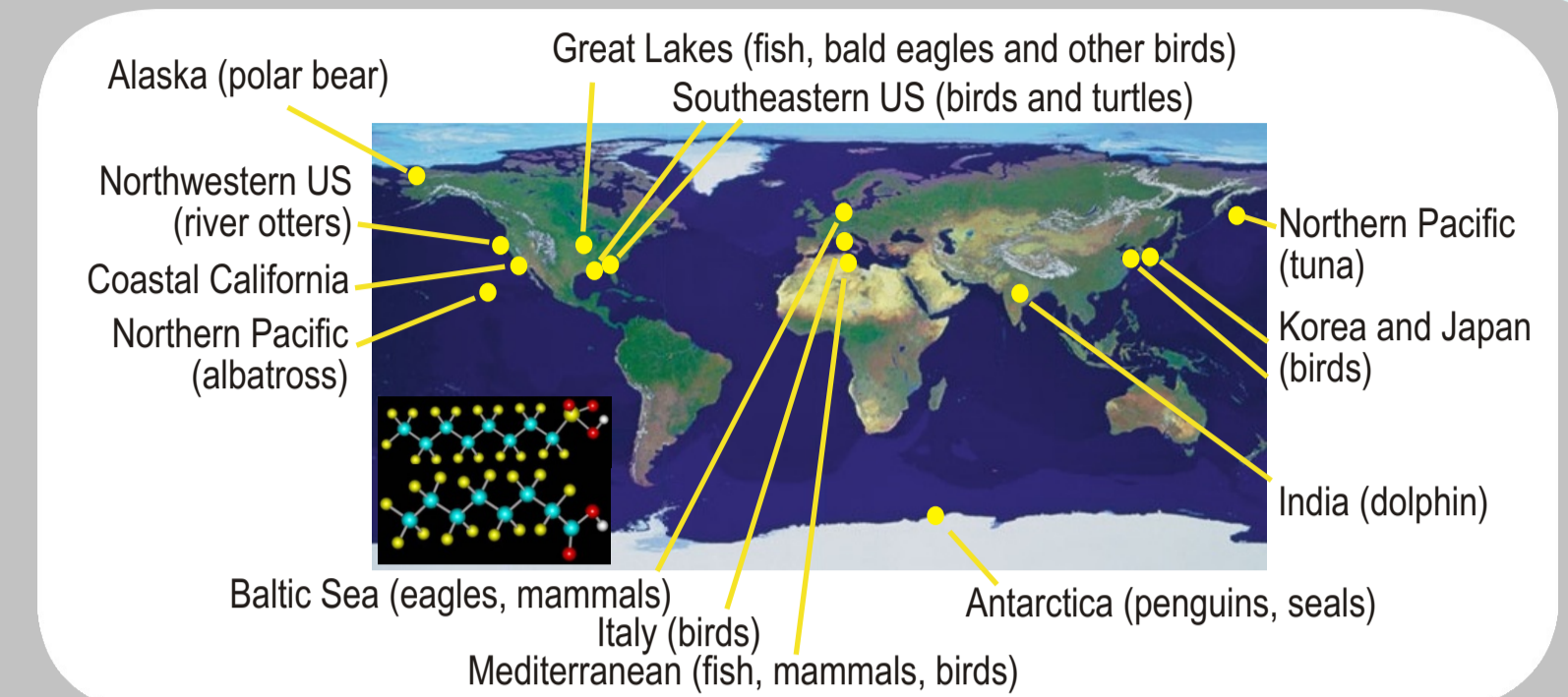
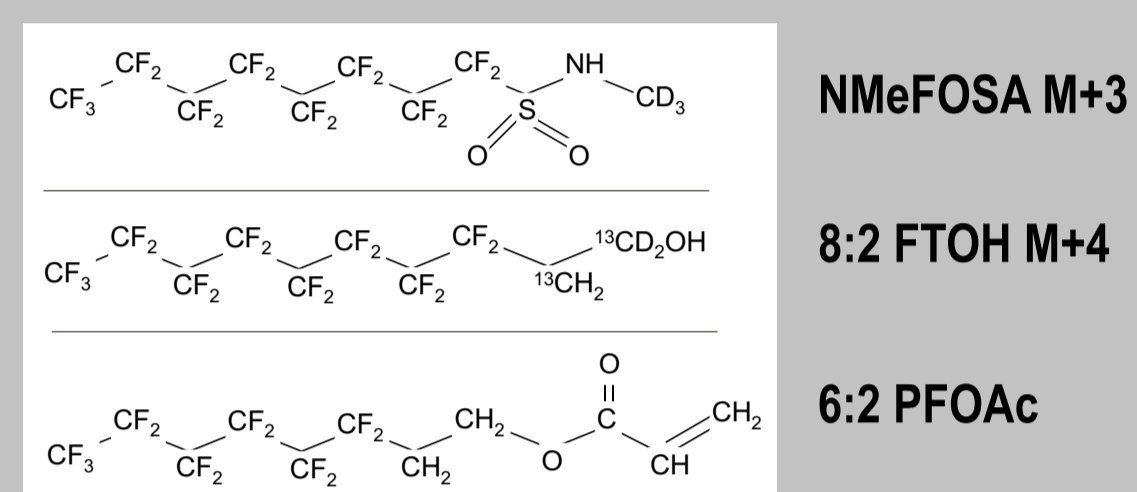


Fig. 1: Global sampling locations for PFCs (adapted from [3])

Materials and Methods

The method used is able to analyse 4:2 FTOH, 6:2 FTOH, 8:2 FTOH, 10:2 FTOH, 6:2 Perfluorooctane acrylate (6:2 PFOAc), NMeFOSA, NEtFOSA, NMeFOSE, and NEtFOSE. Five mass-labelled IS have been applied: **6:2 FTOH M+4**, **8:2 FTOH M+4**, **10:2 FTOH M+4**, **NMeFOSA M+3**, and **NEtFOSA M+5**. The recovery IS added prior to GC-MS analyses were 7:1 and 11:1 fluorinated alcohol (FA).



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Blanks. For most analytes, no blank problems were found. Solvent blanks were <LOD while column blanks could be detected for 10:2 FTOH and NEtFOSA and could be quantified for 8:2 FTOH at 2.6 ± 0.5 pg/ μ L, which is just above the LOQ (see below).

Precision. Within-day (100 pg/ μ L) and between-day (200 pg/ μ L) precision were 4.2-7.4 % and 5.5-9.7%, respectively.

Recoveries. At two concentration levels (100 and 400 pg/ μ L), IS-corrected **solvent recoveries** ranged from 76% (4:2 FTOH) to 160% (NMeFOSE), while **column recoveries** were between 56% (4:2 FTOH) and 320% (NEtFOSA), see Fig. 2.

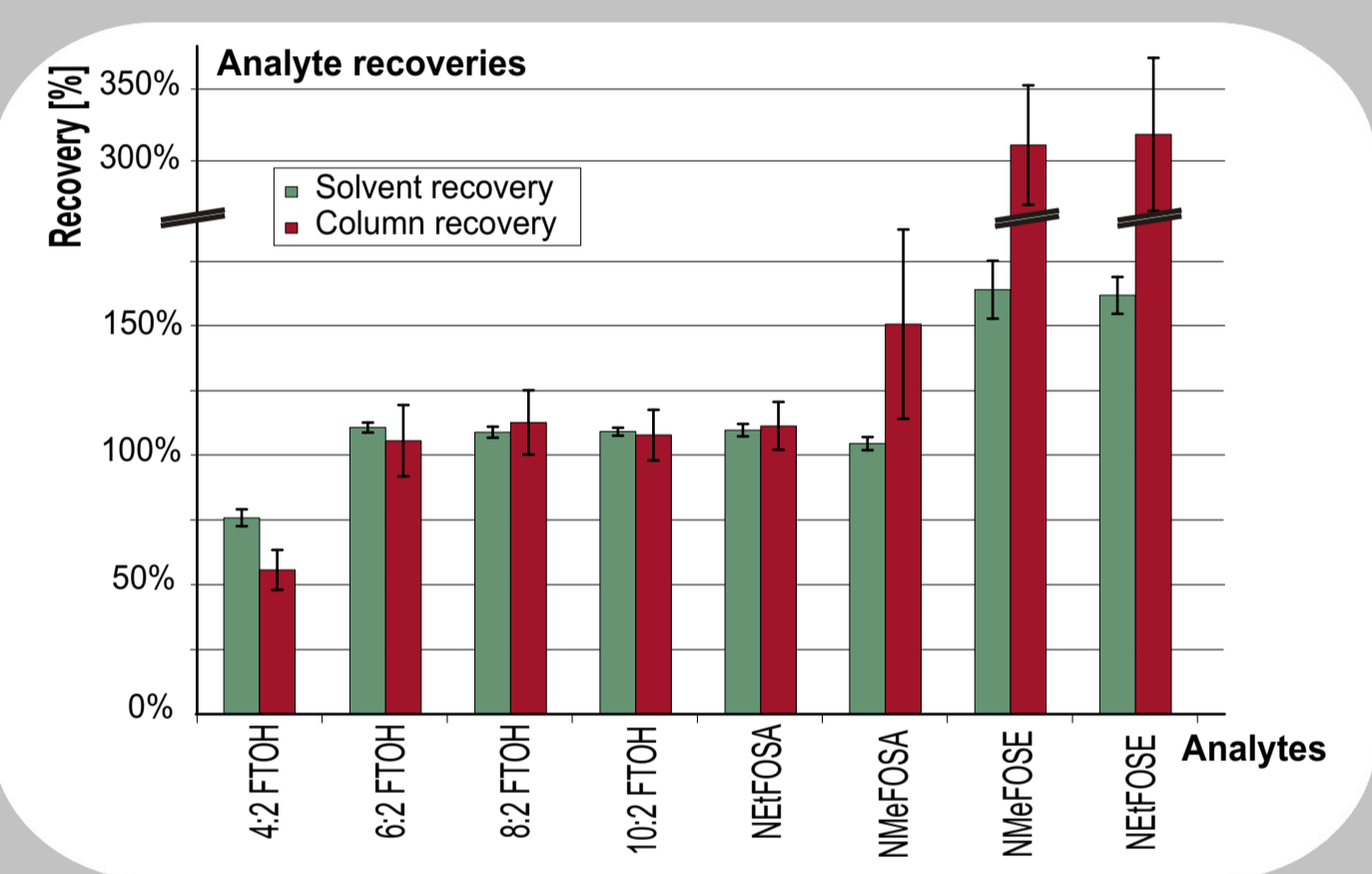


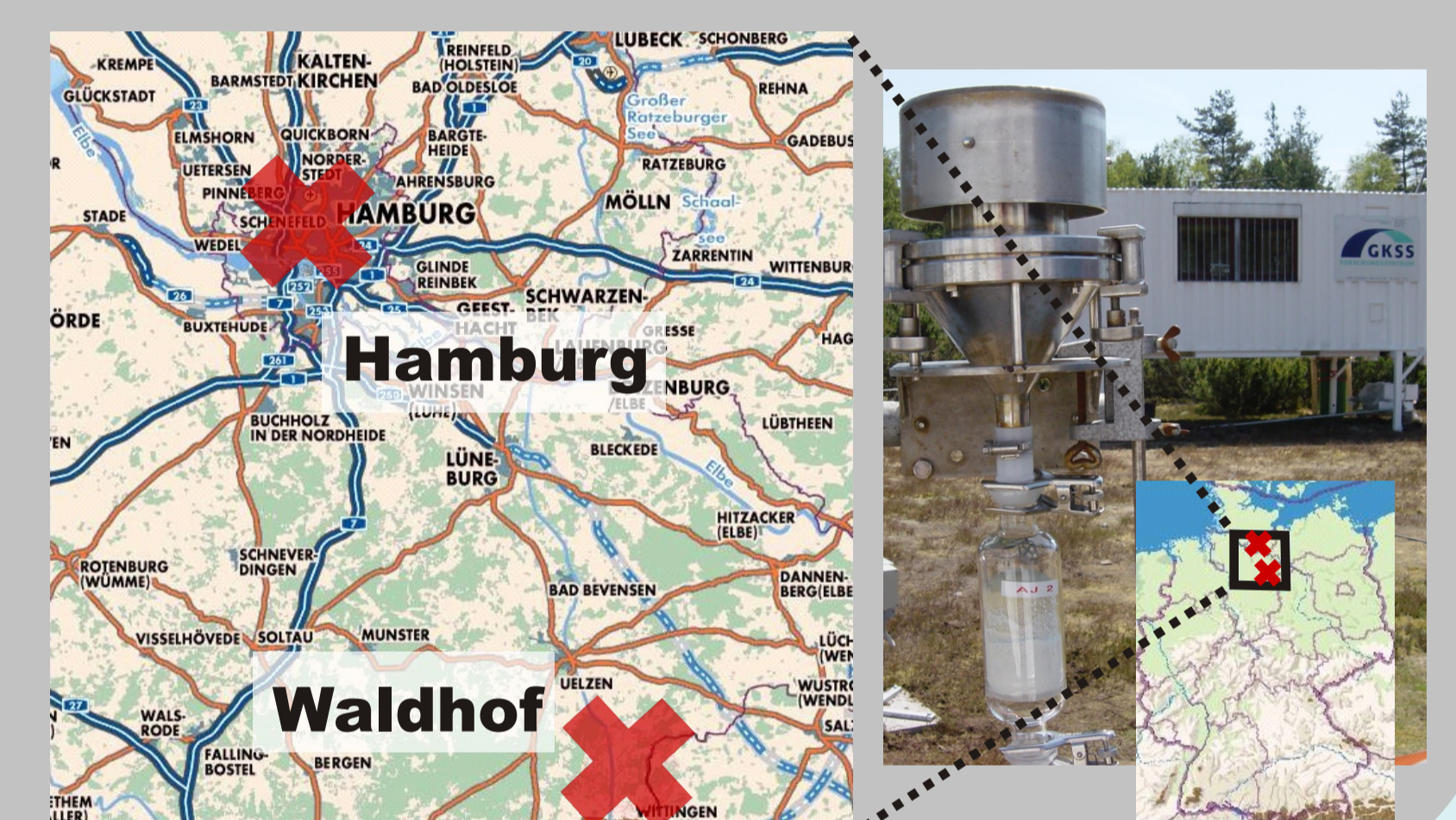
Fig. 2: Solvent and column recoveries (n = 6)

LODs and LOQs were estimated from standard analyses at very low concentrations at a signal-to-noise-ratio (S/N) of 3:1 and 10:1, respectively. Method quantification limits (MQL) were derived from real samples at low concentrations (see Tab. 1).

Tab. 1: Typical LODs, LOQs and MQLs

Analyte	LOD [pg]	LOQ [pg]	MQL [pg/m ³]
4:2 FTOH	0.8	2.6	1.8
6:2 PFOAc	0.3	0.9	-
6:2 FTOH	0.9	2.9	1.4
8:2 FTOH	0.7	2.2	0.4
10:2 FTOH	0.7	2.3	0.2
NEtFOSA	0.2	0.6	0.2
NMeFOSA	0.2	0.8	0.2
NMeFOSE	0.8	2.6	0.4
NEtFOSE	0.9	3.1	0.3

Sampling campaign. Glass fiber filters (GFF) and 25 g of XAD-2 sandwiched between 2 PUF slices were used to take air samples of 850-1600 m³. Samples were taken in metropolitan Hamburg and at a background monitoring site: Waldhof.



Results and Discussion

In the course of the sampling campaign in Northern Germany, samples have always been taken in **parallel** and **field blanks** (individual as well as alltime blanks) have been analysed.

Tab. 2: Blanks and minimum-maximum concentrations (medians) in samples from Hamburg and Waldhof

Analyte	Blanks [ng]	Hamburg [pg/m ³]	Waldhof [pg/m ³]
4:2 FTOH	n.d.	22-120 (43)	3.3-45 (14)
6:2 PFOAc	n.d.	n.d.	n.d.
6:2 FTOH	n.d.-0.8	33-150 (48)	17-120 (58)
8:2 FTOH	<LOQ-1.6	62-270 (93)	33-110 (79)
10:2 FTOH	<LOQ-1.5	16-93 (28)	10-32 (26)
NEtFOSA	n.d.-1.2	1.3-5.9 (2.5)	1.5-3.4 (2.7)
NMeFOSA	n.d.-1.1	3.4-20 (7.0)	3.8-11 (6.3)
NMeFOSE	n.d.-0.8 (4.4)	3.0-89 (14)	0.5-11 (7.9)
NEtFOSE	n.d.-1.1	0.5-27 (2.6)	<MQL-23 (8.1)

Air samples from Northern Germany.

Between April and June, 2005, air samples have been taken in Hamburg (n = 14 and 8 blanks) and Waldhof (n = 8 and 5 blanks). Results are shown in Tab. 2 and Fig. 3.

Airborne PFC concentrations.

Parallel samples coincided very well. GFFs are supposed to contain considerable amounts of mainly particle-bound airborne PFCs as well, but still have to be analysed.

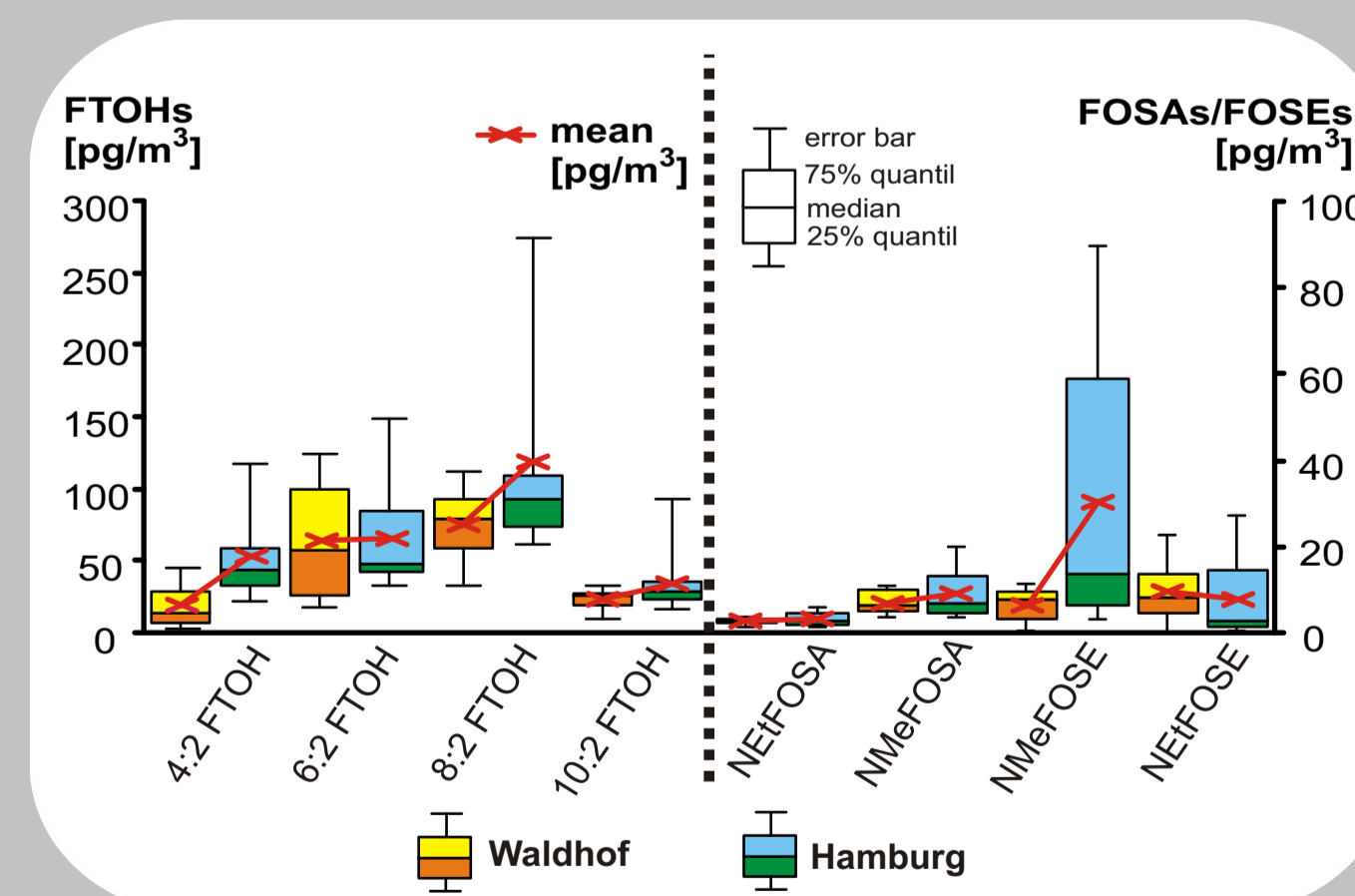


Fig. 3: Airborne PFC concentrations in Northern Germany

Discussion.

For both sampling locations, it can be stated that **FTOH concentrations are generally higher than those of FOSAs and FOSEs**. In Hamburg, 8:2 FTOH is the predominant compound, while in Waldhof, both 6:2 FTOH and 8:2 FTOH are found in rather high concentrations.

Generally, the **big concentration difference** expected between a highly urban area like the Hamburg city centre and a background monitoring site **could not be confirmed**. There are higher concentrations found for most analytes in samples from Hamburg, but not as significant as anticipated. By all means, both sampling locations are only about 100 km apart and are located in Central Europe, so that the highly volatile PFCs might be mixed and distributed rather quickly.

Conclusion: Sampling on R/V POLARSTERN

The method described above has been shown to be valid in terms of sensitivity and analyte recoveries to determine analyte concentrations in environmental air samples. It has been applied to samples taken in the **Hamburg** city centre and **Waldhof**, a background monitoring site in Northern Germany.

Due to the lack of airborne PFC concentration data from the European Arctic, an air sampling campaign was performed on board of research vessel **POLARSTERN** (Alfred-Wegener-Institut (AWI) Bremerhaven) on the way from Bremerhaven to the Norwegian Arctic (Expeditions **ARK/XX-1** and **-2**) in summer, 2004. Analyte concentrations have not been determined yet. Further sampling will be done on the Atlantic transfer of POLARSTERN from Bremerhaven to Cape Town in October and November, 2005 (**ANT/XXIII-1**, Fig. 4).

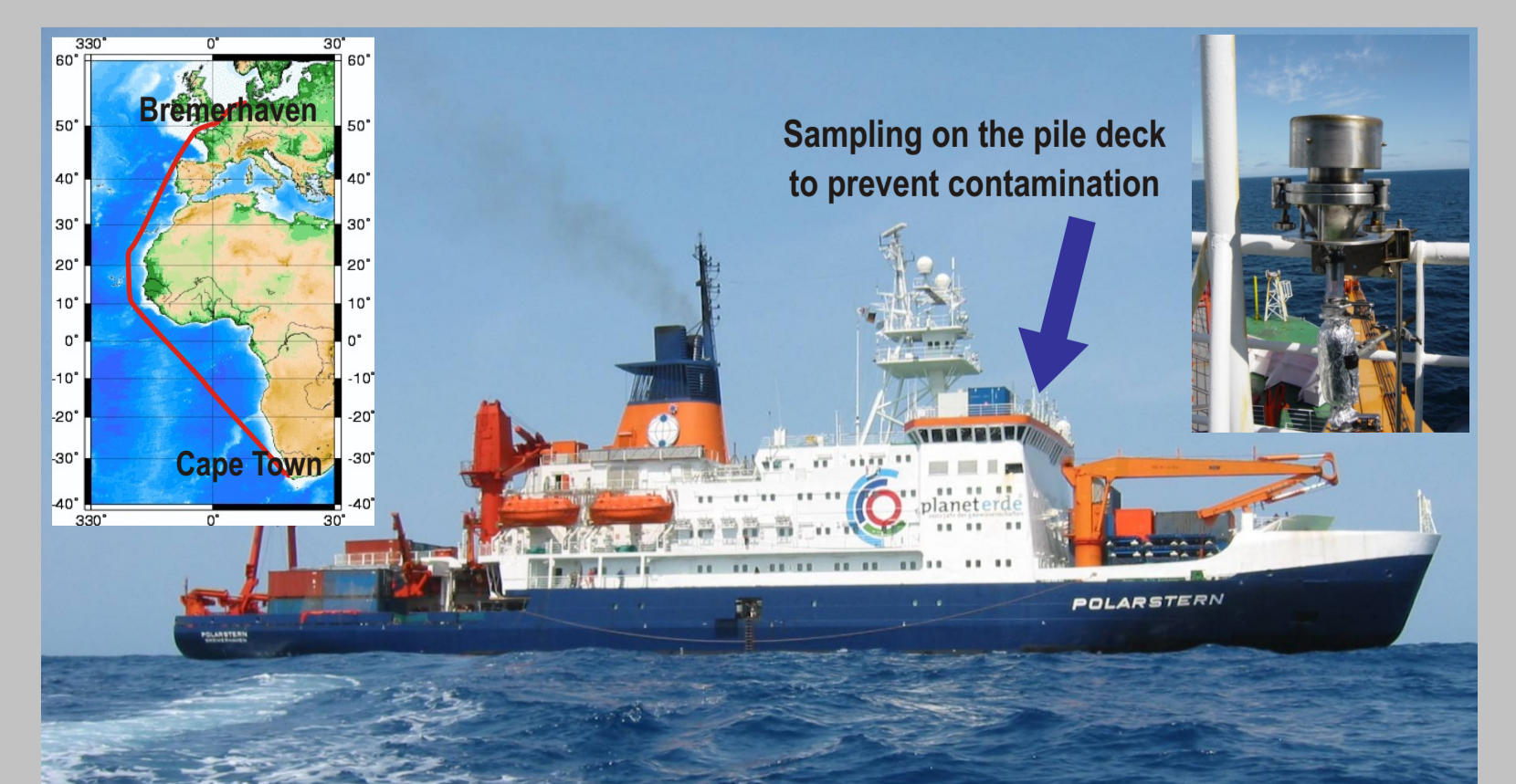


Fig. 4: R/V POLARSTERN (AWI Bremerhaven), ANT-XXIII/1

Literature

- [1] Martin et al. (2002): Anal. Chem., 74 (3): 584-590.
- [2] Stock et al. (2004): Environ. Sci. and Technol., 38 (4): 991-996.
- [3] Giesy & Kannan (2001): Environ. Sci. and Technol., 35 (7): 1339-1342.

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