

Polyfluoroalkyl Compounds in Municipal Wastewater Effluents and Water Samples along the River Elbe, Germany

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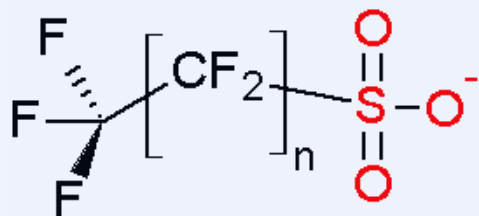
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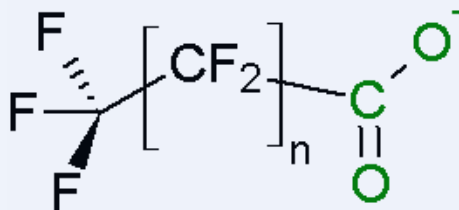
Perfluoroalkyl Compounds (PFCs)

Perfluorinated Acids (PFAs)

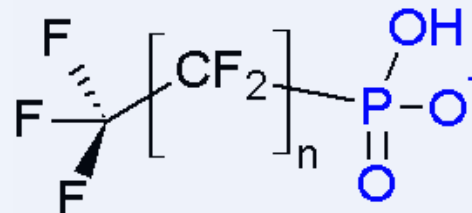
Perfluorinated alkyl sulfonates (**PFSAs**)



Perfluorinated carboxylic acids (**PFCAs**)



Perfluorinated alkyl phosphonates (**PFPAs**)

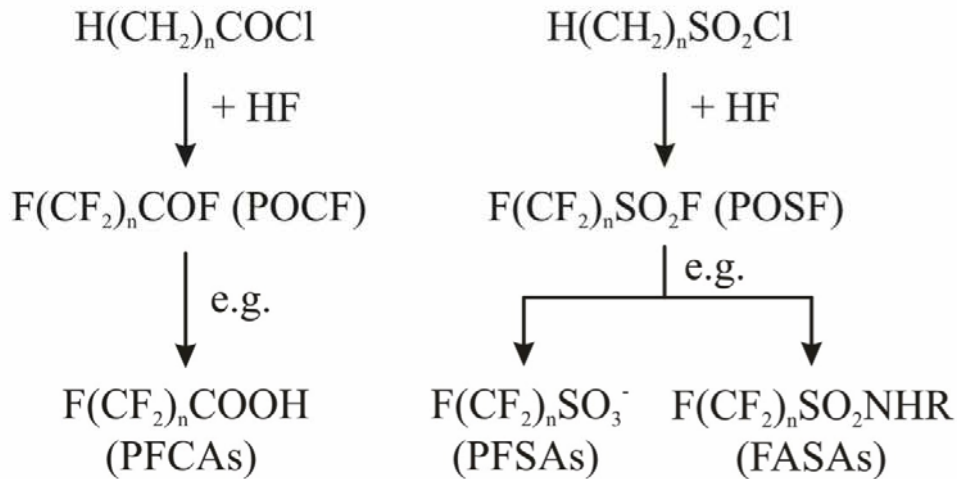


Characteristics of PFCs

- **Fluorinated** organic compounds, **surfactants**, lipophilic and hydrophilic
- **Variety area of applications**
- **Persistent** to heat, acids, and bases, as well as reducing and oxidising agents
- **Bioaccumulate** in the food web, long half-life in humans (PFOS: 8.7 yr/ PFOA: 4.4 yr, in humans)
- **Toxic** - (**PFOS**: endocrine disruptor, **PFOA**: carcinogenic potential)
- non-volatile to semi-volatile and moderately water-soluble
- **Global distribution and ubiquitous occurrence in the environment (water, sediment, air, biota) especially in marine mammals**
- **New candidates in the list of Persistent Organic Pollutants (POPs, Stockholm Convention)**

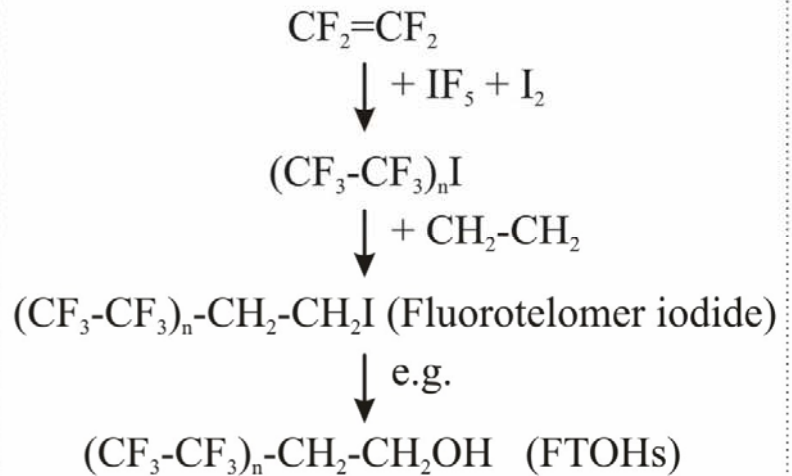
Major Manufacturing Processes

Electrochemical Fluorination (ECF) (since 1970s)



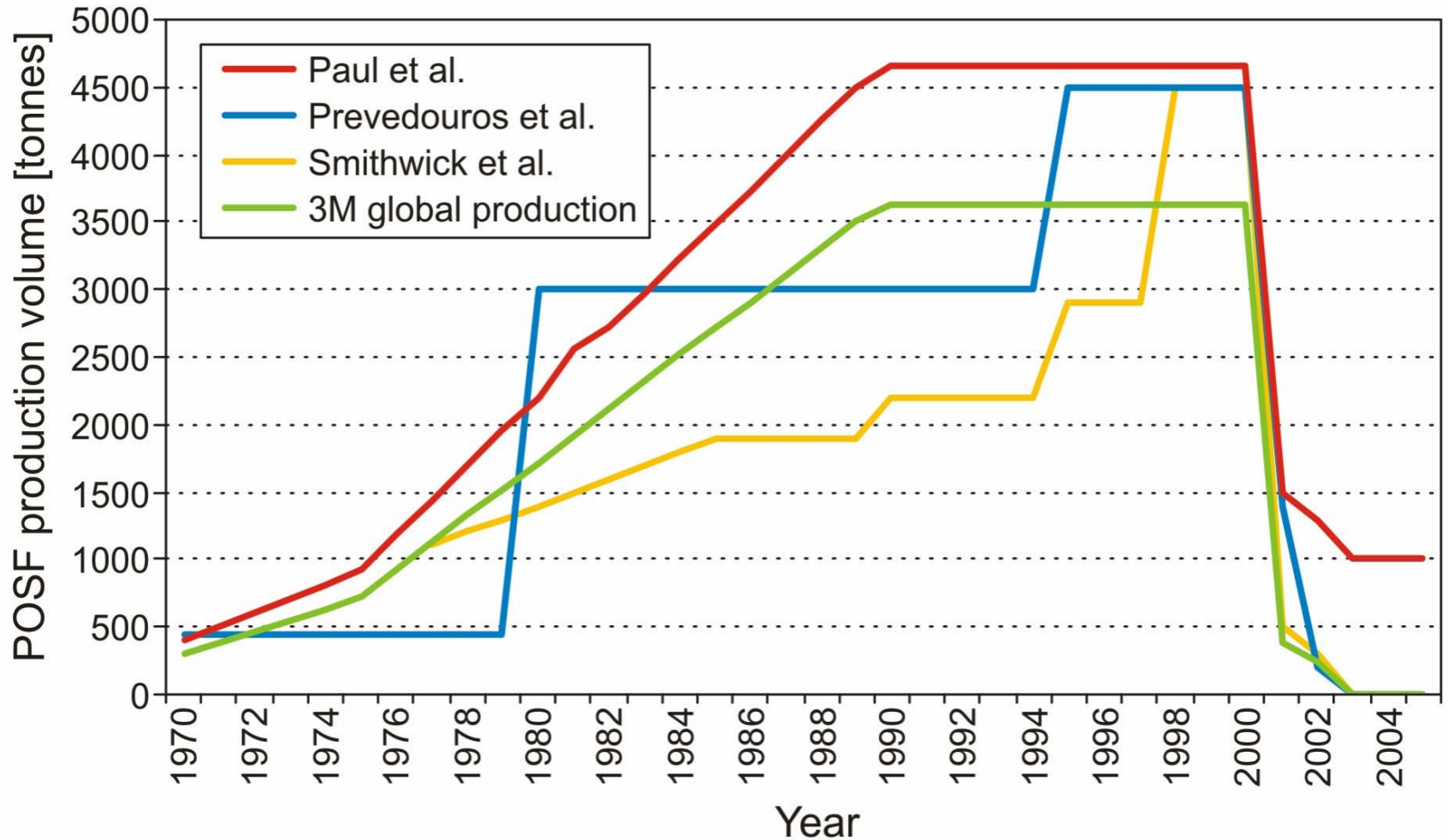
Odd and even number of C-atoms, up to 30% branched

Telomerisation (since 1950s)



Only even number of C-atoms, linear chains

Total Global POSF Production Volume

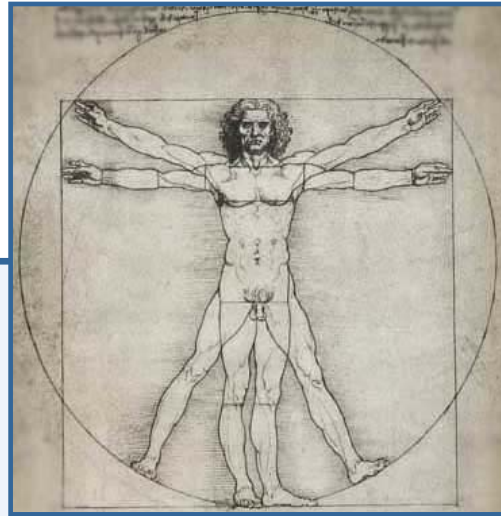


Paul et al. *ES&T*, 2009, 43, 386-392

Utilisation of PFCs



Why are People Contaminated with PFCs?



Direct exposure

- **Drinking water** (Harada et al. 2003)
- **Food** (Falandysz et al. 2006)
- **Inhalation** (air and house dust) (Moriwaki et al. 2003; Shoeib et al. 2005)
- **Hand-to-mouth** intake

Indirect exposure

- **Ingestion/inhalation & metabolism of 'precursors'** (Tomy et al. 2004)

Restrictions of PFCs

- **Phase out agreement of US EPA and 3M** for perfluorooctyl sulfonyl fluoride (**POSF**), which was a major precursor for several PFCs, in **2000**
- In **2006**, **U.S. EPA** launched a voluntary **stewardship program** to reduce perfluorooctanoic acid (**PFOA**) and related chemicals from **facility emissions and products**
- **European Union (EU)** formed a **directive**, which **prohibits the general use** of perfluorooctane sulfonate (**PFOS**) and their derivatives from **June 2008** (but several exceptions)

DIRECTIVE 2006/122/EC OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL
of 12 December 2006
amending for the 30th time Council Directive 76/769/EEC on the approximation of the laws, regulations and administrative provisions of the Member States relating to restrictions on the marketing and use of certain dangerous substances and preparations (perfluorooctane sulfonates)

(Text with EEA relevance)

(1) An OECD (Organisation for Economic Cooperation and Development) hazard assessment has been done on the basis of information that was available by July 2002. This assessment concluded that perfluorooctane sulfonates (hereinafter 'PFOS') are persistent, bioaccumulative and toxic to mammalian species and, therefore, indicate cause for concern.

52.
Perfluorooctane sulfonates
(PFOS)
 $C_8F_{17}SO_2X$
(X = OH, Metal salt (O-M+), halide, amide, and other derivatives including polymers)

→ **However, related PFCs are still being produced by other manufacturers and/or in other countries**

Methodology

- **Sensitive method** to detect 40 PFCs in ppq (water) to ppb (biota) level
- **Reduction of blank contamination:** from sampling to analysis
→ Total replacement of fluorinated materials (e.g. Teflon)

Reduction of Blank Contamination at the HPLC

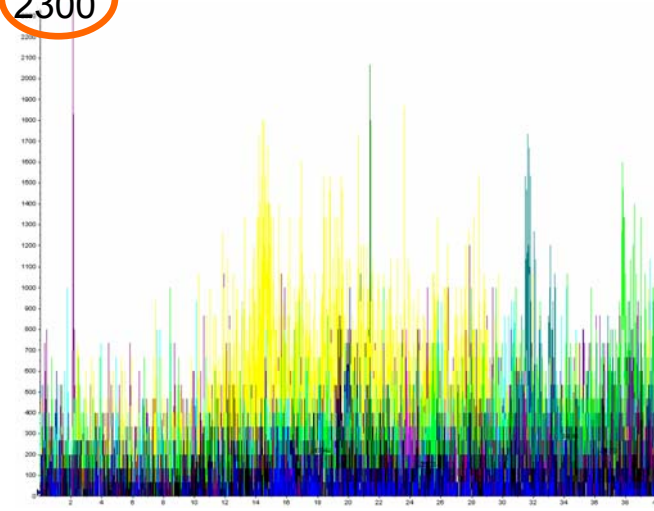
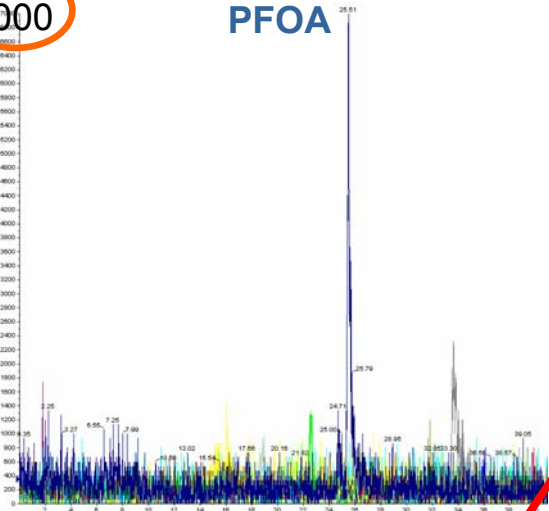
Before HPLC modifications

After HPLC modifications

7000

2300

PFOA



Degassing of the solvent using Helium or sonication

Stainless steel solvent inlet filter

Polypropylen tubings

Septum with Silicone/ aluminium

Guard column: Gemini 5u C18 Mercury (20 x 2 mm)

Guard column: Synergi 2u Hydro-RP Mercury (20 x 2 mm)

Column: Synergi 4u Hydro-RP (150 x 2 mm)

Methodology

- **Sensitive method** to detect 40 PFCs in ppq (water) to ppb (biota) level
- **Reduction of blank contamination:** from sampling to analysis
 - Total replacement of fluorinated materials (e.g. Teflon)
- Use of **standards** with high purity (> 99%)
- Avoid **matrix effects** (signal enhancement and –suppression, other interferences)
 - Solid-phase extraction (SPE) for water samples
 - Effective Clean-up for biota samples
 - Application of 20 mass-labelled standards for quality control
- Improvement of **comparability** (interlaboratory studys)
 - Participation on an international interlaboratory study for water and biota in 2008 (Van Leeuwen et al. 2009)

Analysis

Water

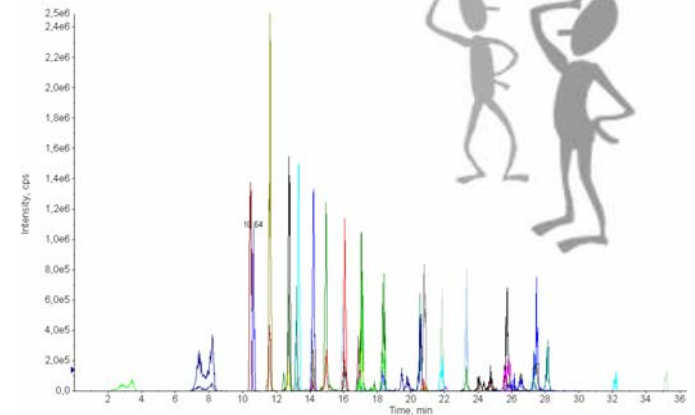
- Solid-phase extraction (SPE) using Oasis WAX cartridges

Biota tissue

- Sonication using acetonitril and clean-up with ENVI-Carb (Supelco)



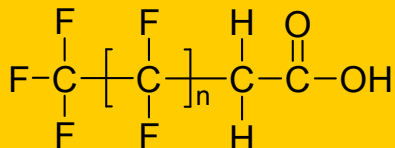
Instrument analysis



Polyfluoroalkyl Compounds (PFCs)

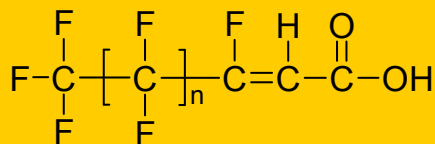
fluorotelomer acids

6:2 FTCA*
8:2 FTCA*
10:2 FTCA*



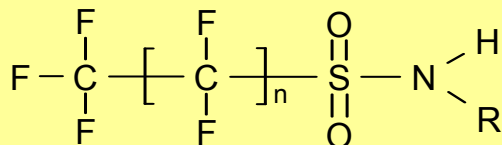
unsaturated fluorotelomer acids

6:2 FTUCA*
8:2 FTUCA*
10:2 FTUCA*



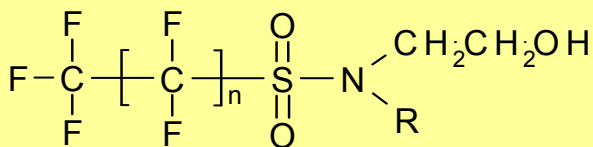
perfluoroalkyl sulfonamides

MeFBSA
PFOSA
MeFOSA*
EtFOSA*



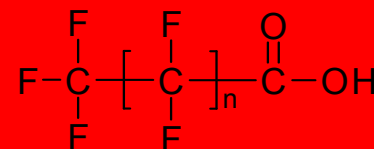
perfluoroalkyl sulfonamido ethanols

MeFBSE
MeFOSE*
EtFOSE*



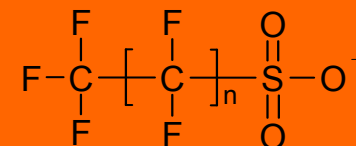
perfluoroalkyl carboxylic acids

n=2 to n=16
e.g. PFOA*



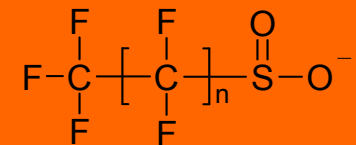
perfluoroalkyl sulfonates

n= 3 to n=10
e.g. PFOS*



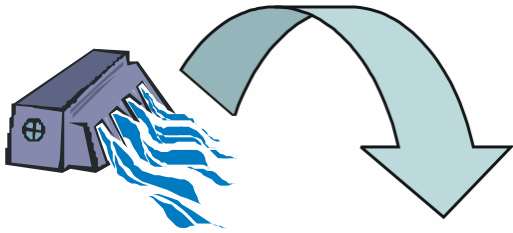
perfluoroalkyl sulfinates

PFH_xSi
PFOSi*
PFDSi



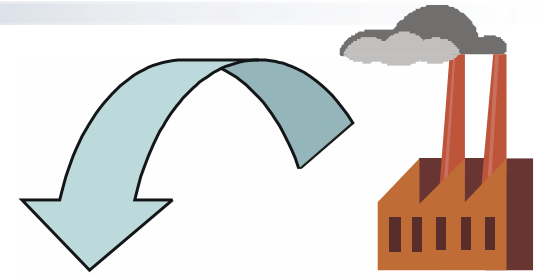
* mass-labelled standard available

How did PFCs Reach Remote Regions?



Direct transport via ocean currents and/or sea-spray

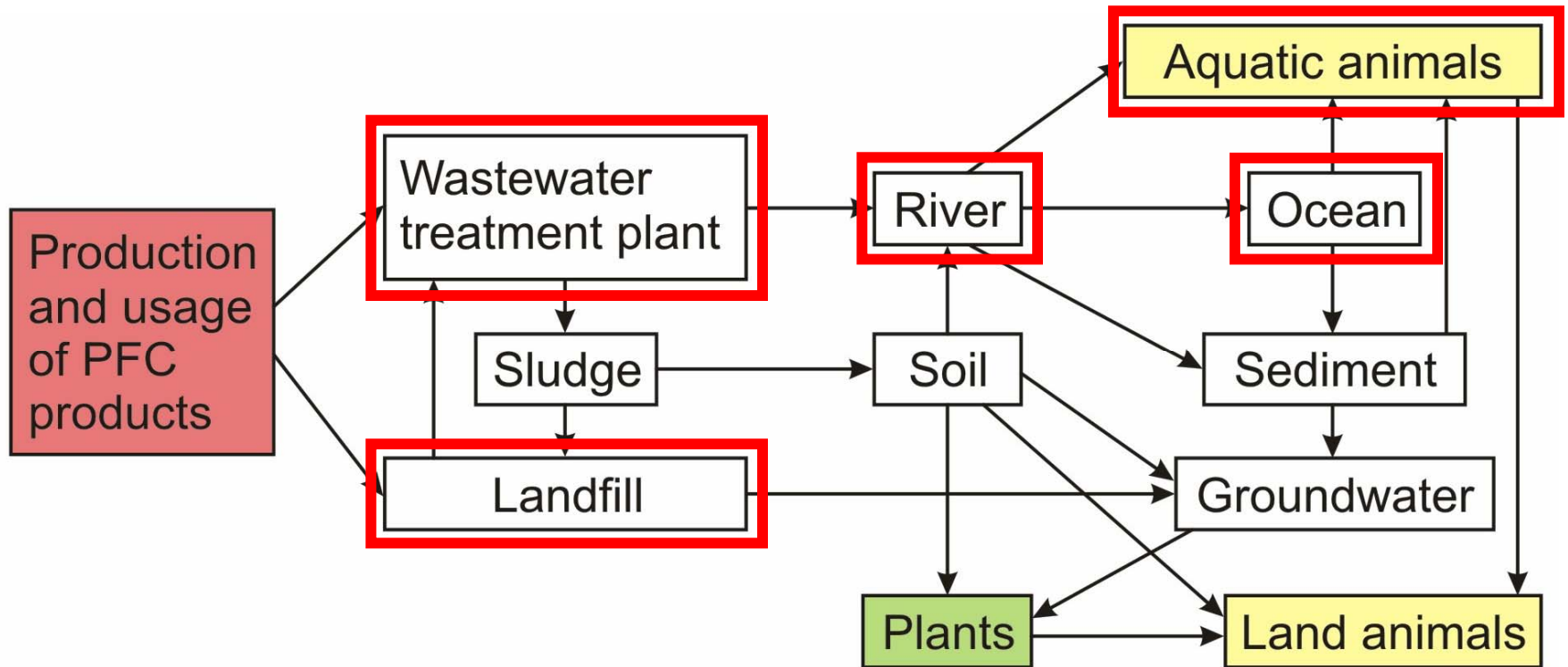
- Detected in sea- and river water and precipitation (Yamashita et al. 2005)
- Ocean currents transport (Yamashita et al. 2005, 2008; Prevedouros et al. 2006)
- Sea spray transport (McMurdo et al. 2008)



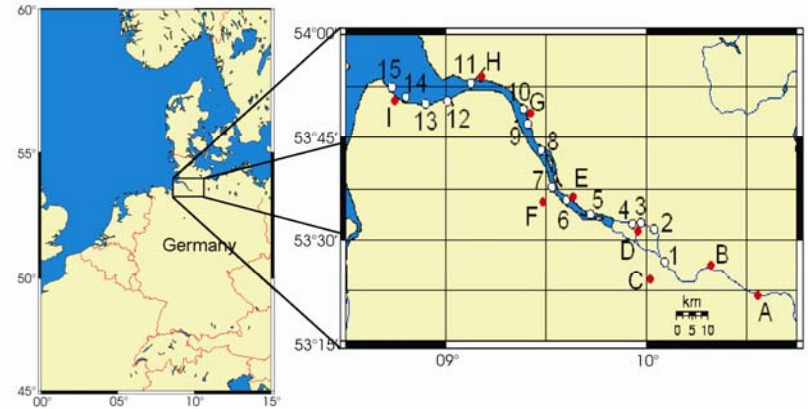
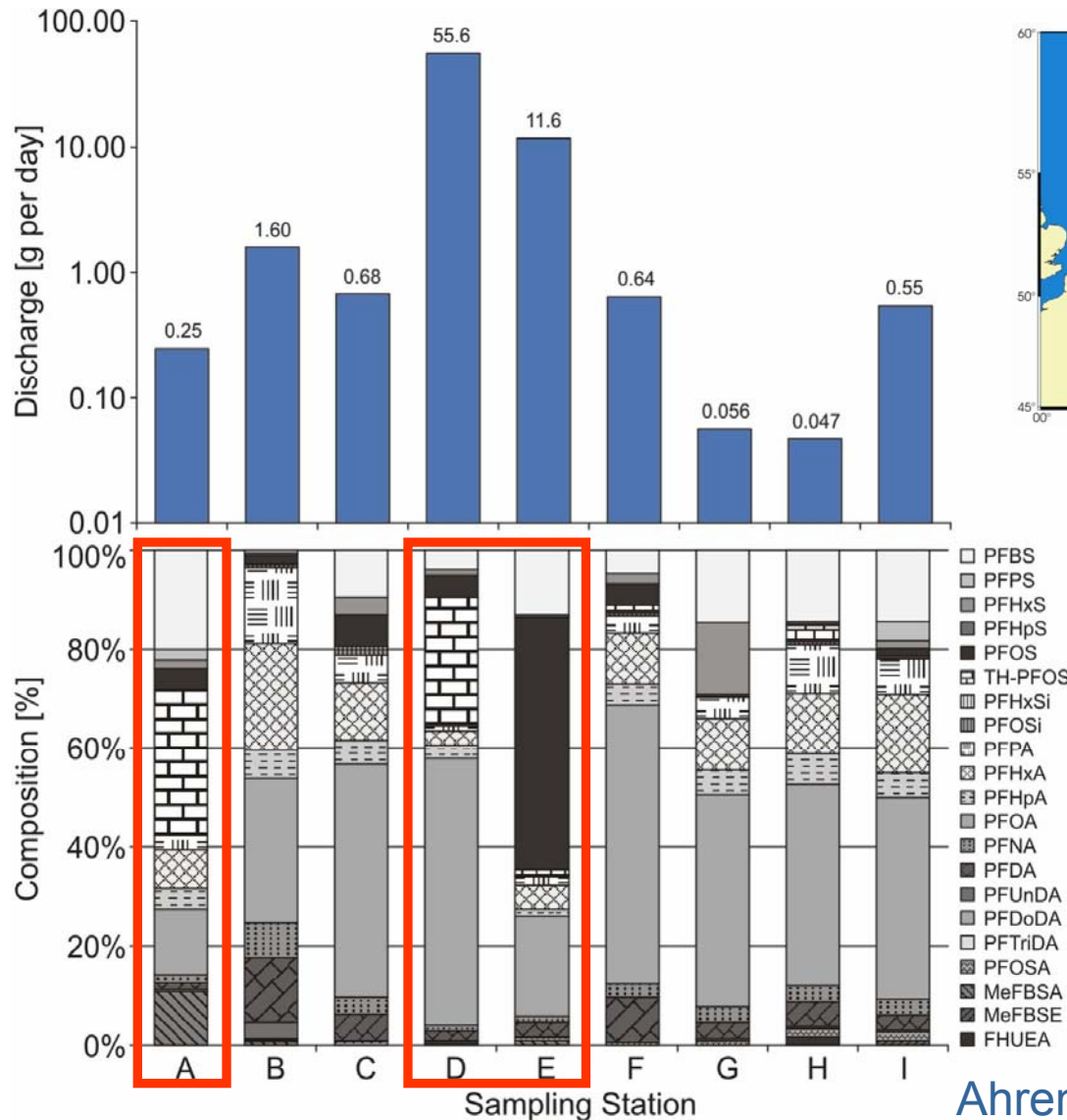
Indirect long-range transport via the atmosphere

- Volatile PFCs have been detected in the atmosphere (Martin et al. 2002; Jahnke et al. 2007)
- Precursor compounds can be decomposed to PF-Acids (Ellis et al. 2004)

Environmental Fate of PFCs



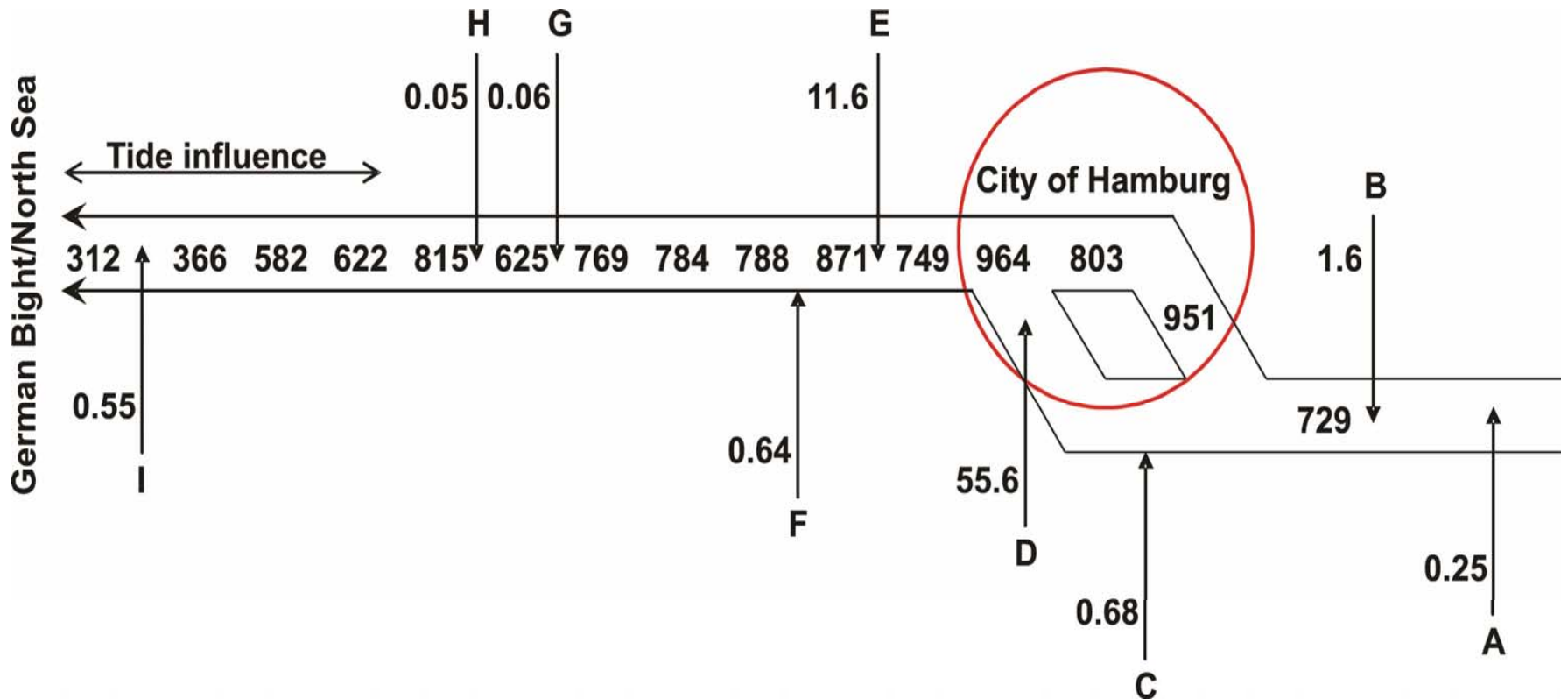
PFCs in Waste Water Treatment Plant Effluents



- WWTP A, D and E with ~30% industrial/commercial waste water
- WWTP D and E were responsible for ~95% of the total discharge into the river

Ahrens et al. *Marine Poll. Bull.*, submitted

Mass Flow of Σ PFCs in g per Day



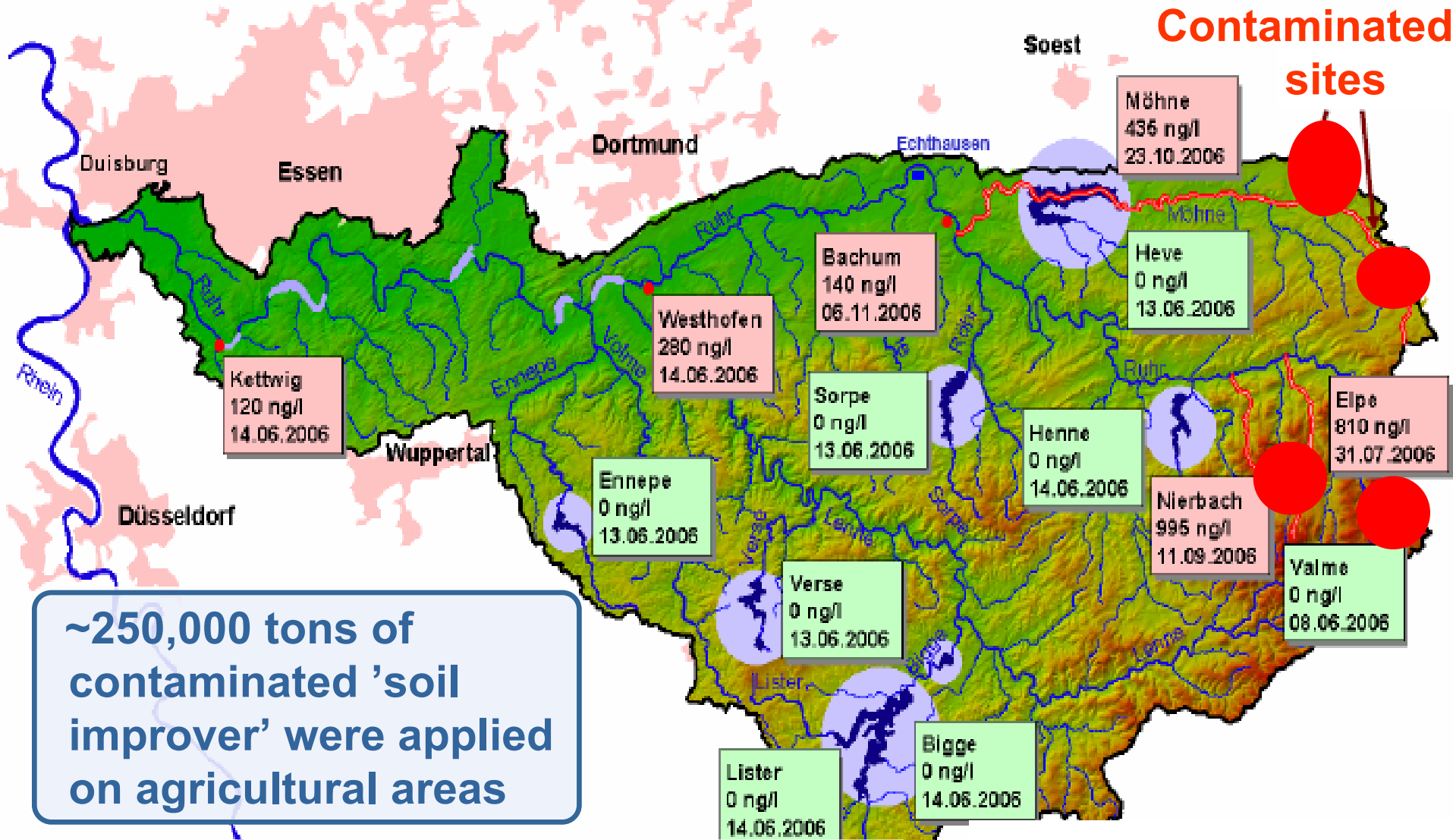
- In **this** area **WWTPs** were not the dominant source, therefore it must exist other point sources like **industrial waste water** or diffuse sources from **surface runoff** or **precipitation**

Ahrens et al. *Marine Poll. Bull.*, submitted

* A to I: Waste water treatment plant effluents

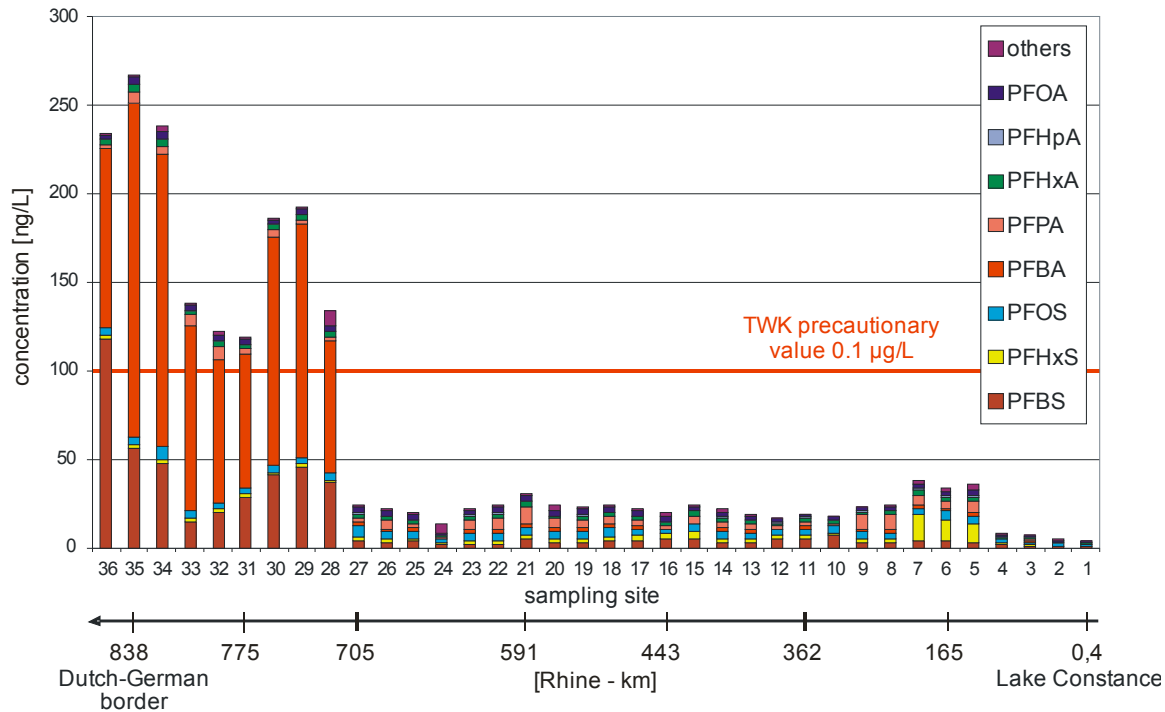
Lutz Ahrens

Contamination of Agricultural Areas in Germany



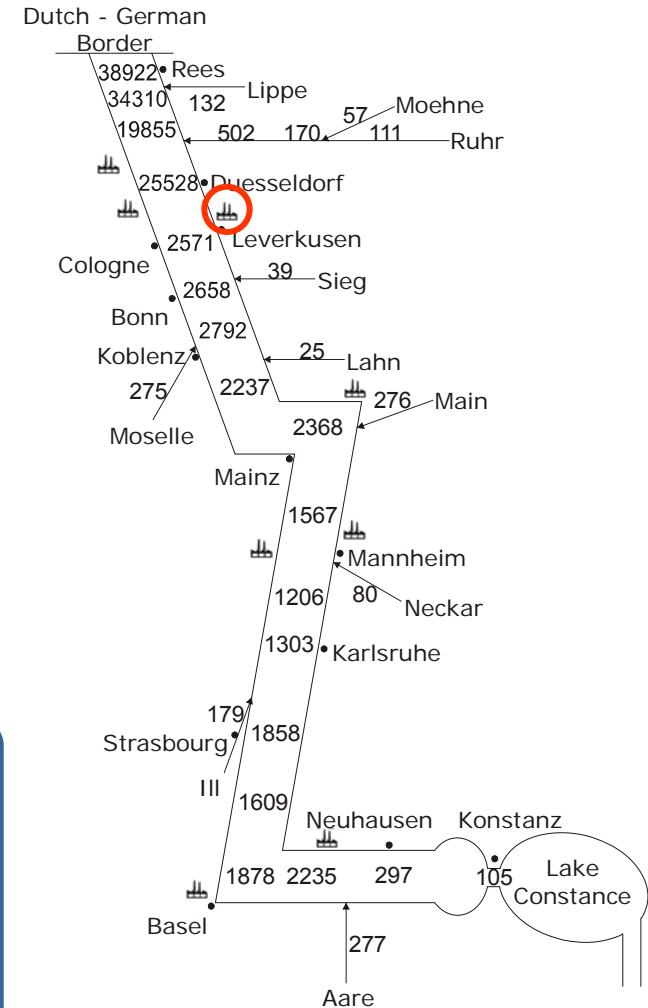
Skutlarek et al. (2006) *Environ. Sci. Pollut.* 13, 299-307

PFCs along the River Rhine



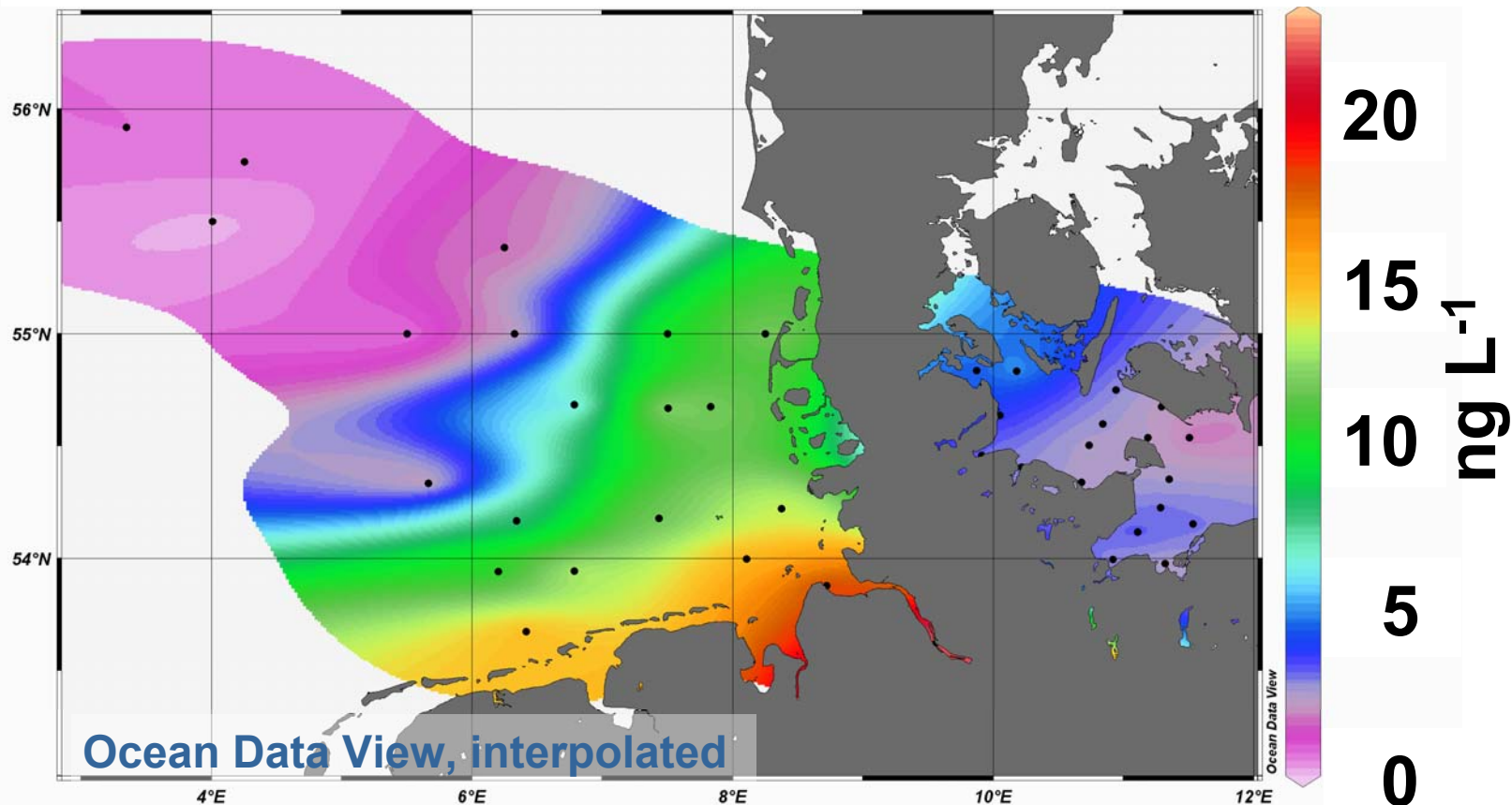
- Increasing concentrations of **PFHxS** between sampling station 4 and 5
- Strong increasing concentrations of **PFBA** and **PFBS** between Leverkusen and Duesseldorf

ΣPFC mass flow in g per day



Diploma work: Axel Möller

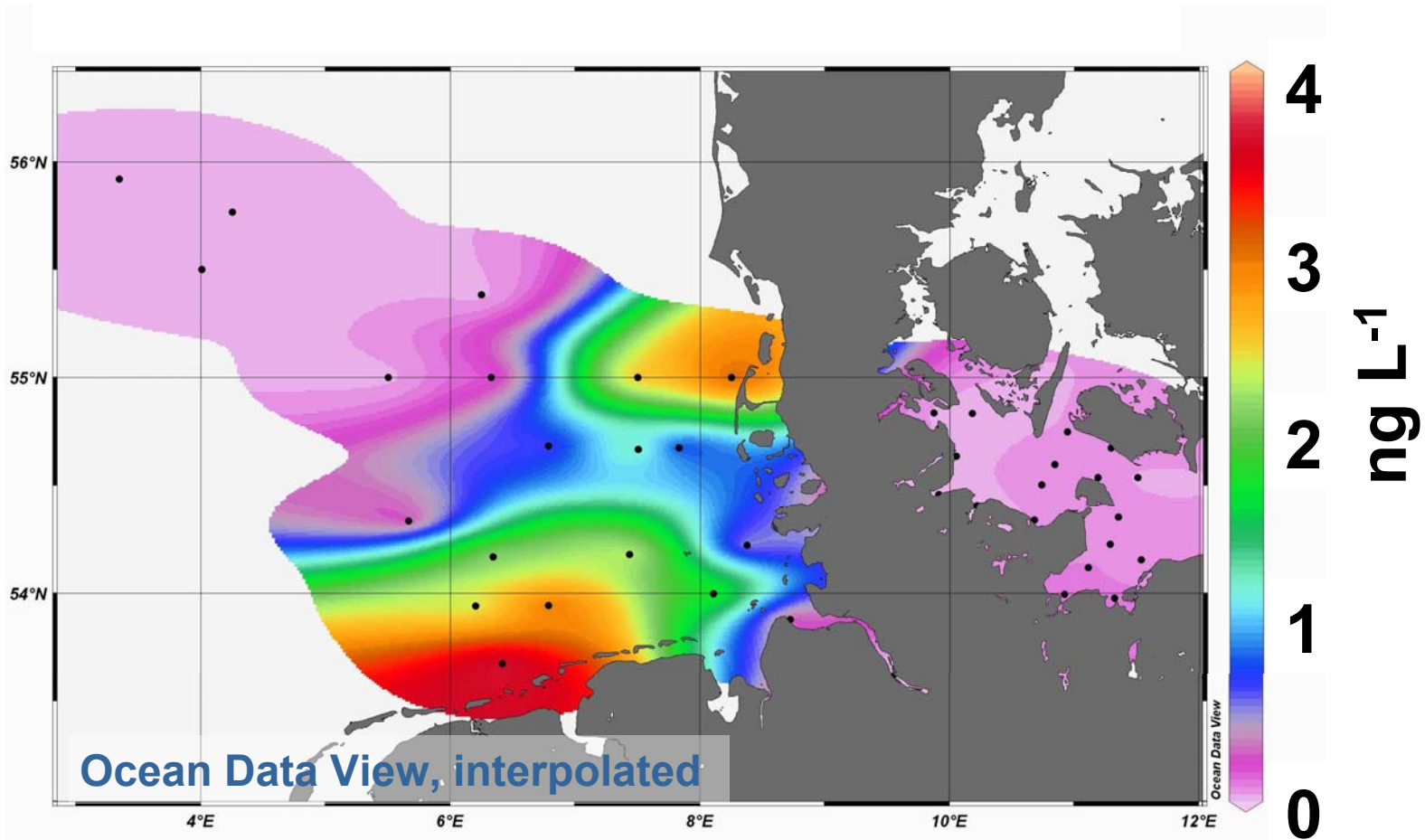
ΣPFC Concentrations in the North and Baltic Sea



- Conc. of ΣPFCs decrease towards the North Sea by a factor of **over 100**

Ahrens et al. *Marine Poll. Bull.*, submitted

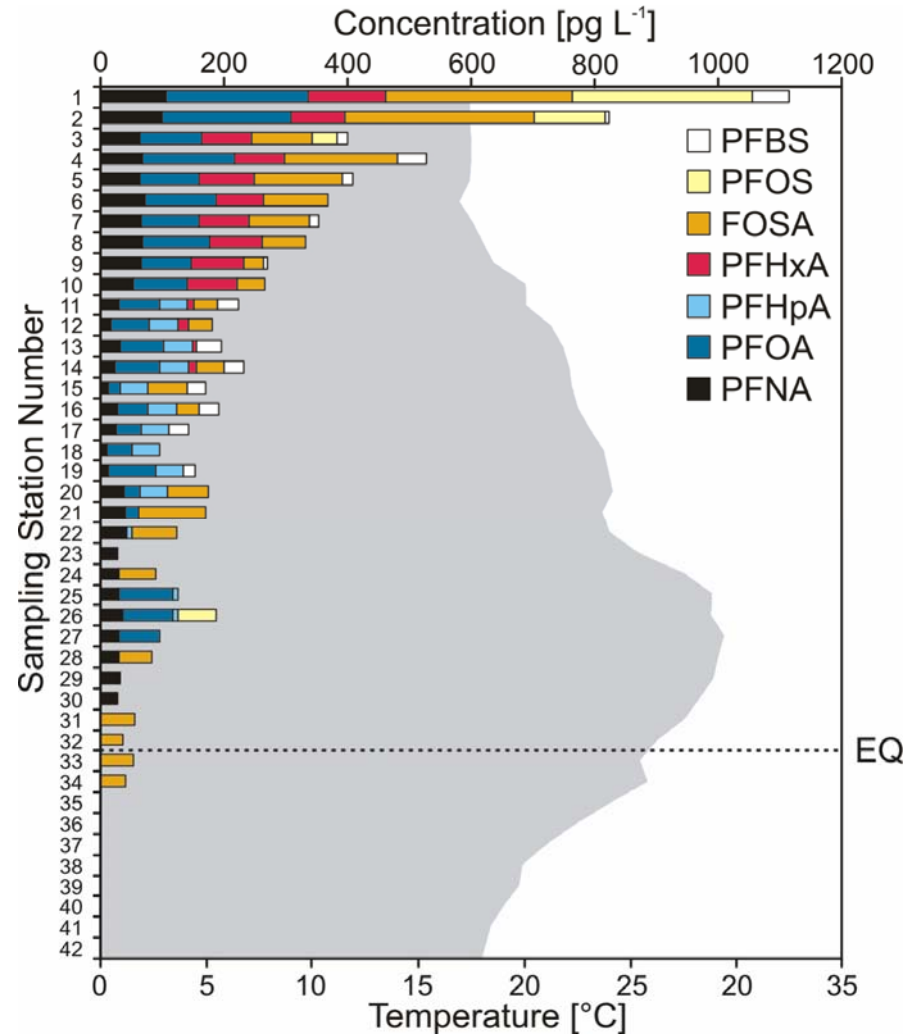
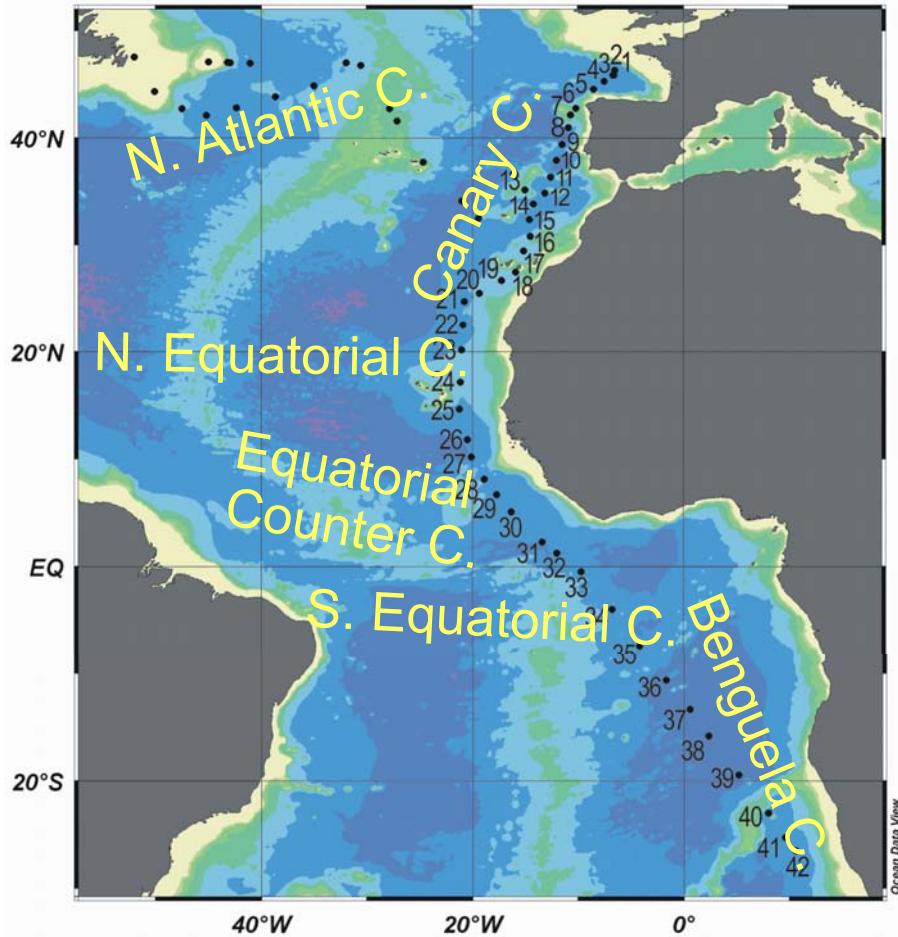
PFBA Concentration in the North- and Baltic Sea



- PFBA was possibly transported from the River Rhine in the German Bight

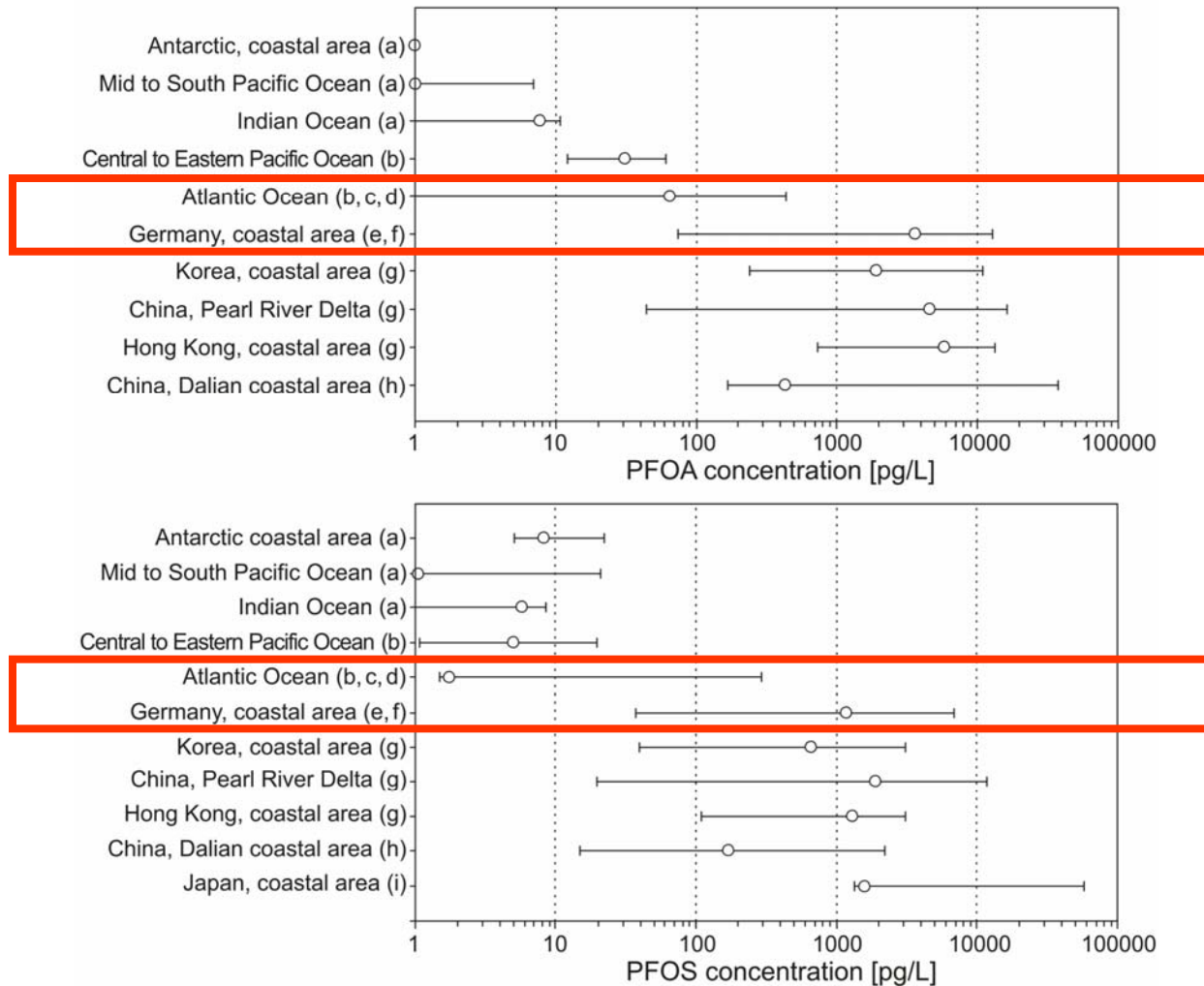
Ahrens et al. *Marine Poll. Bull.*, submitted

PFCs in Atlantic Ocean Surface Water (46°N-26°S)



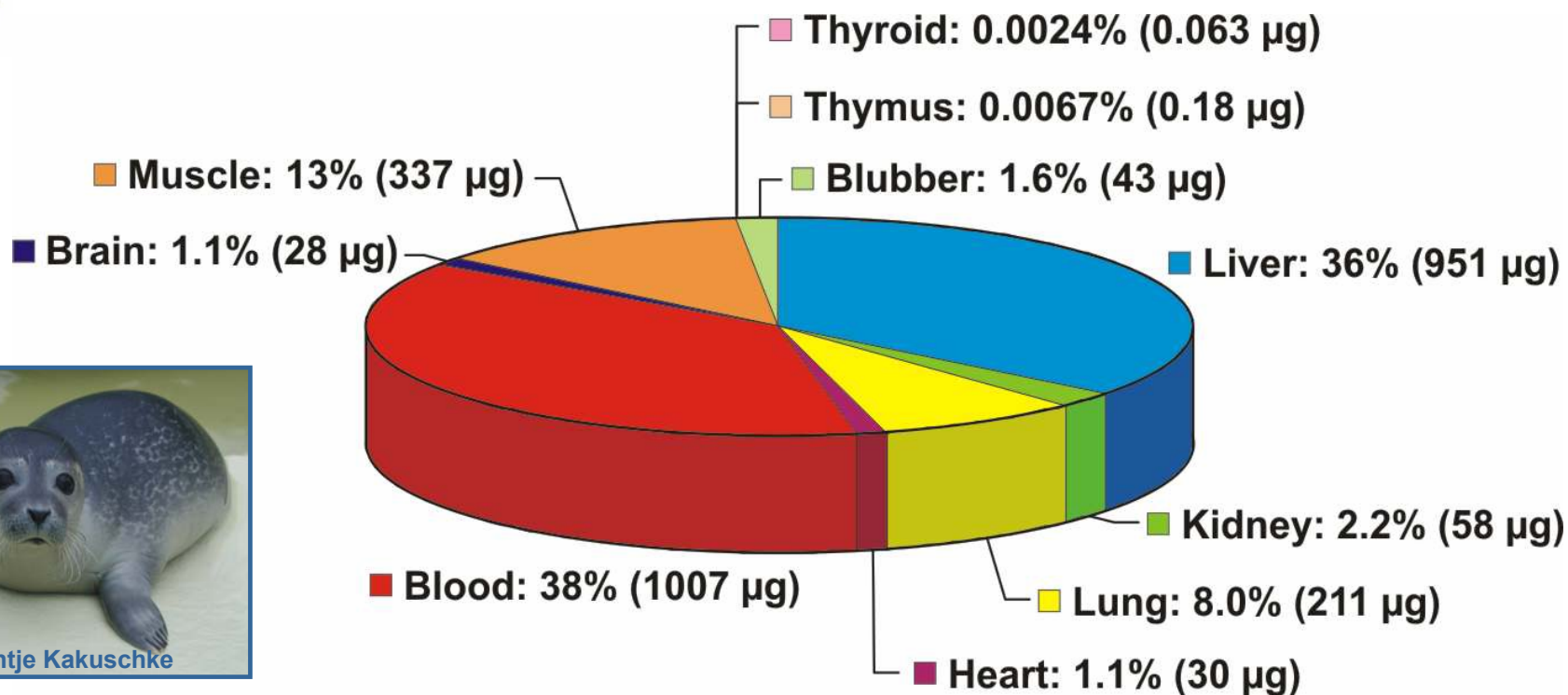
Ahrens et al. *ES&T*, 2009, in press

Overview of PFOA and PFOS in Seawater



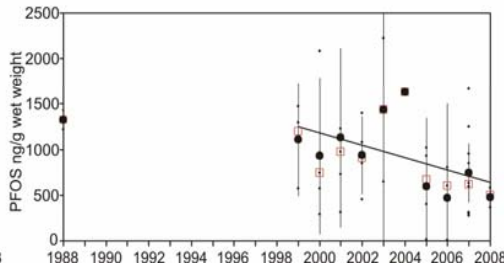
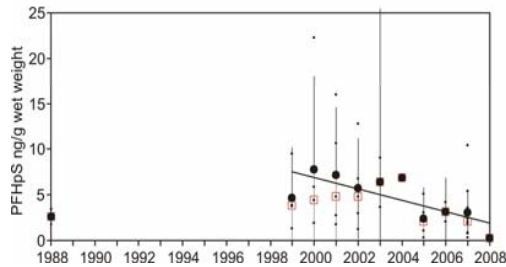
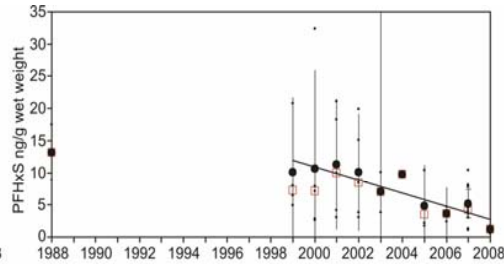
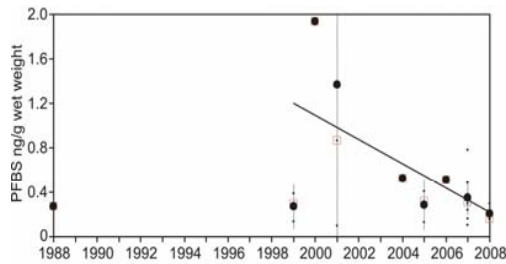
(a) Wei et al. 2008, (b) Yamashita et al. 2005, (c) Theobald et al. 2007b, (d) Ahrens et al. 2009, (e) Caliebe et al. 2004, (f) Ahrens et al. 2009, (g) So et al. 2004, (h) Ju et al. 2008 and (i) Taniyasu et al. 2003) in pg/L

Distribution of PFCs in Harbor Seals

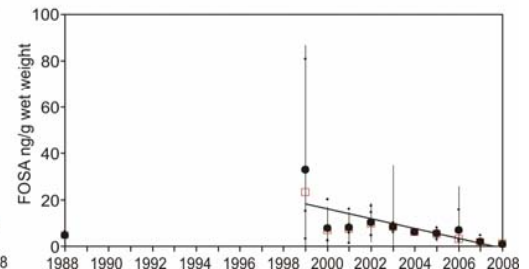
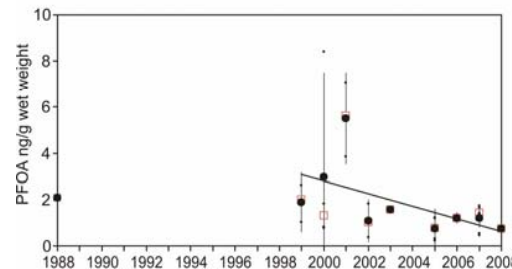
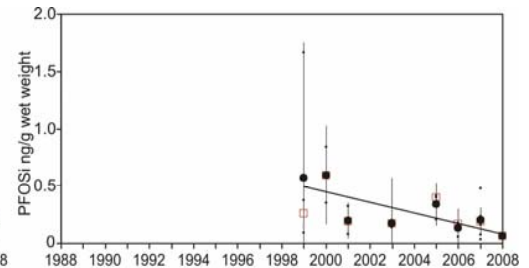
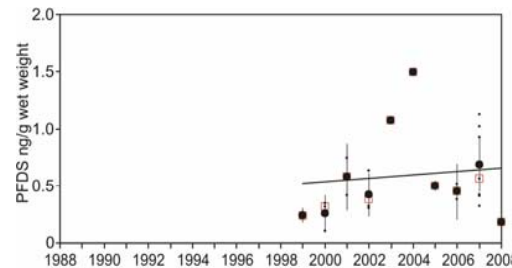


- **Two-third** of the PFCs are accumulated in **blood and liver**
- **PFOS** was the **dominating PFC** (~90% based on \sum PFCs)
- \sum PFCs total body burden: **2665 ± 1207 µg absolut** (n = 4)

Temporal Trend of PFCs in Harbor Seals, 1999-2008

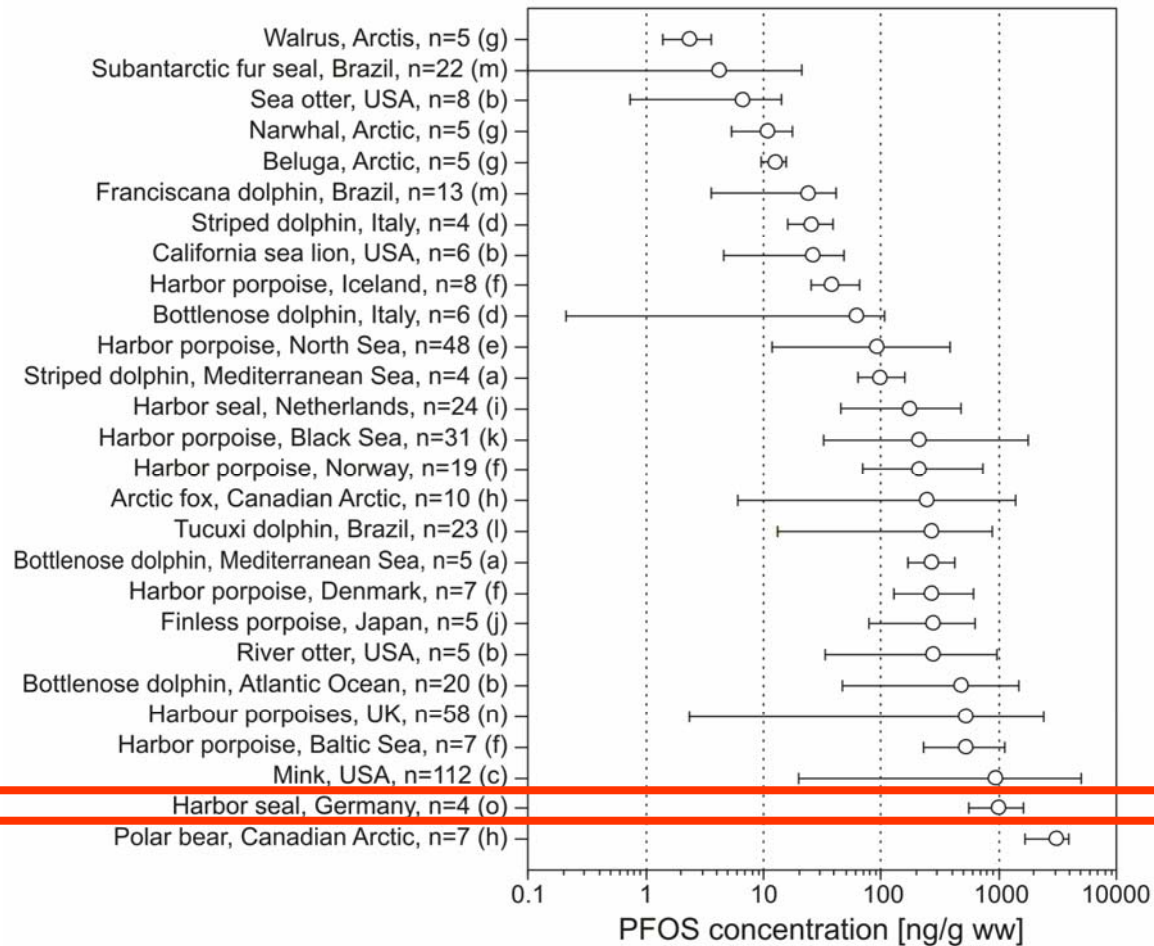


- Declining PFC contamination in harbor seals from the German Bight, Germany



Ahrens et al. *Chemosphere*, in press

Overview of PFOS in Mammals



(a) Tomy et al. 2004a, (b) Leonel et al. 2008, (c) Kannan et al. 2001b, (d) Kannan et al. 2002b, (e) Van de Vijver et al. 2004, (f) Van de Vijver et al. 2003b, (g) Giesy and Kannan 2001, (h) Van de Vijver et al. 2005, (i) Van de Vijver et al. 2007, (j) Martin et al. 2004a, (k) Dorneles et al. 2008, (l) Nakata et al. 2006, (m) Law et al. 2008, (n) Kannan et al. 2002c, and (o) Ahrens et al. 2009 in ng/g ww

Summary

- **Different sources** of PFC contamination in the environment
 - **Conventional waste water treatment plants** are not effective for removal of PFCs from the waste water
 - The river **Elbe, Rhine** are local input sources for the North Sea
 - **But: Where is the origin of the contamination?**
- **Transportation pathways** of PFCs in the environment
 - **Long-range** transport via ocean currents and air
 - **But: What is the main transportation pathway (water or air) for individual PFCs?**
- **Ubiquitous** distribution of PFCs in the environment
 - Over **20** of 40 analysed PFCs were found in water and biota
 - **But: Do presently unknown fluorinated compounds exist?**
- **Composition profile** of PFCs
 - **Replacement** of the **C₈** PFCs (**PFOS** and **PFOA**) by the **C₄** compounds **PFBA** and **PFBS** in the industry
 - **Biota**: especially **long** chain PFCs and **PFOS**
 - **But: Can we localize the source when we know the compound pattern?**
- **Bioaccumulation** of PFCs in the marine food web
 - Accumulation of PFCs (→ **PFOS**) in mammals (→ **blood, liver**) (**also in humans!**)
 - **But: What is the toxicity of individual and sum PFCs?**
- **Temporal and spatial trends** of PFCs
 - **Decreasing** PFC concentrations in the German Bight
 - **But: What temporal and spatial trends do we have in other parts of the world?**

Summary Thoughts...

- Which PFAs, ‘precursors’ and ‘degradation intermediates’ are of **greatest interest**? Existence of other **unknown** PFCs?
- **Sources** and **main transport pathways** of PFCs in the environment?
- Which **waste water treatment system** is most effective for removal of PFCs?
- **Spatial distribution** of PFCs in the environment?
- **Production volume** of the different PFCs?
- **Usage** and **application pattern** of PFCs? Which PFCs?
- **Policy** and **law regulations**?

Thank you for your attention!

