Institute of Coastal Research

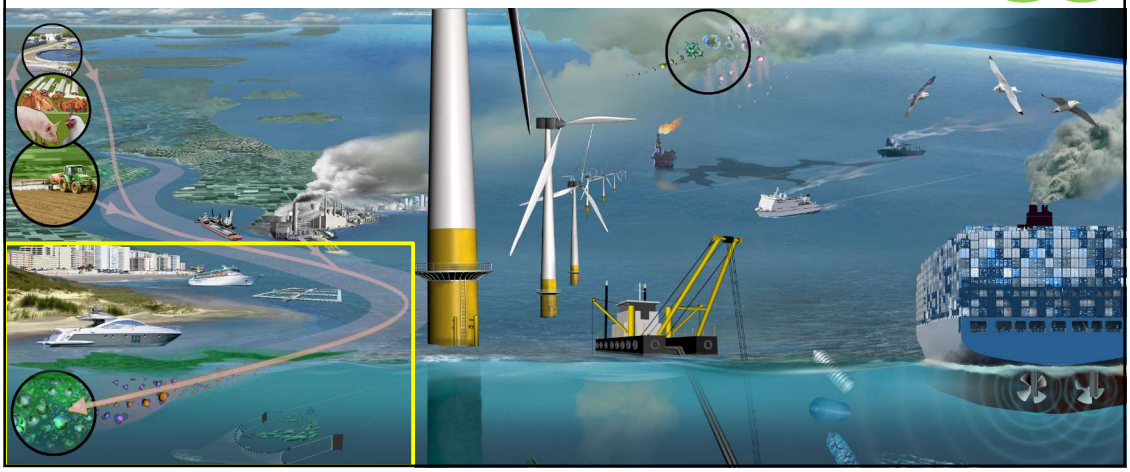
Research Unit *Biogeochemistry in Coastal Seas*

Helmholtz-Zentrum Geesthacht
Centre for Materials and Coastal Research

Emerging contaminants in the catchment-to-sea continuum – Environmental regulations and changes in pollution status

Hanna Joerss – PhD candidate, Universität Hamburg

RU 2 | Topic 2



Organic pollutants in coastal oceans

Helmholtz-Zentrum Geesthacht
Centre for Materials and Coastal Research

- Investigation of coastal areas and catchments as input pathways for pollutants into the marine environment
- Focus on persistent organic pollutants with a potential for long-range transport

? Occurrence, sources, transport and fate
Change of pollution status due to regulations
Scientific basis for future regulations

- Current emphasis on emerging substances like
  - Per- and polyfluoroalkyl substances (PFAS)
  - Alternative flame retardants (aFRs, e.g. aBFRs and OPEs)
  - UV stabilizers and UV filters

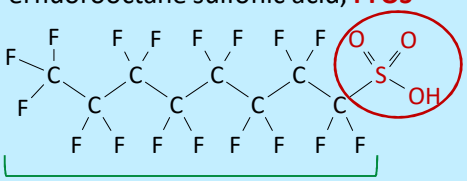
PFAS – properties and uses

Helmholtz-Zentrum Geesthacht
Centre for Materials and Coastal Research

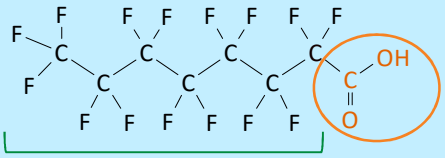
PFAS = **P**er- and Poly**f**luoro**a**lkyl **S**ubstances

fully or partially fluorinated alkyl chain

Perfluorooctane sulfonic acid, **PFOS**



Perfluorooctanoic acid, **PFOA**



hydrophobic fluorinated chain

hydrophilic functional group

- Water-, oil- and dirt-repellent
- High thermal, photolytic and chemical stability
- Wide range of application areas

PFAS – substances of high concern

Helmholtz-Zentrum Geesthacht
Centre for Materials and Coastal Research

! **PFOS** and **PFOA**: global contaminants of high concern

- persistent
- bioaccumulative
- toxic
- undergo long-range transport

➡ **Actions** by industry and regulatory authorities

- **2006** US EPA 2010/2015 **PFOA** Stewardship Program
- **2009** **PFOS** added to Annex B of Stockholm Convention
- **2013** **PFOA** included in candidate list of substances of very high concern under REACH
- **Ongoing** evaluation of **PFOA** under Stockholm Convention

Point of departure

Helmholtz-Zentrum Geesthacht
Centre for Materials and Coastal Research

? Effects of environmental regulations and industry initiatives on pollution status of the catchment-to-sea continuum

- Transition to an unknown amount of less investigated alternatives?
- Differences between developed and developing countries?

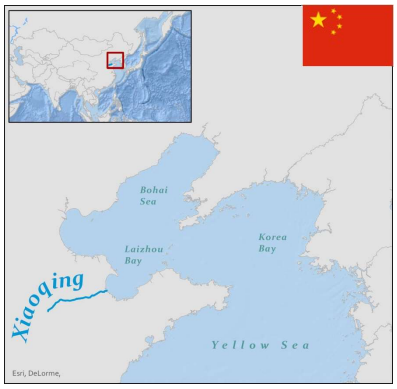
Our PFAS Portfolio

- 38 legacy and 8 alternative PFAS
- Large variety of matrices
- Samples from
  - industrialized regions (Europe, China)
  - high altitude environments (Alps, Tibet)
  - remote marine areas (Atlantic, Pacific)
  - polar regions (Arctic, Antarctica)

© Christian Schmid/HZG © Hannes Grobe/AWI[1]

Sampling locations

Helmholtz-Zentrum Geesthacht
Centre for Materials and Coastal Research

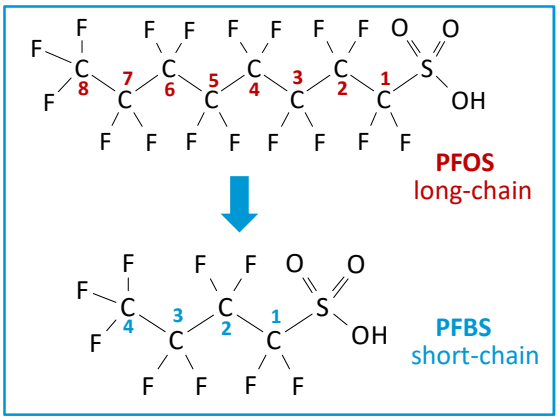


- North Sea including its catchments
- Comparison to China in cooperation with Yantai Institute of Coastal Zone Research
  → major production sites of fluoropolymer industry
  → less regulated

Effects of regulations – shift to alternatives

Helmholtz-Zentrum Geesthacht
Centre for Materials and Coastal Research

1) Shift to short-chain homologues

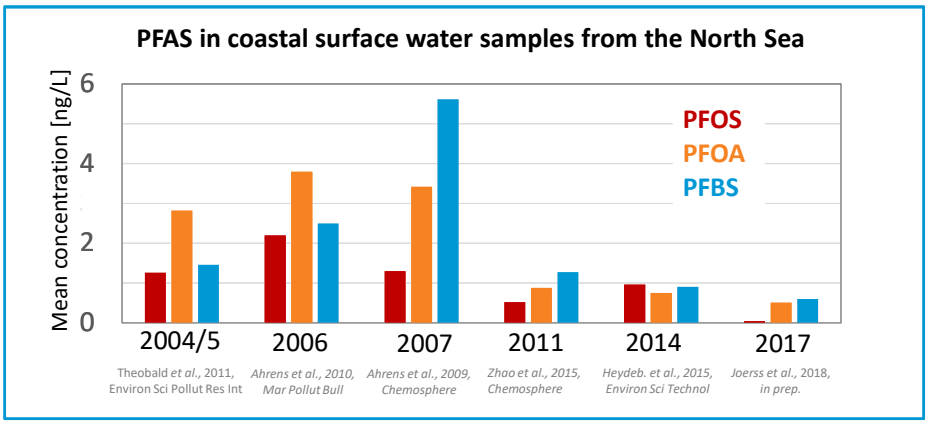


- **Short-chain PFAS:** less toxic and bioaccumulative, **but**
  - more soluble and mobile
  - larger quantities needed

Effects of regulations – shift to alternatives

Helmholtz-Zentrum Geesthacht
Centre for Materials and Coastal Research

1) Shift to short-chain homologues

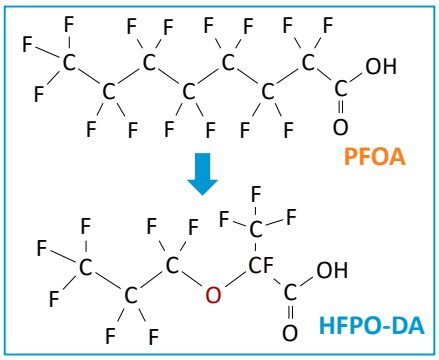


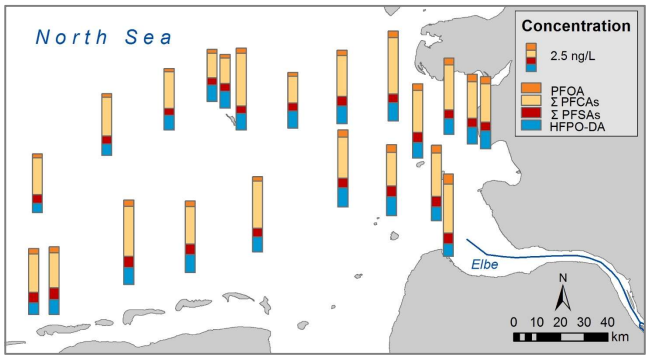
- Decreasing levels of regulated long-chain PFAS **PFOS** and **PFOA** in samples taken after 2006
- Increase of short-chain compound **PFBS** from 2005 to 2007; decreased concentration in samples taken from 2011 onwards

Effects of regulations – shift to alternatives

Helmholtz-Zentrum Geesthacht
Centre for Materials and Coastal Research

2) Shift to PFAS with different functionalities





Joerss et al., 2018, in prep.

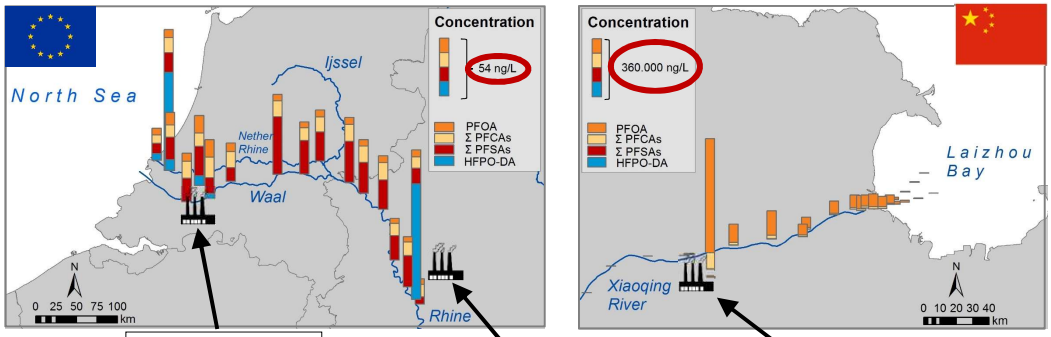
- Fluorinated alternative **HFPO-DA** already one of the dominating PFAS in the German Bight today
- Concerns about replacements
  - similar structures
  - limited data

} problem just shifted ?

Effects of regulations – geographical shift

Helmholtz-Zentrum Geesthacht
Centre for Materials and Coastal Research

Riverine fingerprints of catchments



- Identification of point sources in European and Chinese catchments
- PFAS concentrations several orders of magnitude higher in China
  - PFOA up to 6000 x
  - HFPO-DA 42 x

} higher in comparison to Rhine-Meuse delta

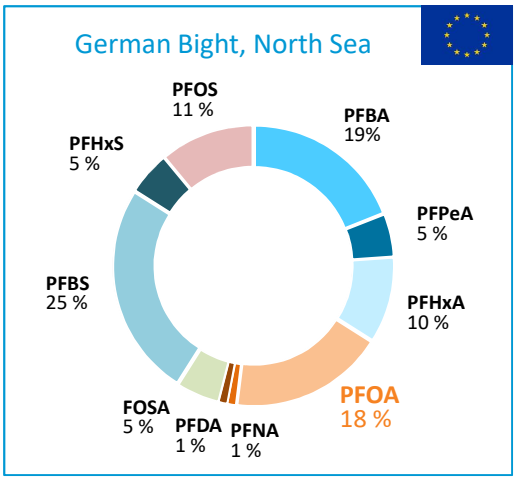
- Significant differences in substance pattern

Heydebreck et al., 2015, Environ Sci Technol

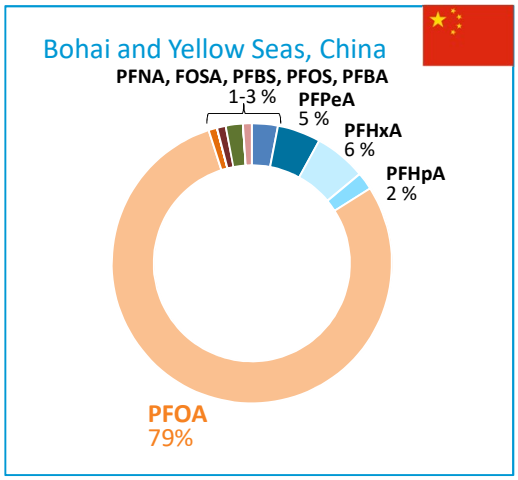
Effects of regulations – geographical shift

Helmholtz-Zentrum Geesthacht
Centre for Materials and Coastal Research

Substance pattern of legacy PFAS in coastal surface waters



Zhao et al., 2015, Chemosphere



Zhao et al., 2017, Sci Total Environ

- Long-chain compound **PFOA** dominating in Chinese seas

Summary and conclusion

Helmholtz-Zentrum Geesthacht
Centre for Materials and Coastal Research

- Data show changes in pollution status of coastal and marine environment as a consequence of regulations exemplified by PFAS
  - shift to alternative substances
  - geographical shift
- Exposure of the environment to controversially discussed replacements demonstrates necessity to evaluate these substances regarding future regulations
- Legacy pollutants which are regulated in Europe or internationally are still highly relevant in countries with lower environmental standards

Data publicly available via coastMap

References

Ahrens, L.; Felizeter, S.; Ebinghaus, R. (2009): Spatial distribution of polyfluoroalkyl compounds in seawater of the German Bight. *Chemosphere* 76: 179–184.

Ahrens, L.; Gerwinski, W.; Theobald, N.; Ebinghaus, R. (2010): Sources of perfluoroalkyl compounds in the North Sea, Baltic Sea and Norwegian Sea: Evidence from their spatial distribution in surface water. *Marine Pollution Bulletin* 60: 255–260.

Heydebreck, F.; Tang, J.; Xie, Z.; Ebinghaus, R. (2015): Alternative and legacy perfluoroalkyl substances: Differences between European and Chinese river/estuary systems. *Environmental Science & Technology* 49: 8386–8395.

Theobald, N.; Caliebe, C.; Gerwinski, W.; Hühnerfuss, H.; Lepom, P. (2011): Occurrence of perfluorinated organic acids in the North and Baltic seas. Part 1: distribution in sea water. *Environmental Science and Pollution Research* 18: 1057–1069.

Zhao, Z.; Xie, Z.; Tang, J-H.; Sturm, R.; Chen, Y-J.; Zhang, G.; Ebinghaus, R. (2015): Seasonal variations and spatial distributions of perfluoroalkyl substances in the rivers Elbe and lower Weser and the North Sea. *Chemosphere* 129: 118–125.

Zhao, Z.; Tang, J.; Mi, L.; Tian, C.; Zhong, G.; Zhang, G.; Wang, S.; Li, Q.; Ebinghaus, R.; Xie, Z.; Sun, H. (2017): Perfluoroalkyl and polyfluoroalkyl substances in the lower atmospheres and surface waters of the Chinese Bohai Sea, Yellow Sea, and Yangtze River Estuary. *Science of the Total Environment* 599–600: 114–123.

Pictures

[1] Polarstern (slide 5): Hannes Grobe, Alfred Wegener Institute - Self-published work, CC BY-SA 2.5, URL: https://commons.wikimedia.org/w/index.php?curid=731714 (accessed: 03/01/2018)