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25.01.2018

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Content

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Emerging contaminants in the coastal and marine environment - Organic UV stabilizers in European and Chinese sediments

Helmholtz-Zentrum Geesthacht
Centre for Materials and Coastal Research

Christina Apel, Jianhui Tang, Hendrik Wolschke, Riccardo Massei, Ralf Ebinghaus

Introduction & Objectives

Organic UV stabilizers are of emerging concern due to

- their large production volumes
- potential for persistence or pseudo-persistence
- potential endocrine disrupting properties

They are widely used in

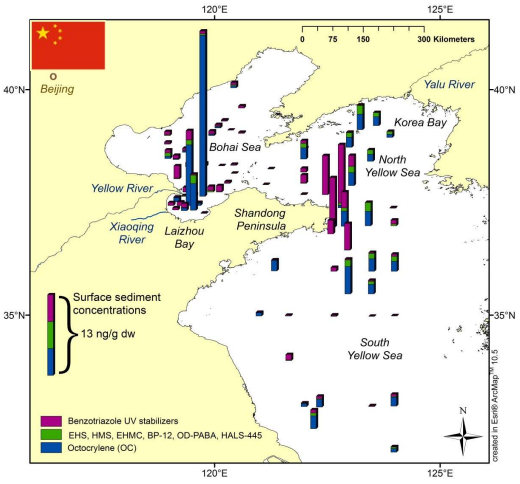
- plastics and other industrial products
- personal care products like cosmetics and sunscreens

Information on the occurrence of UV stabilizers in the coastal and marine environment is sparse. This study for the first time investigates environmental levels of UV stabilizers in the coastal and marine environment in Europe and in China. A comparison is presented between these regions i) Europe with a long industrial history, highly regulated nowadays and ii) China with a rapidly growing, less regulated industry.

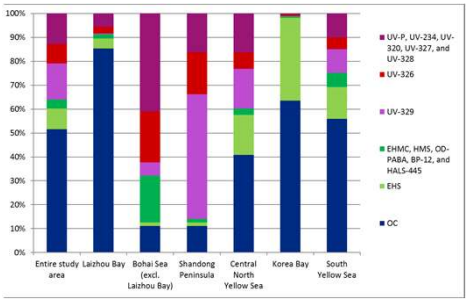
Methodology

Sampling → Freeze-drying and homogenization → ASE extraction and in-cell cleanup → Volume reduction to 150 µL → LC-MS/MS analysis

Results



UV stabilizer concentrations in the surface sediment of Chinese Bohai and Yellow Seas (Apel et al., 2018).

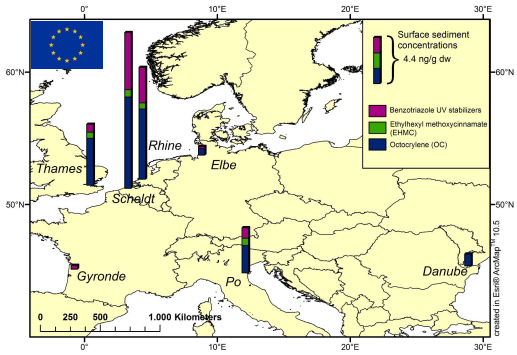


Composition profiles of UV stabilizers in different regions of Chinese Bohai and Yellow Seas (Apel et al., 2018).

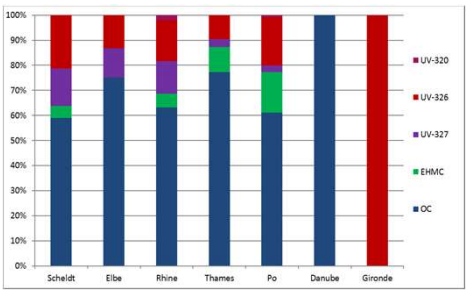
- Environmental levels, pollution profiles, and distribution pattern of organic UV stabilizers were revealed for the first time in European estuaries and Chinese Bohai and Yellow Seas.
- UV stabilizers occur ubiquitously over the entire sampling areas, underlining the importance of further investigations of their impact on these ecosystems.

Organic UV stabilizers in the sediment of Chinese Bohai and Yellow Seas and seven European estuary systems

- UV stabilizers were positively detected in all analyzed sediment samples.
- In the Chinese Bohai and Yellow Seas, characteristic pollution profiles and distribution pattern have been identified. They suggest that these regions are contaminated mainly by indirect sources via riverine inputs.
- In Europe, highest concentrations were found in the Scheldt estuary and Rhine delta. Both rivers are heavily influenced by industry.
- In contrast to other contaminants such as PFASs, environmental levels of UV stabilizers in European estuary systems and the Chinese Bohai and Yellow Seas were in the same concentration range.
- All data will be made publicly available via coastMap
- Next, UV stabilizers will be analyzed in the sediment of the North and Baltic Seas for a comparative study of UV stabilizers in the four seas.



Average UV stabilizer concentrations in the surface sediment of European estuary systems (Apel et al., 2016).



Composition profiles of UV stabilizers in different European estuary systems (Apel et al., 2016).

Publications

Apel, C.; Wolschke, H.; Massei, R.; and R. Ebinghaus (**2016**), *Mitt Umweltchem Ökotox* 3: 63-66.

Apel, C.; Tang, J.; and R. Ebinghaus (**2018**), *Environmental Pollution* 235: 85-94.

Emerging contaminants in the coastal and marine environment – Alternative flame retardants in European, Chinese and Arctic air

Helmholtz-Zentrum Geesthacht
Centre for Materials and Coastal Research

Jing Li, Zhiyong Xie, Wenying Mi, Chongguo Tian, Kay-Christian Emeis, Ralf Ebinghaus

Introduction & Objective

Organophosphate esters (OPEs) are widely used as

- flame retardants (FRs) in plastics, furniture, textile, electric equipment
- replacement substances for regulated/banned FRs, such as PBDEs

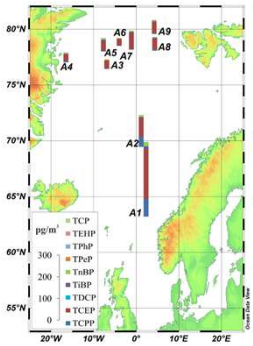
OPEs are of emerging concern because

- their global consumption is rapidly increasing
- they have carcinogenic potential
- they are highly water soluble
- they are persistent and have long life-times in the coastal and marine environment

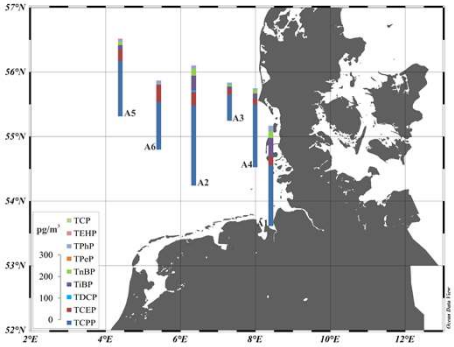
For a more holistic view of OPEs in the coastal zone we combine own experimental data with different models for an improved understanding of the interactions between the gaseous and particulate phases.

We identify and evaluate OPE-fingerprints in the coastal ocean and their long-range transport potential in the North Sea and the North Atlantic, as well as in the Arctic. We compared OPEs in European coastal regions (North Sea) with East Asia (Bohai and Yellow Seas, China).

Experimental Results



Spatial distribution of OPEs in air of the North Atlantic and Arctic



Spatial distribution of OPEs in air of the North Sea (Möller et al., 2011)

OPEs in the atmosphere:

North Sea to the Arctic

Decreasing trend from the North Sea to the Arctic

TCPP dominating in the North Sea, due to regulation of TCEP

TCEP dominating in the European Arctic, indicating higher persistence

Bohai and Yellow Seas

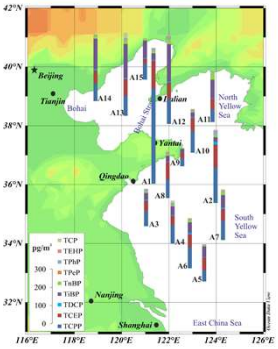
TCEP, TCPP and TiBP dominating

No regulations in China on OPEs

Similar ∑OPE concentrations compared with the North Sea

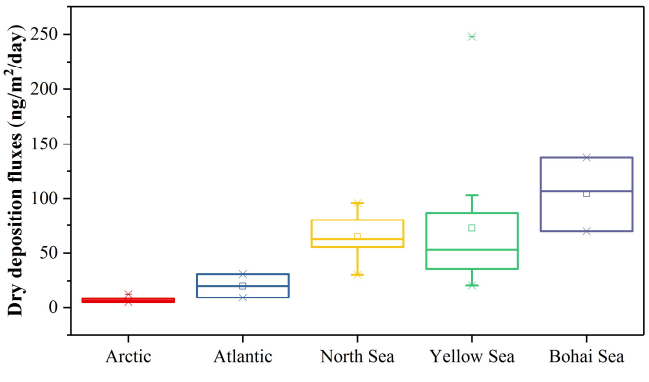
North Sea: 390 ± 120 pg/m³

Bohai and Yellow Sea: 320 ± 160 pg/m³

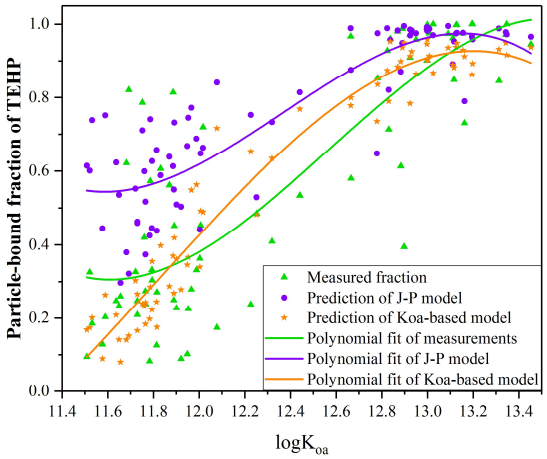


Spatial distribution of OPEs in air of the Bohai and Yellow Seas, China

Modelling Results



Dry deposition fluxes of OPEs



Comparison of predicted and measured particle-bound fraction of OPEs

Dry deposition

- Similar dry deposition fluxes in the North Sea and Yellow Sea
- Higher fluxes in Bohai Sea, and much lower in the Atlantic and Arctic
  - North Sea: 62 ± 22 ng/m²/day; Yellow Sea: 71 ± 61 ng/m²/day
  - Bohai Sea: 105 ± 34 ng/m²/day
  - North Atlantic: 20 ± 15 ng/m²/day; Arctic: 7 ± 3 ng/m²/day

Gas/particle partitioning

- OPEs have low potential to achieve equilibrium between gaseous and particulate phases
- Koa-based model and J-P model perform well for TPhP and TEHP because of their pronounced temperature-dependent partitioning behaviour
- More suitable gas/particle partitioning models are necessary for other OPEs

Publications

Li, J.; Tang, J.; Mi, W.; Tian, C.; Emeis, K.-C.; Ebinghaus, R., Xie, Z. (**2017**): Spatial distribution and seasonal variation of organophosphate esters in the air above the Bohai and Yellow Seas, China. *Environ. Sci. Technol. 52: 89-97.*

Li, J.; Xie, Z.; Mi, W.; Lai, S.; Tian, C.; Emeis, K.-C.; Ebinghaus, R. (**2017**): Organophosphate Esters in Air, Snow and Seawater in the North Atlantic and the Arctic. *Environ. Sci. Technol. 51: 6887-6896.*

- OPE concentrations are 1-2 orders of magnitude higher than for PBDEs and different finger-prints are found in European and Chinese coastal waters
- Modelling the partitioning behavior reveals long-range transport potential to the Arctic

Emerging organic contaminants in the Arctic – Impacts of human activities and climate change

Zhiyong Xie, Jing Li, Ralf Ebinghaus

Helmholtz-Zentrum Geesthacht
Centre for Materials and Coastal Research

Introduction & Objectives

Emerging organic contaminants (EOCs) may reach ecologically sensitive Arctic environments via atmospheric and oceanic long range transport. In cooperation with AWIPEV (Fig.1) we have compiled **the first multi-annual, year-round Arctic time series** for a large number of EOCs since 2011. Concentrations of organophosphate esters (OPEs), dechlorane plus (DPs) and brominated flame retardants (BFRs) in the atmosphere in Ny-Alesund, Arctic are presented.

The objectives of this work are focused on

- screening of new chemicals, e. g. alternative flame-retardants (BFR, OPE, DP) and endocrine disrupting chemicals in Ny-Alesund
- modeling air-sea/snow exchange fluxes in the Arctic
- evaluating the impact of climate change on the remobilization of emerging organic contaminants in polar regions.

Method: Air sampling and analysis

High-volume air samples were collected with an air pump placed on the platform for atmospheric observatory of German station (Fig. 2). Air pump was operated at 15 m^3/h for 7 days to reach a sample volume of 2500 m^3.

- PUF/XAD-2 resin column was used to trap the EOCs in gaseous phase and glass fiber filter was used to collect atmospheric particles.
- XAD-2 based passive air sampler was used to monitor the background of the station (Fig. 3).

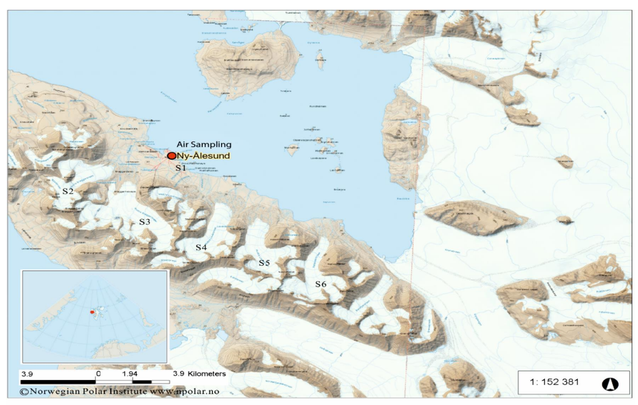


Fig. 1. Map for air sampling at Ny-Alesund, Arctic

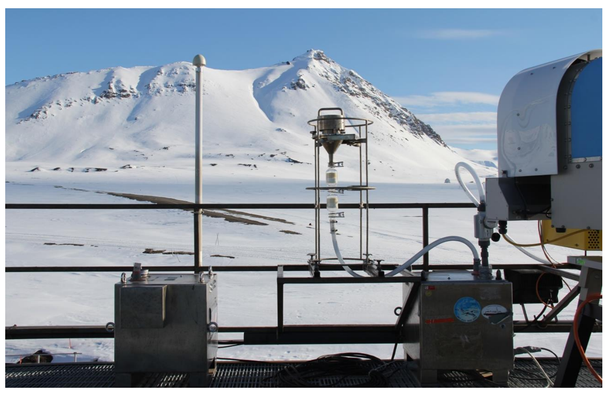


Fig. 2. Air sampling on German Atmospheric Observatory

Fig. 3. Passive air sampling in Ny-Alesund

Result: BFRs and DPs in Arctic air

- **PBDEs:** the pattern showed the predominance of BDE-47 (0.03-2.4 pg/m^3) and BDE-99 (0.02-1.2 pg/m^3) due to their persistence in the environment.
- Significantly high concentrations were present in spring/summer of 2011, which may has been caused by meteorological conditions.
- **HBB** is the major component (0.11-8.3 pg/m^3) among the alternative BFRs selected and its concentrations were higher than BDE-47.
- **BFRs and DPs** showed clearly seasonal variation, e.g relatively low level in Polar night and elevated concentrations in Arctic summer.

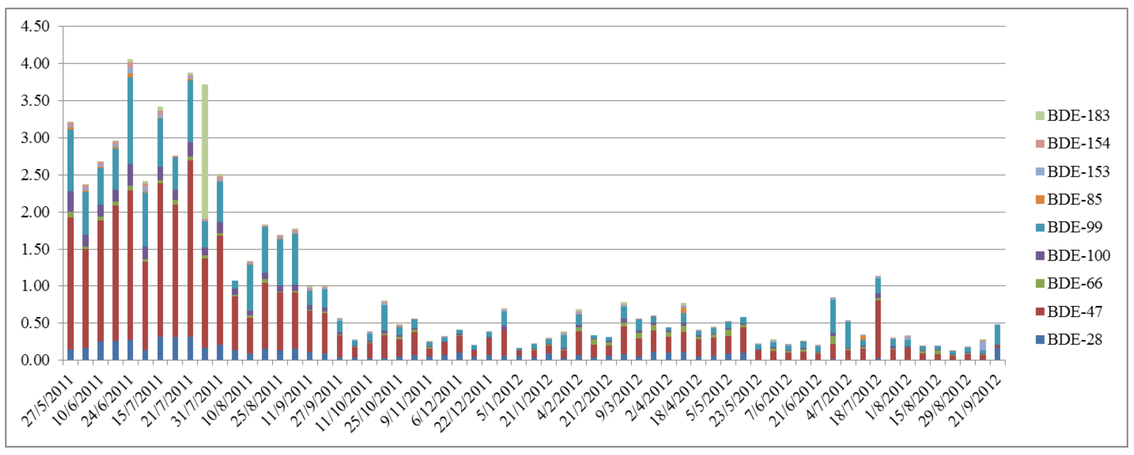


Fig. 4. PBDE (pg/m^3) in Arctic air

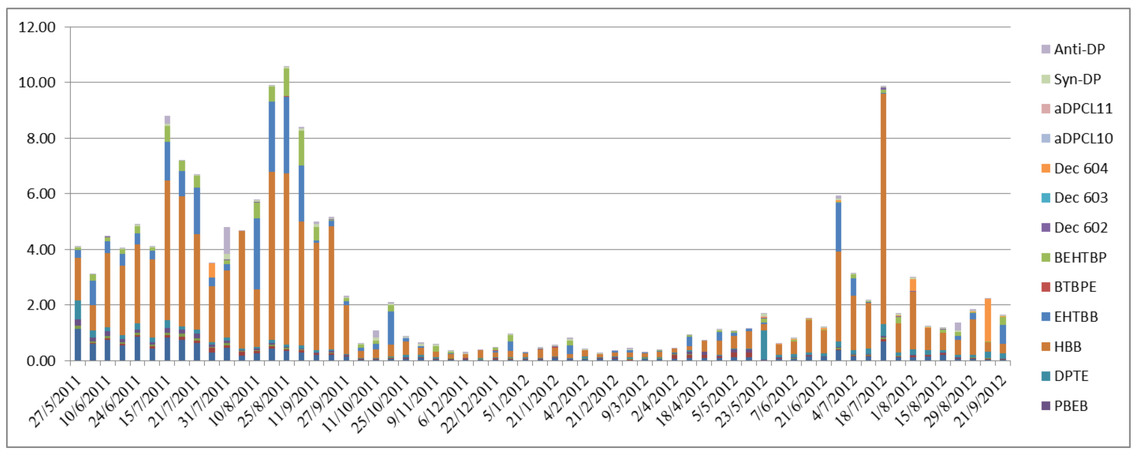


Fig. 5. Composition profile DPs and a-BFRs in Air of Ny-Alesund

Result: OPEs in Arctic air

- Total OPE concentrations (ΣOPEs) ranged from 41 to 1070 pg/m^3.
- Chlorinated OPEs, e.g TCPP and TCEP were the dominant species, which accounted for more than 80% of the ΣOPEs.
- OPEs showed seasonal trends with lower concentration in winter and elevated concentrations from spring to summer.

- Arctic snow and ice can act as a secondary source and release EOCs into the atmosphere during the melting process.
- Alternative BFRs and chlorinated OPEs, e.g. HBB, TCCP and TCEP, are persistent in the Arctic, suggesting more research is required to elucidate their bioaccumulation and toxicity in the Arctic ecosystem.

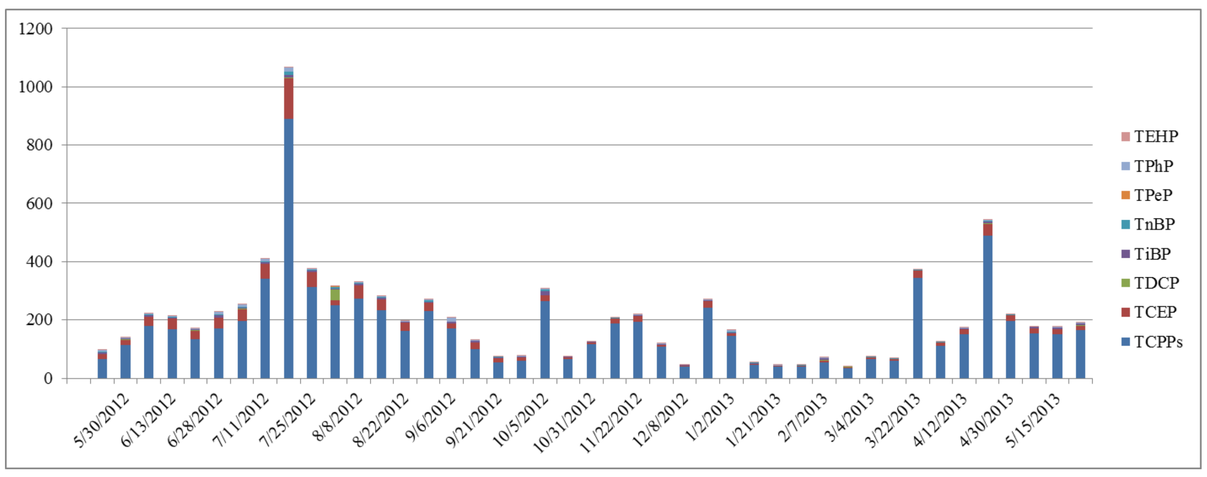


Fig. 6. OPE concentrations (pg/m^3) in Arctic air

Result: Atmospheric deposition flux

The atmospheric particle-bound deposition of ΣOPEs ranged from 4.2 to 8700 ng/m^2/year.
The deposition fluxes of ∑BFR+DP ranged from 0.0005 to 10 ng/m^2/year.

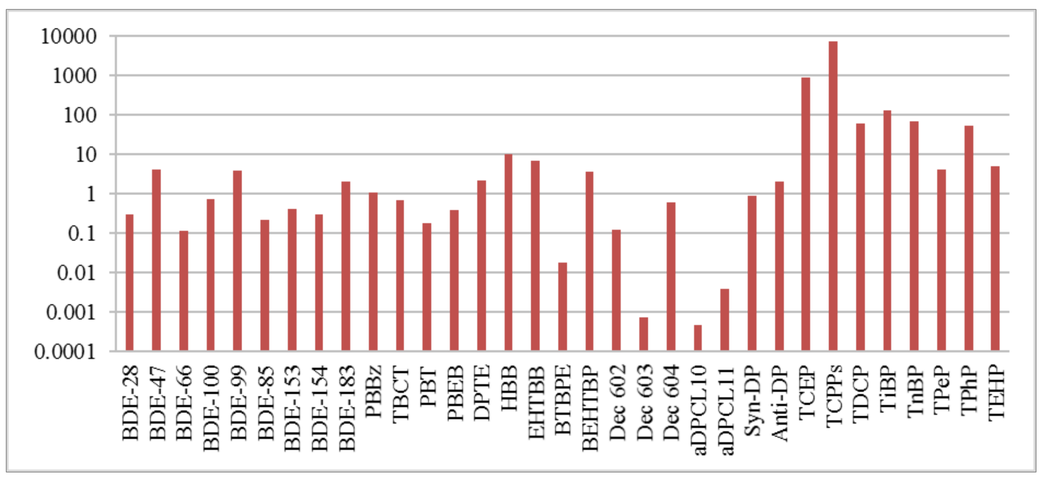


Fig. 7. Atmospheric deposition flux (ng/m^2/year) in the Arctic

Publications

Xie, Z., Wang, Z., Mi, W., Möller, A., Wolschke, H., Ebinghaus, R. (**2015**): Neutral Poly-/perfluoroalkyl Substances in Air and Snow from the Arctic. *Scientific Reports* 5: 8912.
Li, J., Xie, Z., Mi, W., Lai, S., Tian, C., Emeis, K., Ebinghaus, R. (**2017**): Organophosphate Esters in Air, Snow and Seawater in the North Atlantic and the Arctic. *Environmental Science and Technology* 51: 6887-6896.

Impact of different river catchments on the distribution and fate of inorganic contaminants in coastal zones

Anna Reese, Johanna Irrgeher, Tristan Zimmermann, Daniel Pröfrock

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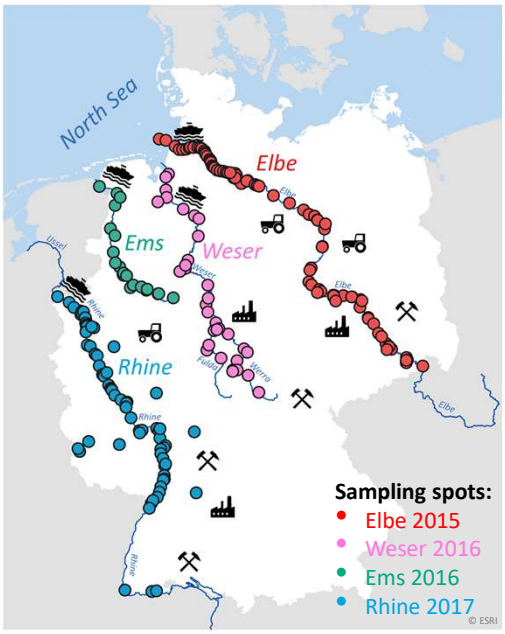
Introduction

The North Sea and its southeastern coastal zones have been affected by pollutants over decades. This is due to various anthropogenic activities in the catchments of the four rivers **Rhine**, **Ems**, **Weser**, and **Elbe** that discharge into this complex ecosystem. The river catchments are highly impacted by anthropogenic activities, which define their individual pollution fingerprint.

- **Novel tools for multielement and isotopic tracer analysis**
- **First in depth characterisation of large catchments**

➔ **Identification of sources, transport pathways and sinks of matter and contaminants**

	Rhine	Ems	Weser	Elbe
source	Switzerland	Germany	Germany	Czech Republic
mouth	Netherlands	Germany	Germany	Germany
length	1233 km (second longest in Central Europe)	371 km	451 km	1094 km (fourth longest in Central Europe)
major impacts	chemical industries, mining, important trade route	major German shipyard in estuary, shipping route, connected to Rhine	highly polluted by potash salt industry, shipping lane, Ports of Bremen	Port of Hamburg, important shipping route, mining



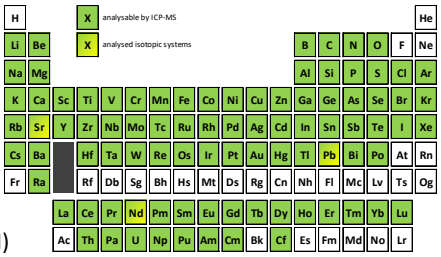
Approaches

Tracers for anthropogenic and geogenic processes

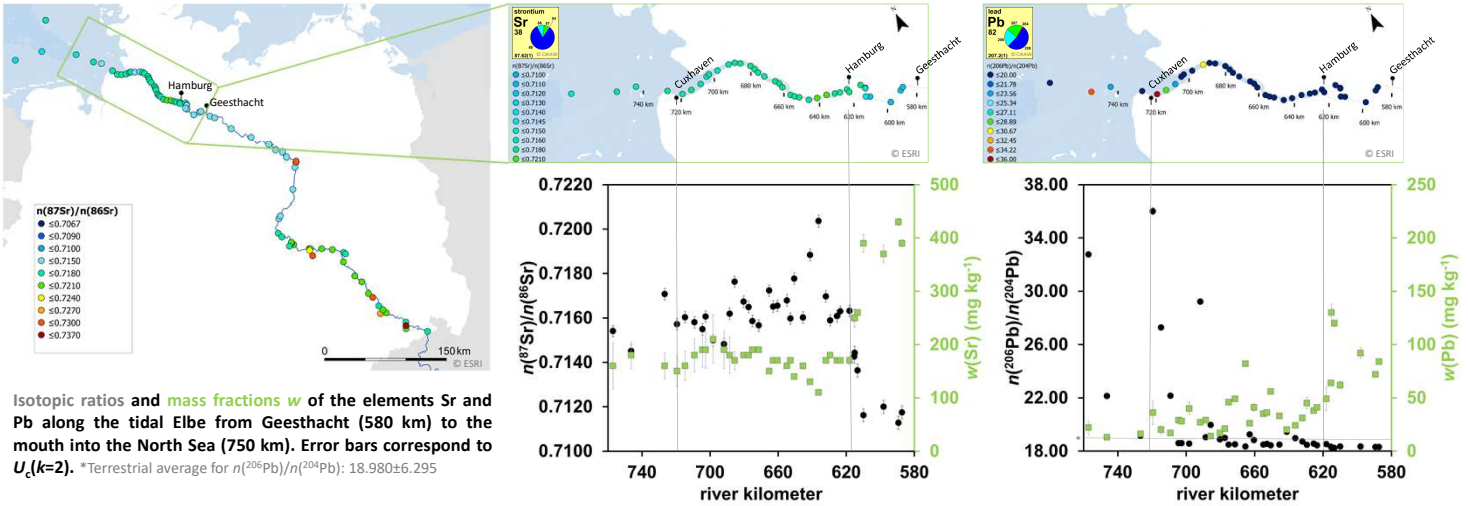
- multielemental concentration patterns
- non-traditional stable isotopes

Statistical tools and data visualisation

- correlation and cluster analysis
- discriminant analysis
- georeferenced data visualisation (ArcGIS® by ESRI)



Selected inorganic tracers analysed in surface sediments from the tidal Elbe[1]



Isotopic ratios and mass fractions *w* of the elements Sr and Pb along the tidal Elbe from Geesthacht (580 km) to the mouth into the North Sea (750 km). Error bars correspond to $U_c(k=2)$. *Terrestrial average for $n(^{206}Pb)/n(^{204}Pb)$: 18.980±6.295

Results

- In the very dynamic area of the tidal Elbe and estuary we observed large variation in **strontium (Sr) and lead (Pb) isotopic signatures**
- The **Elbe's tributaries** contribute with very different isotopic signatures to the main river signature due to the underlying, diverse geology
- **Transport pathways and sinks of sediments can be traced by their isotopic signatures:**
  - **Dredge spoil dumping site for Hamburg's port sediments** in the Elbe estuary carries the same Sr isotopic signature as the sediment from the Port of Hamburg
  - **Extreme Pb isotope ratios** of sediments in the estuary indicate **human interference** (possibly from industrial waste transported by tidal fluxes)

- Development of **novel methods** to generate elemental fingerprints covering the entire periodic table and for the analysis of non-traditional stable isotopes
- Identification of **sources**, **transport pathways** and **sinks** by isotopic variations and end-member modelling

Publications
[1] Reese, A., Zimmermann, T., Pröfrock, D. & Irrgeher, J., in preparation.

From source to sink: physicochemical landscapes and isoscapes for aquatic and marine ecosystem monitoring

Helmholtz-Zentrum Geesthacht
Centre for Materials and Coastal Research

Johanna Irrgeher, Ulrike Kleeberg, Linda Baldewein, Anna Reese, Tristan Zimmermann, Daniel Pröfrock

Introduction

In a novel approach, oceanographic and physical data are combined with chemical information about the chemical form (species), elemental data and information on the isotopic composition of sediment or water to generate physicochemical landscapes and isoscapes. The approach is applied to large scale investigations of marine and estuarine ecosystems on the example of the German Bight catchment.

Physicochemical landscapes

= spatially distributed maps of physicochemical parameters (e.g. elemental distribution, grain size, chemical species) **across terrestrial or aquatic ecosystems**

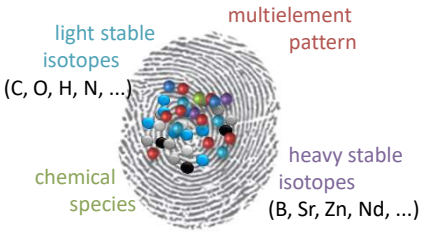
Isoscapes

= spatially distributed isotope patterns (light stable isotopes, non-traditional stable isotopes) **across terrestrial or aquatic ecosystems maps**

Generating spatially resolved physicochemical maps / isoscapes via the combination of a **HYPOTHESIS** with

- geospatial data
- sampling and data acquisition
- predictions
- interpolation and modelling

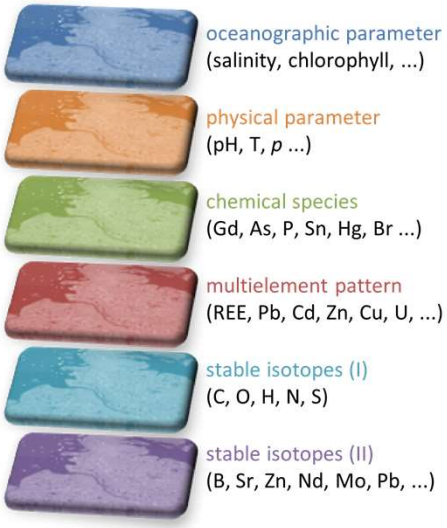
Chemical fingerprint



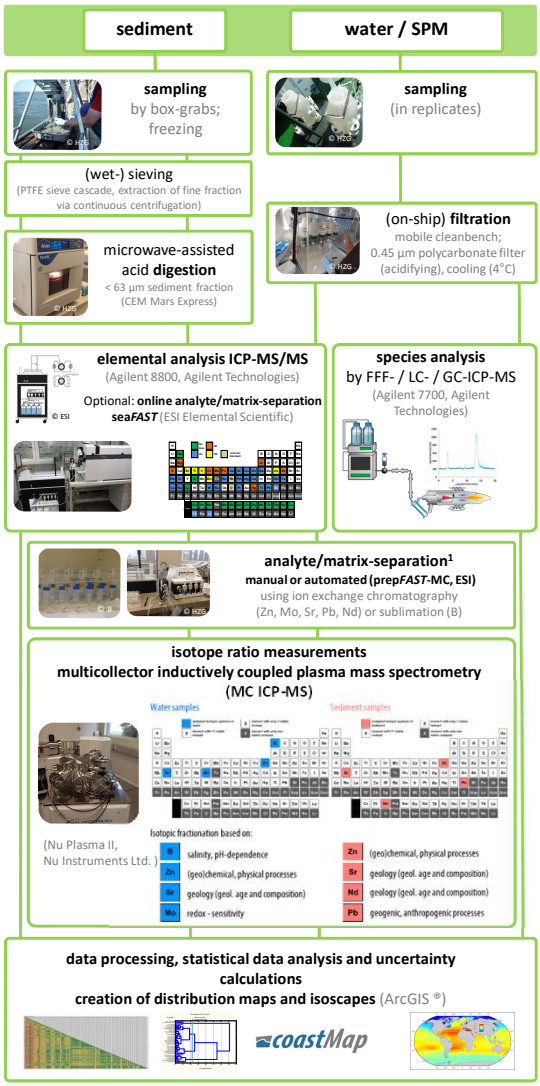
unique intrinsic marker of a sample

identification of sources, transportation pathways and sinks of contaminants within complex ecosystems

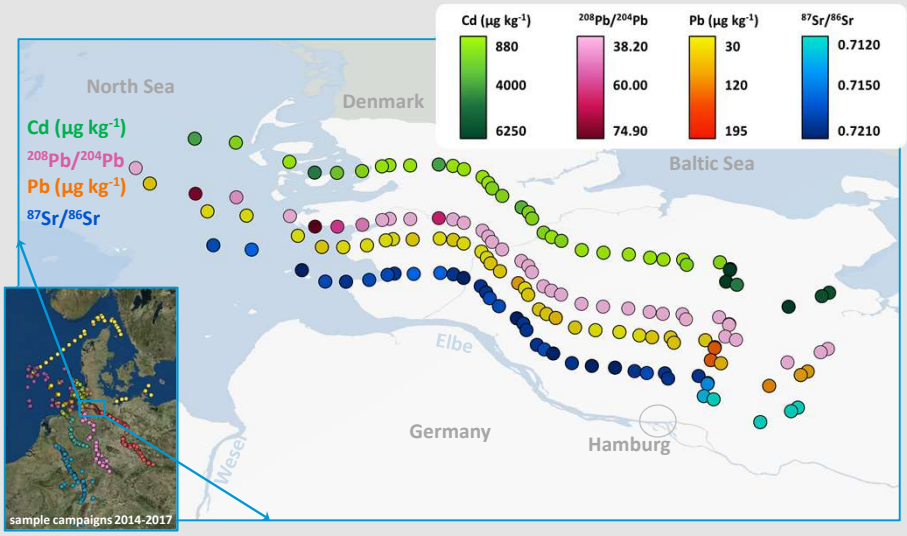
Multi-layer approach



Methodology



Multi-layer elemental and isotopic pattern of the Elbe estuary



Multi-layer elemental isotopic pattern of sediment samples in the Elbe estuary on the example of the Cd mass fraction, the $^{208}Pb/^{204}Pb$ isotope ratio, the Pb mass fraction and the $^{87}Sr/^{86}Sr$ isotope ratio. An extremely large variation of stable Pb isotope ratios with respect to the natural isotopic variation of Pb within a small observation area was found in the Elbe estuary between the Port of Hamburg and the German Bight of the North Sea.

- For the first time, **aquatic physicochemical landscapes** and **isoscapes** of **elements**, their **species** and **non-traditional stable isotopes** are generated on **large scales**.
- **Identification** and **characterisation** of
  - **sources**, transport **pathways** and **sinks** of geogenic and anthropogenic substances
  - **hot-spots** of contamination
  - seafloor **properties**

Publications: [1] Retzmann, Zimmermann, Prohaska, Pröfrock, Irrgeher - Anal. Bioanal. Chem. (2017) 409:5463–5480

Rare earth elements in the German North Sea catchment: analysis of Gd anomalies as proxy to investigate the distribution of emerging contaminants

Tristan Zimmermann, Johanna Irrgeher, Daniel Pröfrock

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Introduction

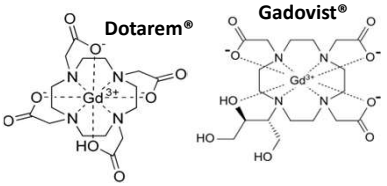
Rare earth elements (REE) are under debate as potential new anthropogenic contaminants, besides engineered nanoparticles [1] or new organic substances [2]. Due to their special chemical properties they play a major role in modern industry, products of everyday life, and medical applications (e.g., gadolinium (Gd) based contrast agents).

Gd based magnetic resonance imaging (MRI) contrast agents

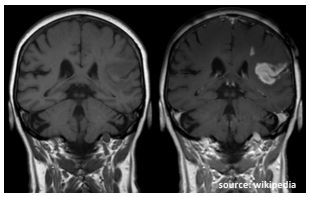
- Gd^{3+} ions are used to improve visibility of body structures during **MRI analysis** (1-3 g Gd/MRI treatment)
- Due to its **toxicity** (LD_{50} 100-200 mg/kg) Gd^{3+} ions are complexed by chelating agents
- Because of their stability contrast agents pass through **waste water treatment plants (WWTP)** and contaminate surface waters

Development of novel tools for the direct determination of rare earth elements in complex matrices

➲ **Tracer to identify transport pathways of emerging contaminants with similar chemical properties**



Chemical structures of two commonly used Gd-based MRI contrast agents

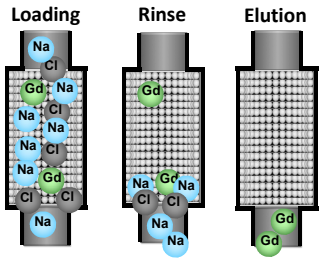


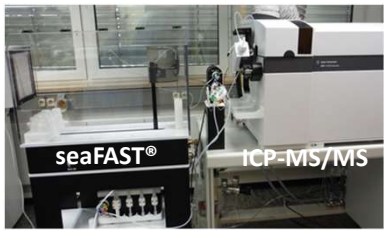
MRI of a brain without (left) and with (right) contrast agent

Methodology

Development of a novel method for REE quantification in complex matrices:

- Fully automated
- Direct seawater analysis
- Detection limits at sub-ng/L range





Analytical instrumentation for REE quantification

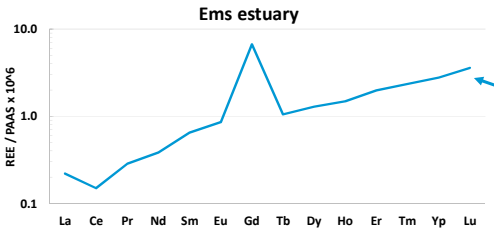
Results

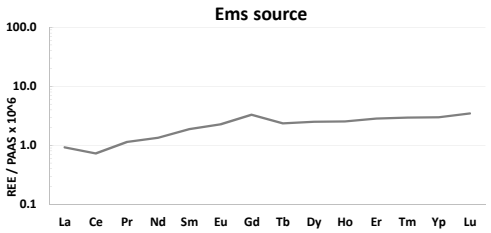
Calculation of the **anthropogenic Gd** amount by extrapolation and normalisation using the Post Archean Australien Shale (PAAS) REE levels.

$$Gd_{anthr} = Gd_{total} - Gd_{nat}$$

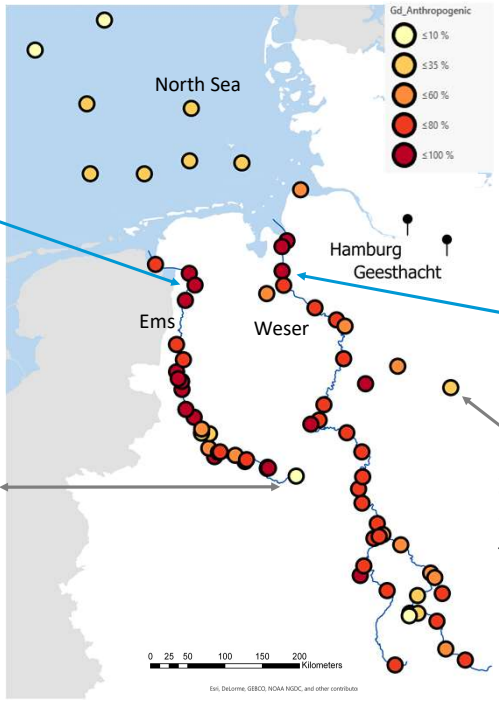
$$Gd_{nat} = Gd_{PAAS} * 10^{(2*\lg(Sm_{PAAS}) - \lg(Nd_{PAAS}))}$$

X_{PAAS} = PAAS normalised X concentration

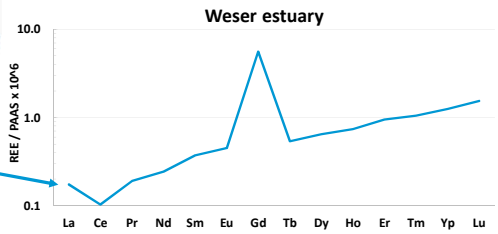


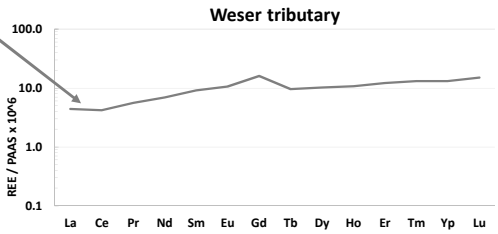


REE pattern normalised to PAAS of Ems (left) and Weser (right) water samples taken in the estuary (blue) and near the source (grey)



Distribution of anthropogenic Gd in the Weser and Ems catchments and selected regions of the German Bight



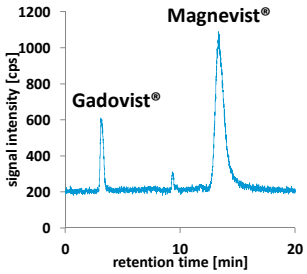


Calculated amount of anthropogenic Gd (in %) for different water samples collected in the Weser, Ems and German North Sea

Speciation of Gd based MRI contrast agents

Identification of the different MRI contrast agents and their individual contribution to the total anthropogenic Gd have been accomplished by speciation analysis.

➲ **Study of potential effects on the environment**



Gd speciation of a water sample taken in the Ems river. Two different Gd- based MRI agents could be identified.

- A significant contamination of Gd was observed in almost all water samples, including those from the North Sea
- The present comprehensive survey is the most extensive study on the distribution of REE as potential new contaminants

Publications: [1] ***J. Anal. At. Spectrom.***, 2015,**30**, 180-190
[2] ***Anal. Methods***, 2017,**9**, 3626-3635
[3] Zimmermann et al. *in preparation*

Research Unit *Biogeochemistry*: Topic 2

coastMap

Universität Hamburg
DER FORSCHUNG | DER LEHRE | DER BILDUNG

Sediments and their role in nitrogen cycling of the North Sea

Helmholtz-Zentrum Geesthacht
Centre for Materials and Coastal Research

Andreas Neumann, Alexander Bratek, Frank D. Bockelmann, Richard Hofmeister, Jana Friedrich, Kai Wirtz

Motivation

- The first biogeochemical habitat atlas of the German Bight
- for a comprehensive understanding of benthic matter fluxes
- to identify and to quantify antropogenic impacts
- on the basis of detailed maps (coastMap).

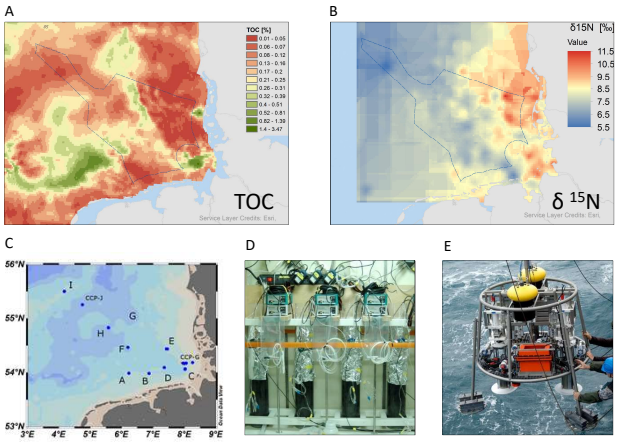


Fig. 1: A) Map of Total Organic Matter (TOC), and B) δ ^{15}N in surface sediment in the souther-eastern North Sea. Maps from coastMap. C) monitoring stations. D) Ex-situ incubations. E) In-situ measurements (FLUXSO).

At a glance

State-of-the-art methods
- in-situ benthic chamber lander (FLUXSO)
- eddy covariance method

Stable isotopes
- natural abundance (^{15}N, ^{18}O)
- enriched in-situ tracer experiments

Comprehensive sampling
- all major sediment types (permeable & impermeable)
- all seasons
- all major transport types (advection, fauna, diffusion)
- all compartments (water column, pore water, sediment)

Partners complement our expertise
- AWI & MPI (in-situ O_2 profiles, eddy covariance)
- Marum (sediment morphology and dynamics)
- Senckenberg (macrozoobenthos)

Modelling
- MOSSCO / OMEXDIA (RU 1)

Added Value
- quantification of ecosystem services (e.g. N-elimination)
- improved ecosystem models
- baseline data for assessment of offshore installations

Key results

① ➢ A coherent dataset of net fluxes at 9 routine monitoring stations (A-I; Fig. 1C) with good spatial and seasonal coverage in 2012 – 2016. Measurement of oxygen and nutrient fluxes with in-situ chambers (SANDY, FLUXSO) and ex-situ whole-core incubations. Our data is complemented by O_2-fluxes in sands (AWI/MPI[1]), sediment dynamics (MARUM), and macrozoobenthos (Senckenberg).

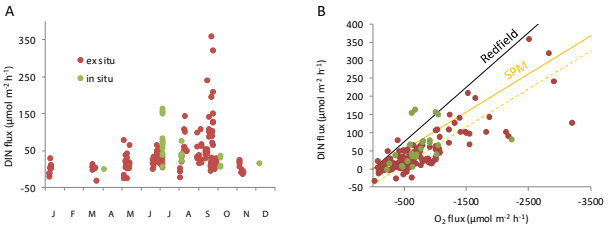


Fig. 2: A) Seasonal variation of benthic DIN fluxes as measured by in-situ (green) and ex-situ (red) incubation. B) Stoichiometric ratio of DIN fluxes and oxygen fluxes.

③ ➢ Current model OMEXDIA_P (MOSCCO) is able to reproduce the general spatial and seasonal pattern of oxygen fluxes. However, the model estimates are low in comparison to measured fluxes.

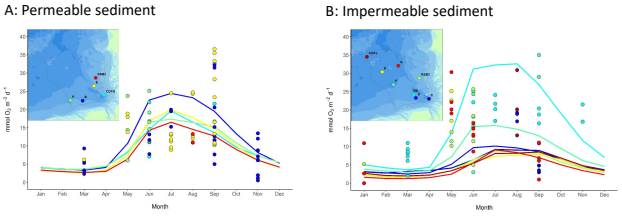
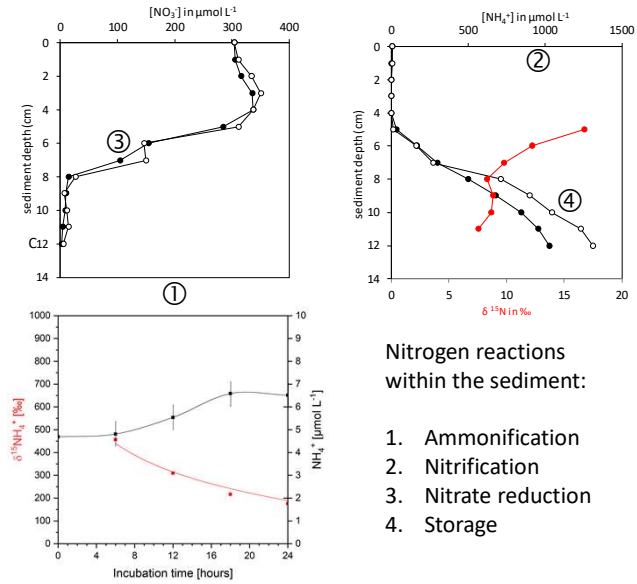


Fig. 4: Seasonal pattern of measured (circles) and modelled (lines) benthic respiration rates of A) permeable and B) impermeable sediment.

② ➢ Quantification of benthic processes (nitrification, denitrification[2], pore water advection, oxygen consumption,) as functions of abiotic site characteristics.



Nitrogen reactions within the sediment:

1. Ammonification
2. Nitrification
3. Nitrate reduction
4. Storage

Fig. 3: A) Nitrate and B) ammonium in the porewater of a permeable sand in the Elbe Estuary. C) Time-course of a isotope dilution experiment during a whole-core incubation to determine the nitrification rate.

- **Quantify the contribution of macrozoobenthos on oxygen and nutrient fluxes**
- **Elucidate the impact of internal N-reactions on the net N-fluxes between sediment and water column**
- **Improve the model for benthic fluxes of oxygen and nutrients (OMEXDIA).**

Publications
1: Ahmerkamp S., Winter C., Krämer K., Beer D. d., Janssen F., **Friedrich J.**, Kuypers M. M. M. and Holtappels M. (2017), Regulation of benthic oxygen fluxes in permeable sediments of the coastal ocean. Limnol. Oceanogr.
2: **Neumann A.**, **van Beusekom J. E. E.**, Holtappels M., **Emeis K.-C.** (2017), Nitrate consumption in sediments of the German Bight (North Sea). Journal of Sea Research.

Long-term changes in nitrogen dynamics in the Elbe estuary

Annika Eisele, Tina Sanders, Justus van Beusekom, Kai Wirtz

Helmholtz-Zentrum Geesthacht
Centre for Materials and Coastal Research

Estuarine filter function

Estuaries are biogeochemical filters attenuating riverine nutrient inputs before they reach the coastal area. Within few decades, the Elbe estuary has changed from a sink to a source of nitrate, and still discharges high nitrogen (N) loads to the North Sea.

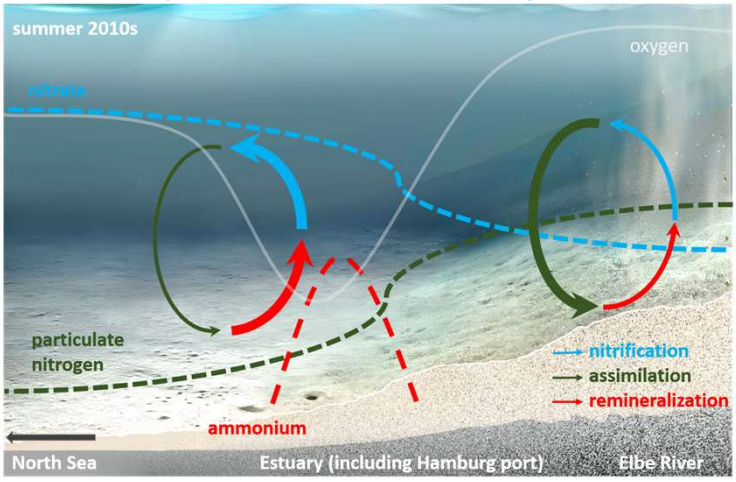
A new generic approach extrapolates station-based data and reveals decadal shifts for estuarine N-retention and budgets

The unique combination of mass flux and stable isotope approaches identifies and quantifies nitrogen cycling hotspots

Our results are crucial for ongoing modeling studies at HZG/RU1 commissioned by our cooperation partners UBA and NLWKN (national authorities) responsible for EU-directives.

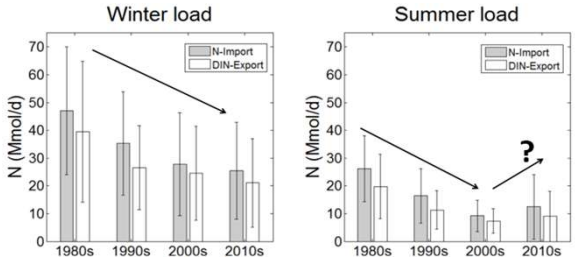
Future goals are to identify forcing factors triggering N losses in the Elbe, to connect altered N-dynamics to dredging activities and to apply a synergetic station-transect approach in other estuaries.

Present N-dynamics in the Elbe estuary



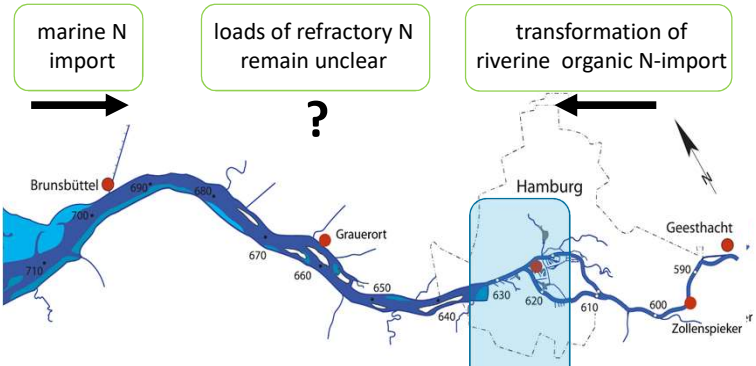
Schematic diagram of the impact of dredging in the port of Hamburg on nitrogen assimilation versus coupled remineralization-nitrification processes.

Trends in nitrogen budget and retention?

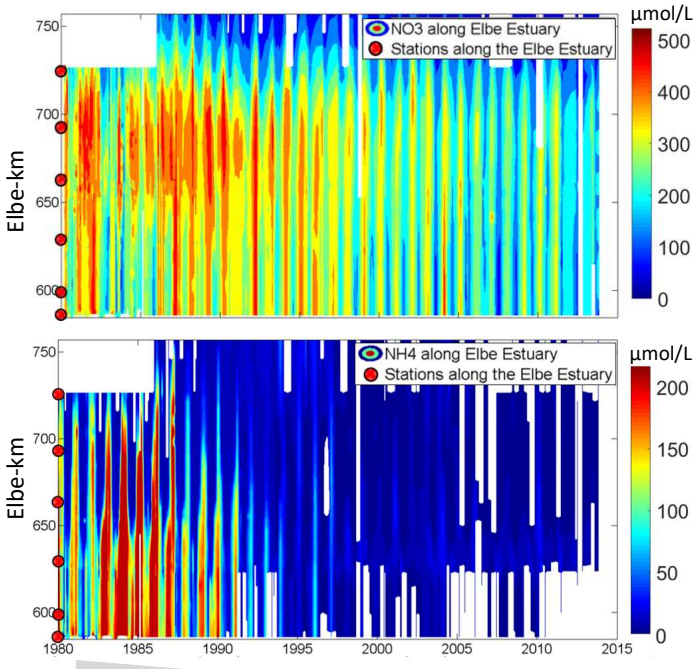


The novel method calculates budgets and retention from station-based time-series data and indicates seasonal and decadal changes. The method accounts for the specific residence time of a water parcel on transit to the coastal area.

Elbe estuary



Long-term decrease in nitrogen (NO_3+NH_4)



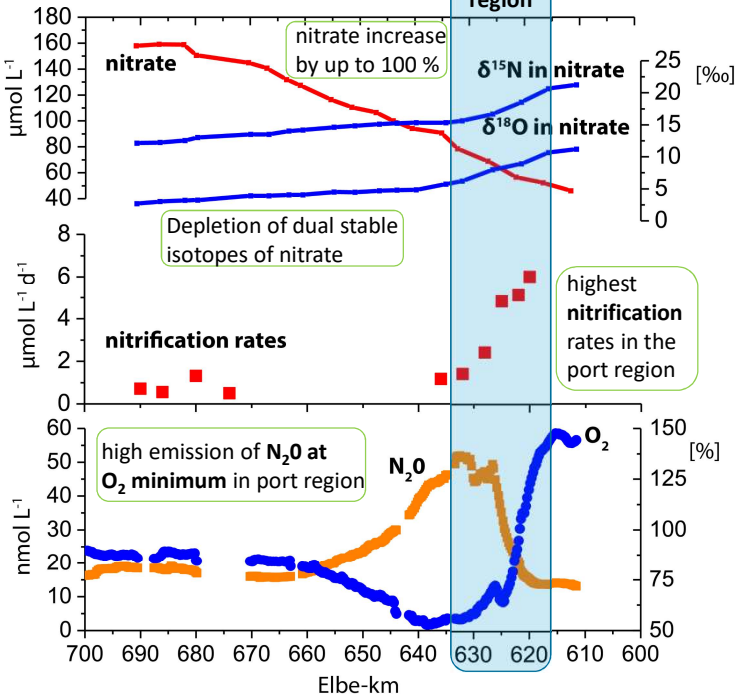
long-term decrease in nitrogen loads

high loads of untreated waste water

intense riverine phytoplankton blooms

morphological changes modified residence times and altered OM turnover

N-turnover situation



Results of transect cruises August 2012 and June 2015

Publications
Sanders et al., 2017, Estuaries and Coasts
Brase et al., 2017, Frontiers in Marine Science
Holzwarth and Wirtz, 2018, Estuarine, Coast and Shelf Science

DANUBIUS-RI

DANUBIUS-RI: International Centre for Advanced Studies of River-Sea Systems

Sina Bold, Jana Friedrich, Justus van Beusekom, Volker Dzaak, Hans-Jörg Isemer

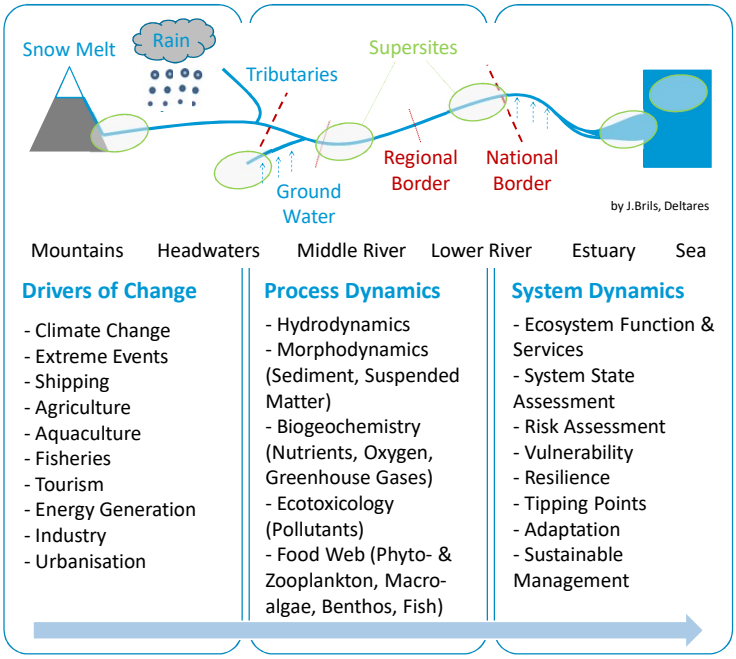
Helmholtz-Zentrum Geesthacht
Centre for Materials and Coastal Research

Addressing Grand Challenges

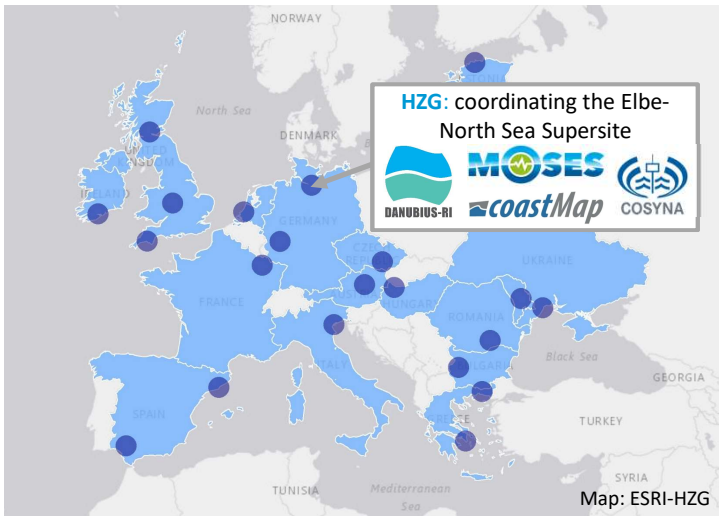
- pan-European **Research Infrastructure (RI)** to study River-Sea Systems, comprising rivers and catchments, transitional waters (e.g. estuaries, deltas) and coastal seas
- to enable research based on **systems approach**, overcoming disciplinary, regional and national boundaries, and to bring together relevant expertise and data
- to better **understand ecosystem functions**, identify cause-effect-relationships, address grand challenges and thus **sustain ecosystem services**

Distributed Research Infrastructure

- **Coordination, Hub & Data Centre**: GeoEcoMar, Romania
- **Technology Transfer Office**: University College Cork, Ireland
- **Nodes**: Observation (Plymouth Marine Laboratory, UK), Analysis (Federal Institute of Hydrology, Germany), Modelling (Institute of Marine Sciences, Italy) and Socio-Economic Impact (Deltares, Netherlands)
- **Supersites**: upper, middle and lower Danube, Elbe, Thamse, Ebro, Po and Nestos, and their respective adjacent seas (additional Supersites under discussion)



Bringing together: 29 Partners from 16 Countries



Enhancing Process and System Understanding

- How are River-Sea Systems changing due to natural and anthropogenic pressures? What are the **drivers** and how are they interacting?
- How are processes and changes in the catchment affecting those further along the **River-Sea Continuum**? What are the timescales?
- How are these changes affecting **ecosystem functioning and services**? How can we sustainably use River-Sea Systems? Which guidelines can be derived from that?
- How are these changes affecting the **resilience** of River-Sea Systems as Socio-Ecologic Systems? What are "tipping points" of such a system or of its components?
- How can we distinguish between **natural variability** and **anthropogenic changes**?
- How can we observe process and system dynamics on a **higher spatial and temporal scale**? How can we predict short and long term changes in River-Sea Systems?

HZG: leading the development of the "Science and Innovation Agenda"

Making a Difference

- provides **access to Research Infrastructure** along several River-Sea Systems
- synthesises and **integrates existing knowledge** on River-Sea Systems
- uses **standardised methods** and provides access to comparable data
- strengthens regional, national and international **collaborations**
- **brings together** research institutes, universities, public authorities, as well as small and medium enterprises
- combines research with **technology development** and its application
- educates and trains young scientists
- develops guidelines for **sustainable management** of River-Sea Systems
- bridges gap(s) between current **European water related policies**, e.g. Water Framework Directive and Marine Strategy Framework Directive
- addresses several **Sustainable Development Goals** (SDGs) of Agenda 2030, particularly SDG 6 (Clean Water and Sanitation) and 14 (Life below Water)

Moving towards DANUBIUS-RI

ESFRI PL Projects Landmarks ROADMAP 2016	DANUBIUS-PP		DANUBIUS-RI
2016	**2016 - 2019**	**2019 - 2021**	**2022 ~ 2050**
Entry in Roadmap of European Strategy Forum for Research Infrastructures (ESFRI)	- H2020 Project - Preparatory Phase - 4 Mio. € (Grant Agreement No. 739562)	- Implementation Phase - European Regional Development Funds?	- Operational Phase - Life Span: 20-30 years

www.danubius-pp.eu // www.danubius-ri.eu

coastMap – The marine Geoportal

Helmholtz-Zentrum Geesthacht
Centre for Materials and Coastal Research

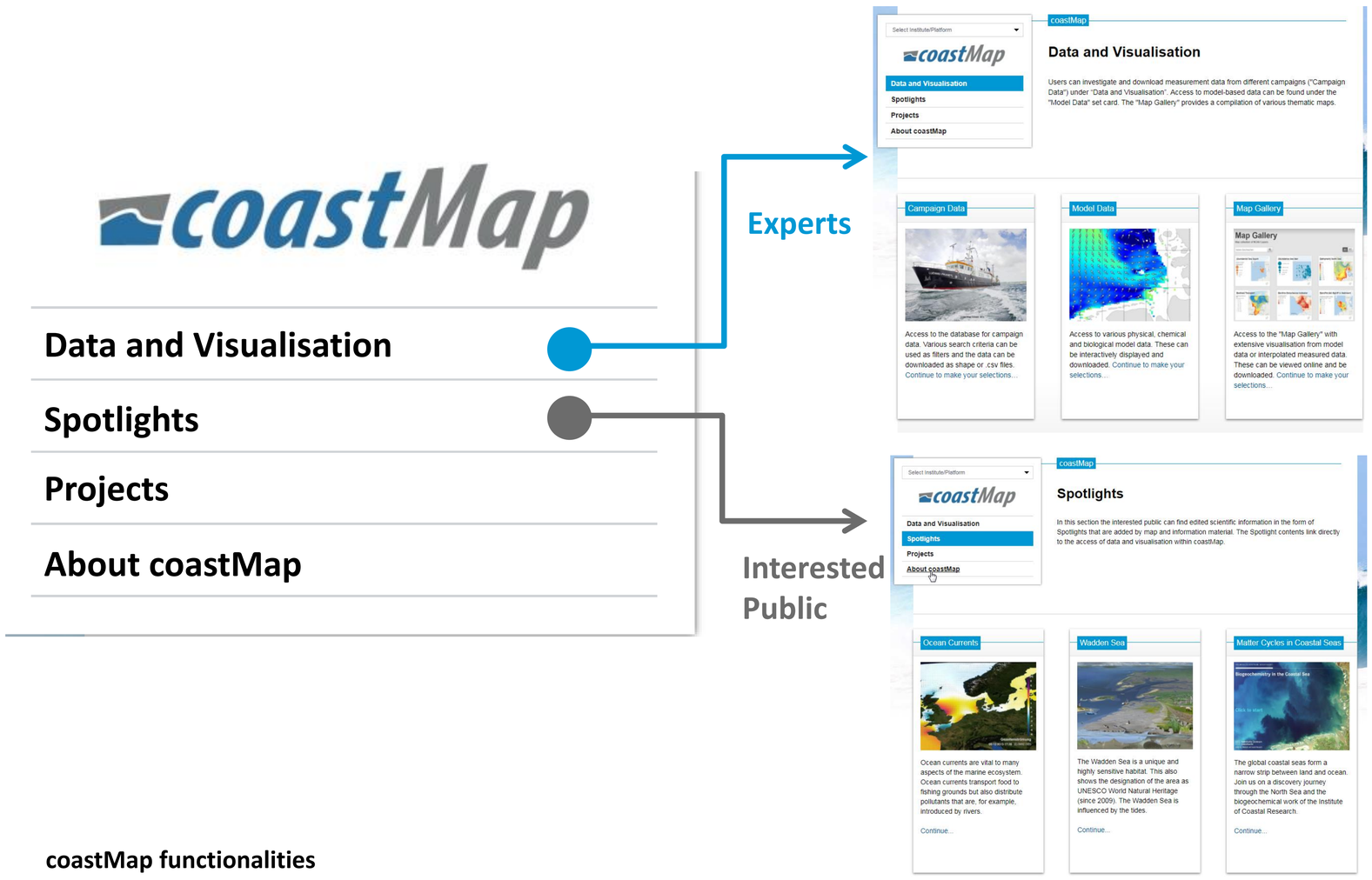
Linda Baldewein, Marcus Lange, Ulrike Kleeberg, Dietmar Sauer

Introduction & Objective

coastMap is the marine Geoportal of the Institute of Coastal Research. It combines analyses and model data on seafloor conditions and those in the overlying water column with a focus on the North Sea and the atmosphere. The motivation behind the development of the coastMap website (www.coastmap.org) is to provide scientific data to both scientists and the interested public.

A variety of tools have been developed to facilitate an optimal data- and workflow. These include advanced data storage for campaign and model data and generic analysis tools for Big Data from numerical models.

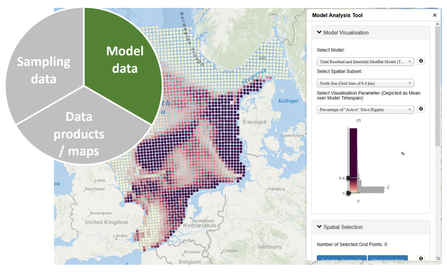
Furthermore, spotlights illustrate the work of scientists in texts intermingled with interactive maps and data exploration tools.



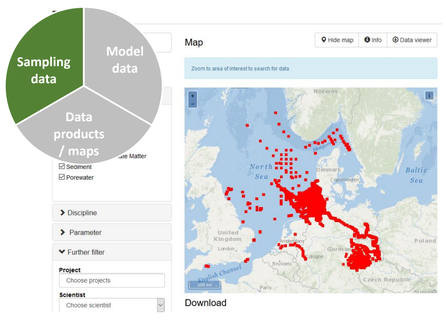
coastMap functionalities

Tools for experts

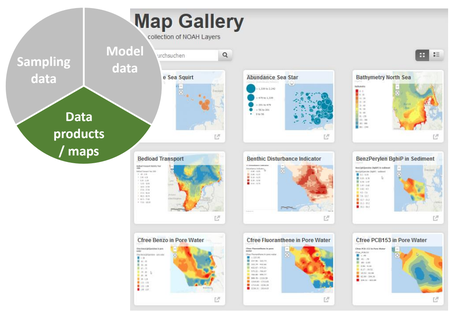
Data storage depends on the data type. The model data, often in the size of several gigabyte, is stored in an innovative Array Data Base Management System. It allows for the integration of high temporal and spatial resolution data in a web-based analysis tool.



The point data collection during sampling campaigns is facilitated with the coastMap campaign planning app. It replaces hand-written campaign notes with an integration of all collected station data, such as the coordinates, in a database at real-time.



Data products and maps are aggregated from model and analysis data. The Map Gallery contains a thematic maps collection, such as for pollution levels. The North Sea Explorer is an interactive WebGIS, allowing to freely select several map layers and several GIS options to generate the desired results of the user.

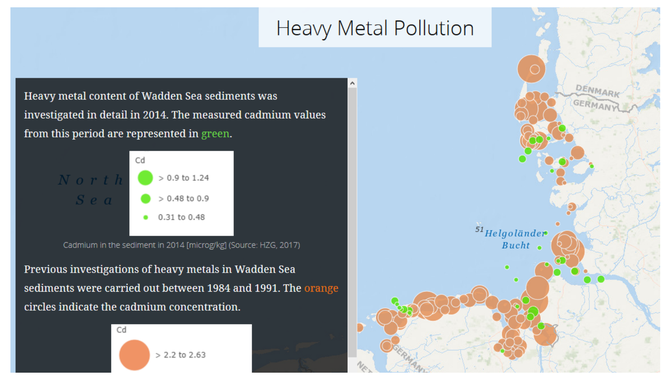


Expert tools

Spotlights for the interested public

Spotlights are popular science writings on different topics of our work. The spotlight texts are augmented by graphics, videos and interactive maps that display the scientific results. The content links directly to the access of data and visualisation within the coastMap expert tools. Currently, the topics of Ocean Currents, the Wadden Sea, Matter Cycles in Coastal Seas and Shipping Emissions are addressed (further Spot-lights to follow).

Start page of the spotlight "Research into Currents"



Interactive map on heavy metal pollution

Technical infrastructure

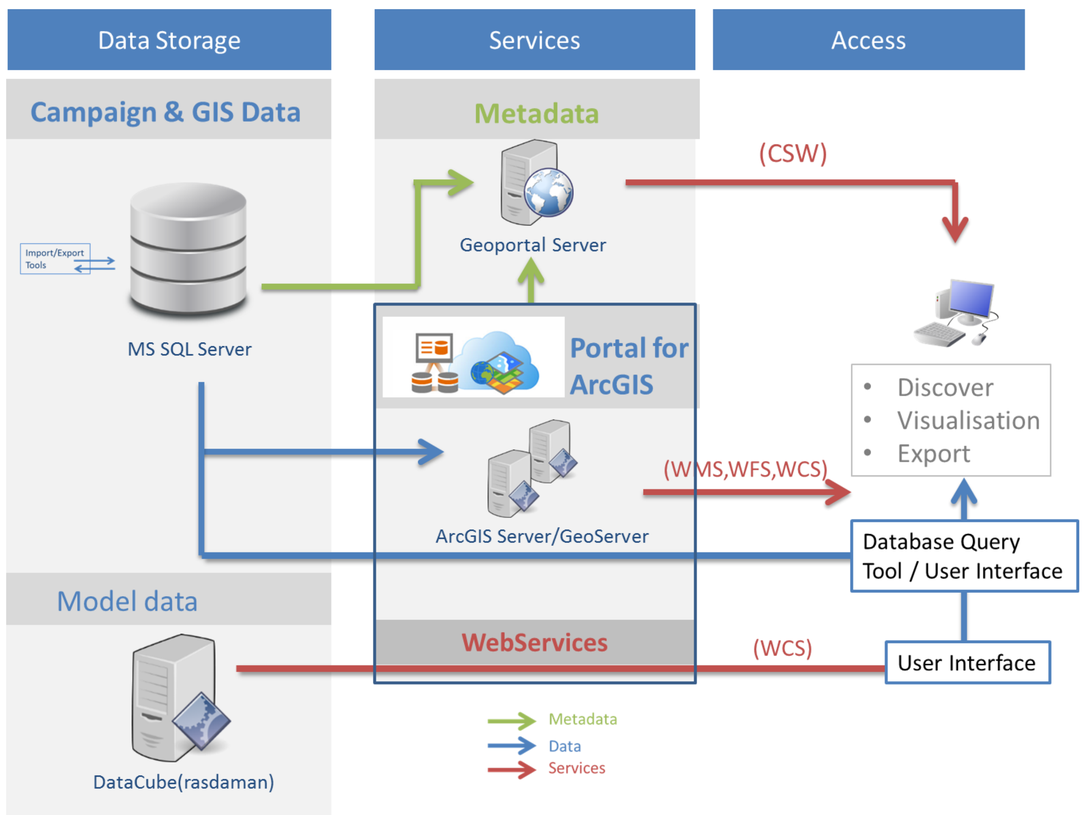


Diagram of the coastMap technical infrastructure, including data, metadata and services flows

- coastMap provides an improved understanding of the marine environment, for example spatially and temporally resolved sea floor conditions.
- It closes the gap between the general public and the scientists by offering a wide range of information, data visualisation and download options.
- It uniquely combines sampling point data with model data and data products in generic tools for data storage, access and analysis.

Modeling ship engine emissions from local to regional scales – a bottom-up approach

Armin Aulinger

Helmholtz-Zentrum Geesthacht
Centre for Materials and Coastal Research

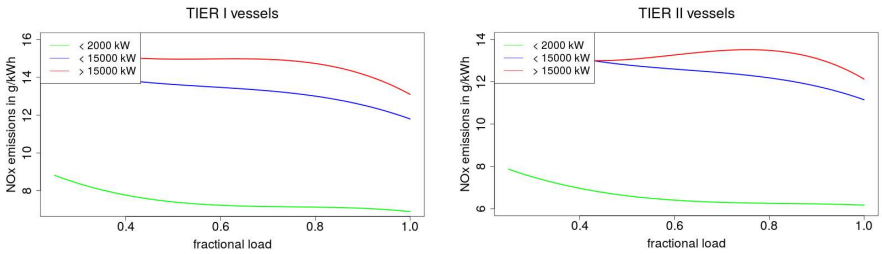
Introduction

Pollutant exhaust from ships is an important factor influencing the air quality in coastal regions and cities with large ports like the city of Hamburg, Germany. Therefore, municipalities are concerned with measures aimed at mitigating air pollution by ships, in particular with NO_x and PM. In terms of planning these measures and evaluating their effectiveness, it is essential to have an emission model that can be run in any temporal and spatial resolution. Most importantly, it should be able to simulate different emission scenarios.
We developed a model that reconstructs the activities sailing, maneuvering and berthing of every single registered ship in the port of Hamburg. Here, we calculate their emissions, such as NO_x, SO_2 and PM_{10} and others.

Ship activities

The Ships' Automatic Identification System was used to reconstruct the tracks of single ships and calculate their energy demand and fuel consumption in time and space.

The model distinguishes three different modes: sailing, maneuvering and berthing.



Load dependent emission factor functions for NOx from ship engines of different sizes; ships complying to the TIER I regulations (left) and TIER II regulations (right).

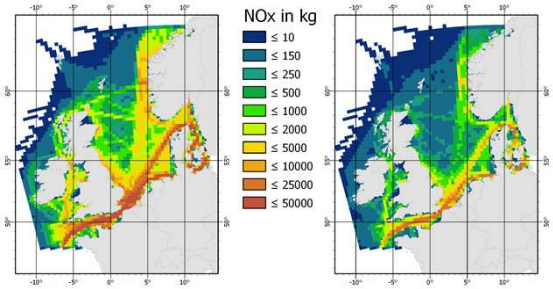
Emission factors

In a cooperation with De Norske Veritas-Germanischer Lloyd load dependent emission factor functions for different ship types and sizes were developed from evaluating more than 400 test bed measurements.
Methods for calculating ship emissions at berth are derived from on-board surveys, asking ship engineers about the engine use and fuel demand while berthing.

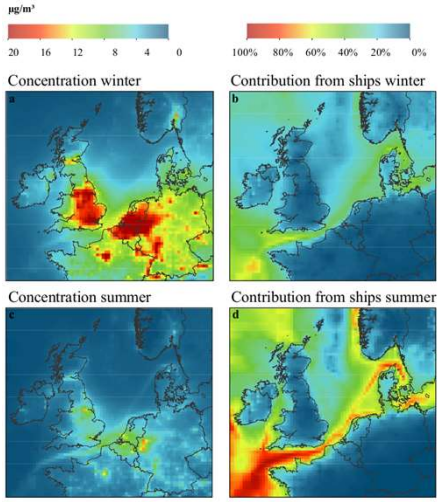
Emission inventories and scenarios

Ship emission inventories were calculated for the North Sea and the port of Hamburg.

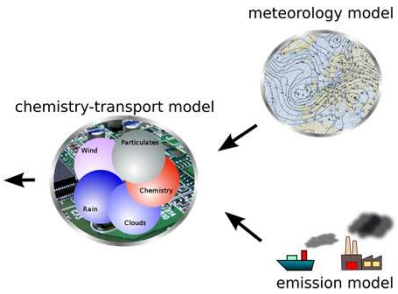
Emission scenarios can be developed based on commercial developments (transportation numbers of goods), political regulations (pollution limits, ship traffic restricted zones, incentives) and technological developments (abatement technologies, alternative fuels).



NOx emissions from ships, prognosed emissions in 2030 without abatement (left) and with all ships complying to TIER III regulations (right).



Relative changes of NOx concentration levels in winter (a) and summer (b) through the influence of shipping emissions (b,d) in 2011.



Air Quality Modeling

Emission inventories are a prerequisite for air quality models. In order to evaluate the impact of emissions on air quality, It is possible to switch on and off certain emission sources.

- Highly flexible bottom-up emission model for shipping emissions.
- Model past, present and future scenarios, both for scientific questions and decision support.

Publications

Aulinger, A., V. Matthias, M. Zeretzke, J. Bieser, M. Quante, A. Backes. 2016: The impact of shipping emissions on air pollution in the greater North Sea region -- Part 1: Current emissions and concentrations. Atmos. Chem. Phys., 16, 739-758.

Matthias V., A. Aulinger, A. Backes, J. Bieser, B. Geyer, M. Quante, M. Zeretzke. 2016: The impact of shipping emissions on air pollution in the greater North Sea region -- Part 2: Scenarios for 2030. Atmos. Chem. Phys., 16, 759-776

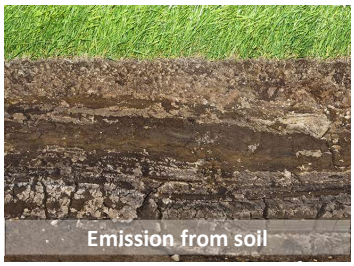
Natural emissions of reactive nitrogen in coastal areas

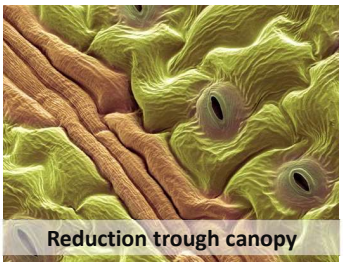
Jan Alexander Arndt, Armin Aulinger, Volker Matthias, Markus Quante

Helmholtz-Zentrum Geesthacht
Centre for Materials and Coastal Research

Natural nitrogen sources and sinks

There are three major sources of reactive nitrogen in the atmosphere that do not originate from anthropogenic sources. The globally largest sources are biogenic emissions from microbial processes in **soil**, the thermic oxidation of fixed nitrogen in thunderstorms by **lightning** and the release of oxidized nitrogen in **vegetation fires**. They account globally for 35% of the total global oxidized nitrogen .
Beside emission, there is a natural sink for nitrogen that affects the flux of biogenic nitrogen to the atmosphere and deposition patterns. This is known as **canopy reduction.**



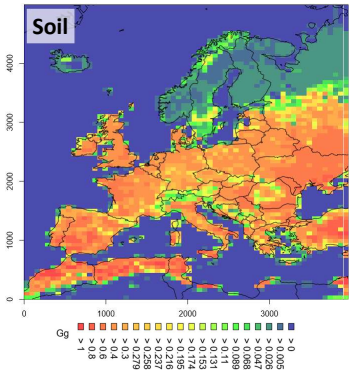


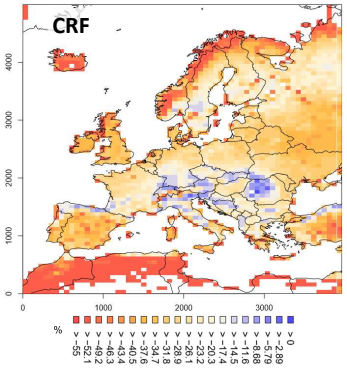
Biogenic emission inventory system & **canopy reduction** function

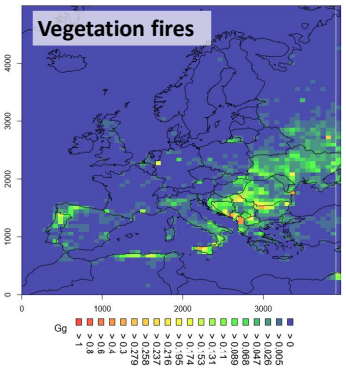
Emission model for Soil NO based on temperature and moisture parameterization with canopy reduction function.

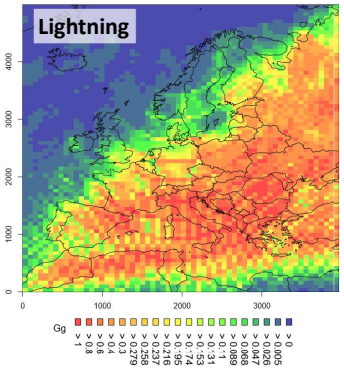
FINN
Satellite derived emission inventory for vegetation fires

LIS/OTD
Satellite derived emission inventory for lightning





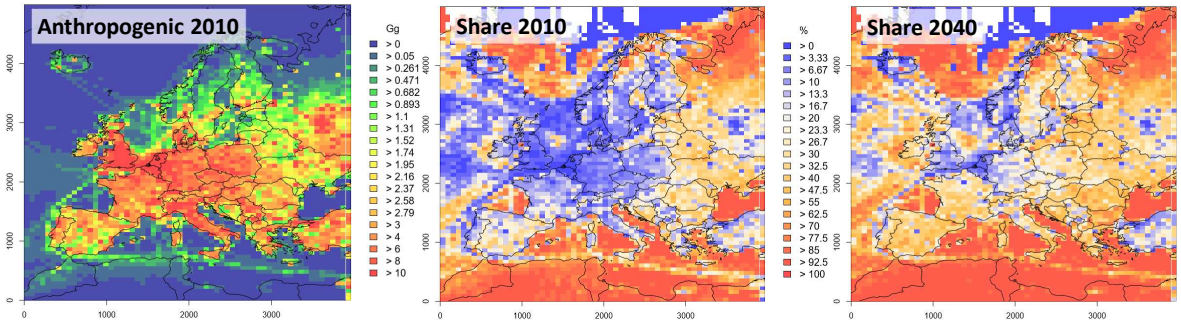




We found **lightning has with 0.6 Tg N total emission the highest share of natural nitrogen emissions in Europe**, which is a surprising new scientific outcome for this region.

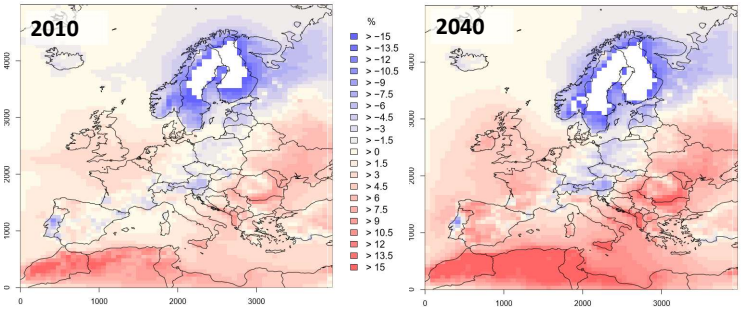
Development in the future: nitrogen 2010 & 2040

Based on the MTFR ECLIPSE Emission scenario we created an Emission Scenario for the 2040 anthropogenic emissions. Based on this scenario, natural emissions will **double** their contribution to the total reactive nitrogen budget.



Impact on deposition

Natural emission influence the deposition patterns of nitrogen. Comparing 2010 and the 2040 scenario with a Chemistry Transport Model, we see a clear intensivation of the patterns created by natural emissions.



- We found lightning to be the largest natural source for Europe, which was not known before.
- We developed and investigated future scenarios of atmospheric nitrogen with a special look at natural emissions which has not been done before.

Publications
Arndt, Aulinger, Matthias: Technical note: Implementation of different Big-Leaf Canopy Reduction functions in the Biogenic Emission Inventory System (BEIS) and their impact on Concentration of oxidized nitrogen species in northern Europe, in preparation

The impact of shipping emissions on air quality in North European harbor cities

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Shipping emissions in North European harbor cities

- Air pollution caused by international shipping is a major source for health damages throughout Europe.
- Nevertheless, it is still one of the least regulated anthropogenic emission sources.
- Therefore it is of interest for research and air quality management.
- The biggest impact of air pollution (NO_x, PM_x, SO_x) is in harbor cities.

Urban Research Domains in North Europe for Air Quality Studies within varying research projects:

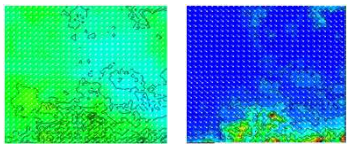
- Gothenburg
- Gdansk-Gdynia
- Riga
- Rostock
- Antwerp
- Rotterdam
- Düsseldorf
- Hamburg

Urban air quality and exposure simulations with chemical transport model (CTM) systems on local scales

Emission inventories

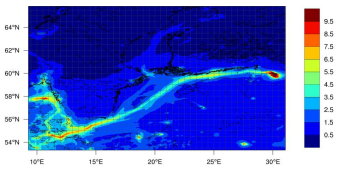
- Urban emissions inventories cover major pollution sources, e.g. industry, traffic, shipping.

Meteorological data



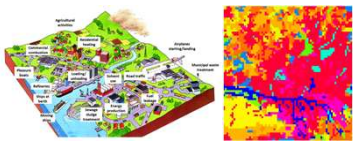
- Meteorological data is required to simulate atmospheric transport processes.

Boundary conditions



- From regional CTM to cover reg. background concentrations.

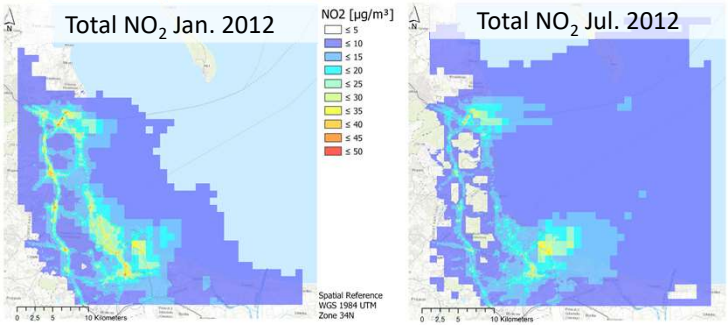
Terrain & land-use data



- Complex urban land cover is integrated to take into account local atmospheric processes.

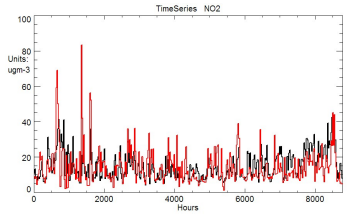
Chemical Transport Model simulations

- The spatiotemporal distribution of exhaust gases and particles is calculated with CTM systems.
- Domain-specific meteorological fields, regional concentrations, as well as detailed and high-resolution emission inventories for emissions of all sectors are created.



Spatial distribution of monthly averaged NO_2 concentrations in the urban agglomerate of Gdansk-Gdynia at the Polish coast for January and July 2012, as a result of CTM simulations with all emissions sources and background concentrations.

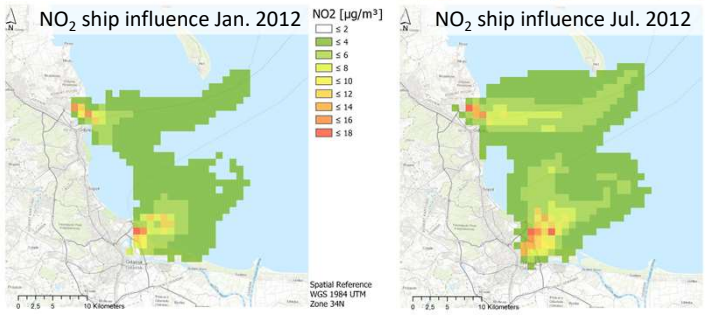
CTM evaluation with air quality monitoring data



Time series for daily NO_2 in 2012 at one measurement station in Gdansk (black line) compared to model output (red line).

Ship impact scenarios

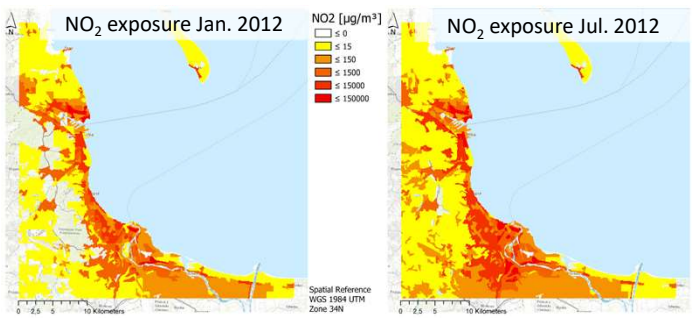
An experiment that excludes the ship emissions is simulated and the difference is calculated to investigate the influence of shipping emissions



Spatial distribution of NO_2 concentrations by shipping activities in the urban agglomerate of Gdansk-Gdynia for January and July 2012.

Exposure calculations

By combining the calculated spatiotemporal concentrations with gridded population densities, the population exposure is calculated.



Spatial distribution of population exposure to NO_2 by shipping activities in the urban agglomerate of Gdansk-Gdynia.

Publications
Ramacher, M. et al. (2017). The impact of Emissions from ships in ports on regional and urban scale air quality. In: C. Mensink und G. Kallos (Ed): Air pollution modeling and its application XXV, p. 309-316, Springer.
Karl, M.: Development of the city-scale chemistry transport model CityChem-EPISODE and its application to the city of Hamburg, manuscript submitted to Geoscientific Model Development, 2018.

- **Ship contribution to air pollution in researched harbor cities ranges from 11-34% for NO_2, 1-10% for $PM_{2.5}$ & 1-29% for SO_2.**
- **CTM simulations are the tool of choice to identify impacts of shipping on urban air quality & exposure in AQM support.**
- **All components of local-scale CTM model system under one roof.**