Age dating of recent tidal sediments by means of Cesium 137 and micropollutants

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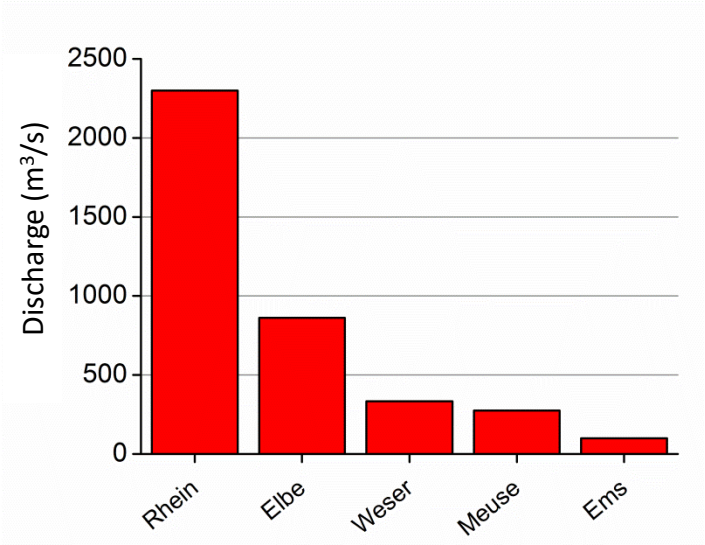
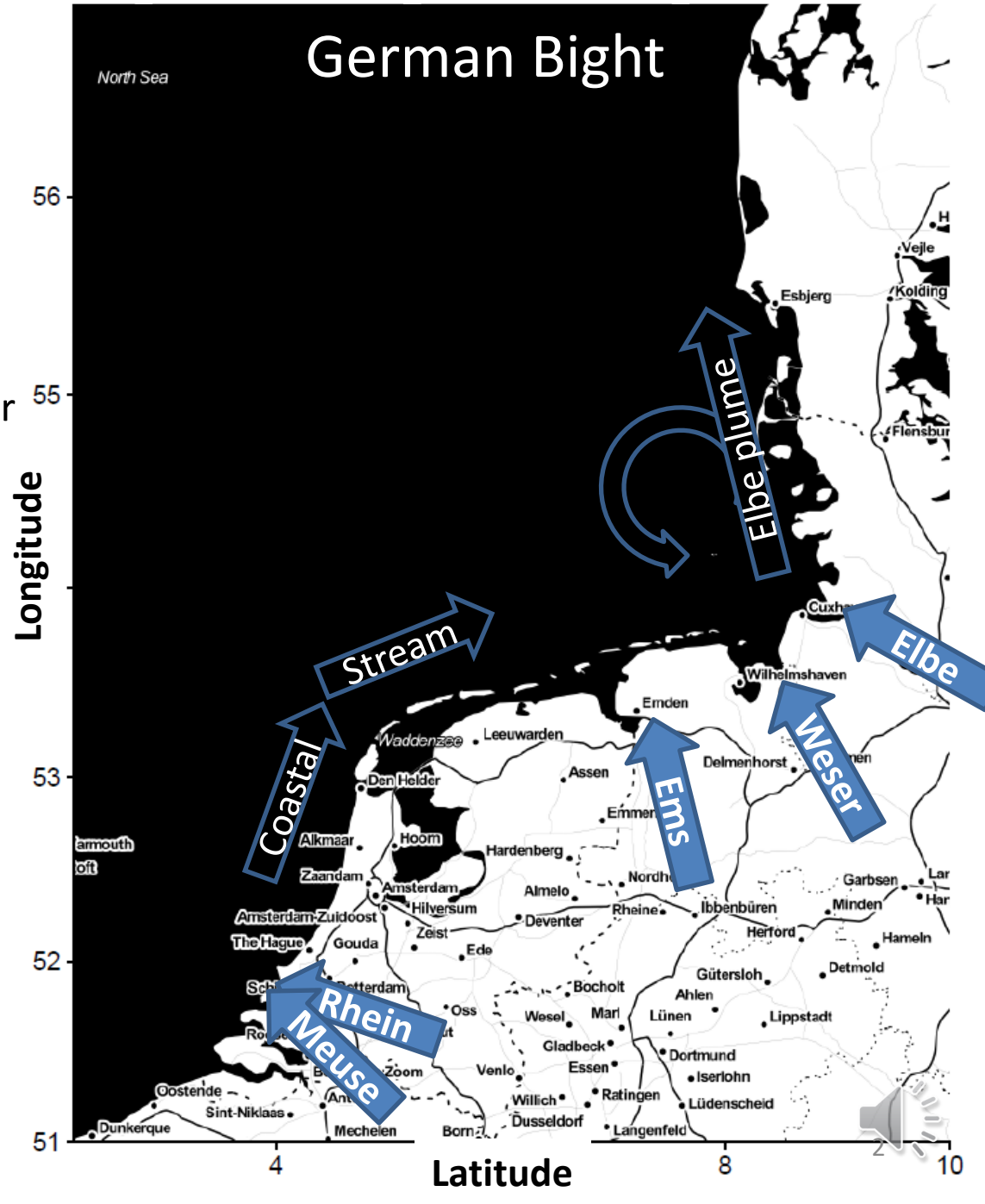
Tidal and coastal areas of the G.B.

- Tidal areas: highly dynamic regions
- Natural transport processes (sediment and particulate matter transport)
- Anthropogenic transport processes (disposal of dredged material - sediment management)





Knowledge gap

- Differentiation between natural transport of contaminated sediments and the transport caused by dredging
- Dwell time of dredged material in estuaries
- Identification of transport paths and deposition sites of dredged materials and associated contaminants
- Quantification of sediment transport and associated pollutants in tidal areas
- Temporal distribution of pollutants

Age dating and analysis of chemical composition

Sediment age dating

1. Option: Age dating of sediments using radioactive isotopes

- Be-7, Pb-210, Cs-137
  limited by their abundance
- Age dating based on Cesium-137
  - Reliable tool
  - Undisturbed sediment profiles
  - Half life of 30,8 years
  - Minimum age of about 35 years back to 1986 (Tschernobyl accident)
    - Tidal areas – fresh sediments

2. Option: Age dating based on chemical composition

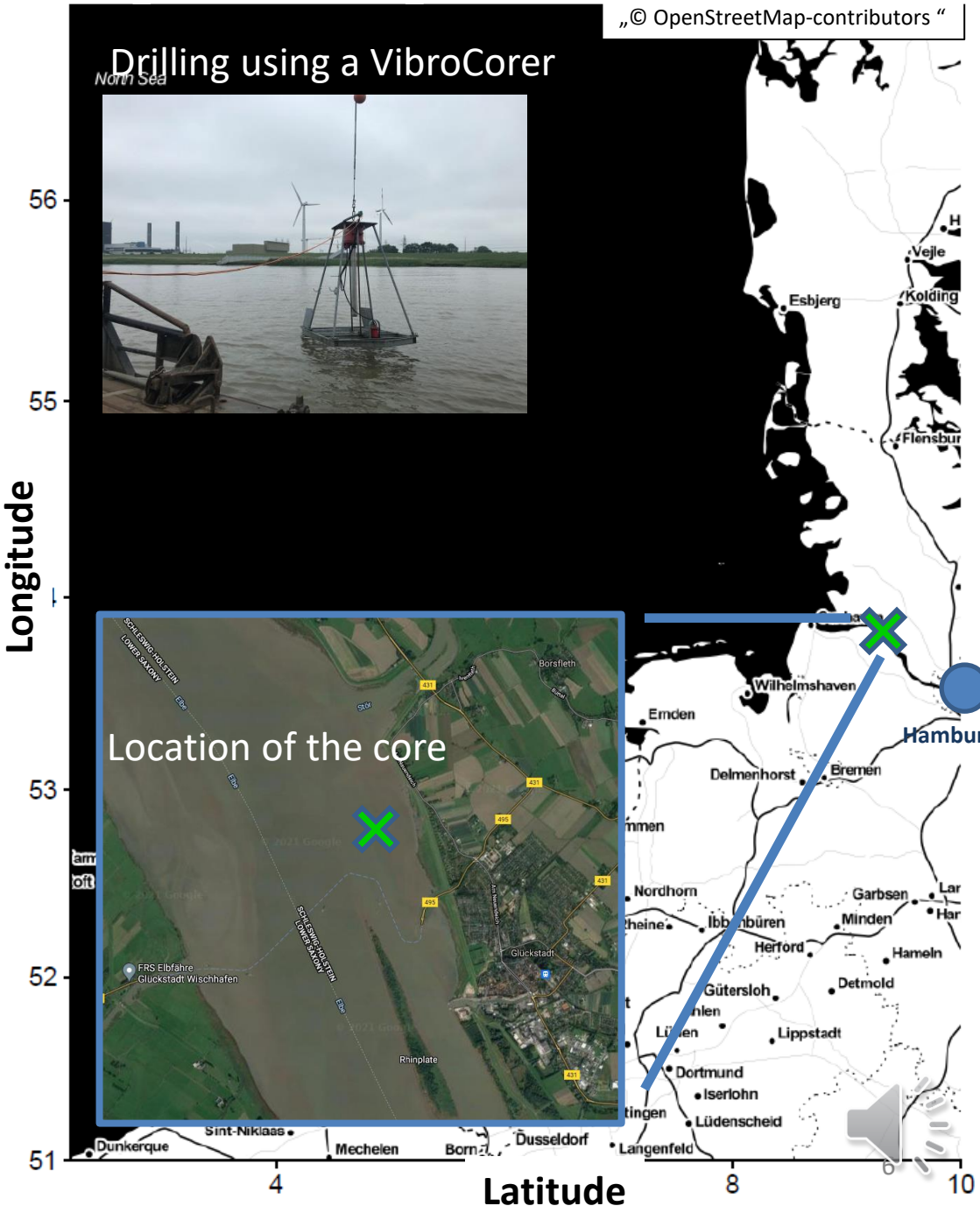
- Comparison of chemical composition with archived samples
- Selection of chemicals used as tracers
- Concentration profiles in sediments vs. concentration trends in particulate matter

Objectives

- Investigating whether emerging pollutants, might be suitable tracers for age dating of young sediment layers
- Combined approach by means of Cs-137 and emerging pollutants

Sampling

- Sampling in scope of a large sampling campaign
- Tidal influence
- Area with regular sediment management
- Flood events (e.g., 2002, 2006, 2013)



Sample preparation and treatment

- Drilling (June 2019) length 140 cm
- Cutting into 2 cm slices
- Each slice
  - Sieving
  - Homogenization
  - Lyophilization
  - CNS analysis (VarioMacro element analyzer)
  - Cs-137 activity measurement (Ge detector)
  - Extraction for LC-MS/MS analysis

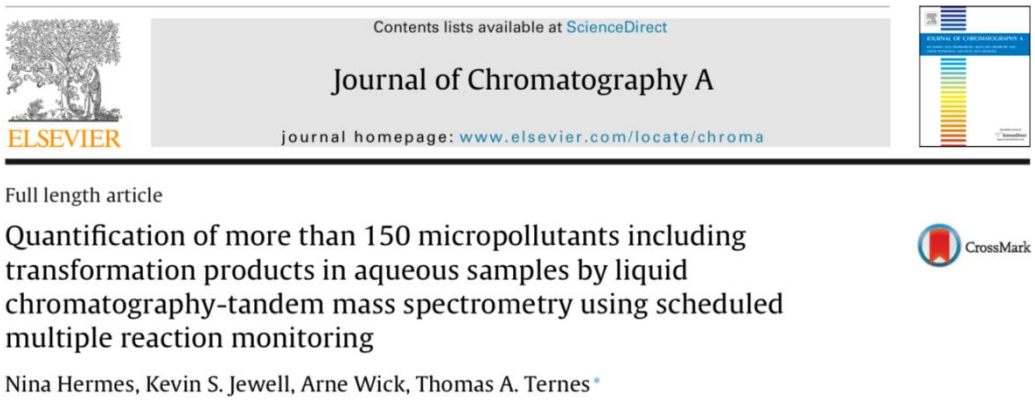
Sediment extraction

- Pressurized liquid extraction
- **Solvent A (MeOH / 2% Formic acid, 50:50)**
  Solvent B (MeOH / Water, 50:50)
- Filling to 30 mL with water
- 10 mL removed and evaporated (50 °C, N_2)
- Filling in 100 µL water and 900 µL ACN
- Centrifugation (6000 RPM, 10 min)
- 100 µL extract mixed with 900 µL of ACN

Method published by:
(Boulard et al. 2020)

Dionex ASE 350 (ThermoFischer)

Analytics: LC-MS/MS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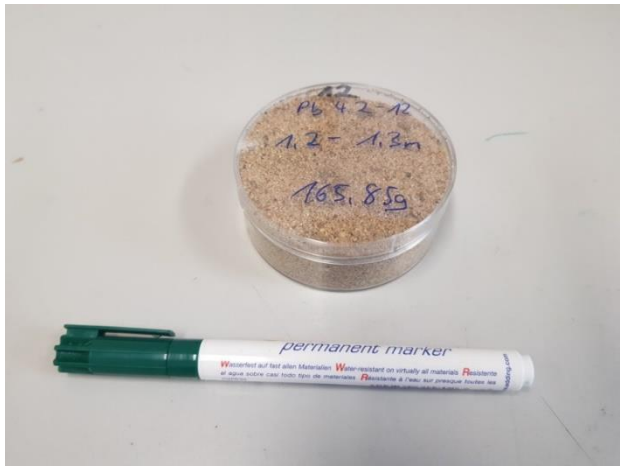
Full length article

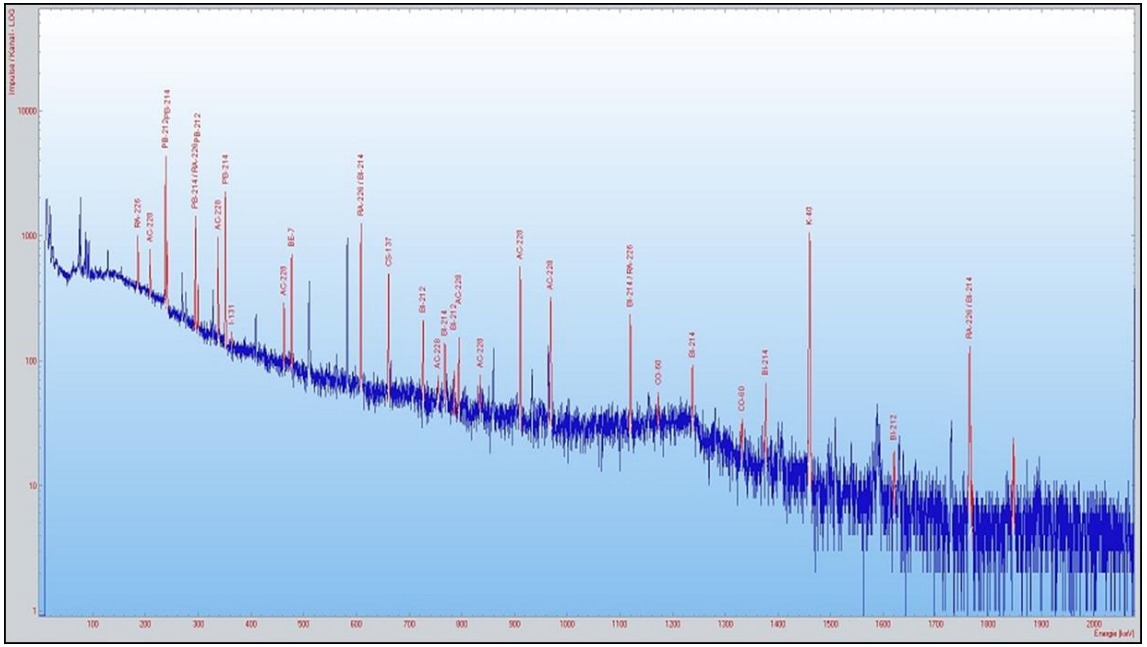
Quantification of more than 150 micropollutants including transformation products in aqueous samples by liquid chromatography-tandem mass spectrometry using scheduled multiple reaction monitoring

Nina Hermes, Kevin S. Jewell, Arne Wick, Thomas A. Ternes*

- **LC:** Agilent Technologies; **MS:** Sciex 6500+; ESI+ and -, Triple Quadrupole
- **Chromatographic Column:** C18 Zorbax Eclipse Plus
- **Eluents:** 0.1% Formic acid (A) and ACN (B)
- **Direct injection:** 80 µL
- Total: **72** compounds of **100**
- **Recovery** for most of the compounds: 70 – 120 %
- **LOQ:** 0.03-3.25 ng/g

Measurement of Cs-137 activities



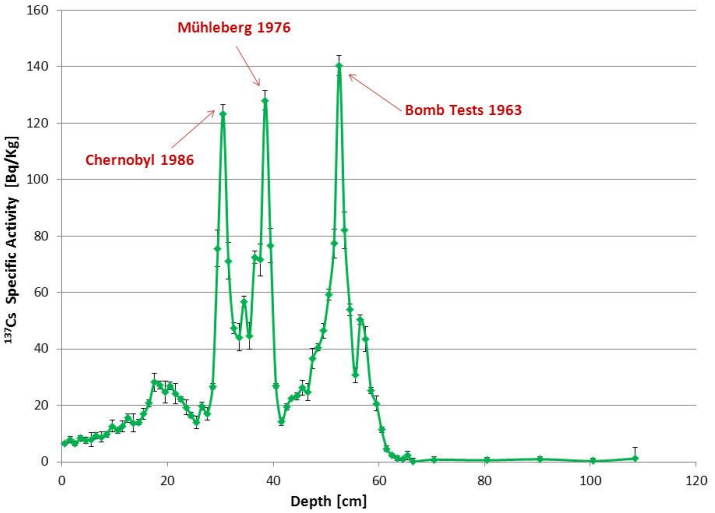


Nondestructive measuring technique

Age-dating using Cs-137

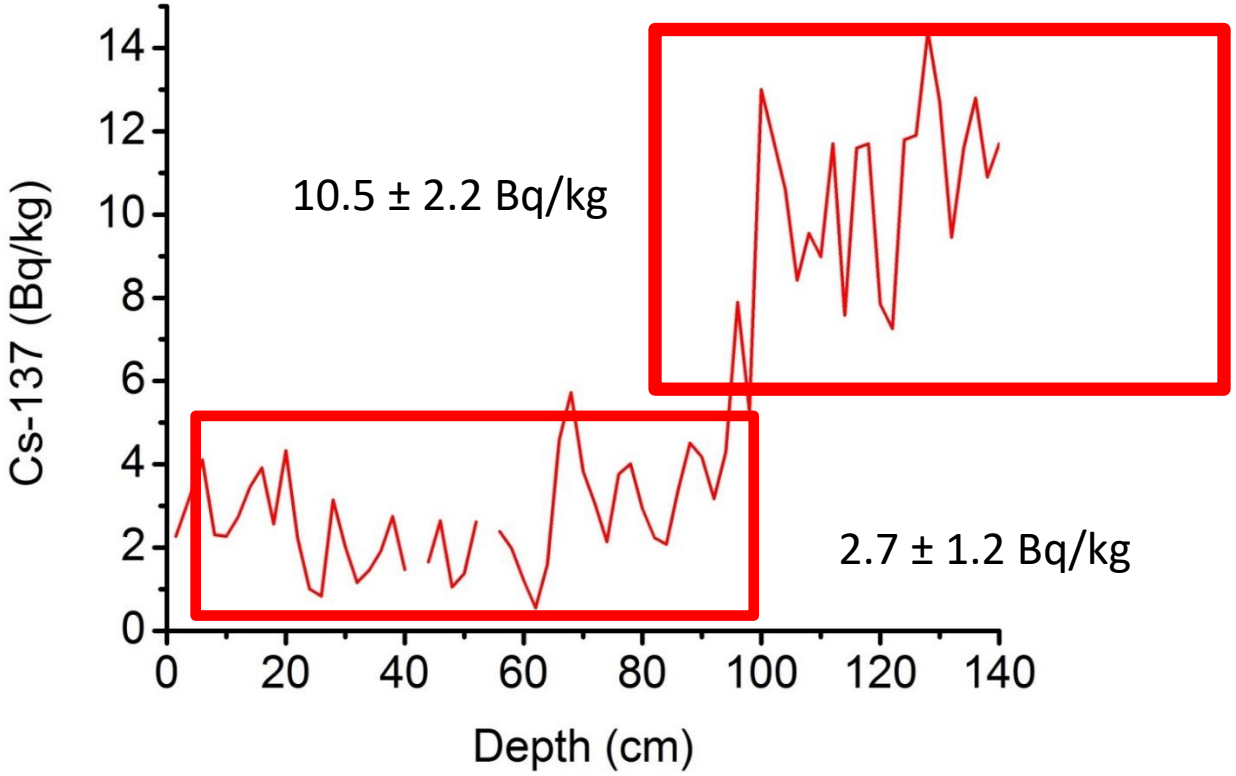
Typical Cs-137 activity of surface sediment samples in the Elbe estuary: 2-4 Bq/kg

Example: Age dating of a sediment core from the lake Biel (Bielersee)



(Pregler, 2014)

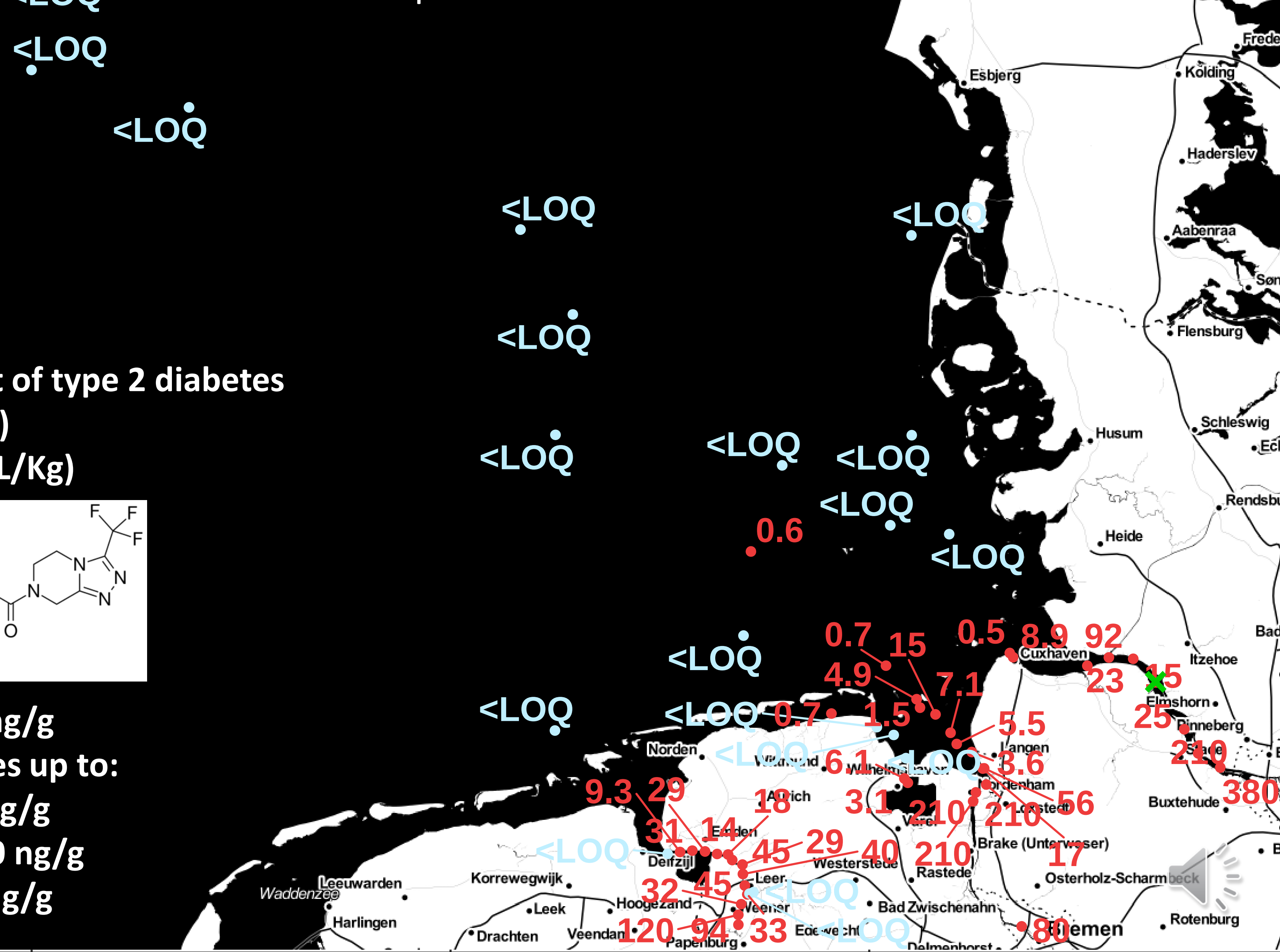
Sediment core – Elbe estuary



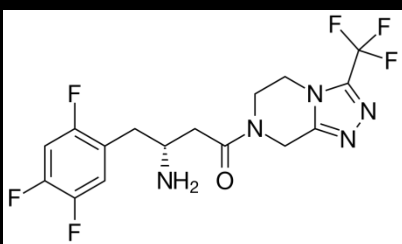
Our previous study:

Sitagliptin

in top 20 cm of sediment



Treatment of type 2 diabetes
Charge: (+)
Kd = 441 (L/Kg)

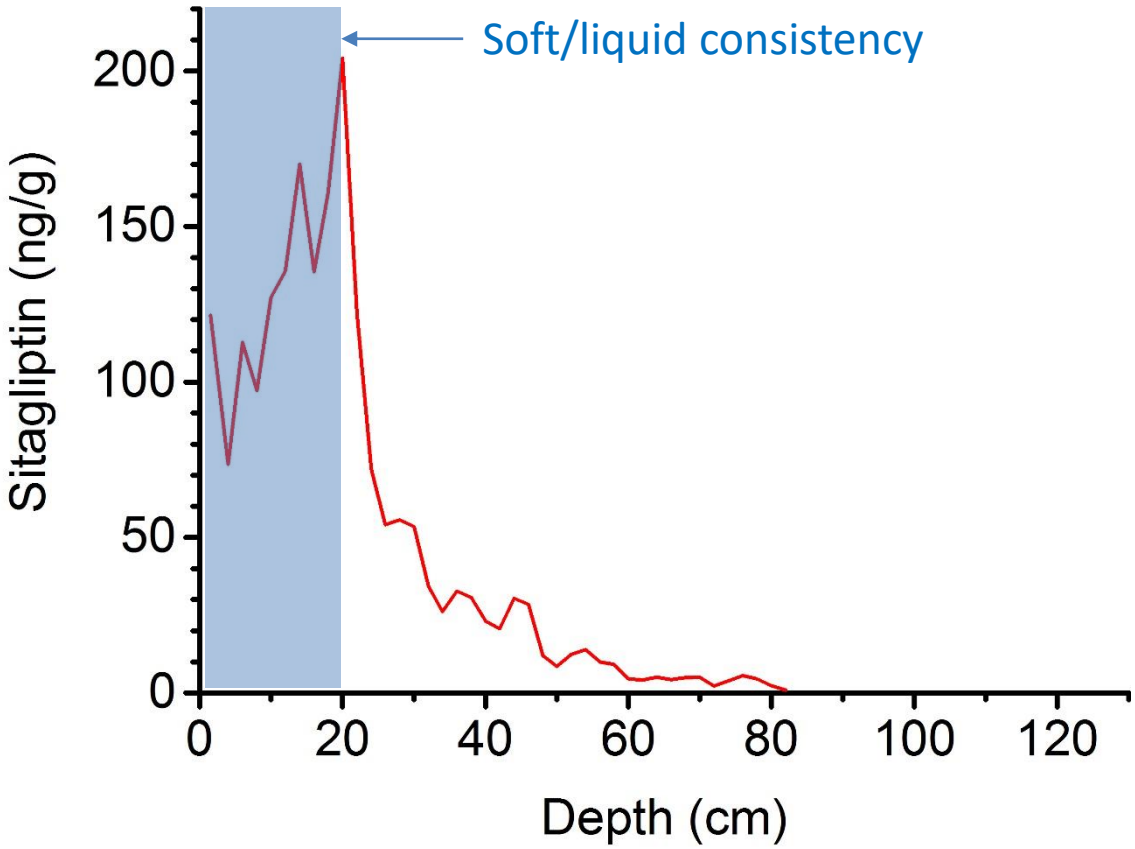


LOQ: 0.6 ng/g
In estuaries up to:
Ems 120 ng/g
Weser 210 ng/g
Elbe 380 ng/g

Sitagliptin

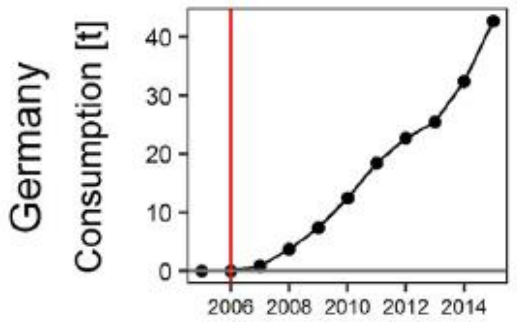
- LOQ: 0.6 ng/g
- Background conc.: <0.5 ng/g
- 2006-13.06.2019
  - 13.5 Years?
  - 6,1 cm/Year in average?

4) Sediment core – Elbe estuary



Boulard et al. 2020: Concentration of sitagliptin in particulate matter of the Rhine:

1)



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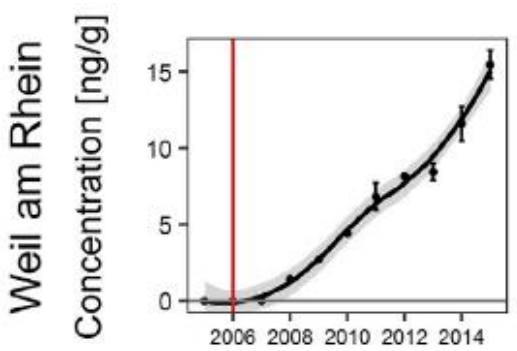

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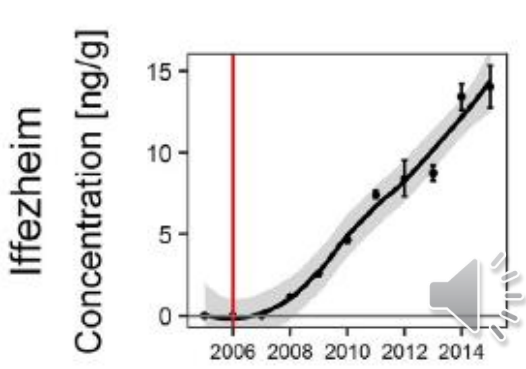

Further compounds

Aliskiren, citalopram and climbazole

- Characteristic pattern in consumption data or steep increase of consumption from 2006

Top 20 cm

- Close to the liquid limit
- Strong data variations

Depth 20 – 82 cm

- Concentration trends generally reflect the consumption data
- Data suggest different sedimentation rates across the profile

Depth 82 cm

- Concentration increases with depths above 82 cm
  → consistent with Cs-137 activity
- 82 cm depth can be used as 2006 approximation

Benefits and limitations

Concentration profiles of micropollutants can be used for age dating of recent sediments

- Cores with undisturbed sediment layers
- Identification of substances with overlapping release dates and concentration trends
  → specific time-stamps
- Specific analysis of catchment area
- Measurement of Cs-137 activity concentrations
  → detailed characterization of the sediment (sufficient length)
- Comparison of several sediment cores

Acknowledgement

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- Hamburg Waterways and Shipping Office (WSA Hamburg)

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Thank you for your attention!