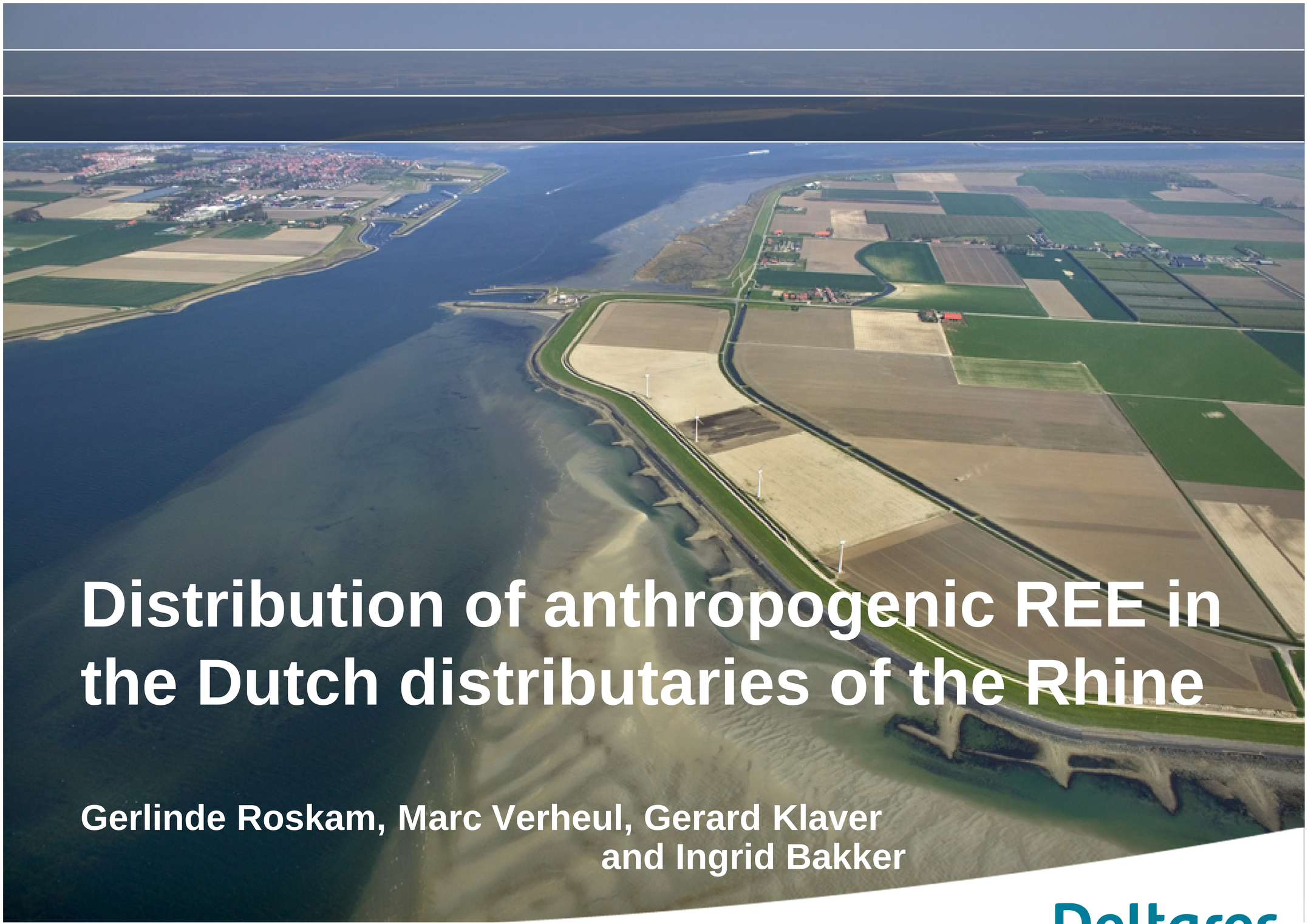

Distribution of anthropogenic REE in the Dutch distributaries of the Rhine

Gerlinde Roskam, Marc Verheul, Gerard Klaver
and Ingrid Bakker

This project was financed by the Dutch Ministry of Infrastructure and the Environment

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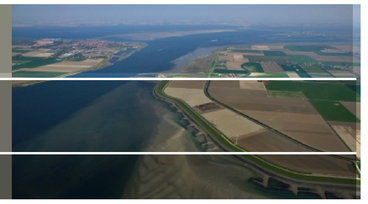
REE = (not at all) Rare Earth Elements



Periodic Table of the Elements

1 1IA 11A	2 IIA 2A	3 IIIB 3B	4 IVB 4B	5 VB 5B	6 VIB 6B	7 VIIB 7B	8	9 VIII 8	10	11 IB 1B	12 IIB 2B	13 IIIA 3A	14 IVA 4A	15 VA 5A	16 VIA 6A	17 VIIA 7A	18 VIIIA 8A
1 H Hydrogen 1.0079																	2 He Helium 4.00260
3 Li Lithium 6.941	4 Be Beryllium 9.01218											5 B Boron 10.811	6 C Carbon 12.011	7 N Nitrogen 14.00674	8 O Oxygen 15.9994	9 F Fluorine 18.998403	10 Ne Neon 20.1797
11 Na Sodium 22.989768	12 Mg Magnesium 24.305											13 Al Aluminum 26.981539	14 Si Silicon 28.0855	15 P Phosphorus 30.973762	16 S Sulfur 32.066	17 Cl Chlorine 35.4527	18 Ar Argon 39.948
19 K Potassium 39.0983	20 Ca Calcium 40.078	21 Sc Scandium 44.95591	22 Ti Titanium 47.88	23 V Vanadium 50.9415	24 Cr Chromium 51.9961	25 Mn Manganese 54.938	26 Fe Iron 55.847	27 Co Cobalt 58.9332	28 Ni Nickel 58.6934	29 Cu Copper 63.546	30 Zn Zinc 65.39	31 Ga Gallium 69.732	32 Ge Germanium 72.64	33 As Arsenic 74.92159	34 Se Selenium 78.96	35 Br Bromine 79.904	36 Kr Krypton 83.80
37 Rb Rubidium 85.4678	38 Sr Strontium 87.62	39 Y Yttrium 88.90585	40 Zr Zirconium 91.224	41 Nb Niobium 92.90638	42 Mo Molybdenum 95.94	43 Tc Technetium 98.9072	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.9055	46 Pd Palladium 106.42	47 Ag Silver 107.8682	48 Cd Cadmium 112.411	49 In Indium 114.818	50 Sn Tin 118.71	51 Sb Antimony 121.760	52 Te Tellurium 127.6	53 I Iodine 126.90447	54 Xe Xenon 131.29
55 Cs Cesium 132.90543	56 Ba Barium 137.327	57-71	72 Hf Hafnium 178.49	73 Ta Tantalum 180.9479	74 W Tungsten 183.85	75 Re Rhenium 186.207	76 Os Osmium 190.23	77 Ir Iridium 192.22	78 Pt Platinum 195.08	79 Au Gold 196.9665	80 Hg Mercury 200.59	81 Tl Thallium 204.3833	82 Pb Lead 207.2	83 Bi Bismuth 208.98037	84 Po Polonium [208.9824]	85 At Astatine 209.9871	86 Rn Radon 222.0176
87 Fr Francium 223.0197	88 Ra Radium 226.0254	89-103	104 Rf Rutherfordium [261]	105 Db Dubnium	106 Sg Seaborgium	107 Bh	108 Hs [269]	109 Mt [268]	110 Ds [269]	111 Rg [272]	112 Cn [277]	113 Uut unknown	114 Uuq	115 Uup Ununpentium	116 Uuh Ununhexium	117 Uus Ununseptium unknown	118 Uuo Ununoctium unknown

Lanthanide Series	57 La Lanthanum 138.9055	58 Ce Cerium 140.115	59 Pr Praseodymium 140.90765	60 Nd Neodymium 144.24	61 Pm Promethium 144.9127	62 Sm Samarium 150.36	63 Eu Europium 151.9655	64 Gd Gadolinium 157.25	65 Tb Terbium 158.92534	66 Dy Dysprosium 162.50	67 Ho Holmium 164.93032	68 Er Erbium 167.26	69 Tm Thulium 168.93421	70 Yb Ytterbium 173.04	71 Lu Lutetium 174.967
Actinide Series	89 Ac Actinium 227.0278	90 Th Thorium 232.0381	91 Pa Protactinium 231.03588	92 U Uranium 238.0289	93 Np Neptunium 237.0482	94 Pu Plutonium 244.0642	95 Am Americium 243.0614	96 Cm Curium 247.0703	97 Bk Berkelium 247.0703	98 Cf Californium 251.0796	99 Es Einstelnium [254]	100 Fm Fermium 257.0951	101 Md Mendelevium 258.1	102 No Nobelium 259.1009	103 Lr Lawrencium [262]

Alkali Metal | Alkaline Earth | Transition Metal | Basic Metal | Semimetals | Nonmetals | Halogens | Noble Gas | Lanthanides | Actinides

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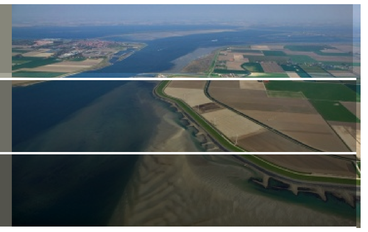
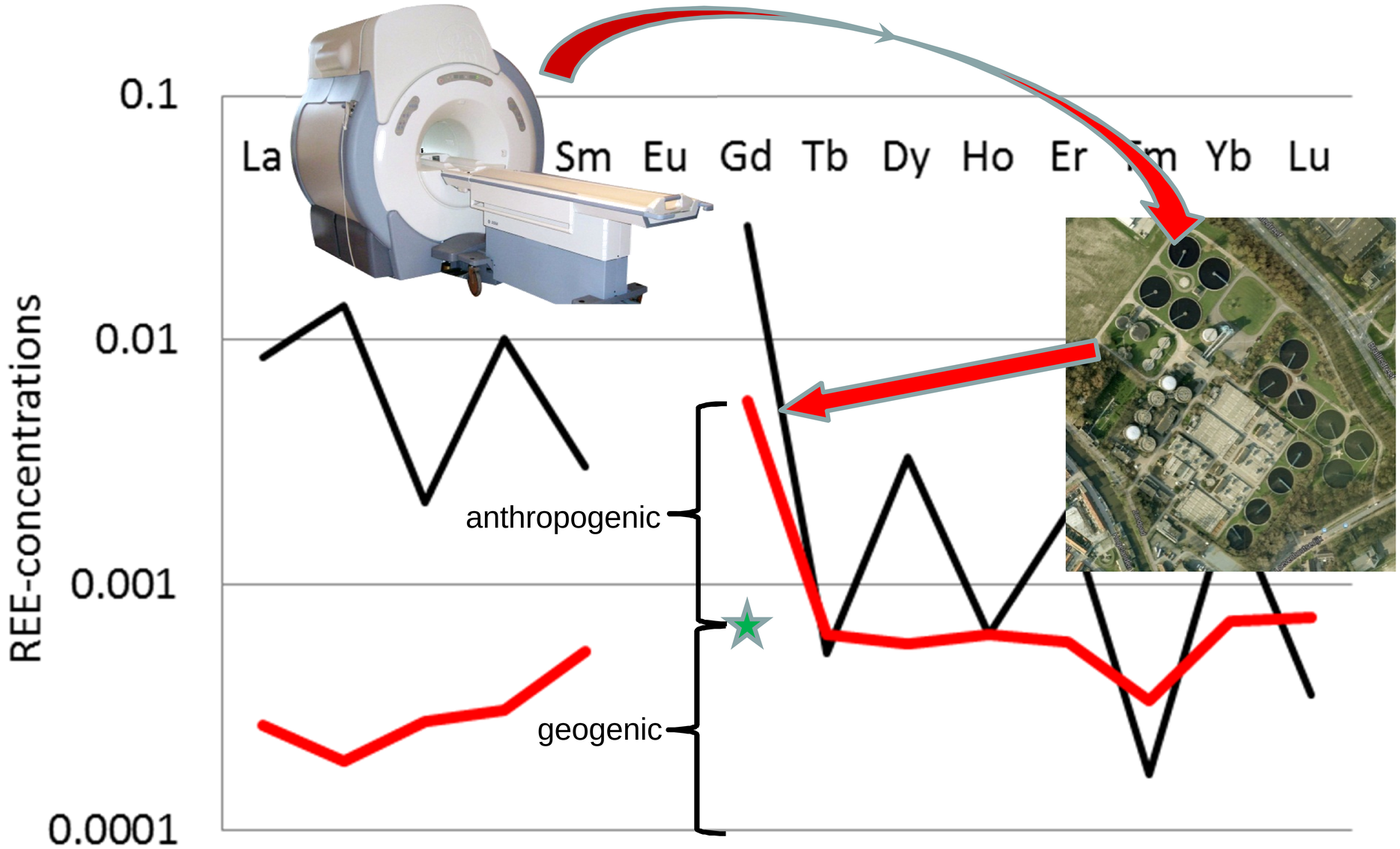
Normalisation





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Available REE-data

<u>Marine environment</u>

- 92 monitoring locations
- 43 sampled every 3 years

- REE-content in < 63 μm fraction of sediment

<u>Rhine, Meuse and distributaries</u>

- 16 monitoring locations points
- sampled monthly (biweekly at Lobith)

- REE concentrations BEFORE (total water) and AFTER filtration + REE-content of suspended matter

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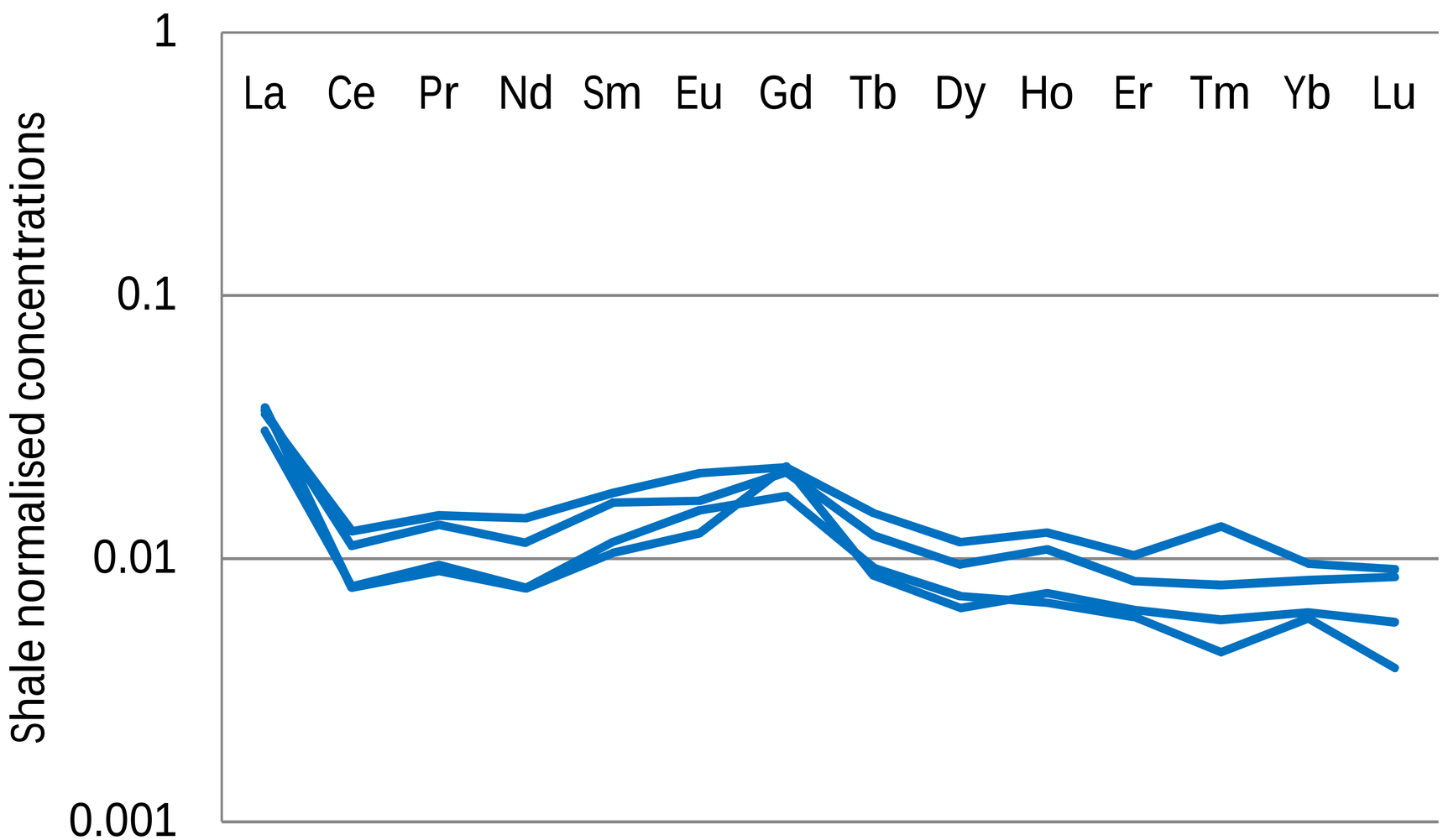
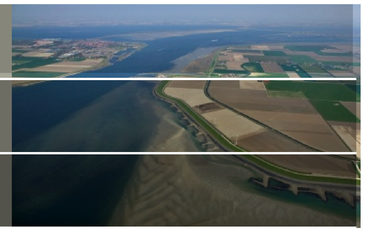
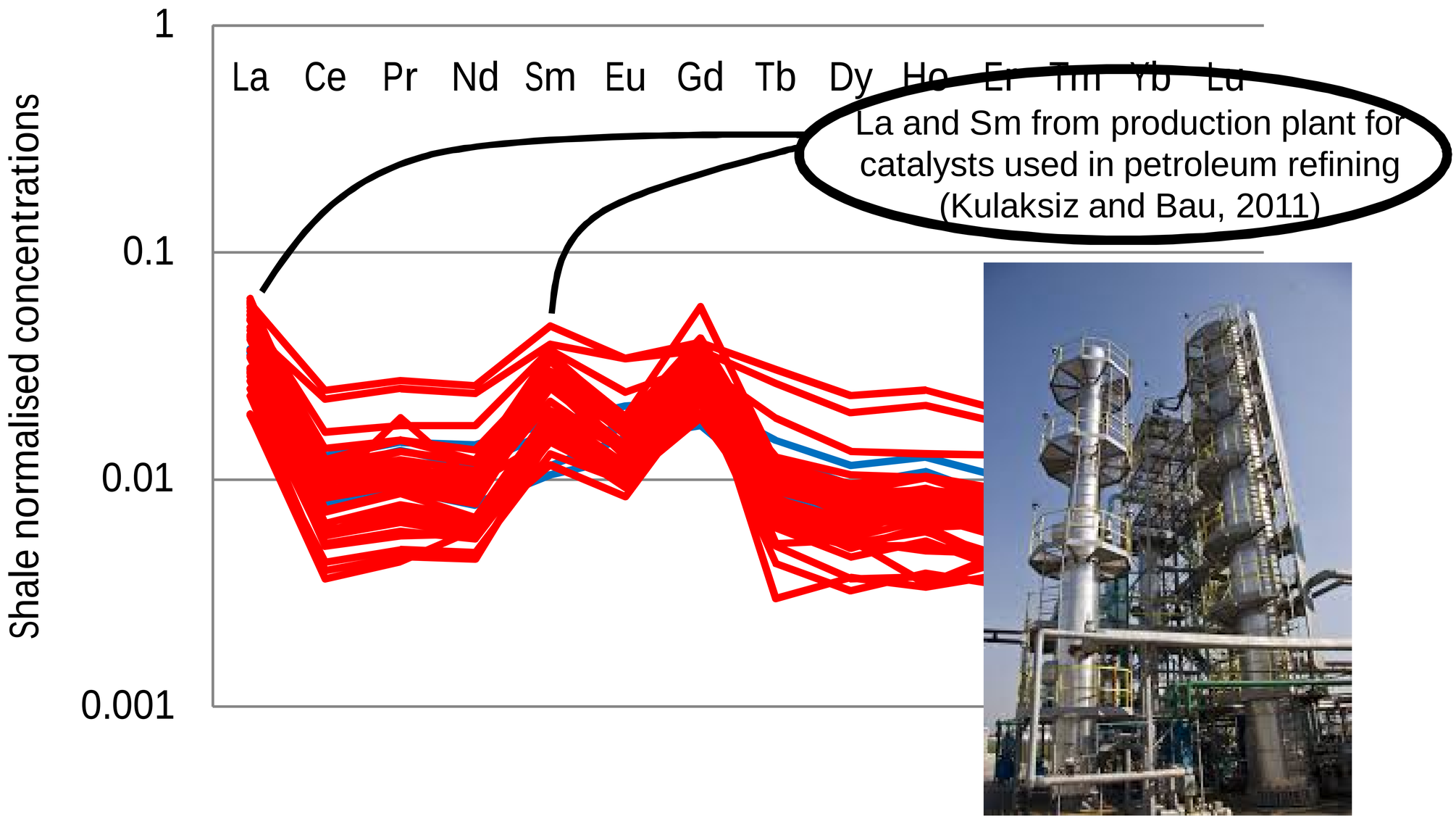
Lobith - before filtration - Jan/Feb 2011



Deltares

Lobith - before filtration - 2011





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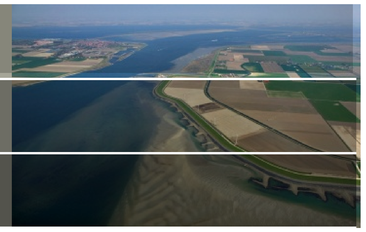
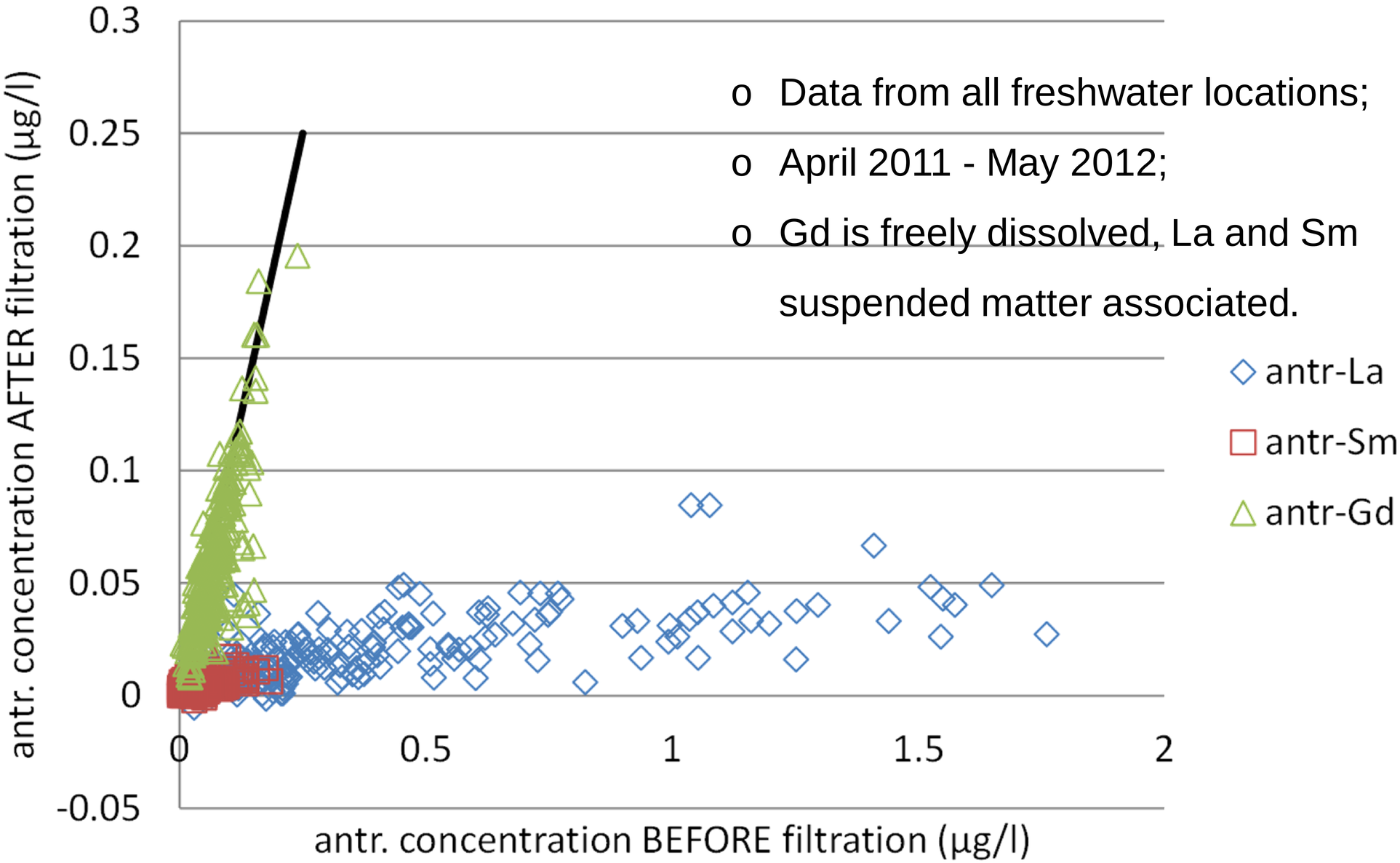
Anthropogenic Gd, La and Sm



- Data from all freshwater locations;
- April 2011 - May 2012;
- Gd is freely dissolved, La and Sm suspended matter associated.



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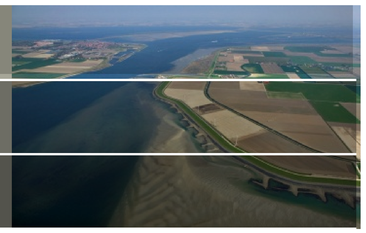
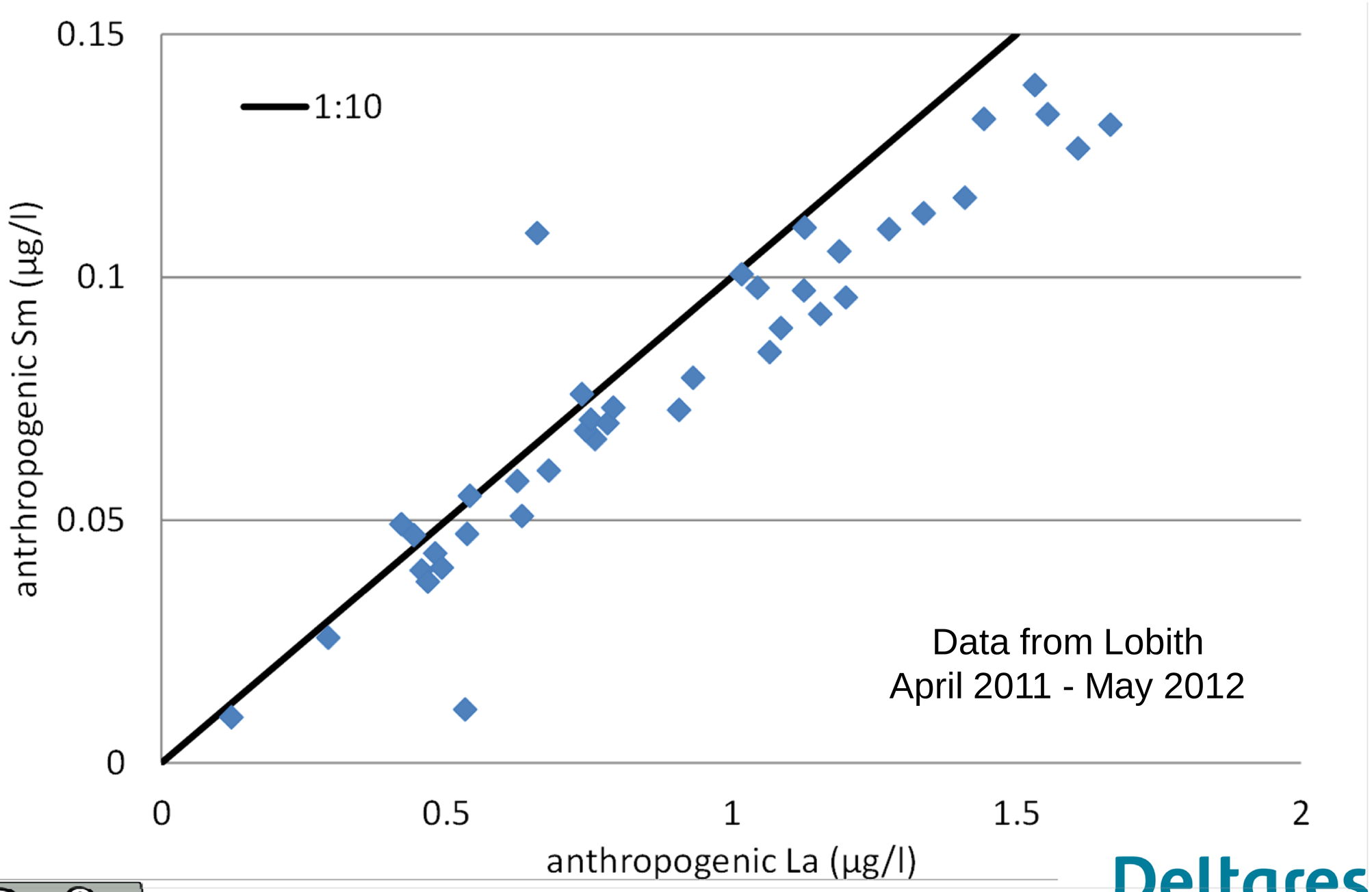
Ratio anthropogenic La:Sm





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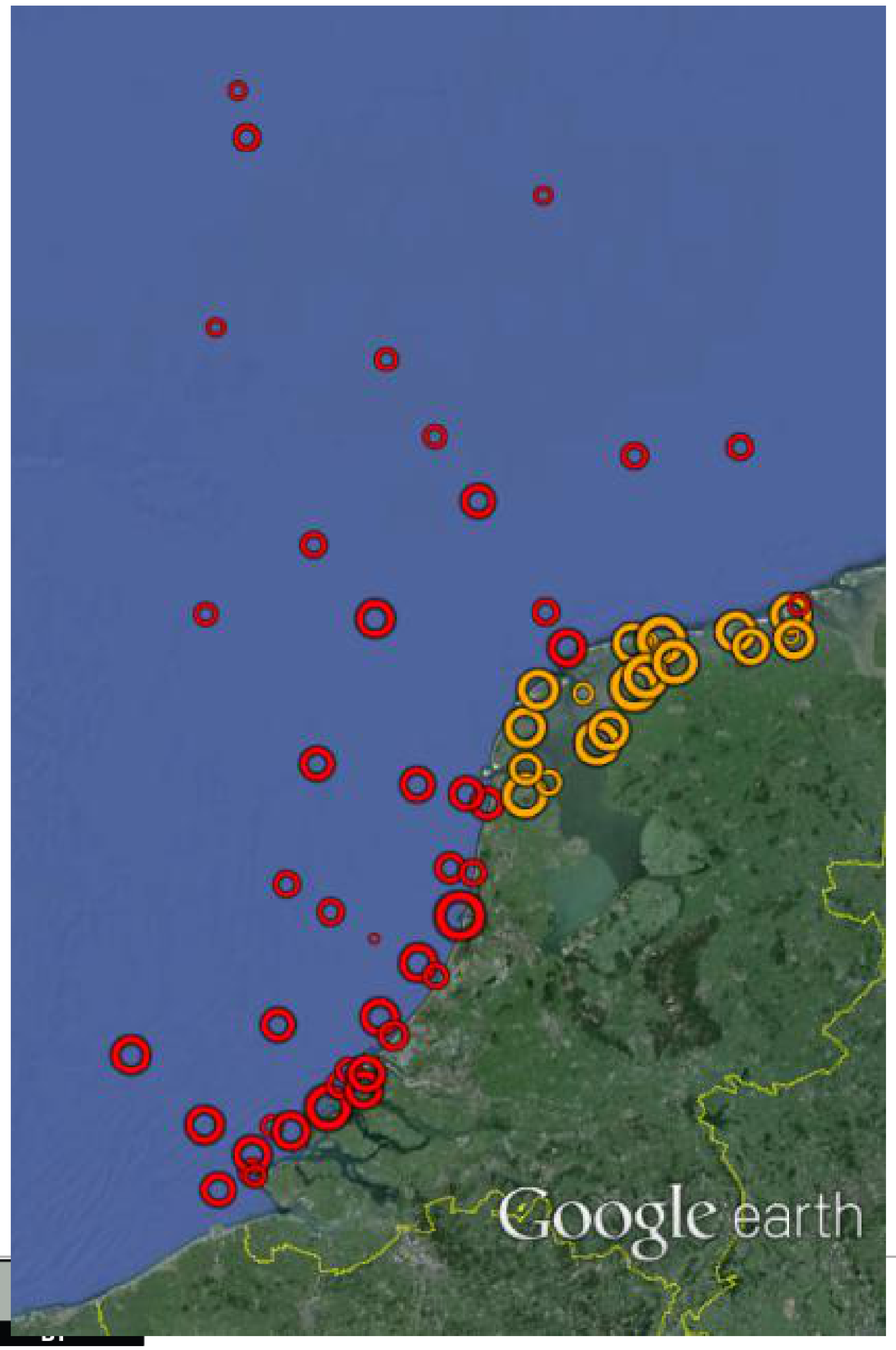
La-anomaly in the North Sea and Wadden Sea



- Data from 2008 + 2009;
- Sediment fraction < 63 µm;
- Doubts about the way the samples were prepared;
- Quality of analysis is limited;
- Anomalies range from about 1 to 1.3;
- Generally larger anomalies close to the coast.

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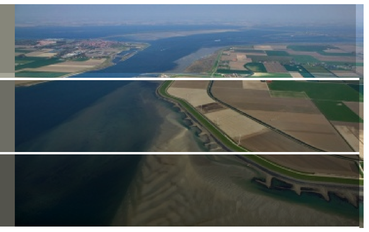
Following two routes



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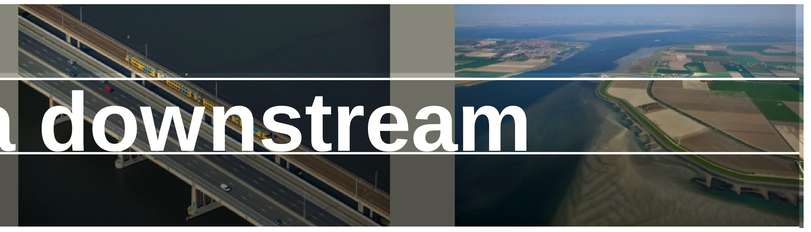
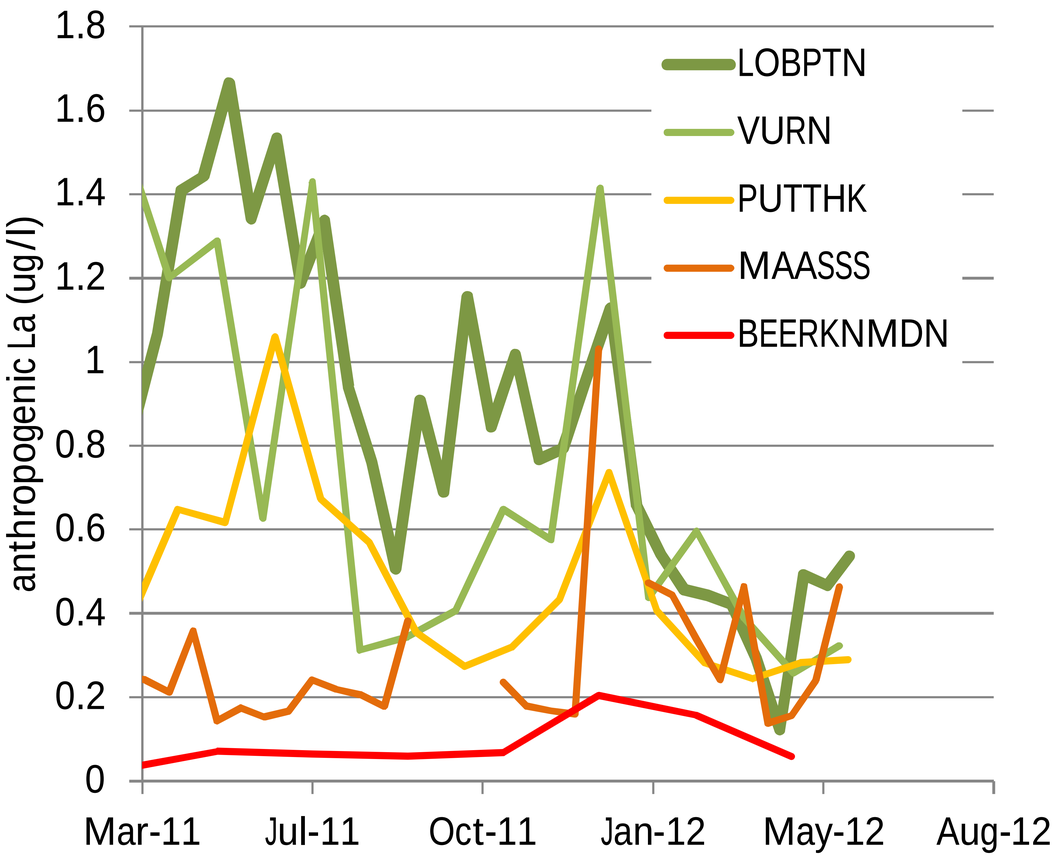
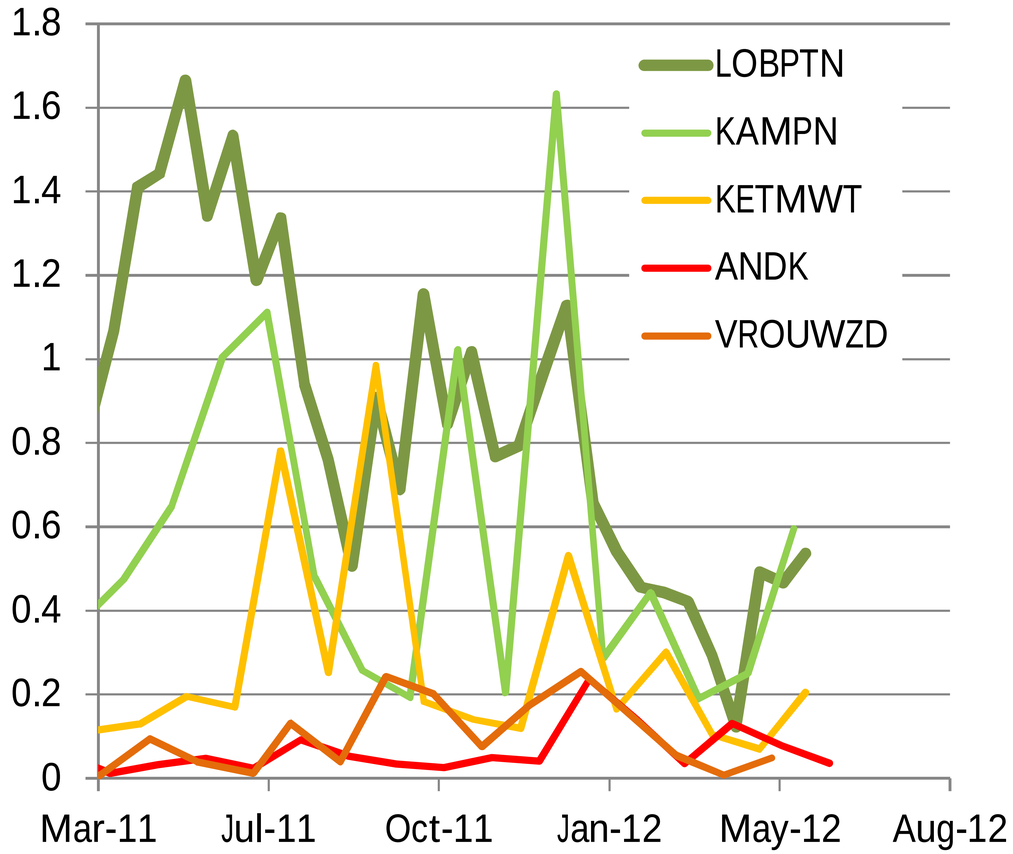
Decrease in anthropogenic La downstream



towards the North Sea



towards Lake IJsselmeer



- Anthropogenic La in total water samples
- Data April 2011 - May 2012

Just sedimentation?

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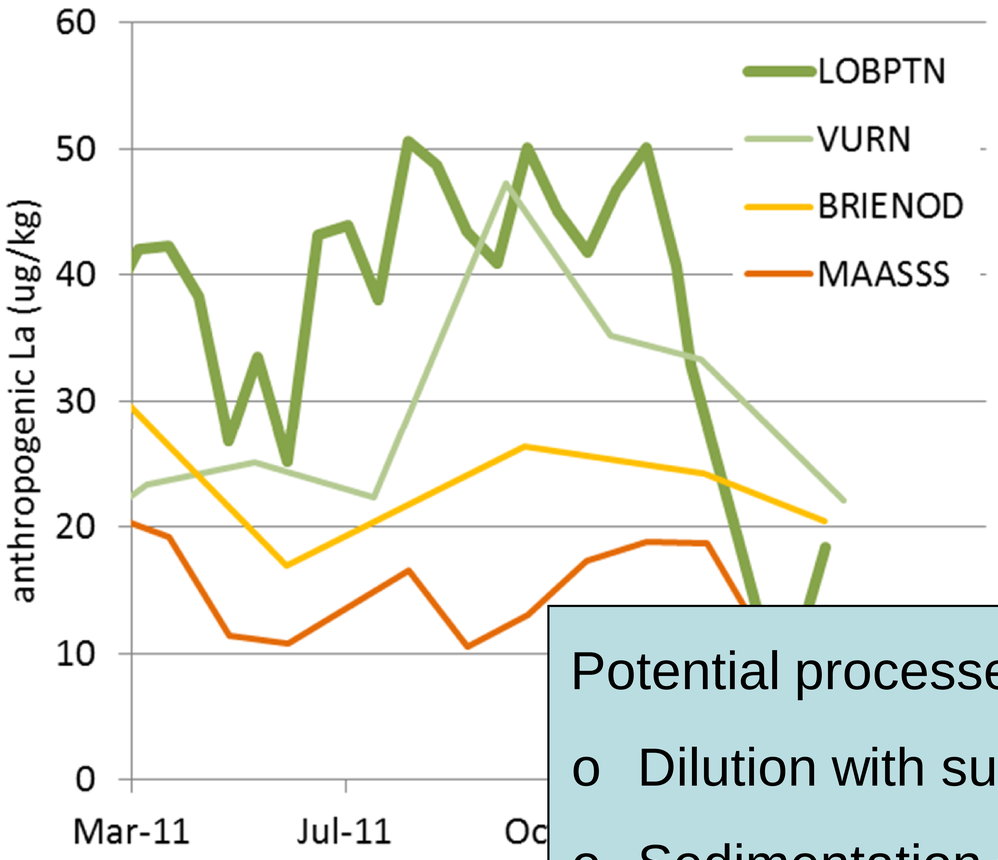
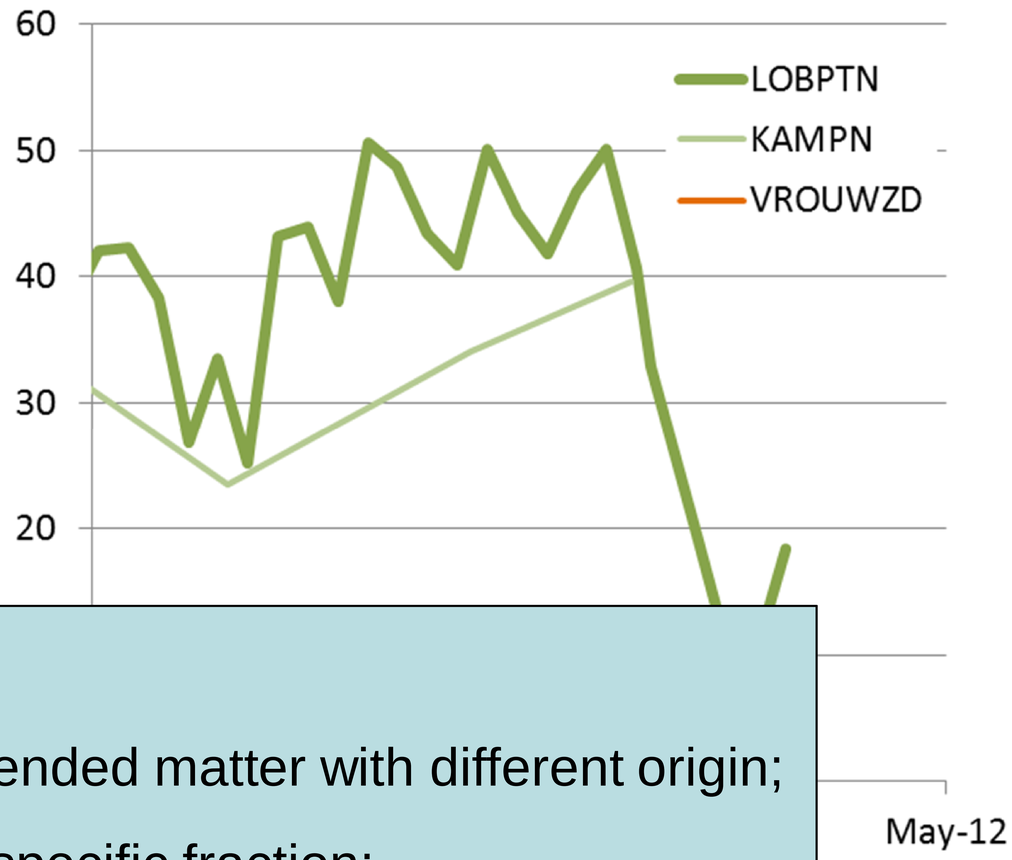
Decrease in anthr. La in suspended matter

towards the North Sea



towards Lake IJsselmeer



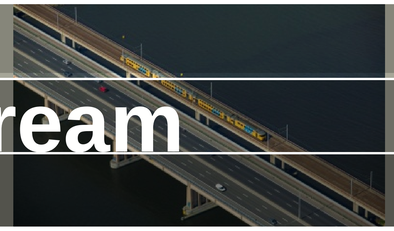
Potential processes:

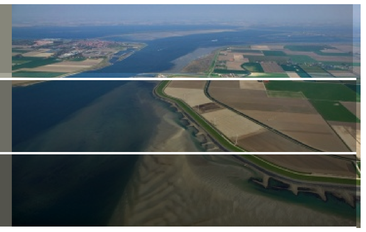
- Dilution with suspended matter with different origin;
- Sedimentation of specific fraction;
- Resuspension of older sediments.

- Anthropogenic La in total water samples
- Data April 2011 - May 2012

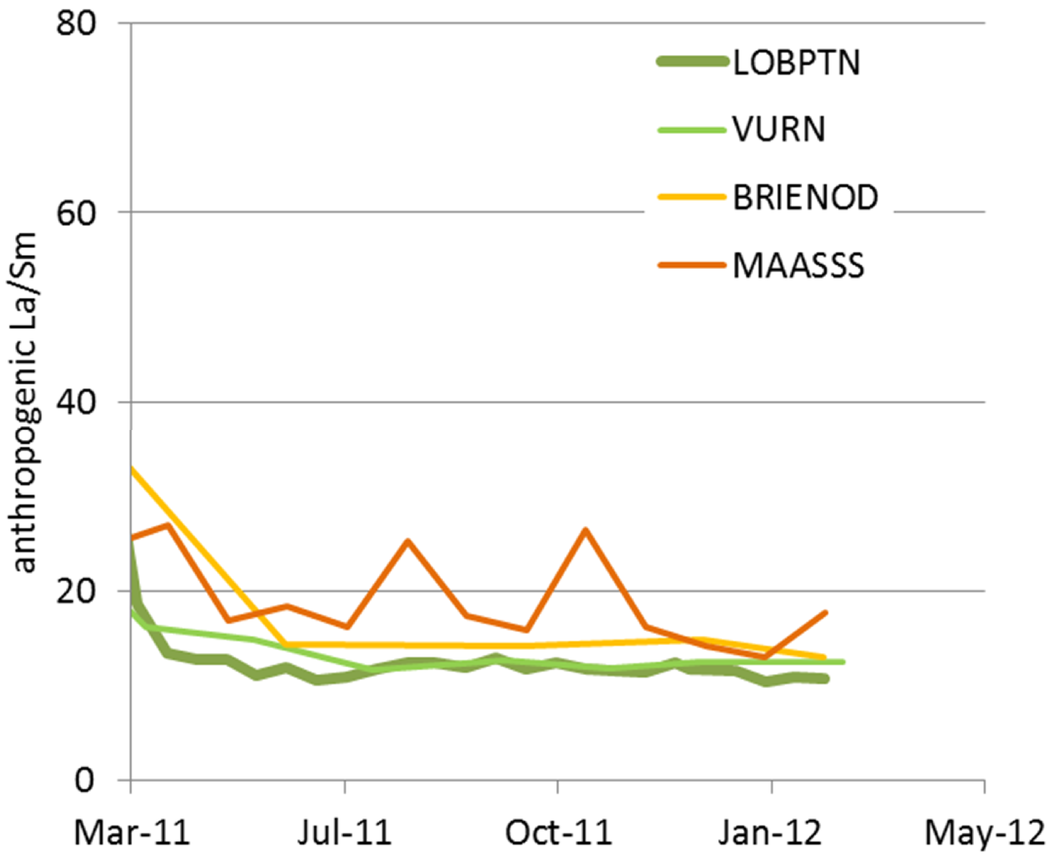
Deltares

Decrease Sm/La ratio downstream

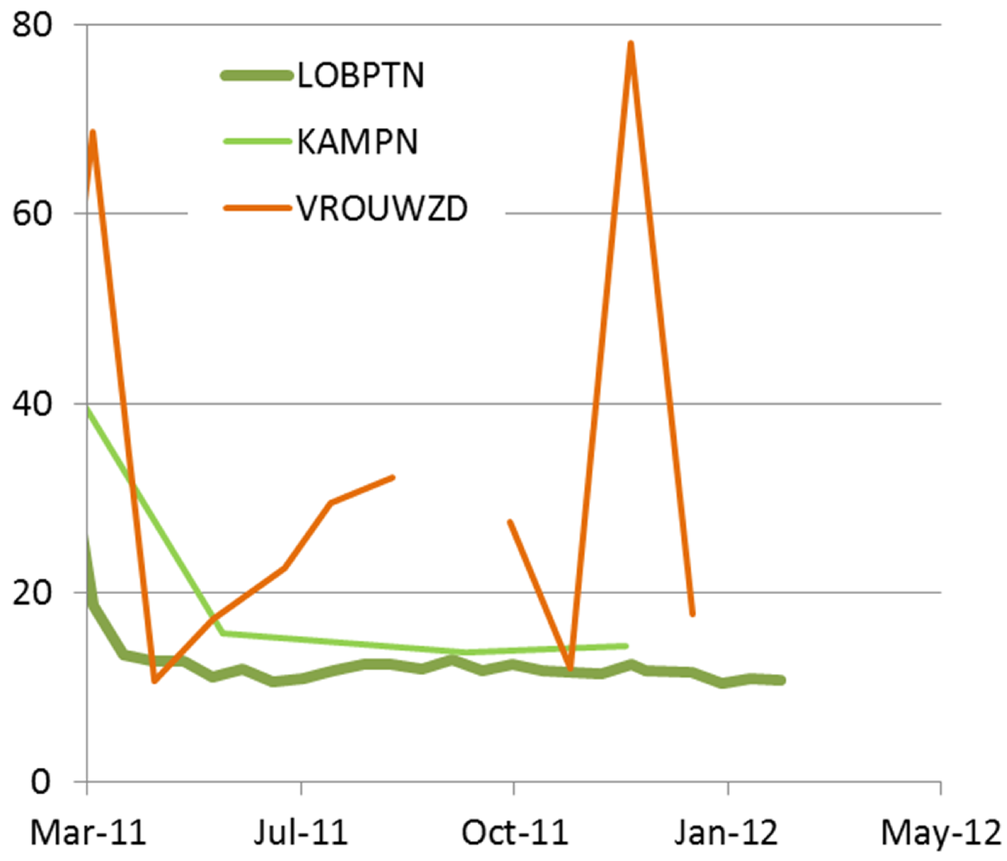




towards the North Sea



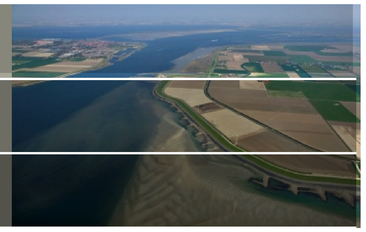
towards Lake IJsselmeer



- Ratio anthr. La/anthr. Sm in suspended matter
- Data April 2011 - Feb 2012

Deltares

Conclusions

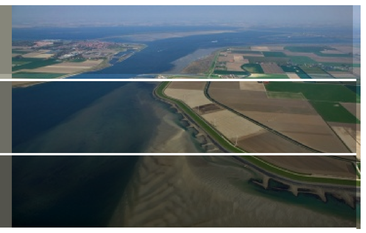


- Sedimentation causes a strong decrease in the anthropogenic La- and Sm-concentrations towards the North Sea and Lake IJsselmeer;

- Based on the La/Sm ratio in the suspended matter, we can conclude that some resuspension of older sediments takes place, mainly in Lake IJsselmeer;

- Behaviour of different size fractions of suspended matter cannot be deduced from this data set.

Questions that are still open



- Can we use the La- and Sm-anomalies for dating sediments?

  → Sample sediment cores and measure the La- and Sm-anomalies in different layers.

- Are La and Sm associated with a specific size fraction? And if so, is this fraction properly sampled with a centrifuge?

  → Sample different size fractions and determine La- and Sm-content

- How strong is the association of La and Sm with suspended matter?

  → Perform online continuous leach ICP-MS analysis with increasing HNO_3 concentrations.

- What happens at the fresh water - salt water interface with La and Sm?

  → Perform online continuous leach ICP-MS analysis with increasing salt concentrations.