



Water quality of Lake Paranoá - Toxicologically relevant inorganic traces and sum parameters

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**Subproject 5
Water Quality**

**Final Workshop - Project IWAS ÁGUA DF
Integrated Water Resources Management
in Distrito Federal – DF
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Situation, Lake Paranoá

- used for recreational activities, energy generation, fishery, and as receiving reservoir for effluents of two sewage treatment plants (tertiary treat.)
- political decision to use Lake Paranoá as future drinking water reservoir
- few data available concerning basic parameters of the water quality
- lack of information about the occurrence of organic micropollutants in the lake



<http://www.ufz.de/iwas-sachsen/index.php?en=18049>



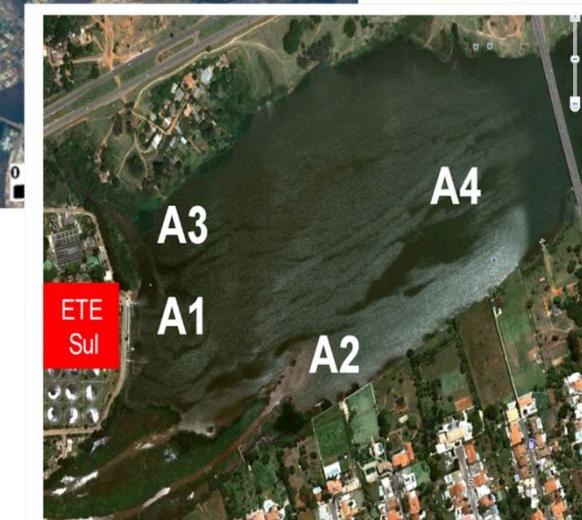
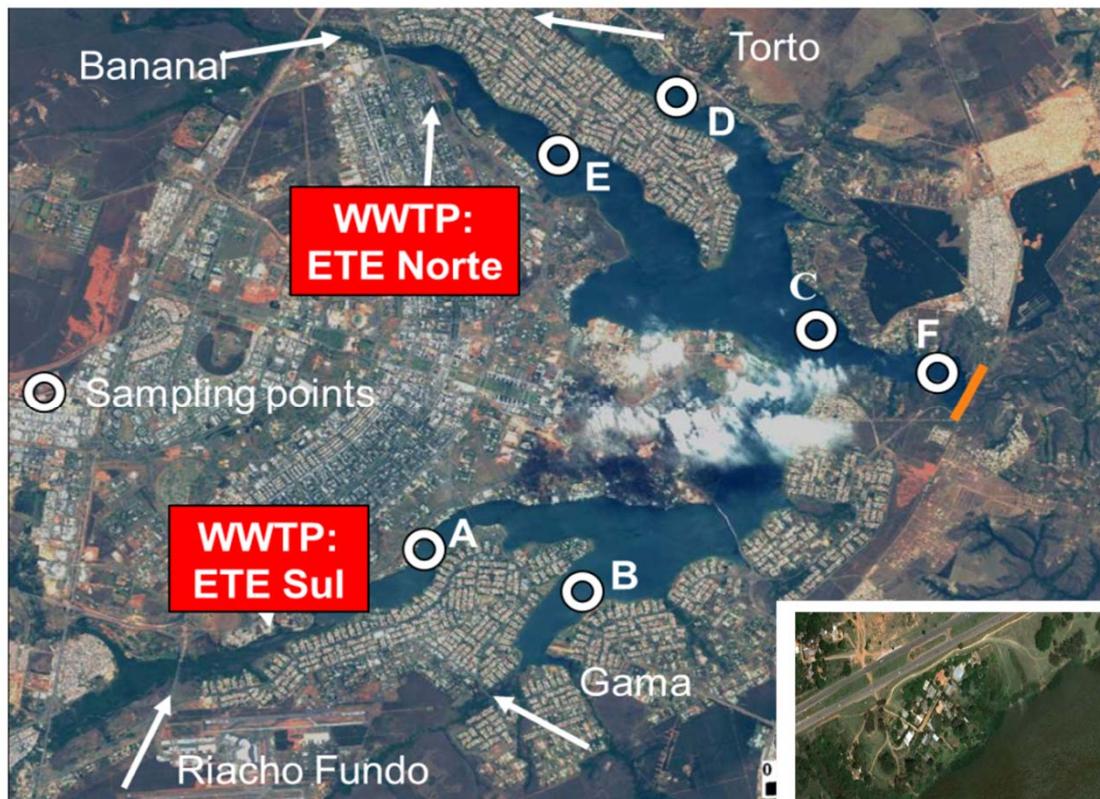
Subproject 5 – Water Quality

Objectives

- **to gather detailed data and information concerning factors which impact water quality in the Federal District**
- **to monitor water quality, to specify sampling points and sampling campaigns**
- **to screen contaminants relevant for water quality, including metals, organic sum parameters, and organic micropollutants**
- **to evaluate data and to look for trends and conclusions for further required water analysis**
- **to adapt and implement analytical methods in Brasilia (Caesb)**



Sampling



Sites selection and strategy

- A to E (Caesb), F (new)
- main tributaries (4)
- effluent WWTP (Norte, Sul)
- grab samples
- 1 m b.s.
- depth profile in C
- sampling during wet and dry season
- daily composite samples (WWTP)
- sediments (A1,2,3,4), porewater



google earth



Outline, water quality of Lake Paranoá

- **inorganic compounds**
 - anions, phosphorous, (heavy)metals, metalloids
- **DOC, advanced DOC characterization**
 - gel chromatography with online OC- and UV-detection
 - SAK (254 nm)
- **sediments**
 - heavy metals and phosphorous
 - colloids and nanoparticles
- ***organic micropollutants*** (→ WG Worch et al.)



Basic inorganic parameters, Lake Paranoá (A-F)

| pH | Elect. Cond. μScm ⁻¹ | Cl ⁻ mgL ⁻¹ | NO ₃ ⁻ mgL ⁻¹ | P μgL ⁻¹ | SO ₄ ²⁻ mgL ⁻¹ | Ca ²⁺ mgL ⁻¹ | Mg ²⁺ mgL ⁻¹ |
|-----------|------------------------------------|--------------------------------------|---|------------------------|--|---------------------------------------|---------------------------------------|
| 7.5...8.0 | 80 ... 110 | 6 ... 8 | 2 ... 7 | 22 (m) | 6 ... 10 | 8.82 (m) | 0.99 (m) |

Metals, As, B, Se, Si conc. (mean val. (m)), Lake Paranoá (A-F)

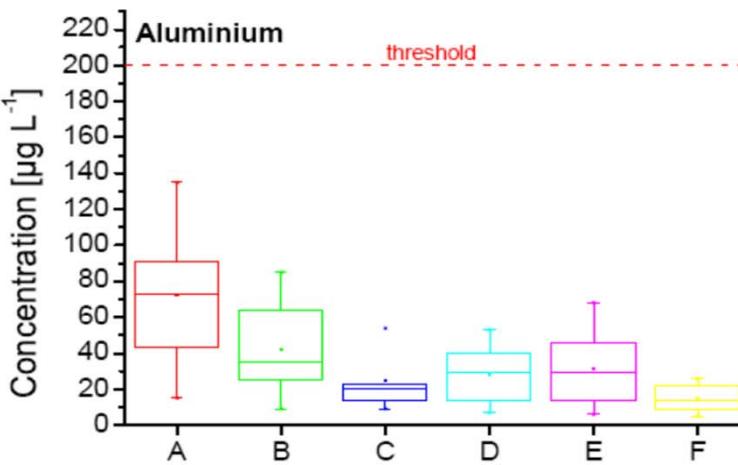
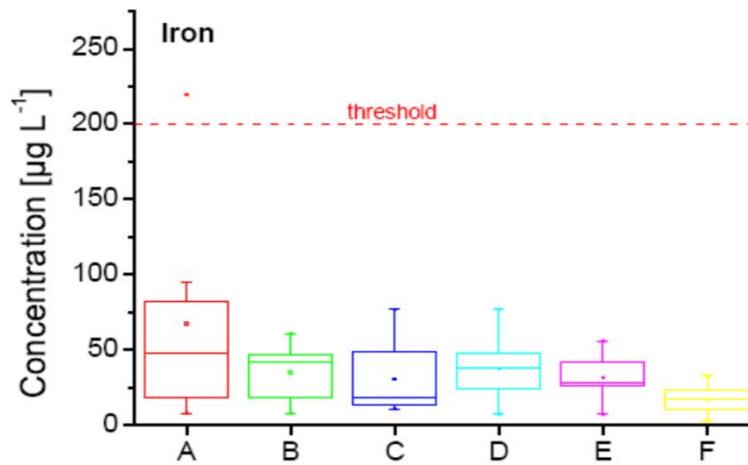
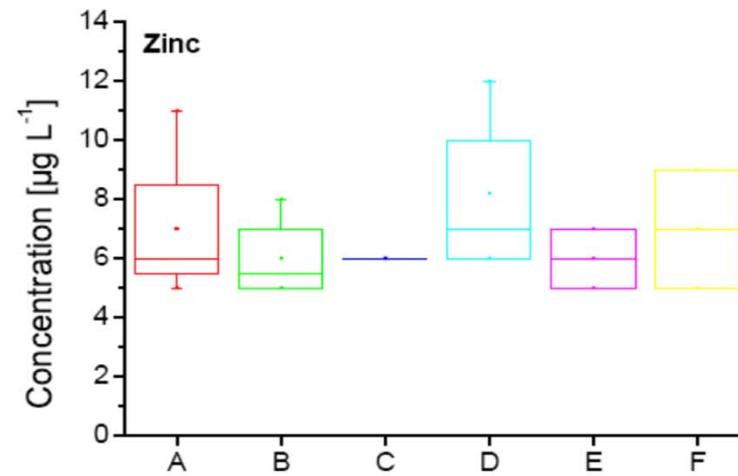
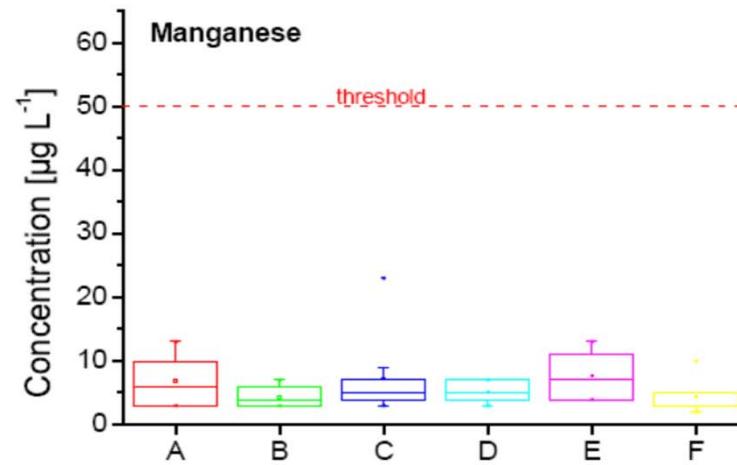
| | Al | As | B | Cd | Cr | Cu | Fe | Mn | Na | Ni | Pb | Se | Si | Zn |
|-------------------|------------|-------|------|-----|-----|------|------------|-----------|-------------------------|-----|-------|-------|------|-------------|
| μgL ⁻¹ | 34 | < 10* | 11 | < 2 | < 2 | < 10 | 31 | 5 | 8110 | < 5 | < 10* | < 10* | 2750 | 6 |
| GER | <u>200</u> | 10 | 1000 | 3 | 50 | 2000 | <u>200</u> | <u>50</u> | <u>2x10⁵</u> | 20 | 10 | 10 | - | <u>5000</u> |
| BRA | 200 | 10 | - | 5 | 50 | 2000 | 300 | 100 | 2x10 ⁵ | 70 | 10 | 10 | - | 5000 |

Jul`10 to Feb`13; n = 70 per metal, n = 11 per site

threshold value for drinking water (GER, BRA), indicator value, WHO (Zn), *ICP-MS

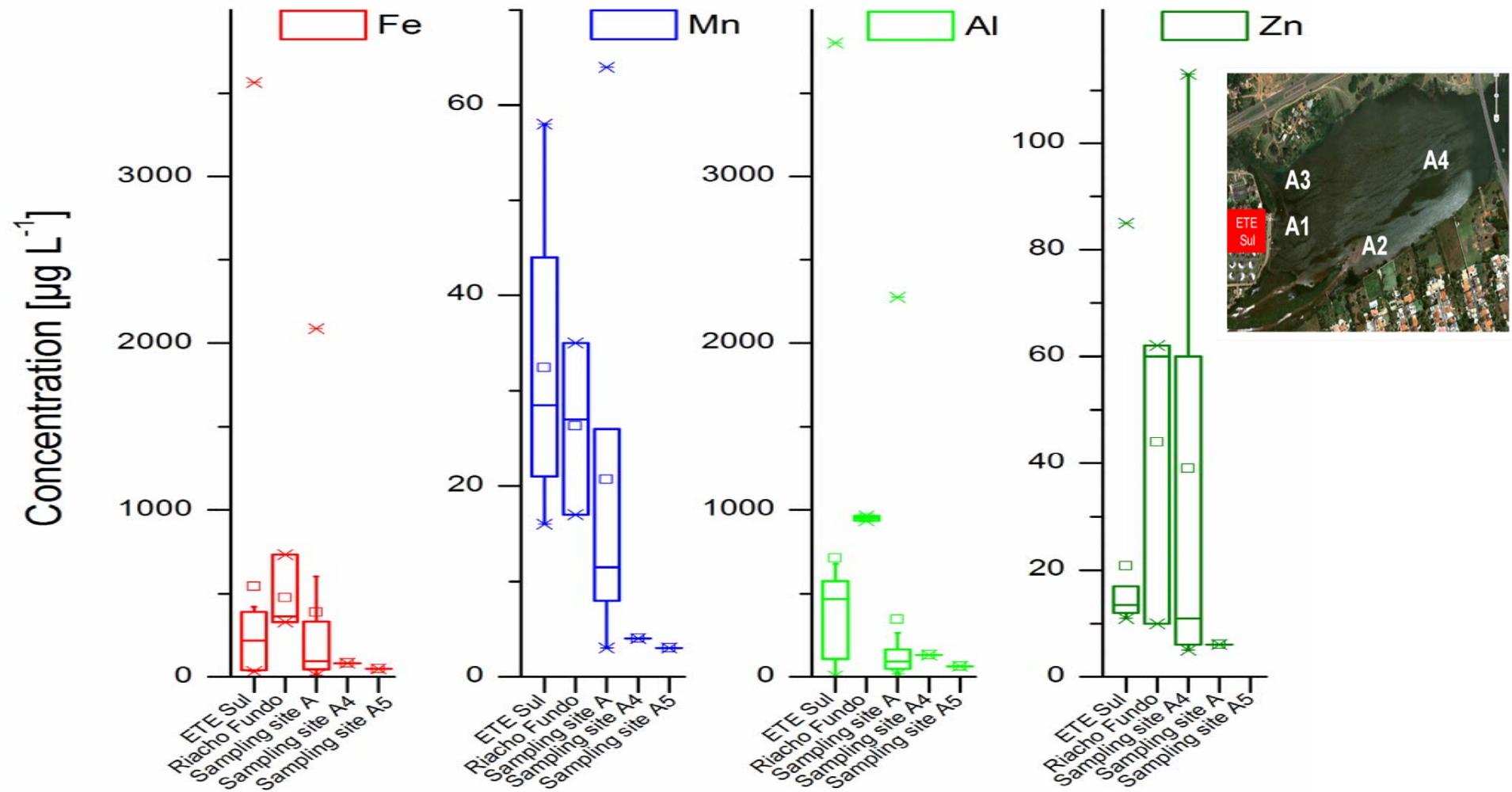


Metal concentrations, spatial distribution



sampling sites A (n = 10), B (n = 10), C (n = 10), D (n = 10), E (n = 8) and F (n = 8) during May, July, September and November 2011; threshold indicates the German drinking water threshold

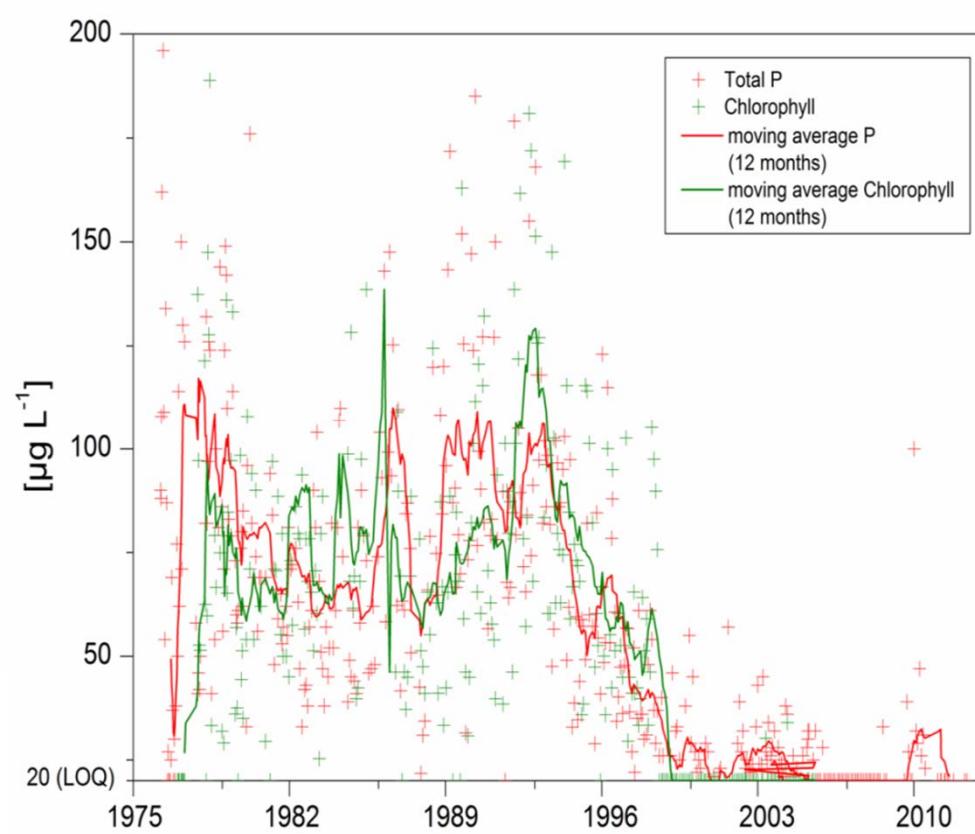
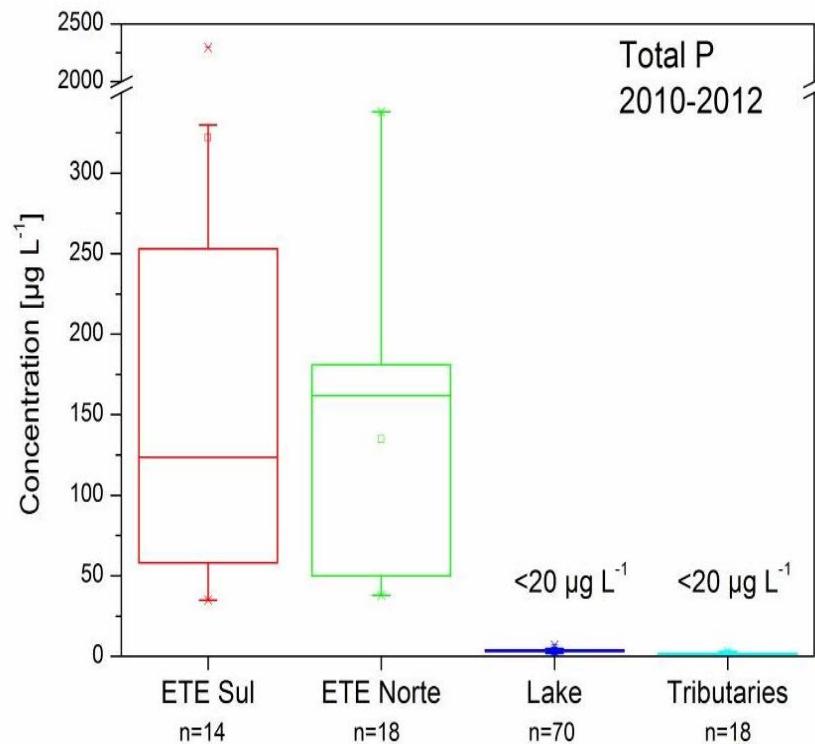
Discharge from WWTP and tributaries



effluent WWTP ETE Sul ($n = 11$), Riacho Fundo ($n = 4$), from Dec. 11 to March 12, A ($n = 10$), A4 ($n = 1$) und A5 ($n = 1$) 8

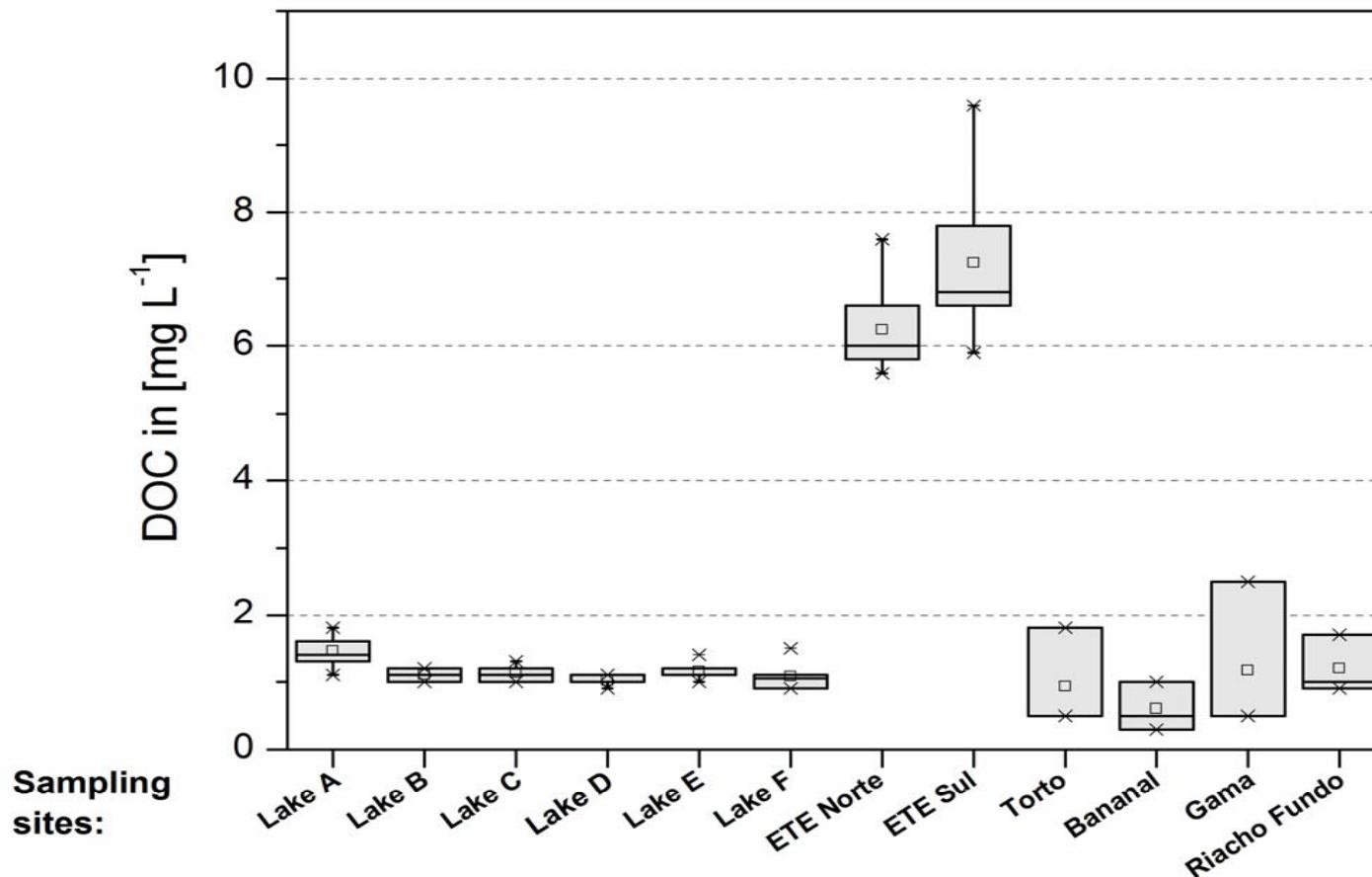


Phosphorous, discharge from WWTP and tributaries



Dissolved organic carbon (DOC)

Natural organic matter (NOM), humic substances (HS)



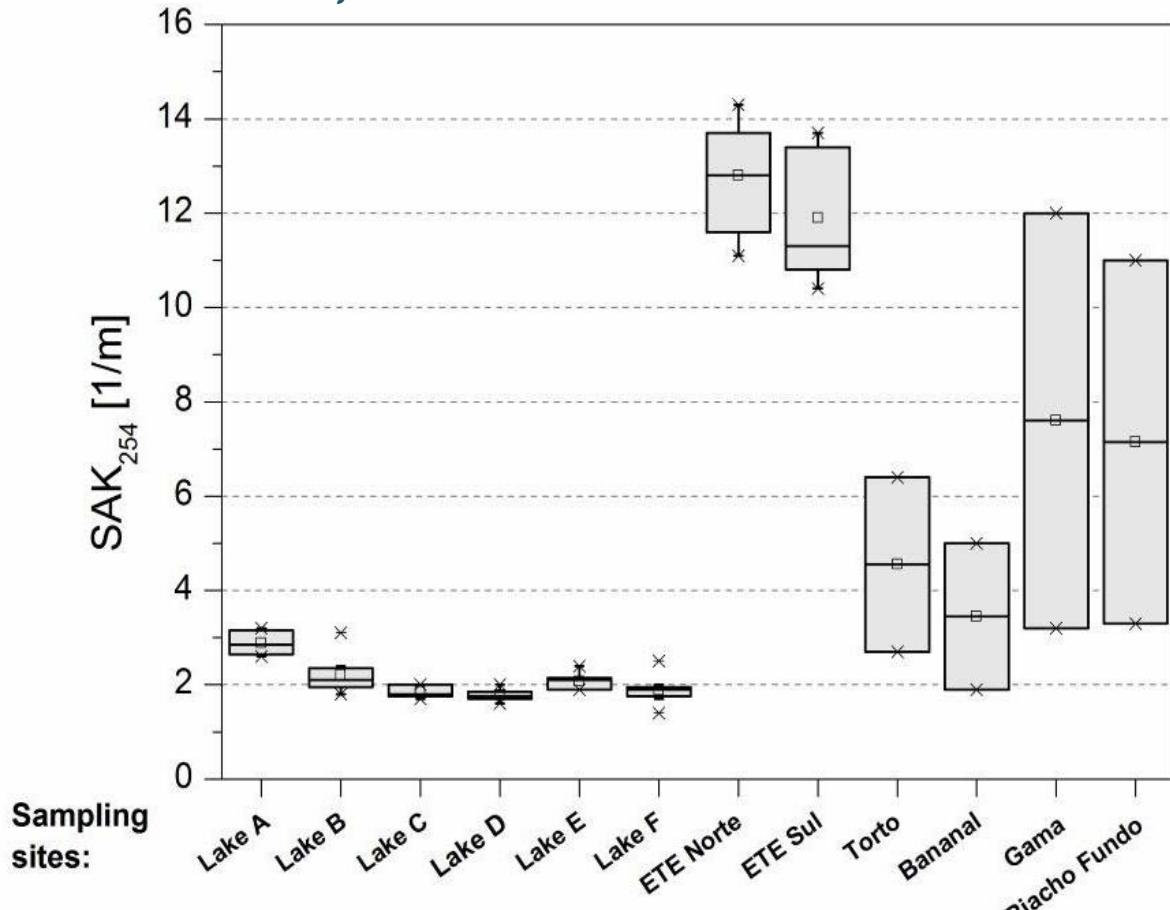
A to F ($n = 6$ per site), WWTP effluents ($n = 6$ ETE Sul, $n = 4$ ETE Norte) and in the tributaries ($n = 3$); data from 2010 to 2013.



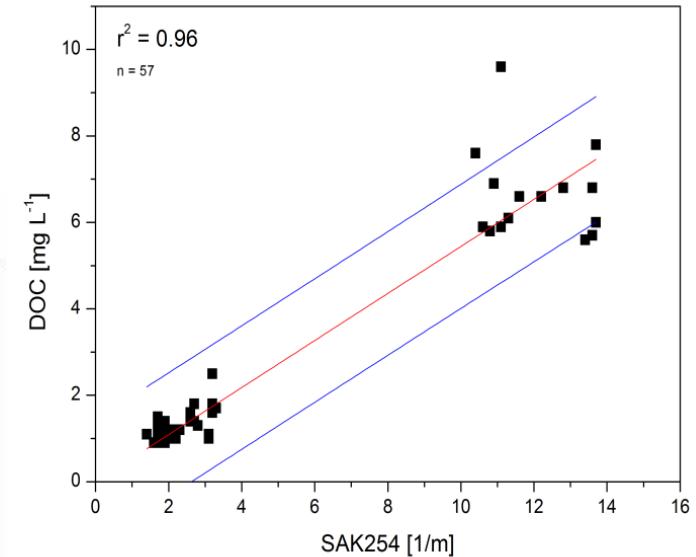


Spectral Absorbance at $\lambda = 254$ nm

indication for unsaturated bonds, lone pair electrons, and/or aromatic structures

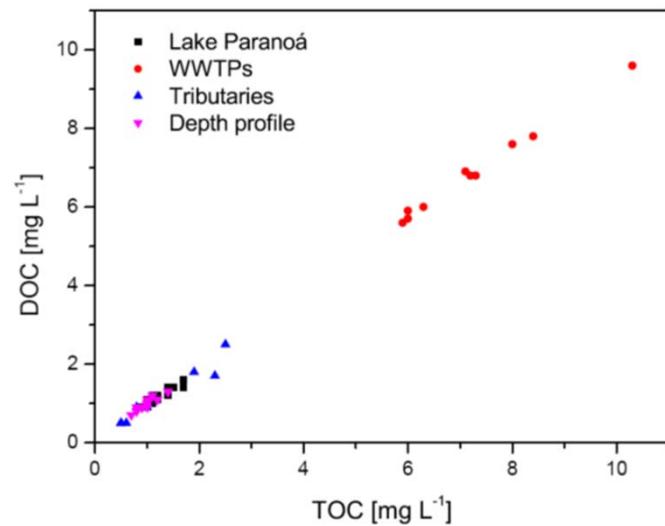
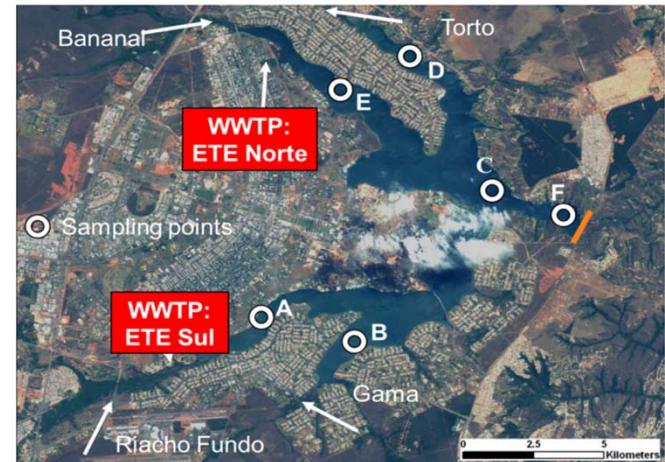
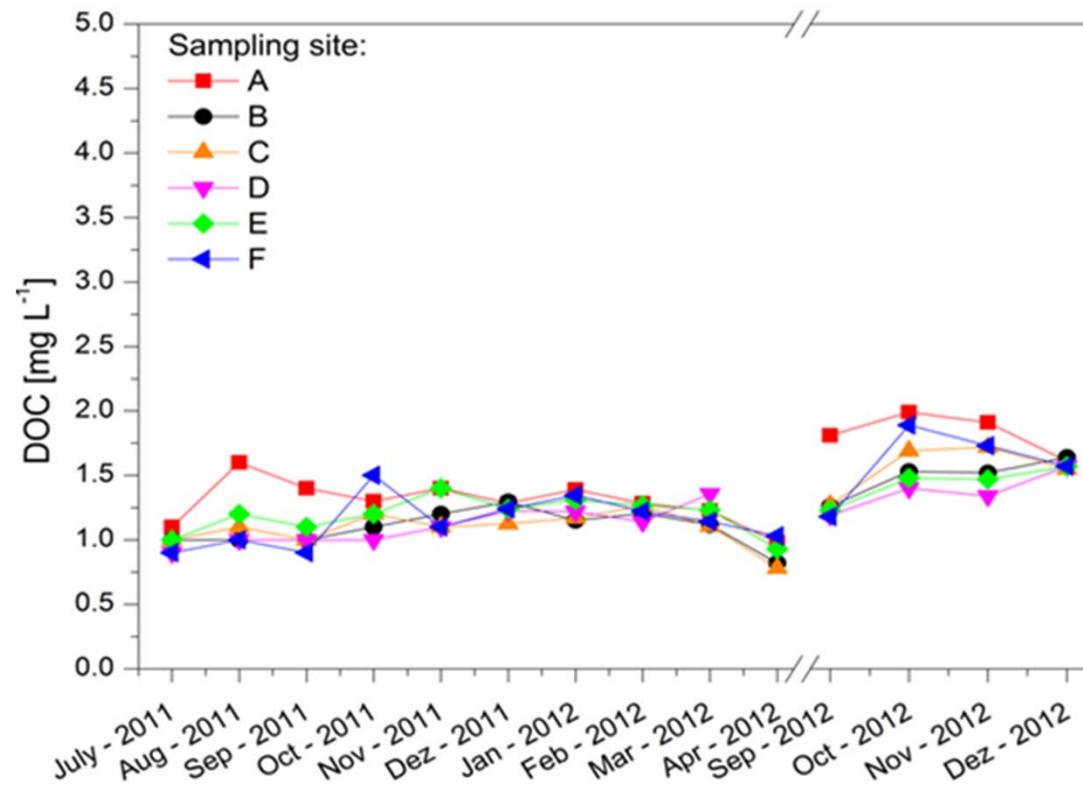


$$s\text{SAK} = \text{SAK}(254 \text{ nm}) / \text{DOC} = 1 \dots 2 \text{ L/(mg m)}$$





DOC, season

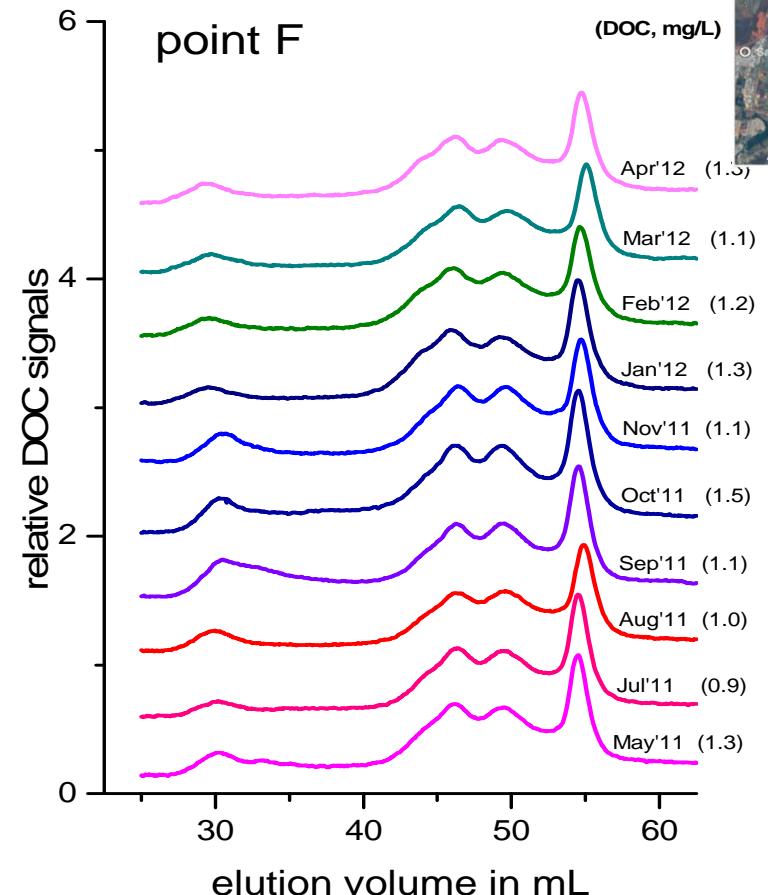
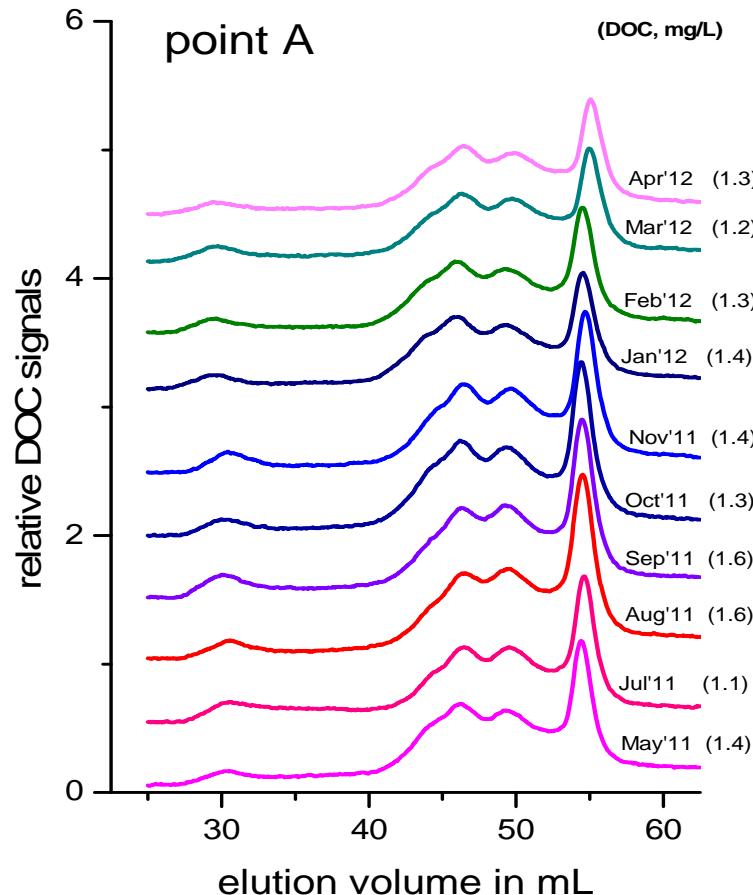


- low variation in depth
- low particulate fraction (POC), (lake, WWTP, tributaries)



DOC – character, seasonal and spatial distribution, I

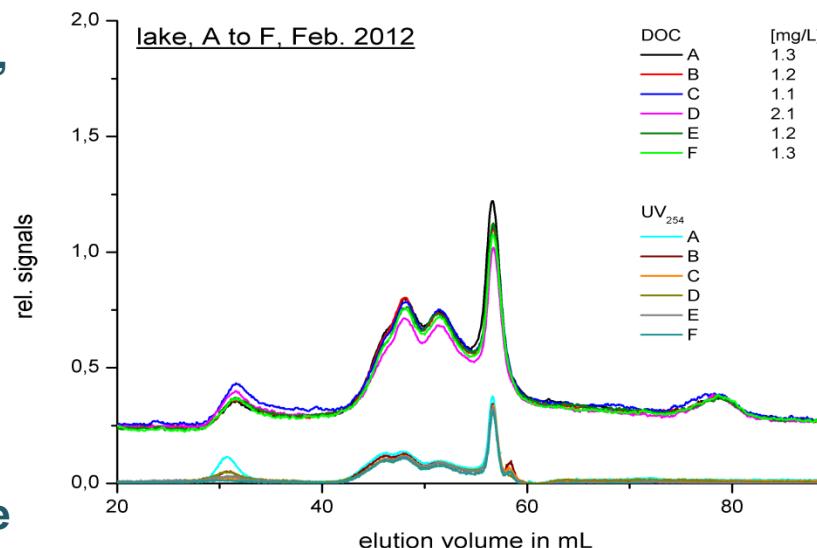
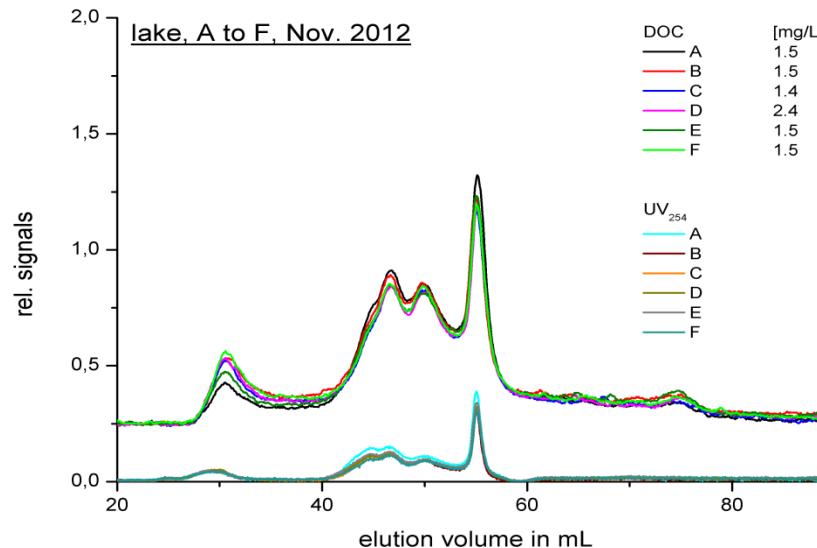
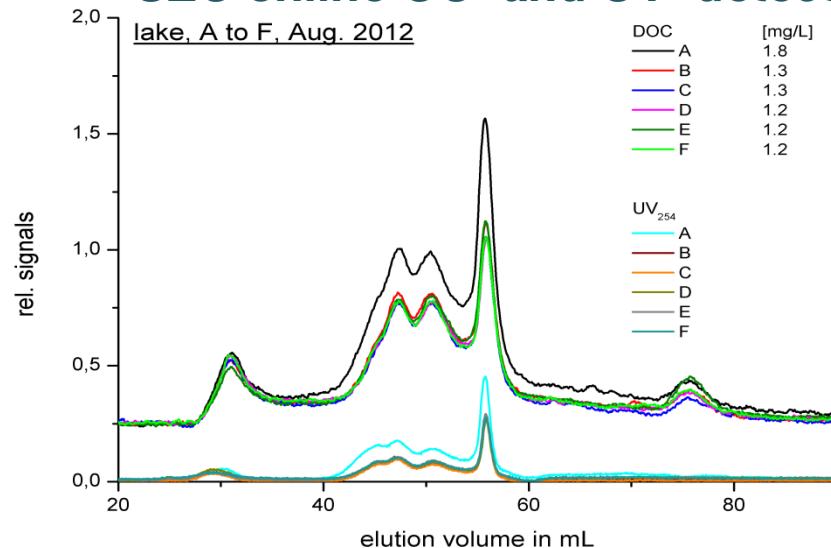
Size Exclusion Chromatography, online OC- and UV- detection



low variation in season: the molecular weight distribution of the DOC in the lake is very similar (A, F), no big difference between May'11 to April'12

DOC – character, seasonal and spatial distribution, II

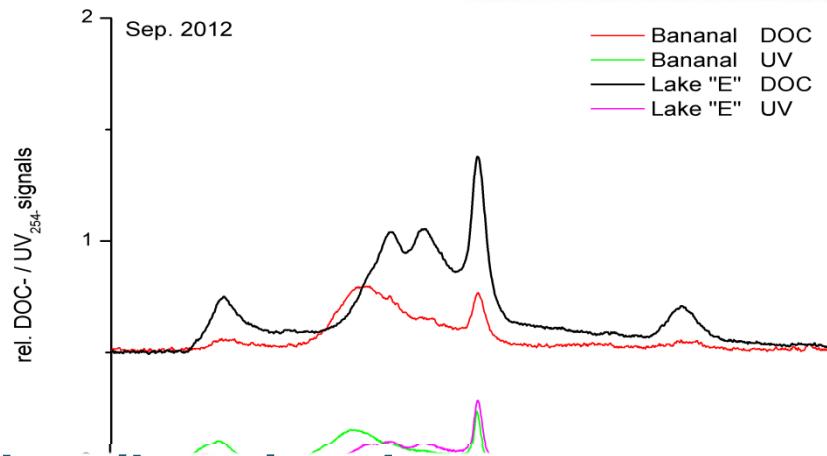
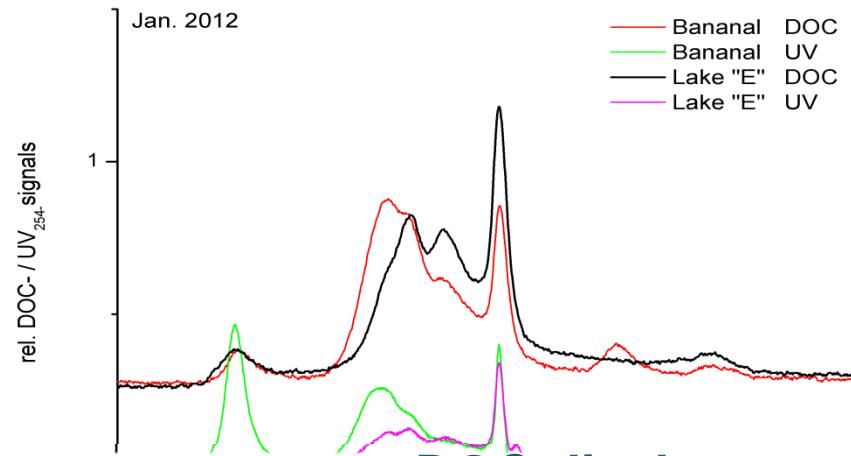
SEC online OC- and UV- detection



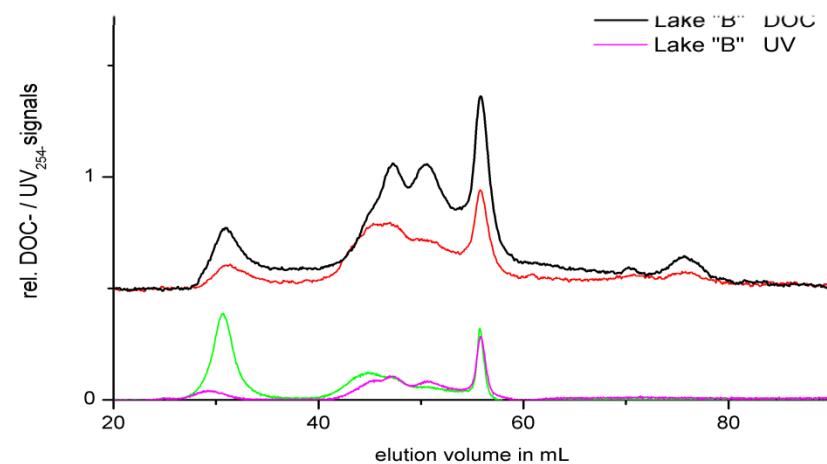
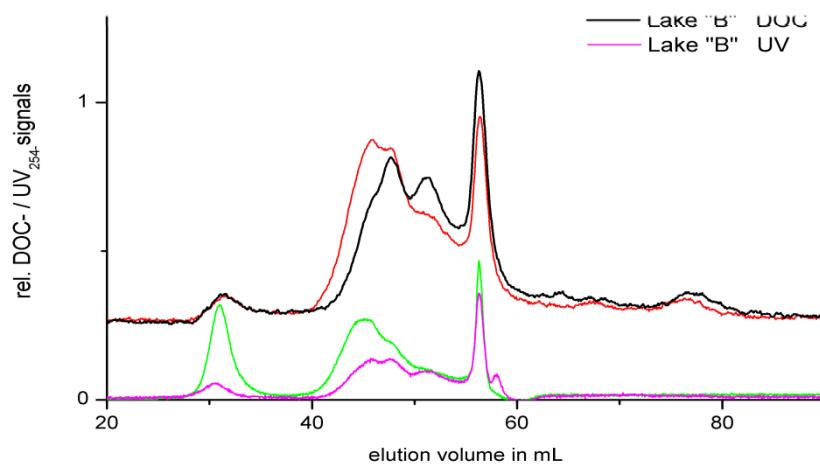
- low amount of high molecular weight subst., most subst. belong to a MW between 4000 and 400 g/mol (PEG), showing aromatic and unsaturated functional groups
- the molecular weight distribution of the OM in the lake is quite similar (A to F),
- low variation in season, and in sampling site



DOC – discharge of tributaries *SEC online OC, UV detection*



**DOC discharge of the tributaries shows
higher molecular weight distribution**





Sediments

Geoaccumulation index I_{Geo} (Müller 1986), clay rock standard

| I_{geo} Class | | As [mg/kg] | Cd [mg/kg] | Pb [mg/kg] |
|-----------------|---|------------|------------|------------|
| | Background | 13 | 0,3 | 20 |
| 0 | Not polluted | 19,5 | 0,45 | 30 |
| 1 | Not polluted to moderately polluted | 39 | 0,9 | 60 |
| 2 | Moderately polluted | 78 | 1,8 | 120 |
| 3 | Moderately polluted to strongly polluted | 156 | 3,6 | 240 |
| 4 | Strongly polluted | 312 | 7,2 | 480 |
| 5 | Strongly polluted to very strong polluted | 624 | 14,4 | 960 |
| 6 | Very strong polluted | 1248 | 28,8 | 1920 |

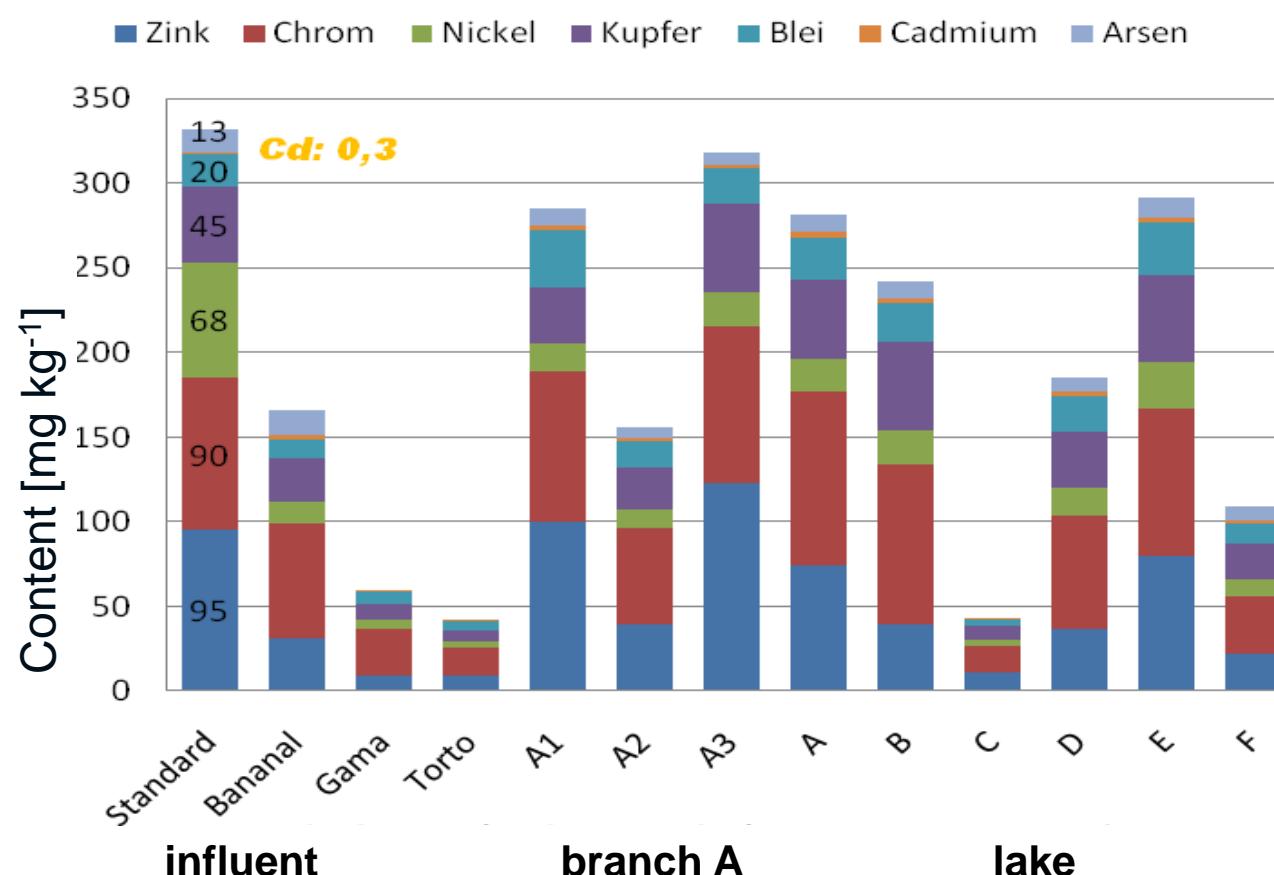
$$I_{geo} = \log \frac{C_n}{1,5 \cdot B_a}$$

C_n concentration in the sediment (in mg/kg)

B_a natural background (from silt-standard) (in mg/kg)



Sediments, heavy metals



class 0

not polluted

not for

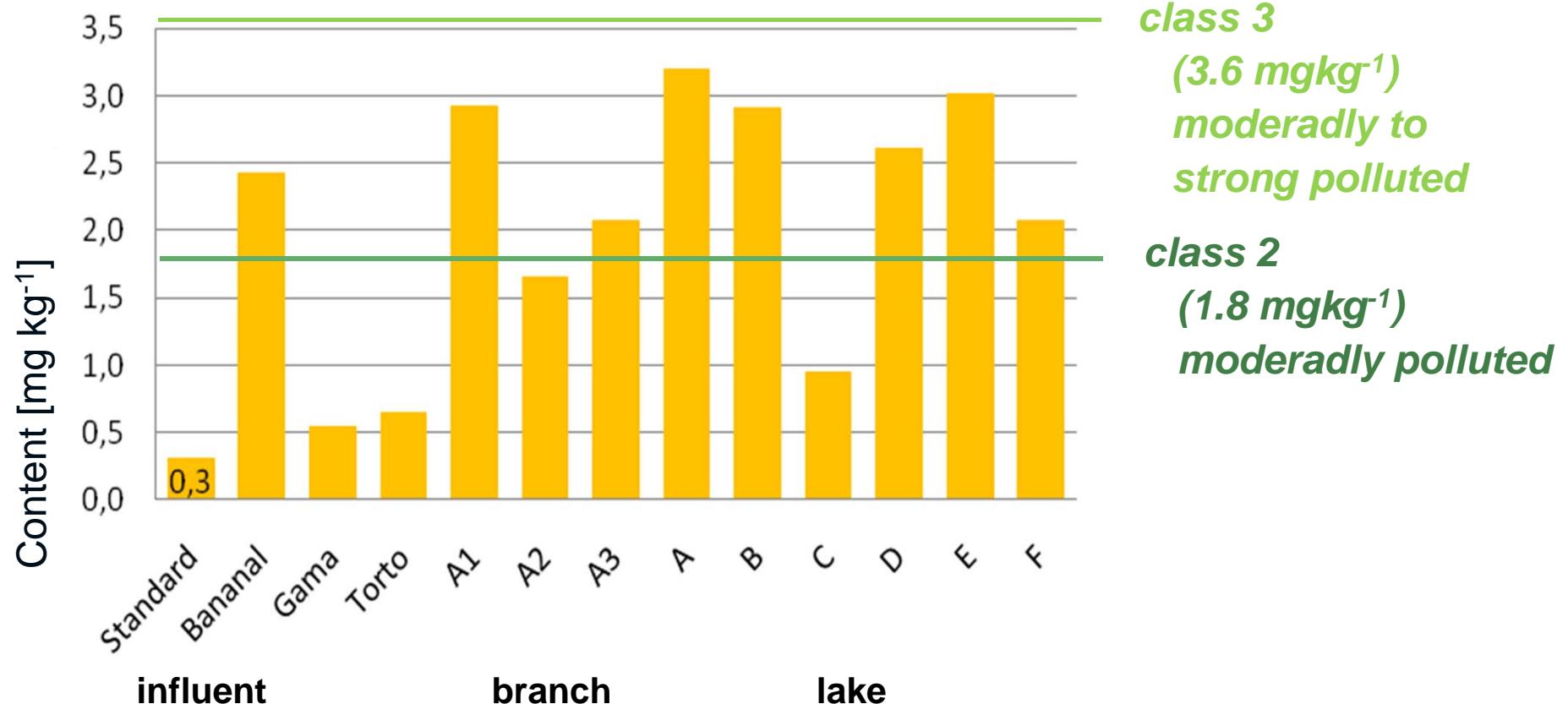
Pb, Cd

Pb: A1, E
class 1

*not polluted
to moderately
polluted*

- sampling during Dec'11 and Jan'12
- digestion of dried sediments with H_2SO_4/HNO_3 , analysis by ICP/OES

Sediments, Cadmium

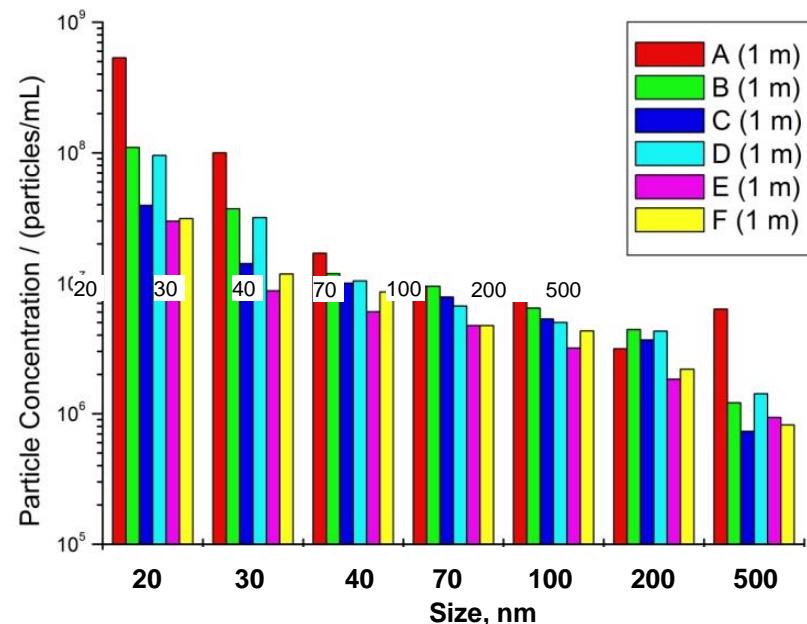


- sampling during Dec'11 and Jan'12
- digestion of dried sediments with $\text{H}_2\text{SO}_4/\text{HNO}_3$, analysis by ICP/OES



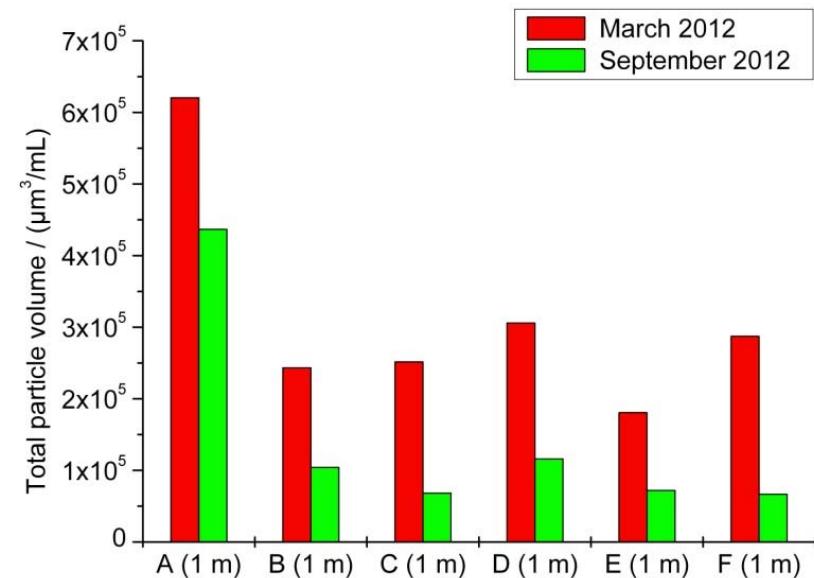
Colloids and Nanoparticles – TZW, Tröster

LIBD (Laser Induced Breakdown Detection)



Particle size distribution

- concentrations up to 1.8×10^9 particles/mL
(sampling point A, 20 nm, March '12)
- pareto-like size distributions for A to F
- high number conc. of particles < 100 nm



Spatial distribution in the lake

- highest concentrations at sampling point A
- temporal variations (rainfall period)
- sampling point F concentrations within the lowest range



Summary and Conclusions

- low variation during measuring periods (lake)
- significant impact of the WWTP and the tributaries

Inorganic basic parameters

- the two WWTP effluents are significantly higher for Al, B, Zn; different pattern in the tributaries

Organic sum parameters (DOC, SAK)

- low DOC: 1 – 2 mg L⁻¹; WWTP effl. DOC: 5 to 10 mg L⁻¹, higher variation and higher DOC in the tributaries
- similar molecular weight distribution (MWD), tributaries higher MWD

Sediments

- good sediment quality (class O, not polluted rainy season, grab sample); not valid for Cd, Pb and total P (not shown)
- Phosphorous bound in the particulate fraction (pore water, aqueous extracts, not shown)

-
- the raw water reaches almost all drinking water shreshold numbers (inorganic parameters)
 - low DOC (flocculation, low THM FP)



Acknowledgements

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