Fate of pharmaceuticals in settleable particulate material and lake sediments

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Consumption of pharmaceuticals

- Use increases all over the world
- In Finland total consumption varies from kilograms to tons per year
  - ibuprofen
    - 114 000 kg in 2010
    - 1% increase from 2009
  - paracetamol
    - 151 000 kg in 2010
    - 9% increase from 2009
  - bisoprolol
    - 635 kg in 2010
    - 7% increase from 2009

Finnish Medicines Agency 2011
www.fimea.fi/laaketieto/kulutustiedot

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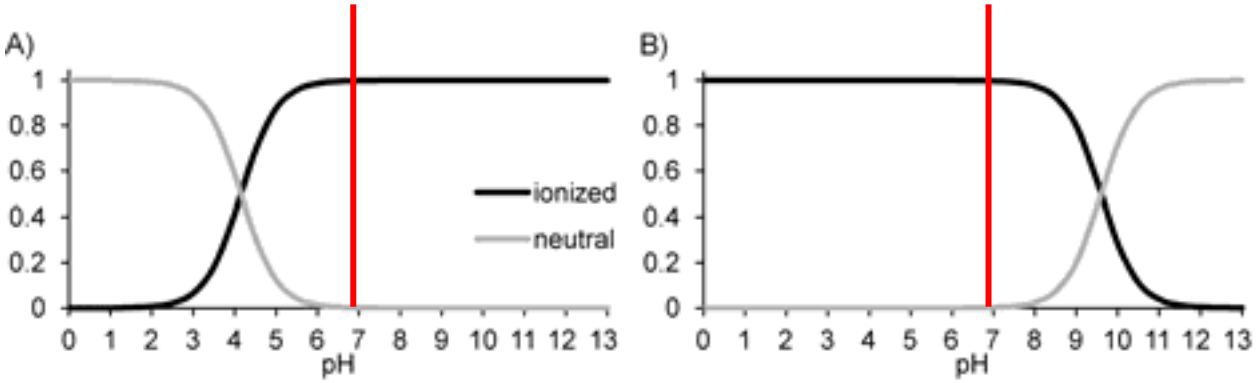
Ionization of pharmaceuticals

- Can occur as neutral, acidic, basic or zwitter form in environmentally relevant pH (pH 6-8)
- The proportion of ionized and neutral forms depends on pH and pKa



Naproxen, pKa 4.15

Citalopram, pKa 9.6

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Sorption of pharmaceuticals

- Ionized
  → ionic interactions
  → not solely dependent on lipophilic partition
  (unlike nonpolar compounds)
- Organic material, minerals and biofilms often negatively charged
  – Sorption of cationic compounds higher than that of anionic ones
  – Desorption unknown
- Large variation in the sorption depending on the properties of the solid material

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Pharmaceuticals in the environment

- Main route of entrance via wastewater treatment plants after human use
- Removal efficiency in WWTP varies considerably
  - ibuprofen almost totally eliminated
  - diclofenac and carbamazepine only slightly, if at all
- Concentrations in surface waters usually in ng/l range
  - Occurrence in particles, sediments and biota much less studied

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Fate of pharmaceuticals in the aquatic environment

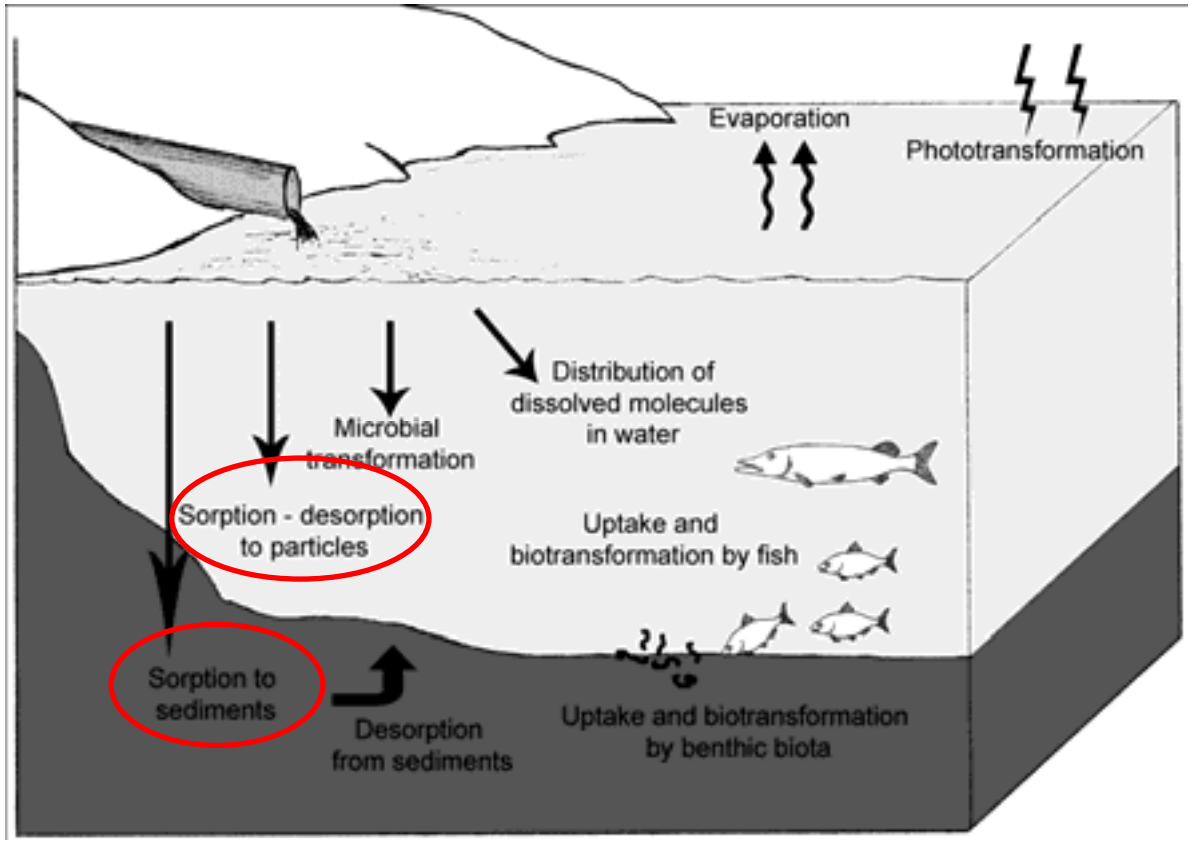

Figure: Lahti M. 2012

First objective:

Are pharmaceuticals susceptible for sedimentation?

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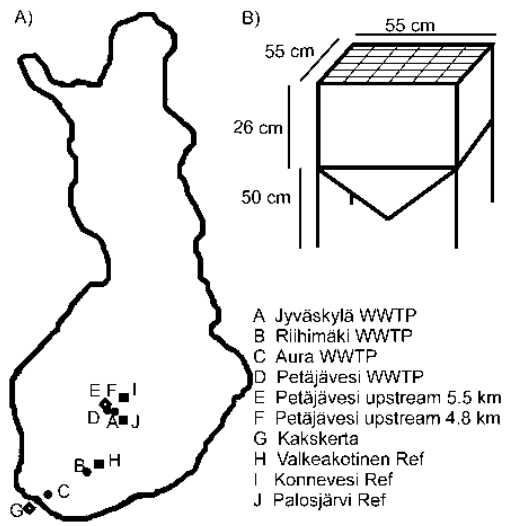
Sampling of SPM

- Settleable particulate material (SPM) collected from ten sites
  - Vicinity of wastewater treatment plant (A-D)
  - Rural sites (E-G)
  - Reference sites (H-J)
- Funnel-like stainless steel collector
  - Area 0,25 m^2
  - Volume 90 l
  - Collection time 60-80 days (summer)



Lahti M. & Oikari A. 2011. Pharmaceuticals in settleable particulate material in urban and non-urban waters. Chemosphere 85:826-831

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Analyses

- 17 pharmaceuticals
  - e.g. anti-inflammatories, anti-depressants, antibiotics, betablockers
- Ultrasonic and solid phase (SPE) extraction
- LC-MS/MS analysis
- Also dry weight, LOI and TOC analyzed

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Characteristics of SPM

	Location	Year	dw (%)	LOI (% dw)	TOC (% dw)	Deposition rate kg dw m^{-2} y^{-1}
A	Jyväskylä WWTP	2008	14.4	20.0	13.4	5.0
A	Jyväskylä WWTP	2009	11.2	29.2	12.4	53.2
B	Riihimäki WWTP	2008	3.1	37.6	7.9	103
C	Aura WWTP	2008	15.7	16.4	5.6	70.9
D	Petäjävesi WWTP	2009	7.9	20.2	9.0	6.4
E	Petäjävesi upstream 5.5 km	2009	4.9	18.0	7.8	4.0
F	Petäjävesi upstream 4.8 km	2009	6.4	19.0	7.9	2.8
G	Kakskerta	2009	8.1	15.8	5.9	3.3
H	Valkea-Kotinen Ref	2009	1.2	82.7	36.1	1.1
I	Konnevesi Ref	2008	1.7	38.4	-	0.3
I	Konnevesi Ref	2009	3.4	34.9	14.0	0.6
J	Palosjärvi Ref	2008	1.7	44.4	19.7	0.4
J	Palosjärvi Ref	2009	1.5	39.2	15.8	0.6

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Pharmaceuticals in reference sites

- Pharmaceuticals not detected in reference sites
- Ibuprofen and ofloxacin detected in rural Lake Kakskerta
  → no widespread contamination of the environment

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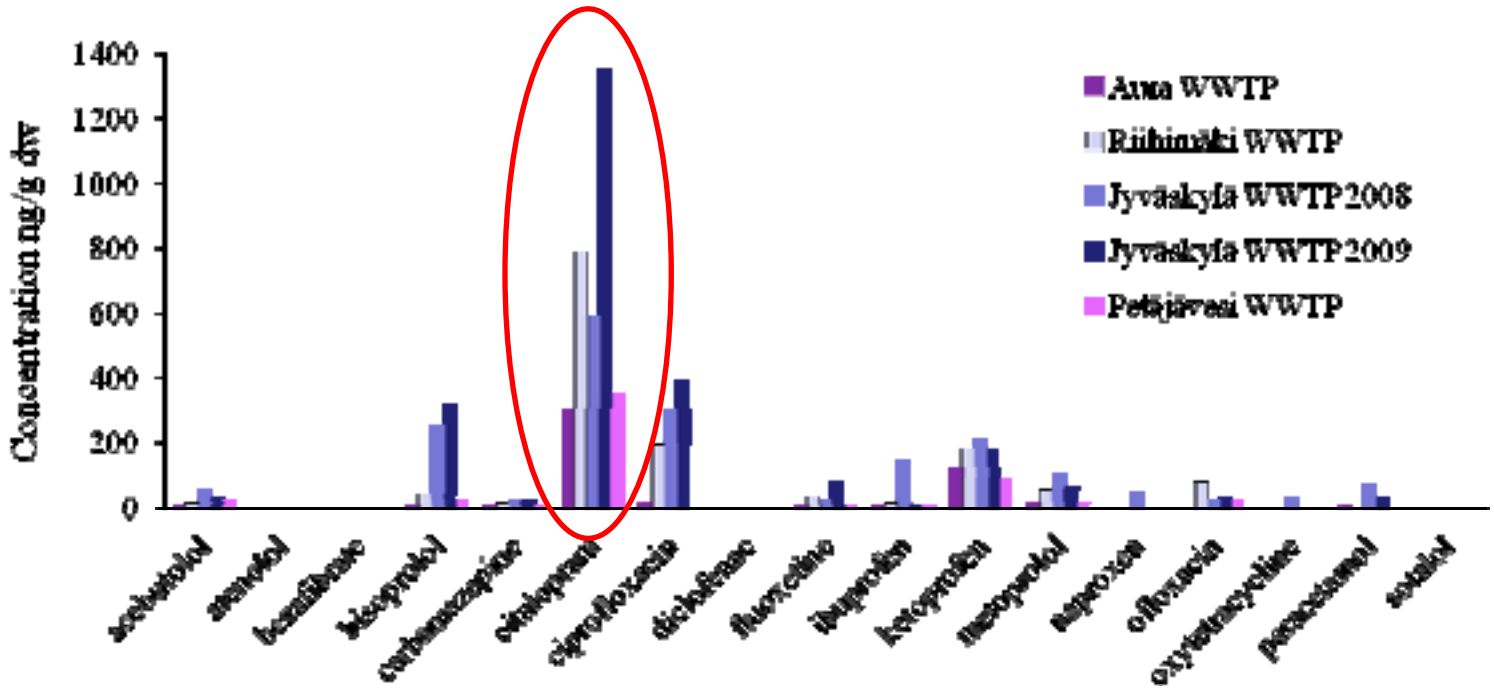
Pharmaceuticals in SPM



- Several pharmaceuticals were found from SPM near WWTP
  - Especially citalopram, bisoprolol and ciprofloxacin
  - Concentrations highest in Jyväskylä WWTP

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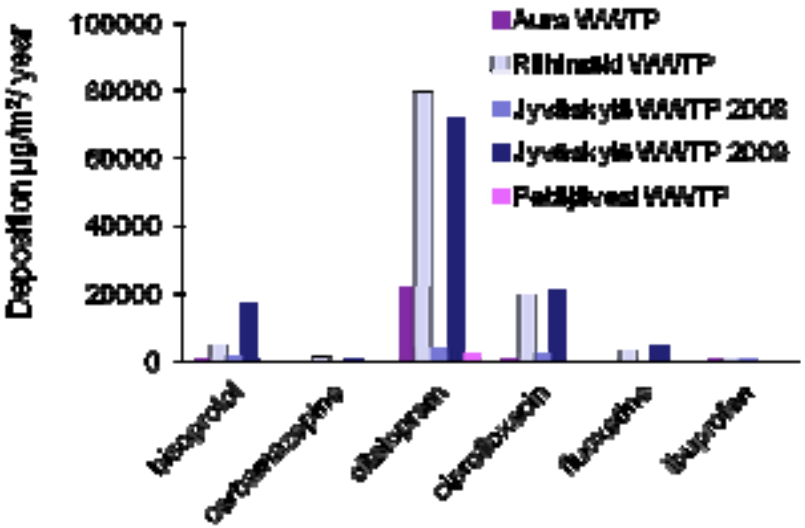
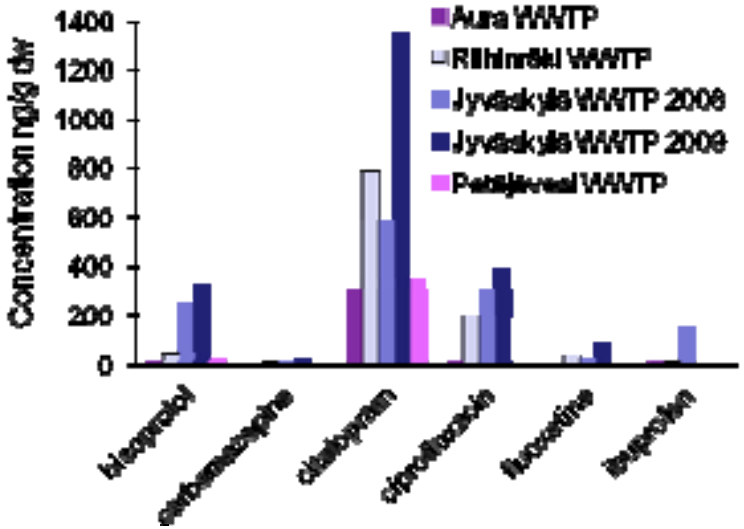
Pharmaceuticals in SPM





- Annual deposition highest in Riihimäki WWTP due to high amount of SPM

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Some findings

- Pharmaceuticals in SPM near WWTP differs from those found in wastewater

  (Vieno N. 2007 PhD thesis)

  → Different pharmaceuticals occur in dissolved and sorbed phases

  → Measuring only dissolved fraction may underestimate the release of pharmaceuticals from WWTPs

- Question emerged: Are benthic habitats contaminated by pharmaceuticals?

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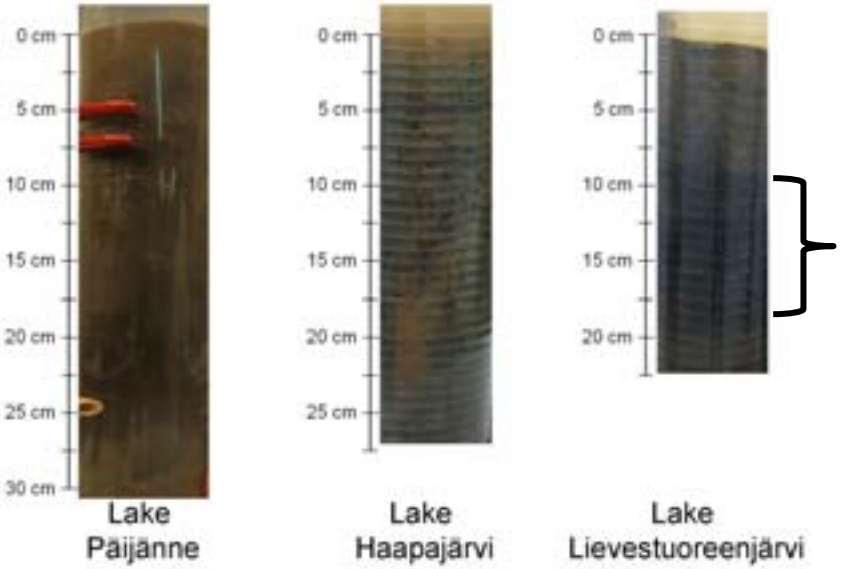
Sampling of sediment

- Sediment cores from three lakes
- Divided to 2-2.5 cm slices
- Analysed for pharmaceuticals
- Also fecal sterols, LOI and TOC analysed



Lahti M. & Oikari A. 2012. Vertical distribution of pharmaceuticals in lake sediments – Citalopram as potential chemomarker. Accepted Environmental Toxicology and Chemistry

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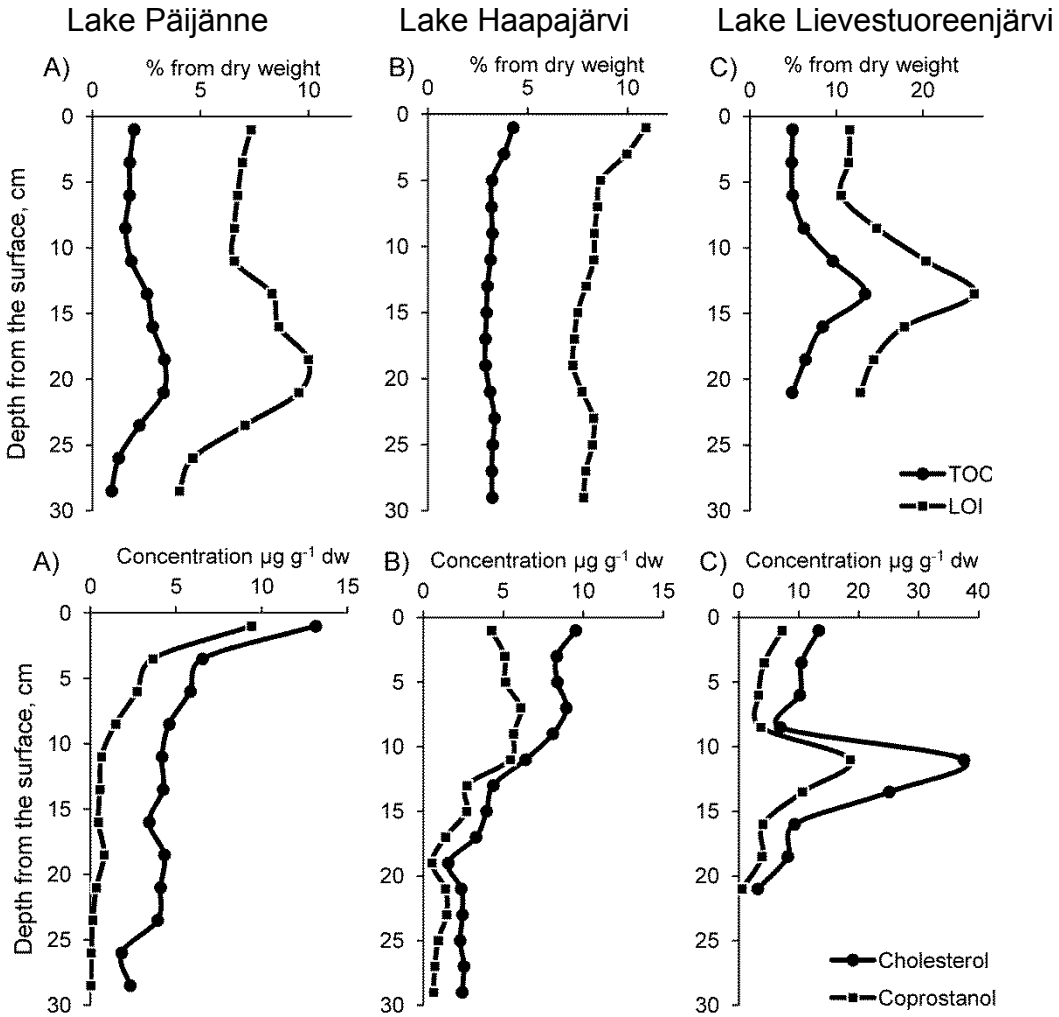
LOI, TOC and fecal sterols in sediments



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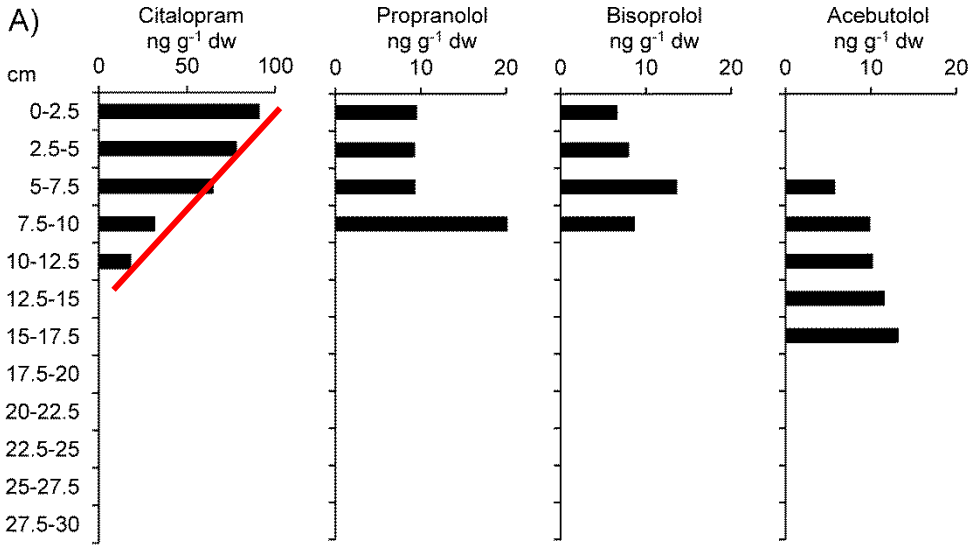
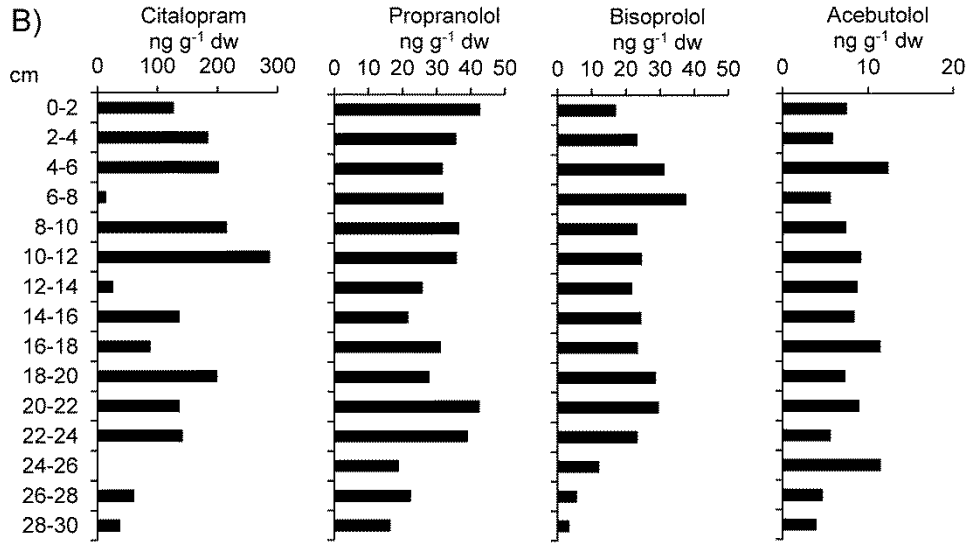
Pharmaceuticals in sediments

Lake Päijänne



Lake Haapajärvi



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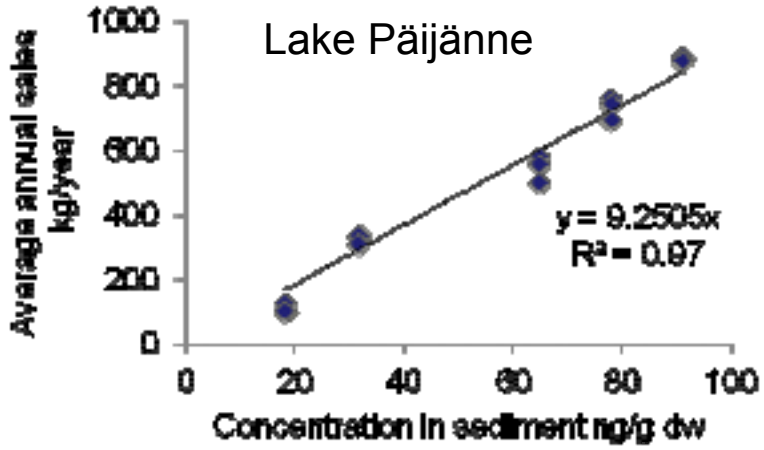
Consumption and occurrence of citalopram

- The age of the sediment layers were evaluated as three different alternatives (Options 1–3)
- Average annual sales were calculated from sales reports (Finnish Medicines Agency, 2011 www.fimea.fi/laaketieto/kulutustiedot)
- Citalopram came to markets in Finland in 1990



→ Could citalopram and other drugs be used for dating of sediments?

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Main conclusion: Sediments clearly contaminated by pharmaceuticals

Further perspectives

- Destruction of habitats?
- Bioavailability of drugs?
- Organisms exposed?

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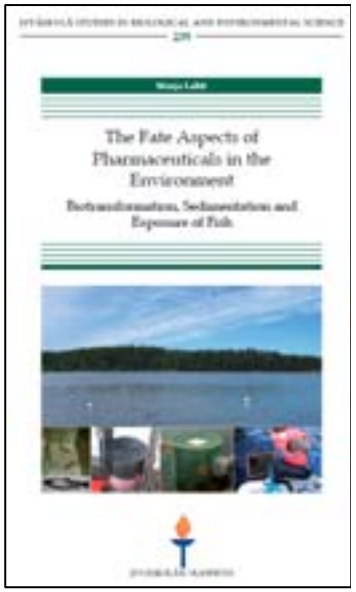
Funding sources:

Maa- ja vesitekniikan tuki ry

EnSTe -graduate school



THANK YOU FOR YOUR ATTENTION!

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