Emission inventories for priority substances at catchment levels: Solving the PAH source conundrum with an array of in-stream tools

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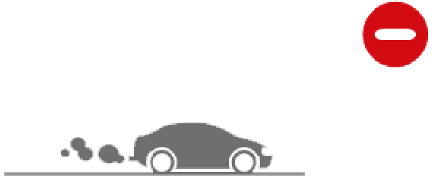
BAD CHEMICAL STATUS
PAH EQS exceedance most common reason

- All surveillance sites in Luxembourg exceed EQS for high-molecular weight PAH
- Same trends in the neighboring regions (Rhine-Mosel Commission)
- PAH often considered as ubiquitous with important atmospheric immission
- Fatalistic attitude upon improving the situation (little concrete measures in RBMP)
- Scarce efforts to investigate spatial differentitation and sources more thoroughly



PAH SOURCES AND DYNAMICS

What the literature says

- Exports from catchments > current atmospheric deposition (urban areas)
- Street deposits major source
- Soils often secondary source
- Accumulation in soils in vicinity of traffic
- Building up of stocks in sewers (first flushs)
- Role of combustion derived carbonaceous particles
- Contaminated industrial sites (historical)

EMISSION INVENTORIES

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One scheme for all compounds?

TIER	BUILDING BLOCKS	EXPECTED OUTPUT	RESULTS FOR THE INVENTORY
STEP 1: ASSESSMENT OF RELEVANCE			
	Information sources identified in Art. 5 of EQS directive, see section I.1	Decision of relevance	List of relevant and less relevant substances
STEP 2: APPROACHES FOR RELEVANT SUBSTANCES			
1. Point source information	• Data on point sources • Emissions factors	• Availability of data • Quality of data • Identification of gaps	• Point source emissions • Listing of identified data gaps
2. Riverine load approach	add: • River concentration • Data on discharge • In stream processes	• Riverine load • Trend information • Proportion of diffuse and point sources • Identification of gaps	• Rough estimation of total lumped diffuse emissions • Verification data for pathway and source orientated approaches • Listing of identified data gaps
3. Pathway orientated approach	add: • Land use data • Data on hydrology • Statistical data • …….. • ……..	• Quantification and proportion of pathways • Identification of hotspots • Information on adequacy of POM	• Pathway specific emissions • Additional spatial information on emissions
4. Source orientated approach	add: • Production and use data e.g. from REACH • SFA • Substance specific emission factors • …….. • ……..	• Quantification of primary sources • Complete overview about substance cycle • Information on adequacy of POM	• Source specific emissions • Total emissions to environment and proportion to surface waters

- Is this adapted to secondary pollutants with diffuse sources and a strong affinity for solids?

SUBSTANCE FLOW ANALYSIS
Regionalized emission balances

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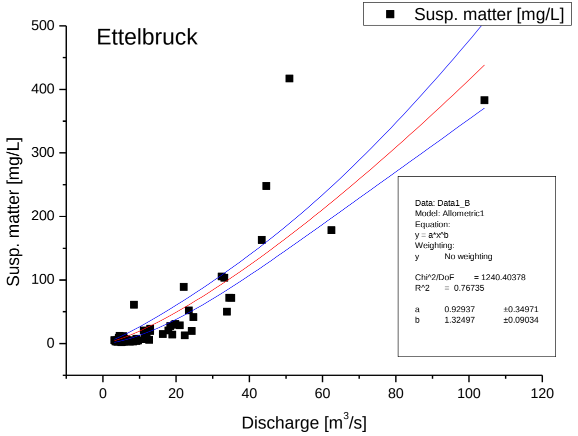
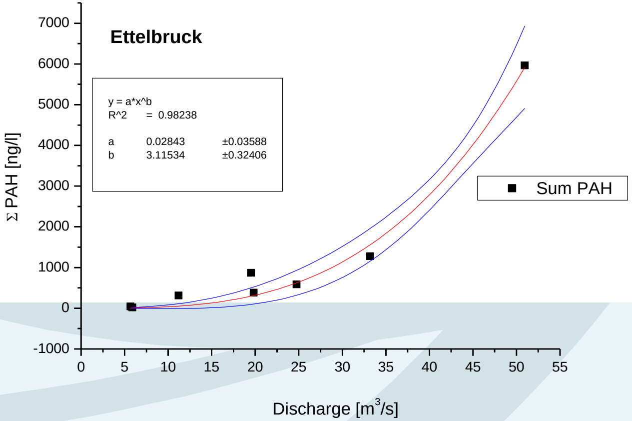
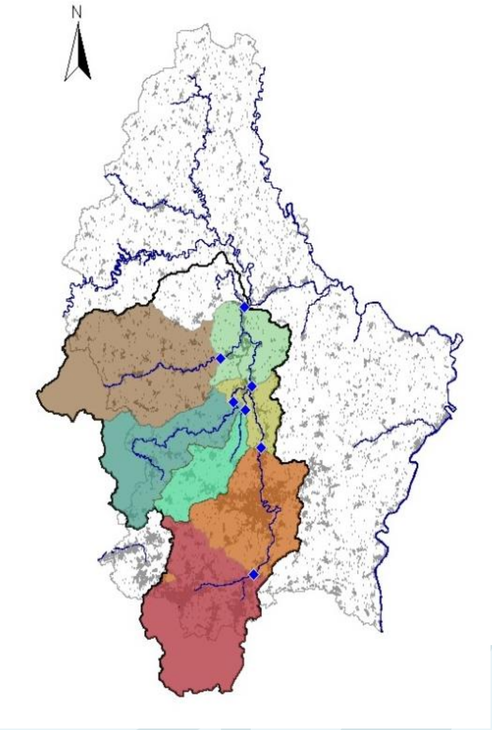
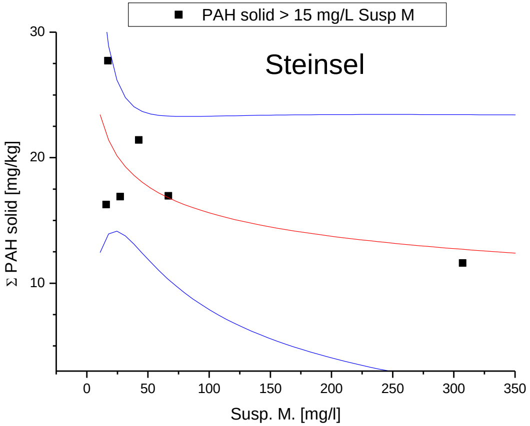
- Substance flow analysis in different catchment
- Establishment of Q-C relationships
- Calculation of catchment loads
- Characterization of pollution level in different hydrological situations
- Contribution of WWTPs and urban runoff

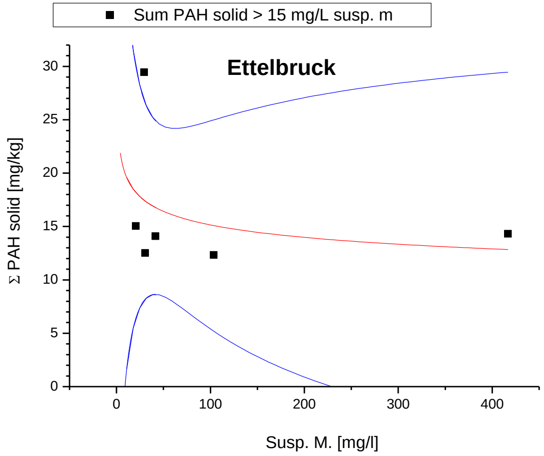


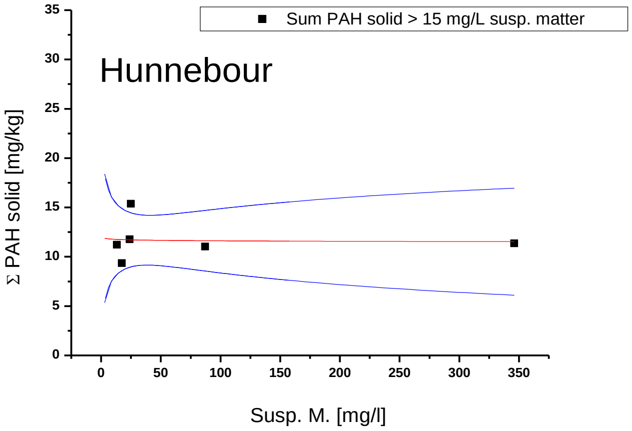




SUSPENDED MATTER POLLUTION
Source discrimination



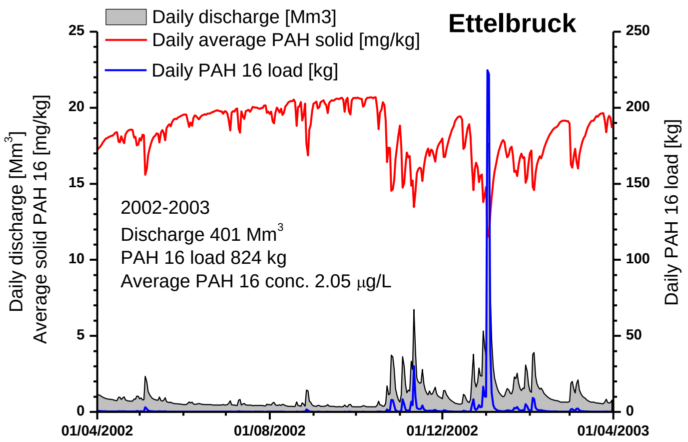


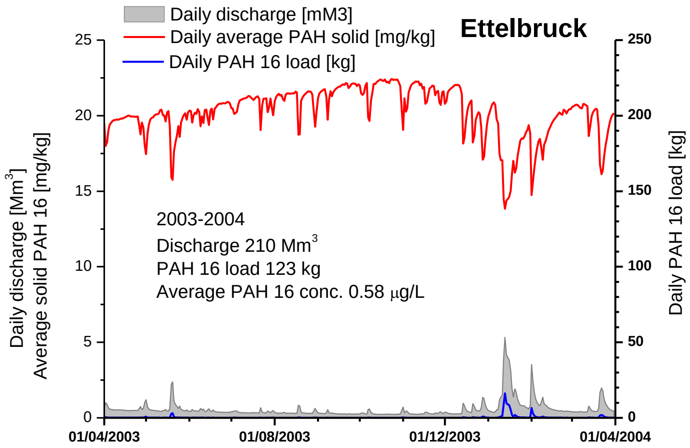


- Solid contamination levels allow for objective comparison in different hydrological situations and catchments (SPM as main carrier)
- High levels of SPM indicate strong catchment wide erosion and background levels of (alluvial) contamination

CATCHMENT BALANCES

Yearly variability - uncertainties





	Steinsel 2002-2003	Ettelbrück 2002-2003	Steinsel 2003-2004	Ettelbrück 2003-2004
Yearly discharge [Mm^3]	183	401	99	210
Yearly load PAH [kg]	241	824	56	123
Yearly average concentration PAH [µg/L]	1.32	2.05	0.58	0.58
Yearly average concentration SPM [mg/L]	95	160	33	37

- Yearly loads are governed by SPM yield – read: hydrological events
- SPM pollution levels is the more objective measure

CONTRIBUTION BY URBAN AREAS

WWTPs vs runoff pollution

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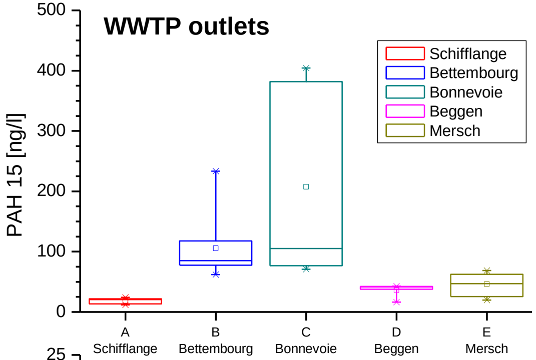
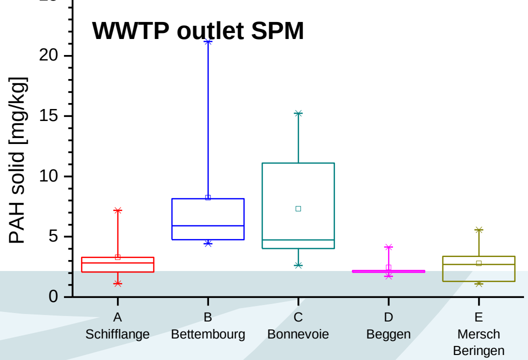
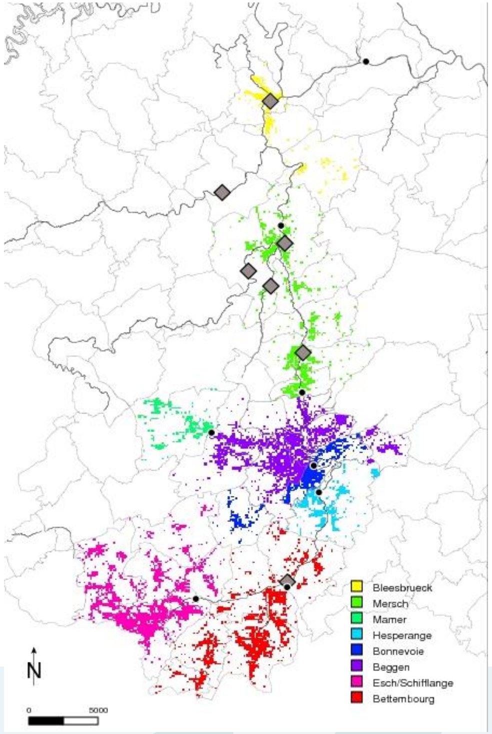
- Contribution of WWTPs: medians of measurement campaigns
- Contribution of surface runoff
  - Combined sewers

    Difference between effective precipitation on impervious surfaces and discharge of WWTPs
  - Separative sewers: Effective precipitation
  - Median concentrations: measurements/literature

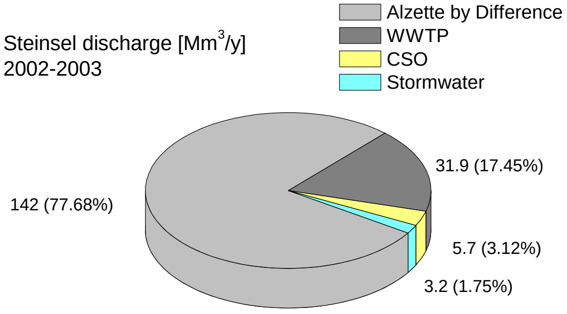


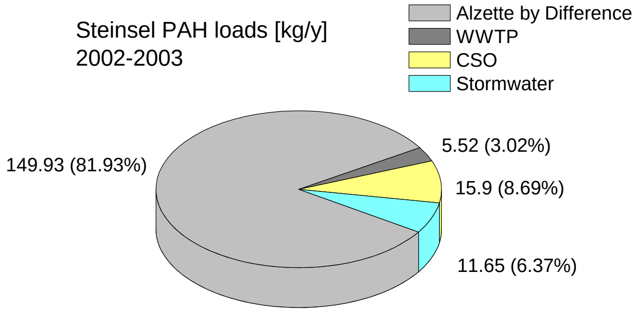


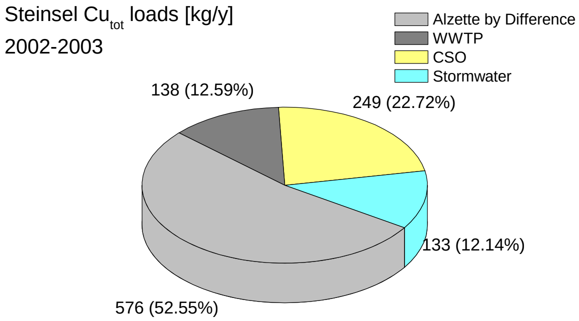


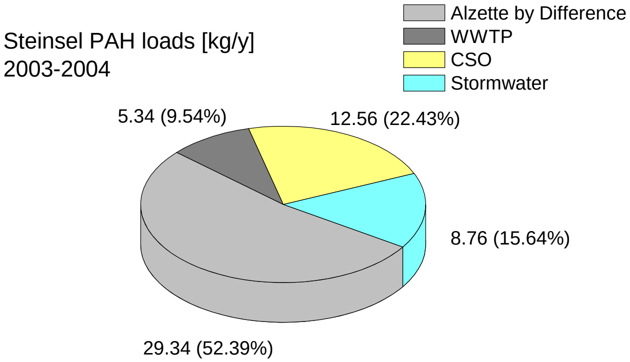
CONTRIBUTION PATTERNS

Runoff as the main source?









- The contribution of WWTPs and urban runoff is much smaller for PAH than for metals
- The contribution is largely dependent on the hydrological season (wet year vs. dry year)

FLOOD EVENTS
Source mobilisation and transport dynamics

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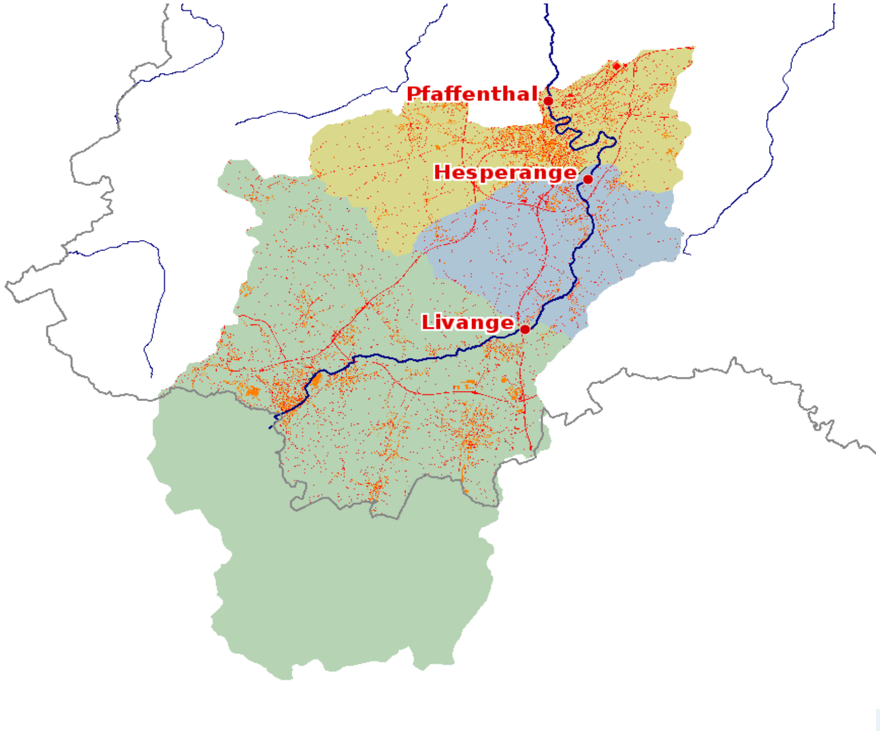
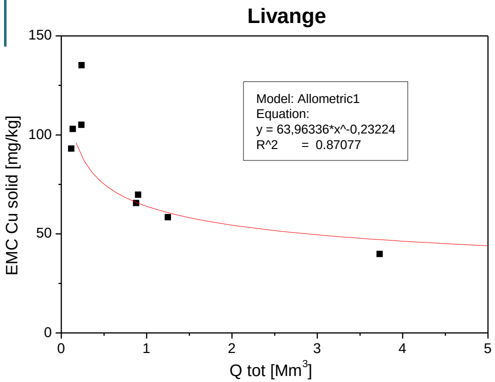
- Follow-up project on urban runoff through in-stream balances
- 3 triggerd autosamplers in a longitudinal profile from industrial region to strongly urbanized segments
- Event based balancing and peak analysis in flood waves

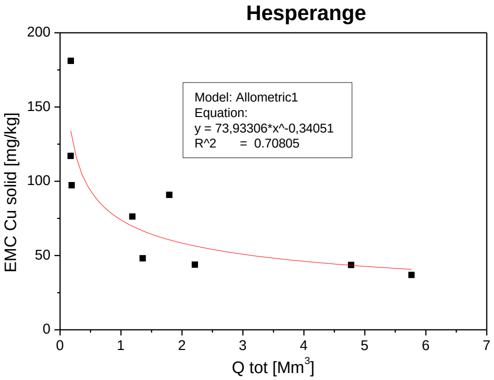


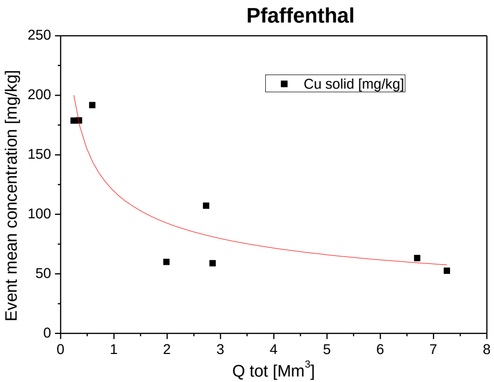
- Can we depict fast urban runoff contributions in chemographs?

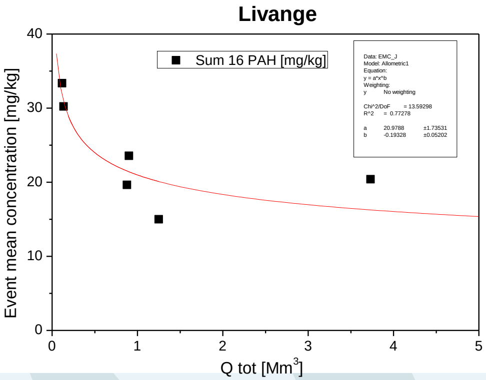
EVENT MEAN CONCENTRATIONS

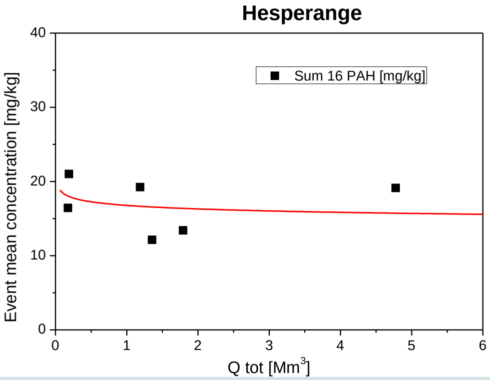
Fingerprinitng the sources

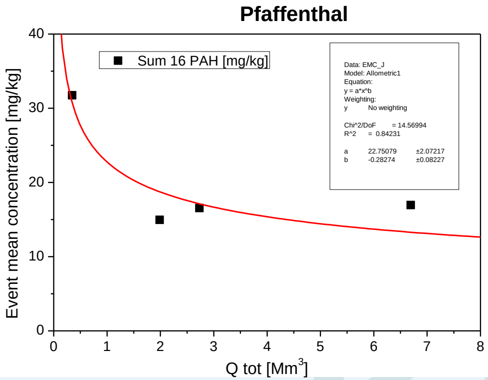












- EMC for Copper and PAH show higher solid contamination in small events (Cu > PAH)
- Small events have higher contributions of first-flushes vs catchment erosion

SPATIAL VARIABILITY

Limited outreach of PAH pollution

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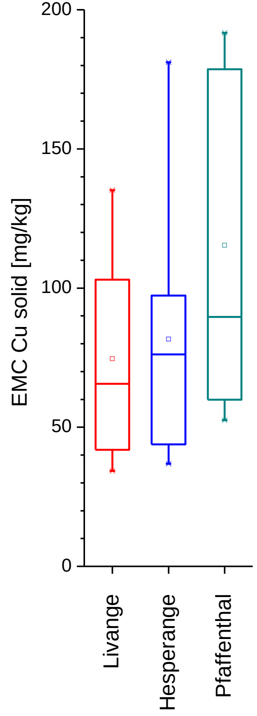
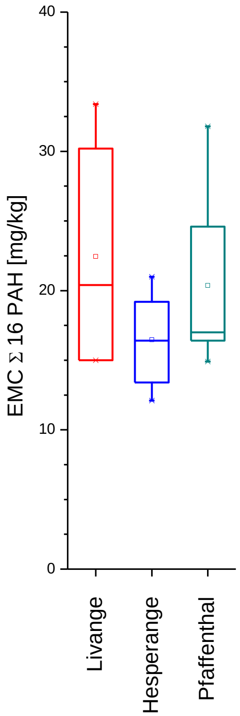
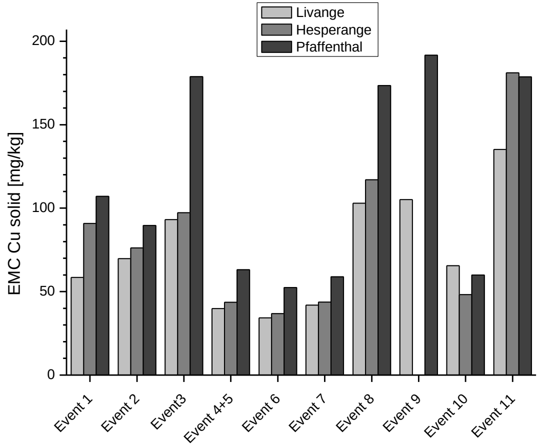
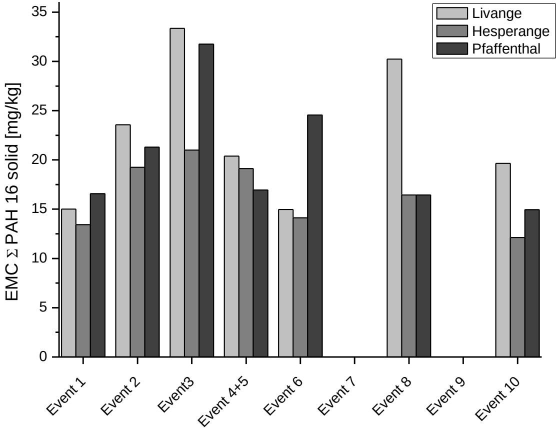




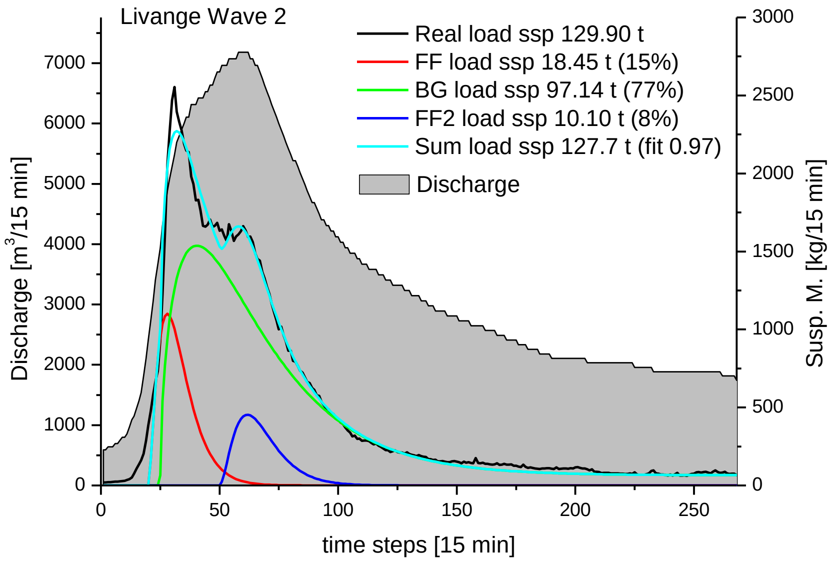


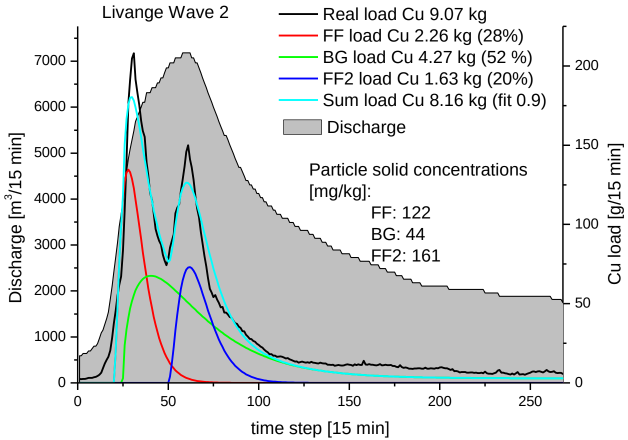


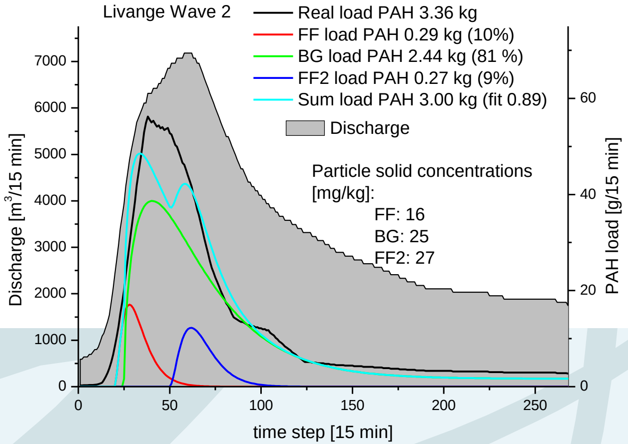
- PAH pollution and Copper pollution behave differently in longitudinal profile
- Sources seem to be diverse and variably mobilisable

MASS FLOW COMPONENTS

Deconvoluting flood waves





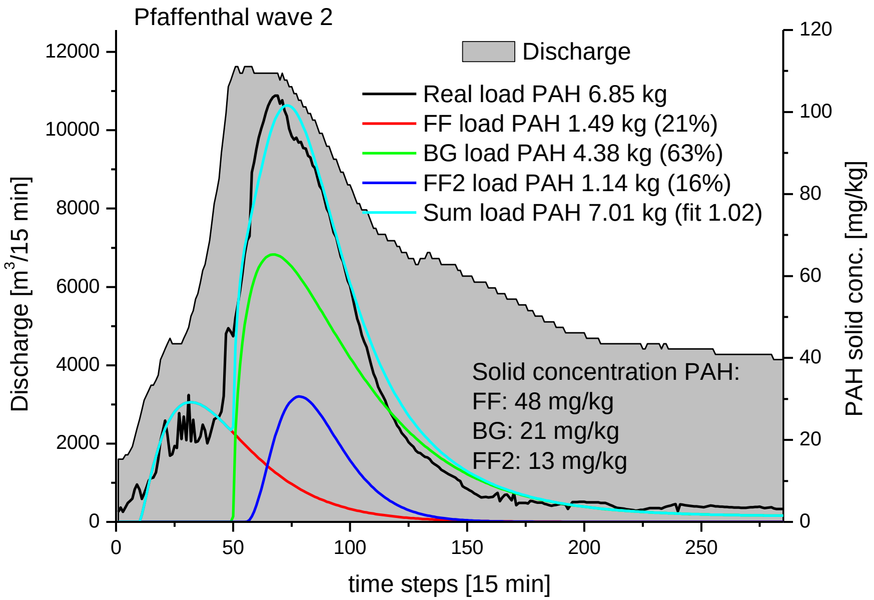


- First we identify and fit SPM loads (turbidity signal)
- Then we allocate a pollution to each SPM source

MASS FLOW COMPONENTS

Deconvoluting flood waves

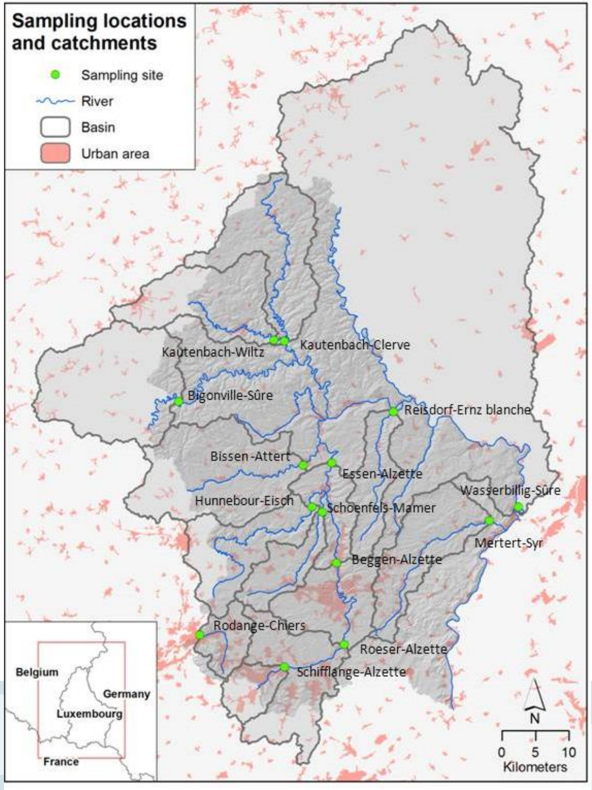
	Event load PAH [kg]	First Flush load fraction [%]	FF conc. [mg/kg]	BG conc. [mg/kg]
Livange	3.36	29 %	16 (27)	25
Hesperange	3.61	22 %	33 (29)	18
Pfaffenthal	6.85	37%	48 (13)	21

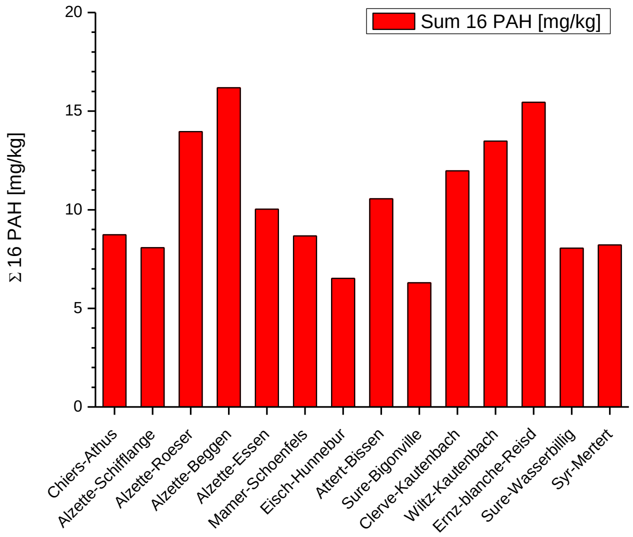


- First flush contributions can be below background contamination
- Contamination levels of first flush vs. background are variable downstream

LARGE SCALE PICTURE
Catchment properties and PAH pollution

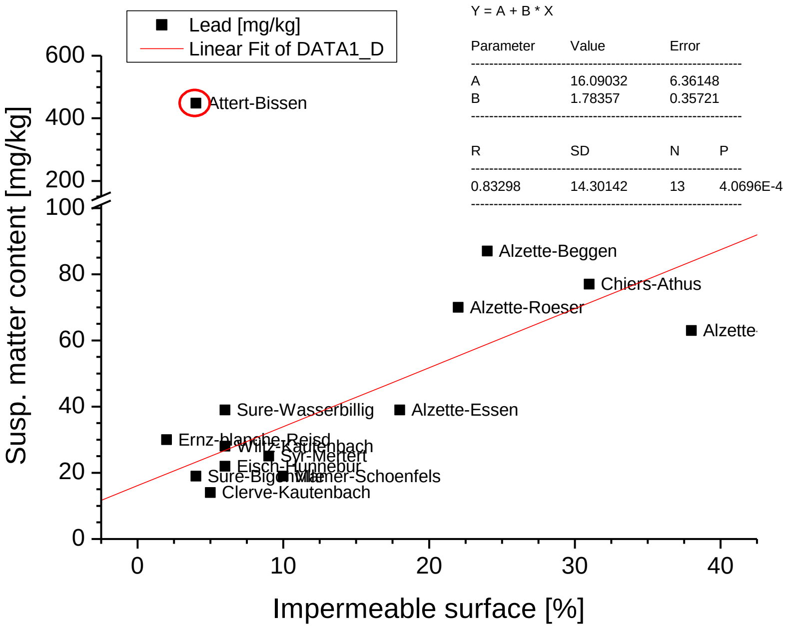
- Country wide sampling with sediment nets at low-flow
- Large variety of catchment properties (land use)

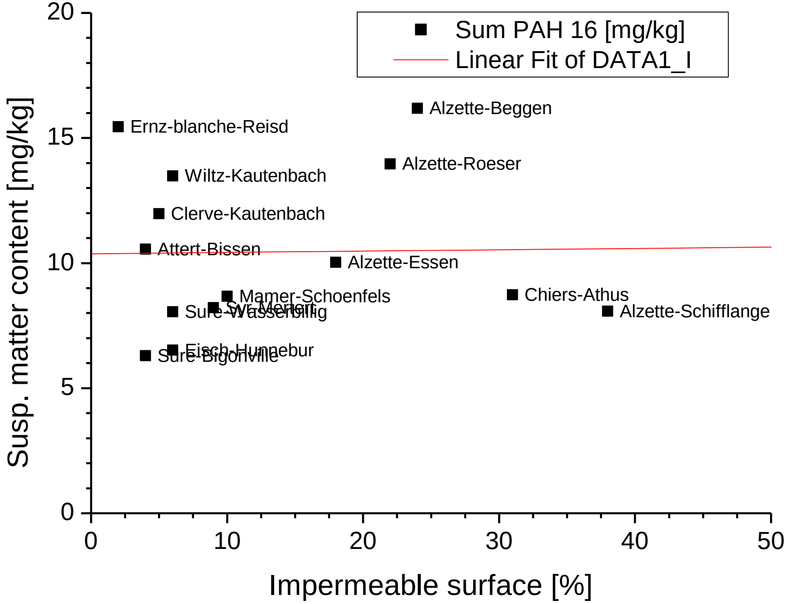




LOW FLOW PATTERN

The random nature of PAH sources

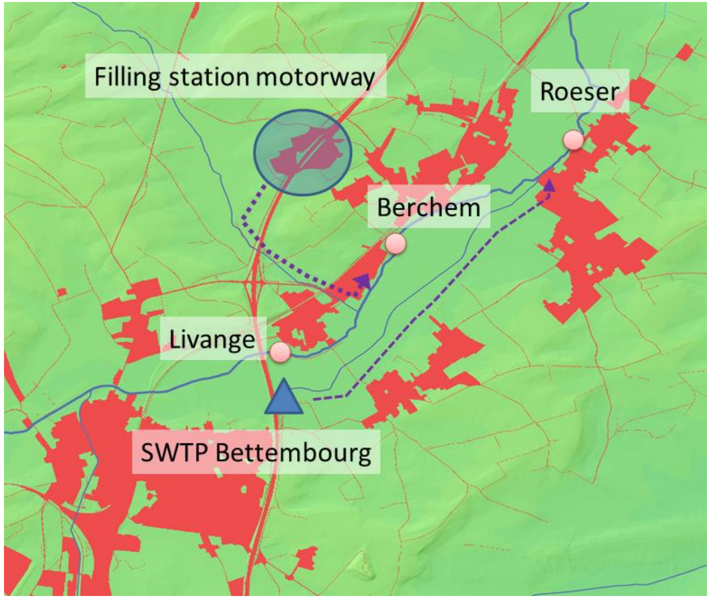




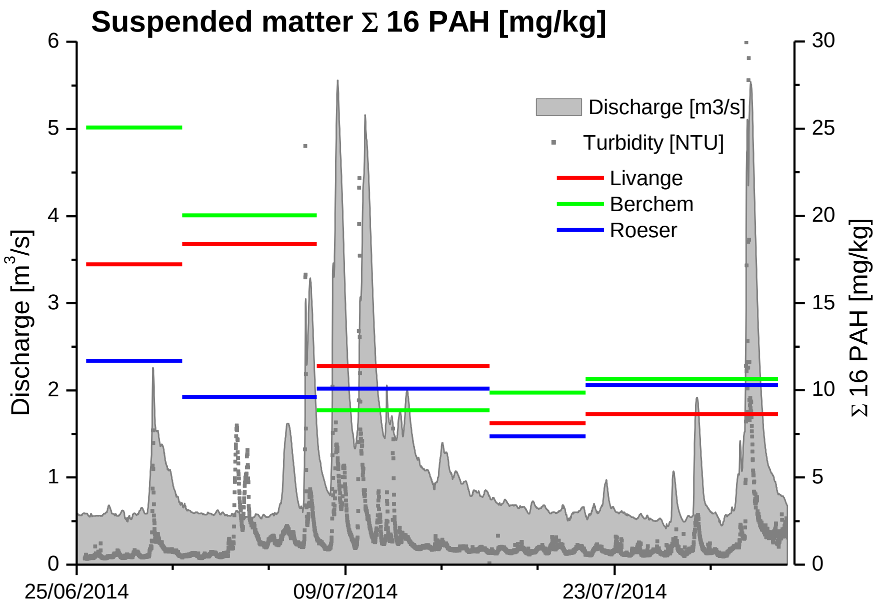
- Metals correlate well with impermeable surfaces while PAH do not at all
- Alluvial contaminated sites as probable sources for PAH

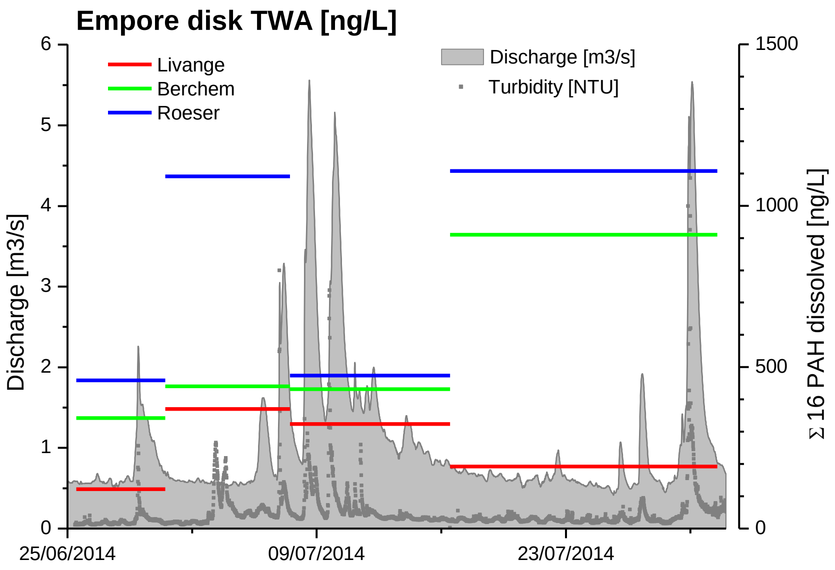
TRACKING THE SOURCES
How small scale is the problem?

- Combined passive sampler campaign (SPM nets & Empore disks for dissolved fraction)
- Longitudinal stretch of 4 km length with 3 monitored sites
- Different pollution sources
  - Urban + historical background (Livange)
  - Gas station (Berchem)
  - WWTP with known PAH pollution (Roeser)



SPATIAL DISCRIMINATION
Sources reveal under low flow

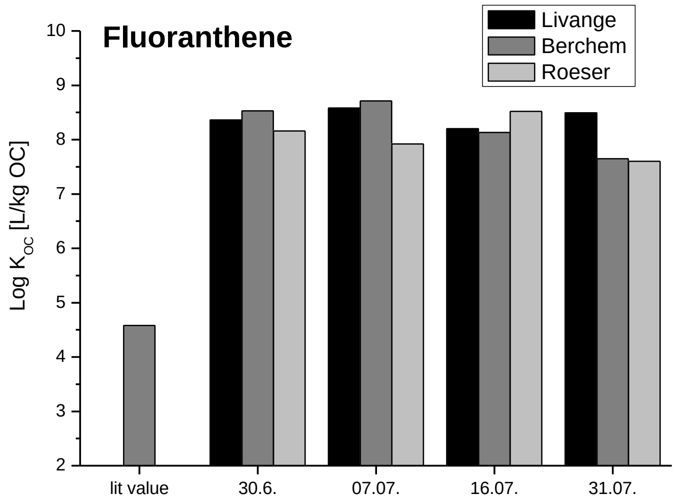


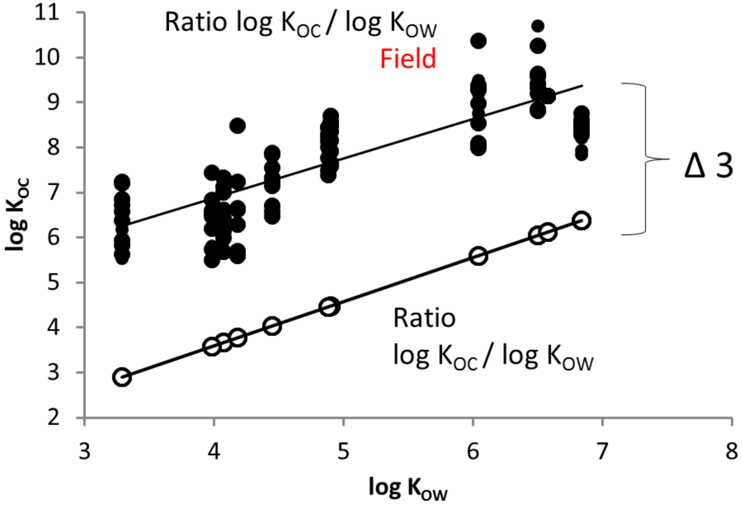


- Differences in SPM contamination can only be observed prior to the floodwave
- Empore disk TWA show highest input by dissolved PAH downstream of the fresh sources (WWTP, Gas station)

FAR FROM EQUILIBRIUM

Apparent log K_{oc} higher than literature values

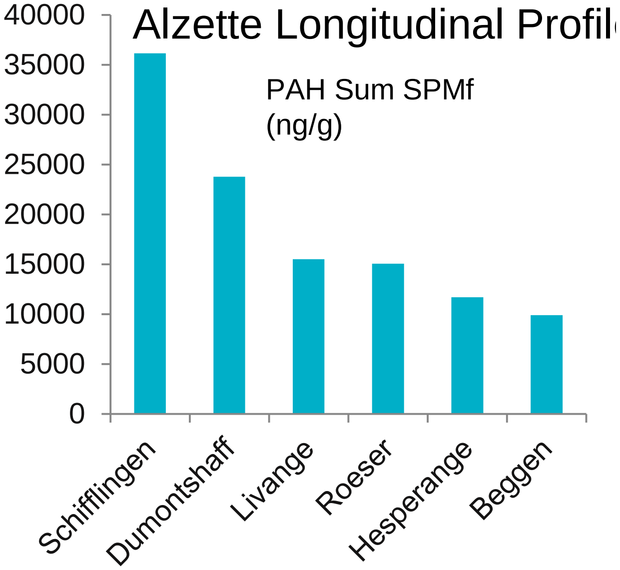


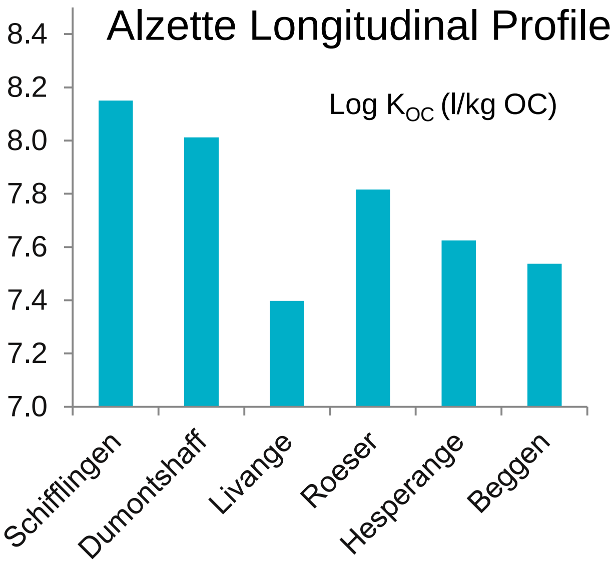


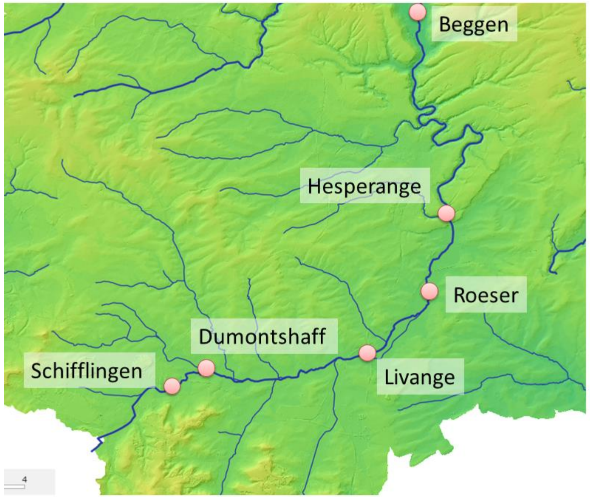
- Apparent log K_{oc} calculated with SPM and Empore disks are 3 orders of magnitude higher than expected from literature regressions
- Differences between the 3 sites are < 1 log unit and largest under low-flow conditions

SOURCE DISCRIMINATION

The potential of log K_{oc} to reveal aged contamination



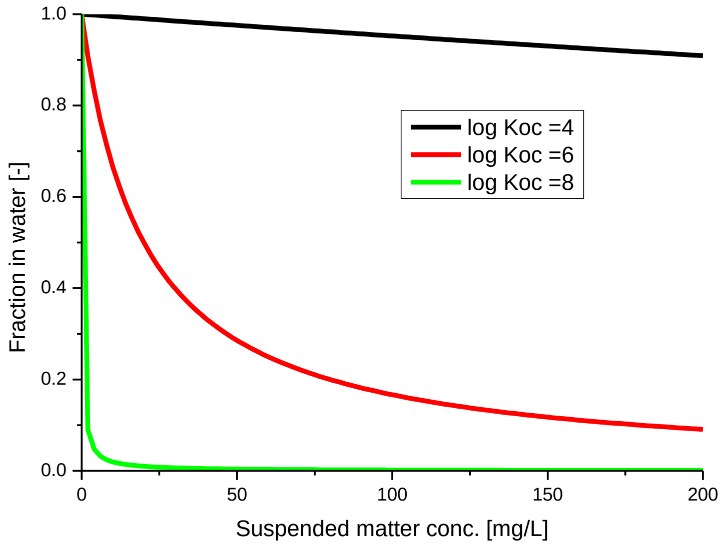


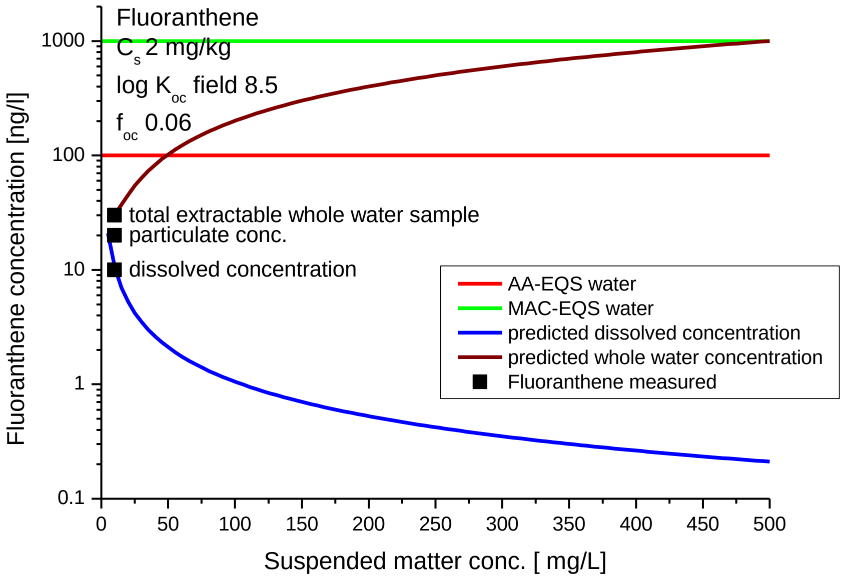


- The south of Luxembourg is a historical steel working area
- SPM contamination and log K_{oc} are decreasing downstream of the source

IMPLICATIONS FOR MOINTORING

Relevance of log K_{oc} for whole water extraction?





- With field K_{oc} up to 3 orders higher than expected suspended matter concentration impacts EQS-evaluation heavily
- Are these EQS relevant under these conditions (bioavailability)?

SUMMARY & CONCLUSIONS

- PAH EQS exceedences are one of the main reasons of chemical status failure
- Several investigations with different approaches suggest that urban runoff is not the main source of PAH in Luxembourgish catchments
- Instead, suspended sediment profiles under low-flow suggest very localized contaminations
- The outreach of these pollutions is very limited in longitudinal profiles (-> erratic conclusions on upstream situation)
- Apparent log K_{oc} of suspended sediments are 3 orders of magnitude higher than literature values (implications for whole water sampling, SPM impact)
- Log K_{oc} have the potential to discern fresh from old PAH pollution sources
- Longitudinal profiles at low flow with combined SPM and Empore disk sampling can be used to pinpoint pollution sources