



Diffuse Pollution of Soil and Water: Long-term Trends on Large Scales

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Water & Earth System Science
Competence Cluster



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Industrialization and urbanization, which consequently increased pressure on the environment to cause degradation of soil and water quality over more than a century, is still ongoing. The number of potential environmental contaminants detected in surface and groundwater is continuously increasing; from classical industrial and agricultural chemicals, to flame retardants, pharmaceuticals, and personal care products. While point sources of pollution can be managed in principle, diffuse pollution is only reversible at very long time scales if at all. Compounds which were phased out many decades ago such as PCBs or DDT are still abundant in soils, sediments and biota. How diffuse pollution is processed at large scales in space (e.g. catchments) and time (centuries) is unknown. The relevance to the field of processes well investigated at the laboratory scale (e.g. sorption/desorption and (bio)degradation kinetics) is not clear. Transport of compounds is often coupled to the water cycle and in order to assess trends in diffuse pollution, detailed knowledge about the hydrology and the solute fluxes at the catchment scale is required (e.g. input/output fluxes, transformation rates at the field scale). This is also a prerequisite in assessing management options for reversal of adverse trends.



1. Subsurface heterogeneity causes high uncertainty in location of point sources

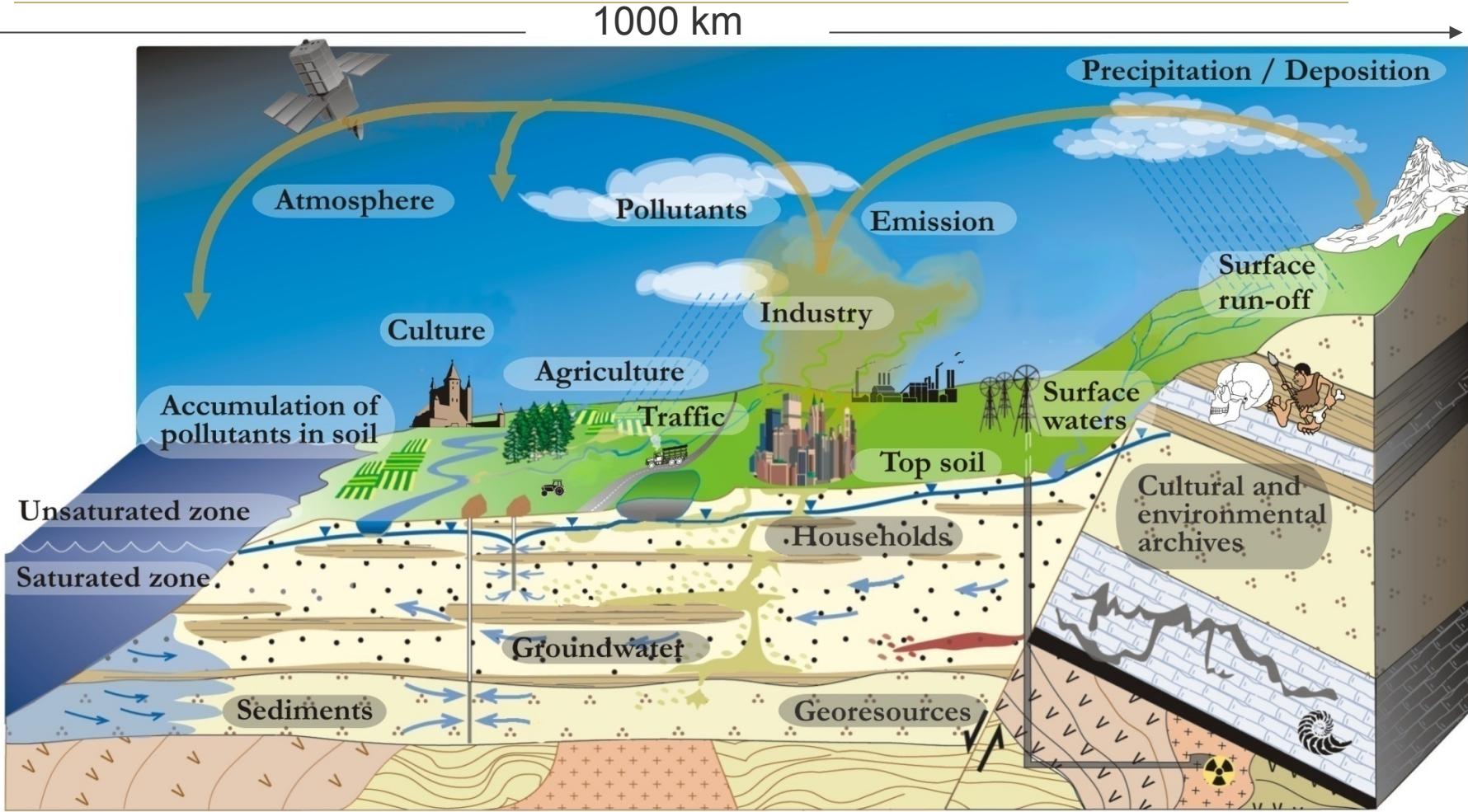
→ Most important reason for failure of site remediation (despite all progress in remediation technologies)

2. Natural attenuation works

→ But not efficient in sources (time scales are too long) and not for all compounds (steady state plumes for degradable compound, long plumes for stable compounds such as chlorinated solvents)



Water cycle + diffuse pollution

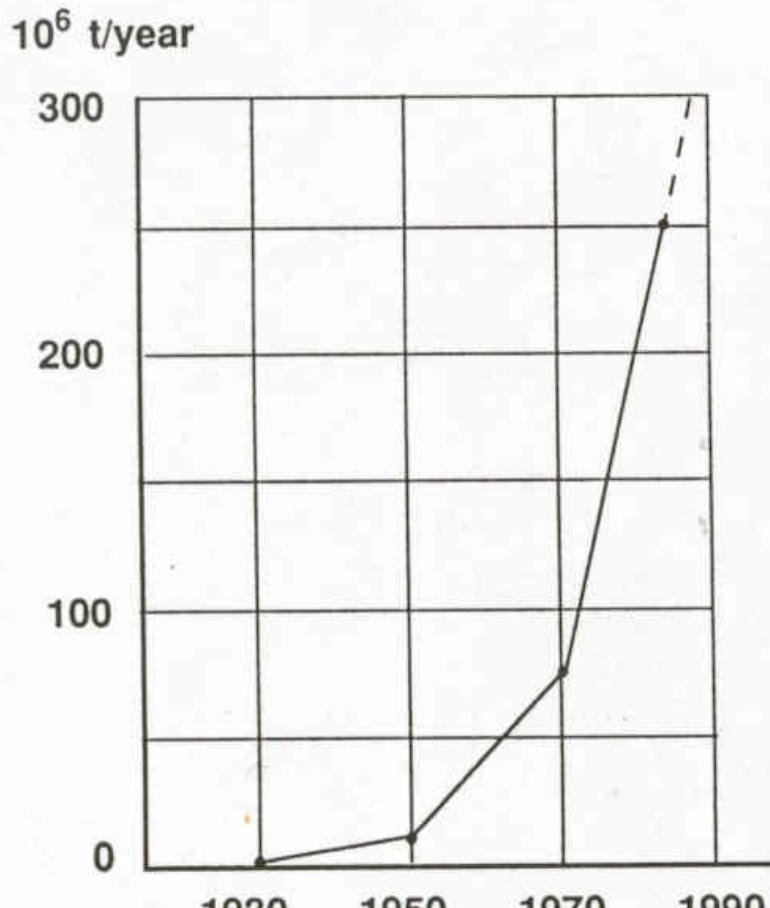


*Man, however much he may like to pretend the contrary, is part of nature.
Can he escape a pollution that is now so thoroughly distributed
throughout our world? (Rachel Carson 1907 – 1964; Silent Spring, 1962)*



Increasing production – numerous compounds

Development of the global annual production of synthetic organic material since 1930

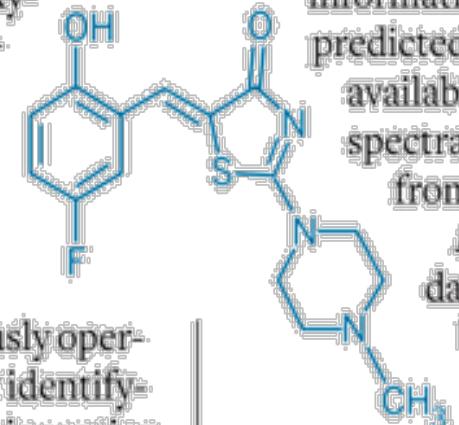


(Source: UNEP, 1987)

The discovery and production of new organic chemicals has grown exponentially:
50 000 000 registered in CAS (09/2010)

part of a 199-page patent document and is (5Z)-5-[(5-fluoro-2-hydroxyphenyl)methylene]-2-(4-methyl-1-piperazinyl)-4(5H)-thiazole, CAS RN 1181081-51-5.

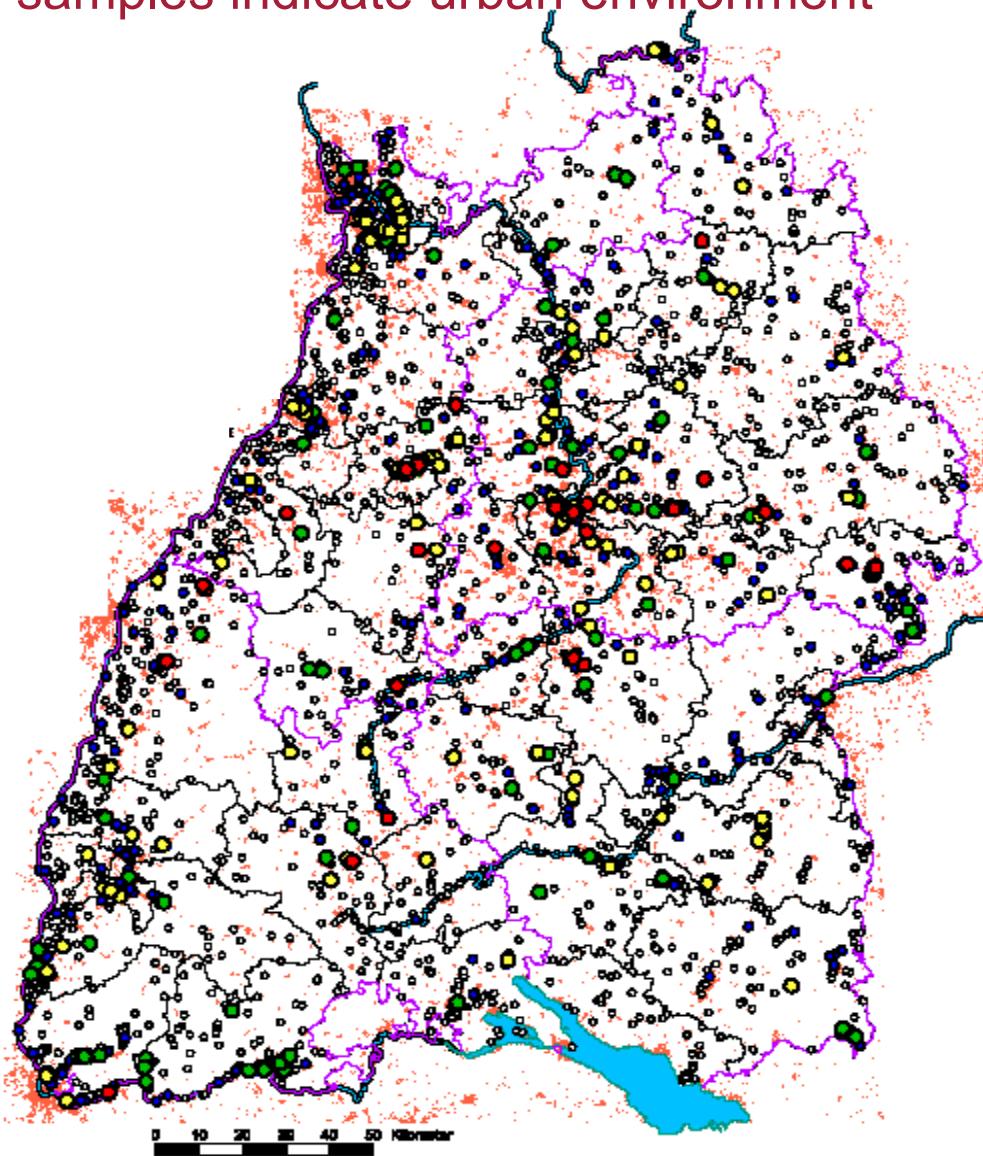
The 50 million publicly disclosed substances represent a consequential milestone. The CAS Registry has been continuously operated for the purposes of uniquely identifying chemical substances since its inception,



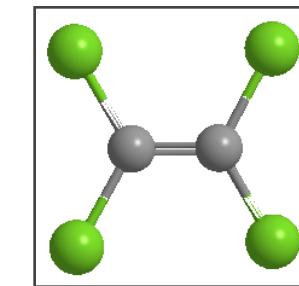


PCE “Footprint“ in groundwater

→ Chlorinated solvents in groundwater samples indicate urban environment



Tetrachloroethene
(PCE)



Sampling campaign 1998

Conc. in mg/l

n.d.

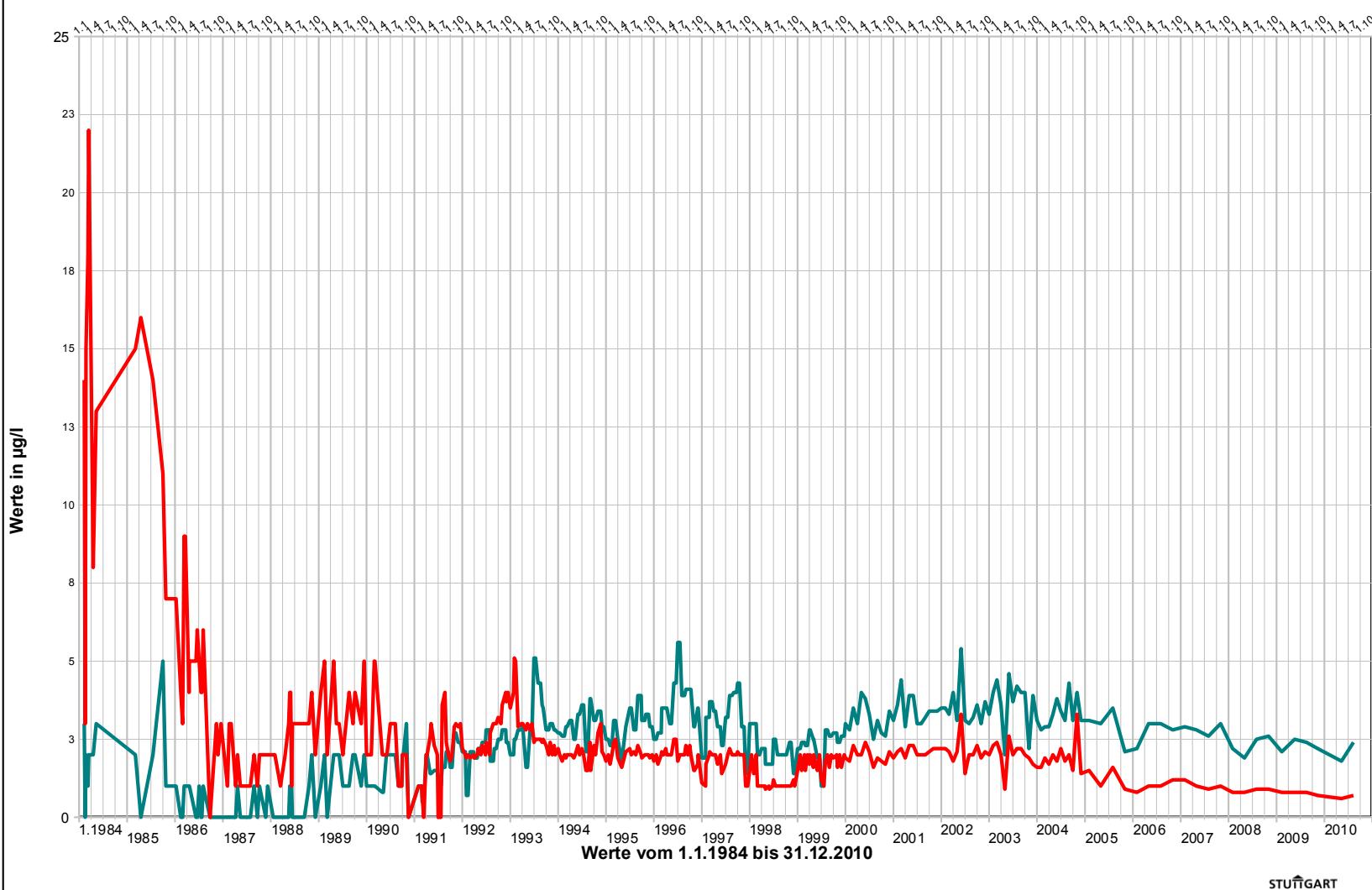
- < 0.0010
- 0.0011 – 0.0050
- 0.0051 - 0.1000
- > 0.1000

LFU -Baden Württemberg



Not much change in almost 30 years despite expensive remediation efforts

Parameter-Trendvergleich für Messstelle 0063/511-4





Diffuse nitrate pollution

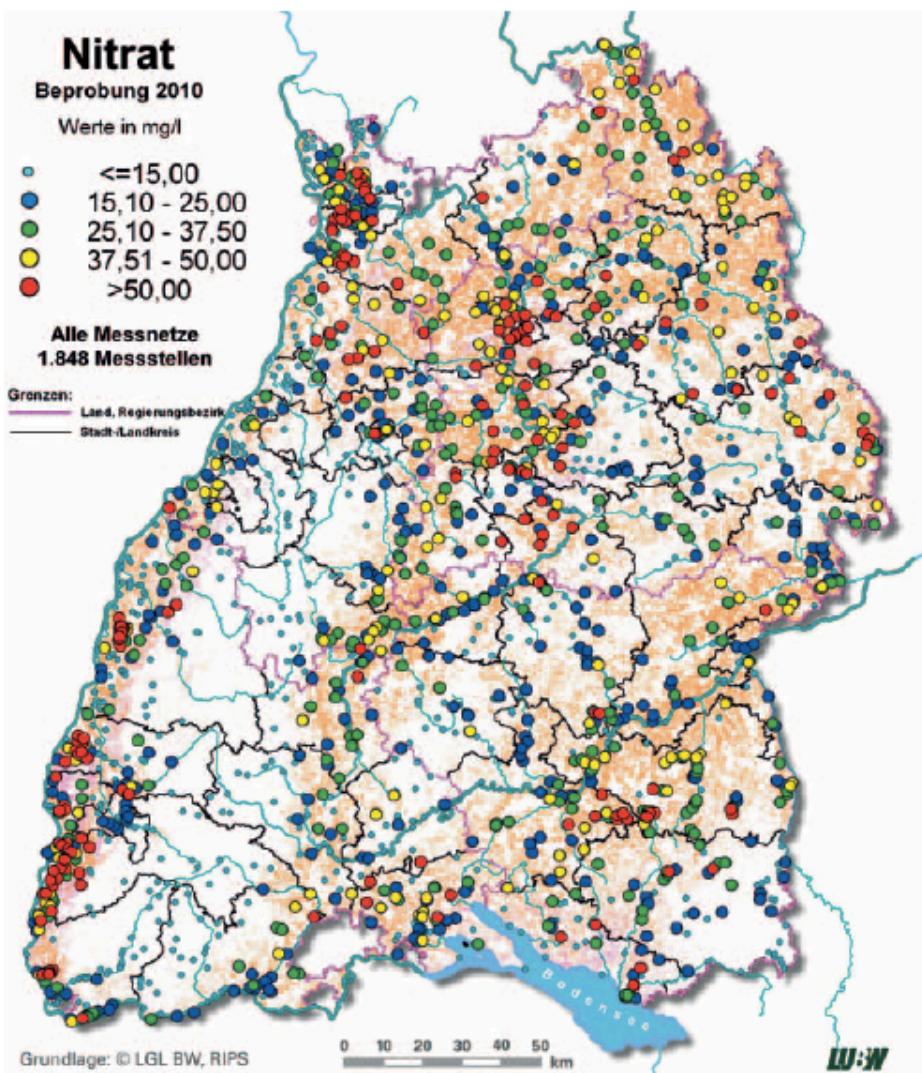


Abbildung 2.4-2: Nitratgehalte 2010 an den Landesmessstellen
Kartenhintergrund: braune Flächen: Ackerbau; violette Flächen: Weinbau, Obstbau

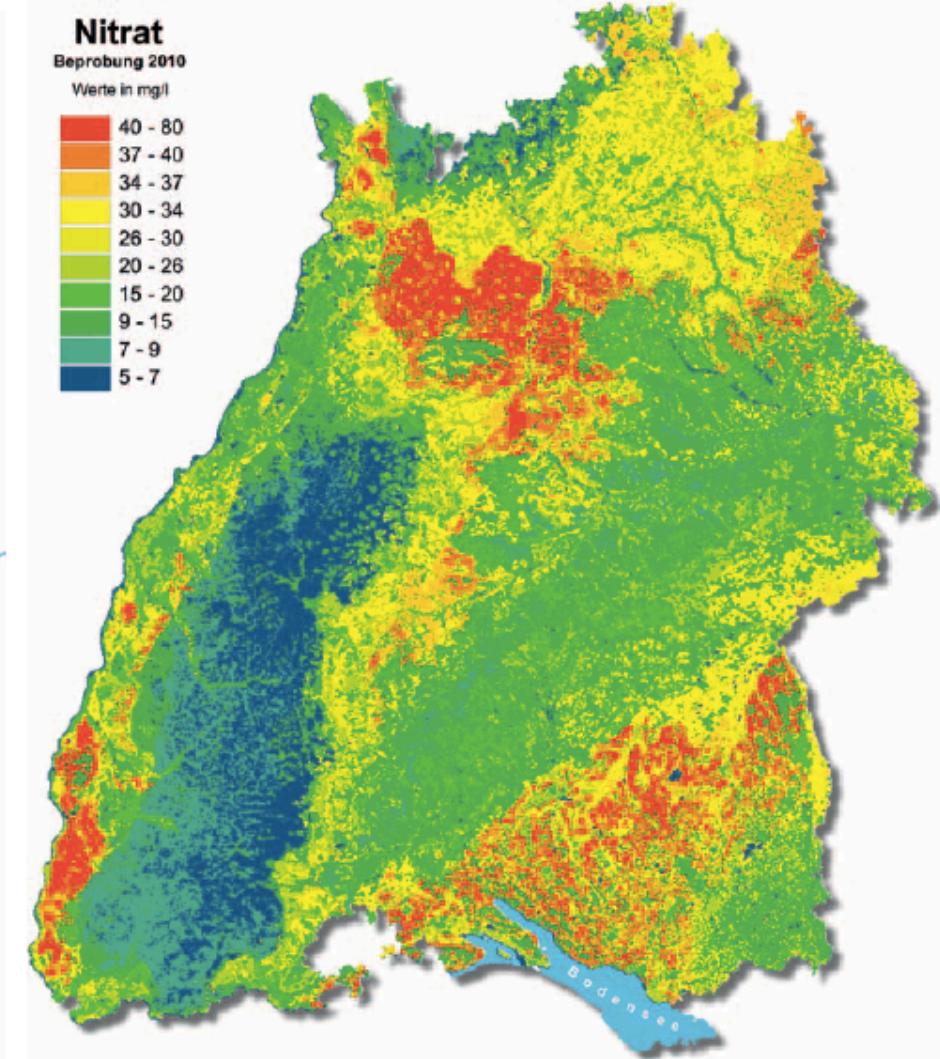


Abbildung 2.4-3: Verteilung der Nitratgehalte 2010 im oberflächennahen Grundwasser; regionalisierte Darstellung nur oberflächennaher Messstellen mit Messungen von September bis Oktober 2010 (Datengrundlage: 1.475 von insgesamt 1.774 Landesmessstellen, da ein Teil der Messstellen in tiefen Aquifern verfiltert ist oder für Messstellen keine Aquifer- oder Landnutzungszuordnung vorliegt)



Not much change in almost 20 years

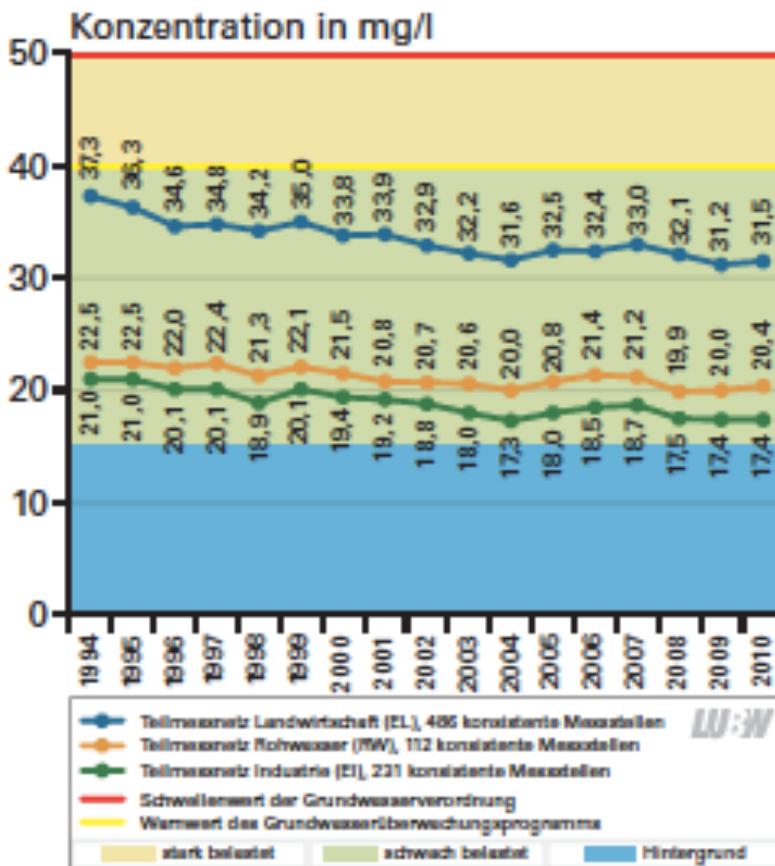


Abbildung 2.4-7: Entwicklung der Nitratmittelwerte zwischen 1994 bis 2010 bei konsistenten Messstellengruppen im Beprobungszeitraum jeweils zwischen Anfang September und Ende Oktober

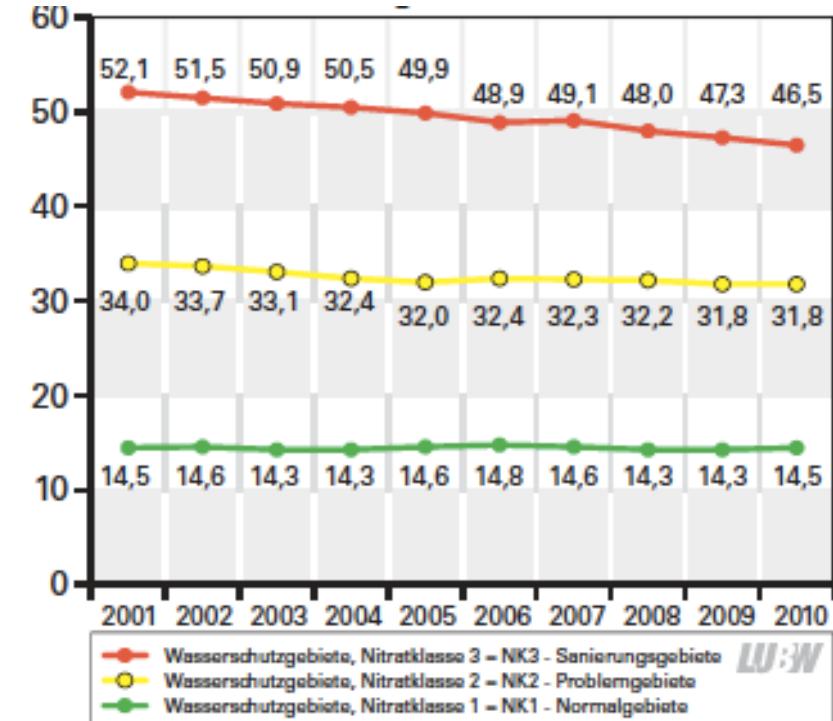
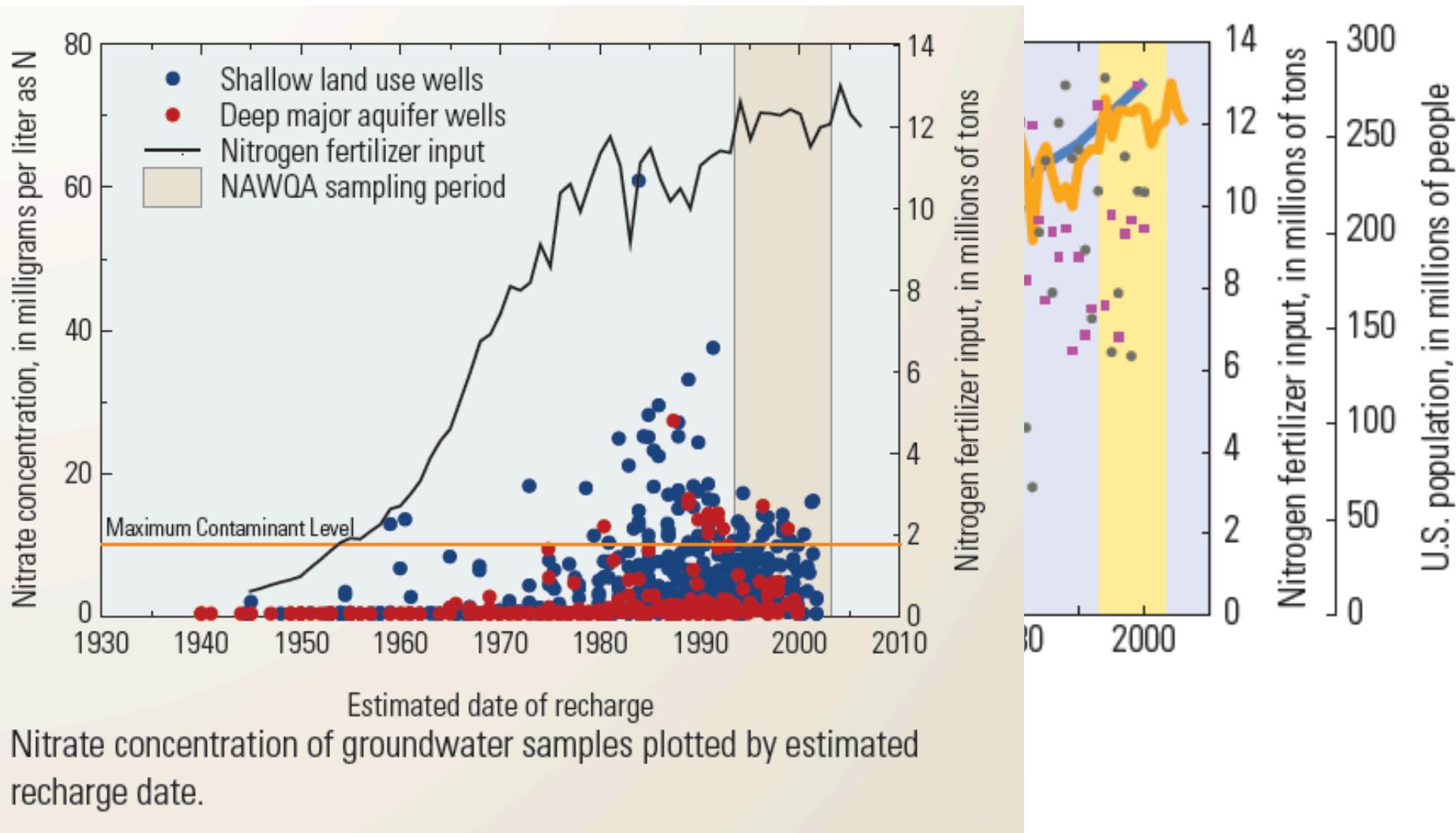


Abbildung 2.4-9: Entwicklung der jährlichen Mittelwerte für Nitrat von 2001 bis 2010 für konsistente Messstellen und konsistente Wasserschutzgebiete nach SchALVO-Einstufung über alle zur Verfügung stehenden Nitratwerte (SchALVO-Einstufungsbasis: 2001), Abk. siehe Text. Datenquelle: alle Landesmessstellen und alle Kooperationsmessstellen der Wasserversorgungsunternehmen in WSG, die für die WSG-Einstufung maßgebend sind

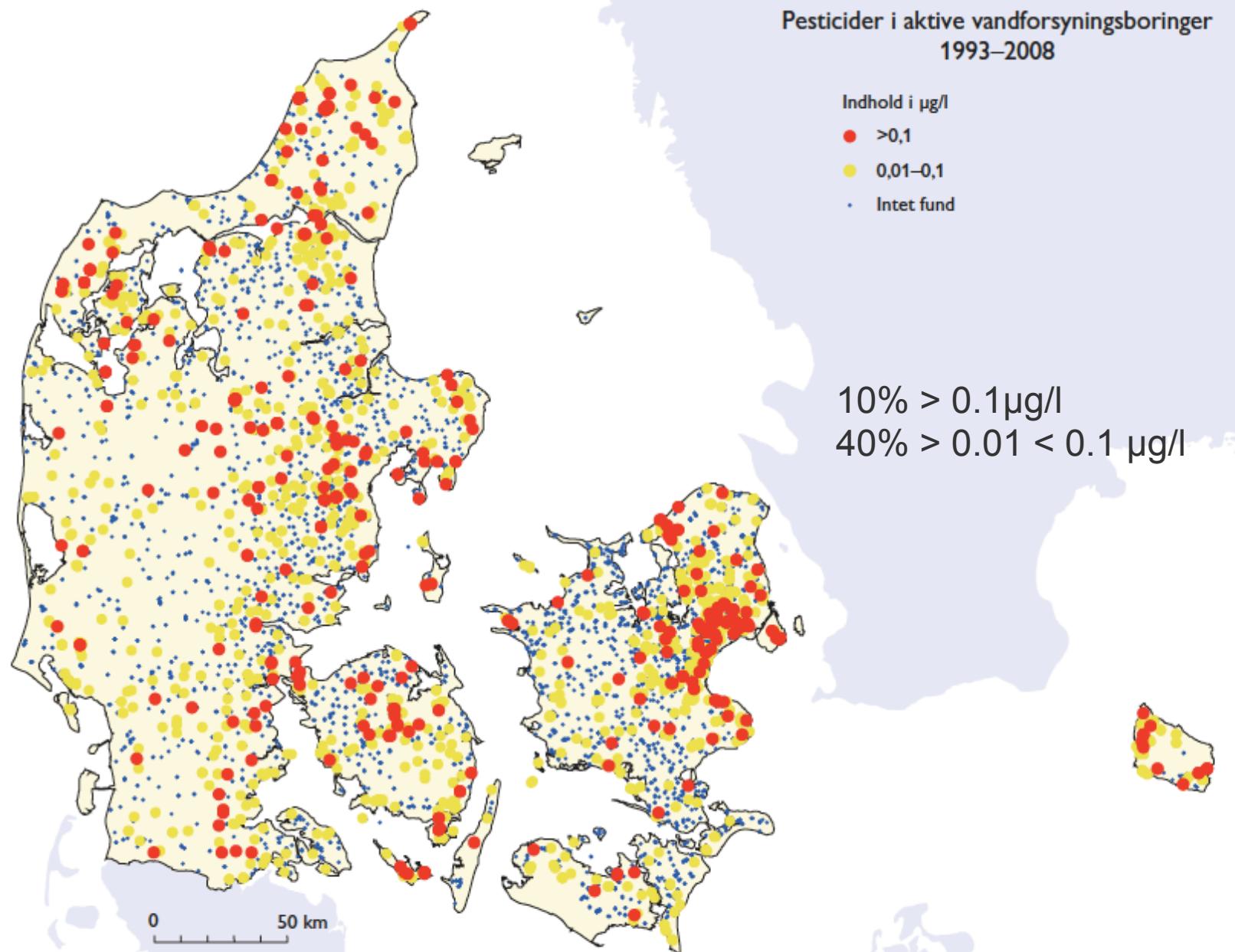


Trends in nitrate



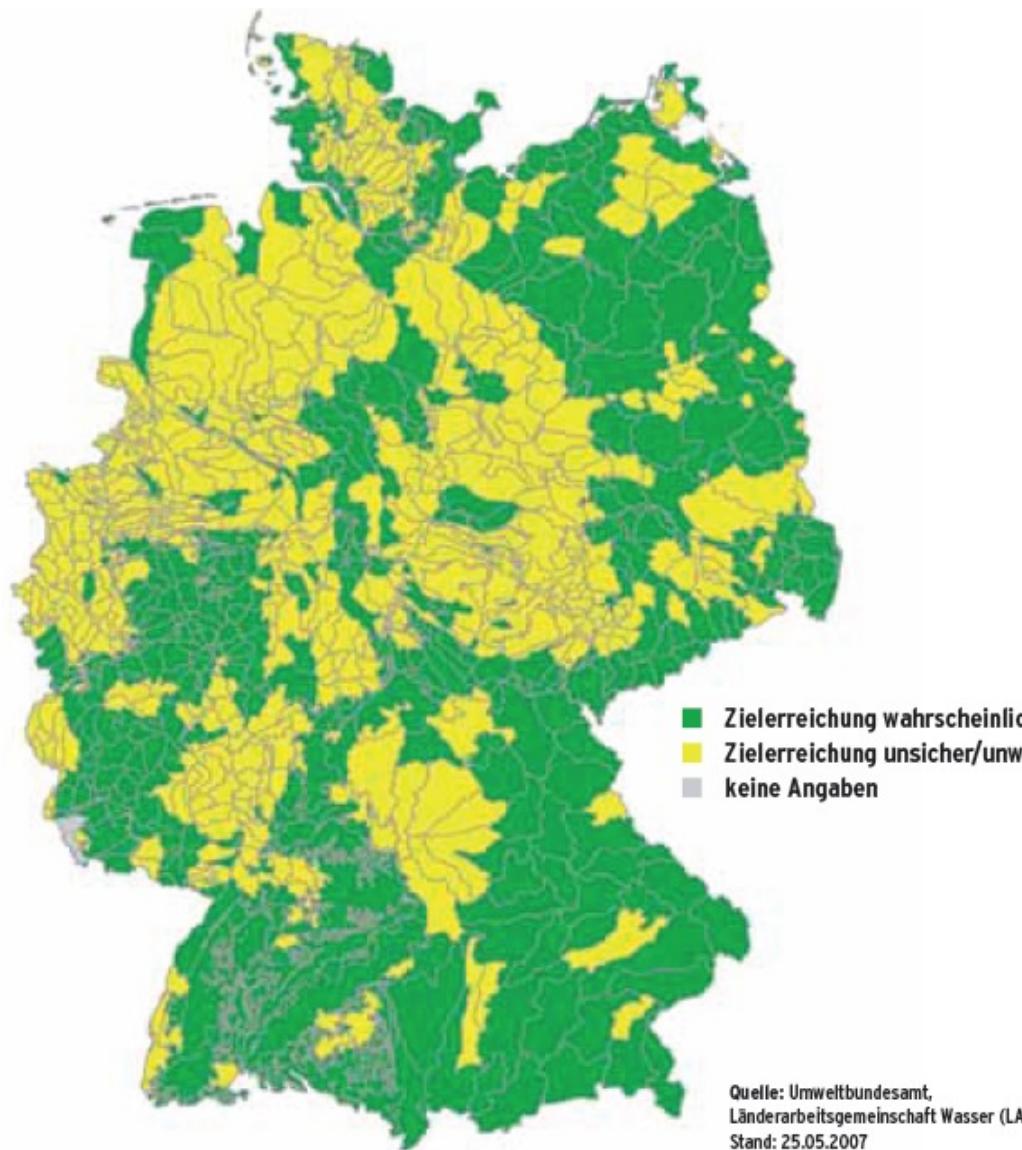
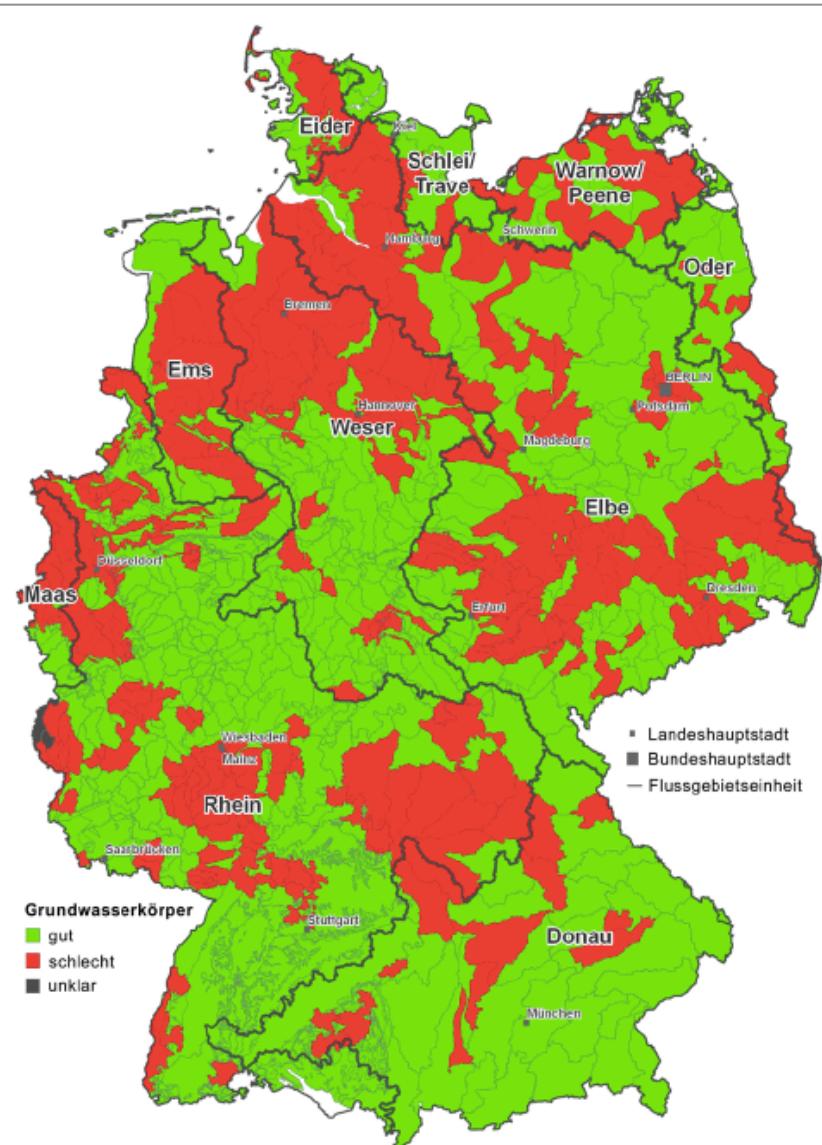


Pesticides in Groundwater: Denmark





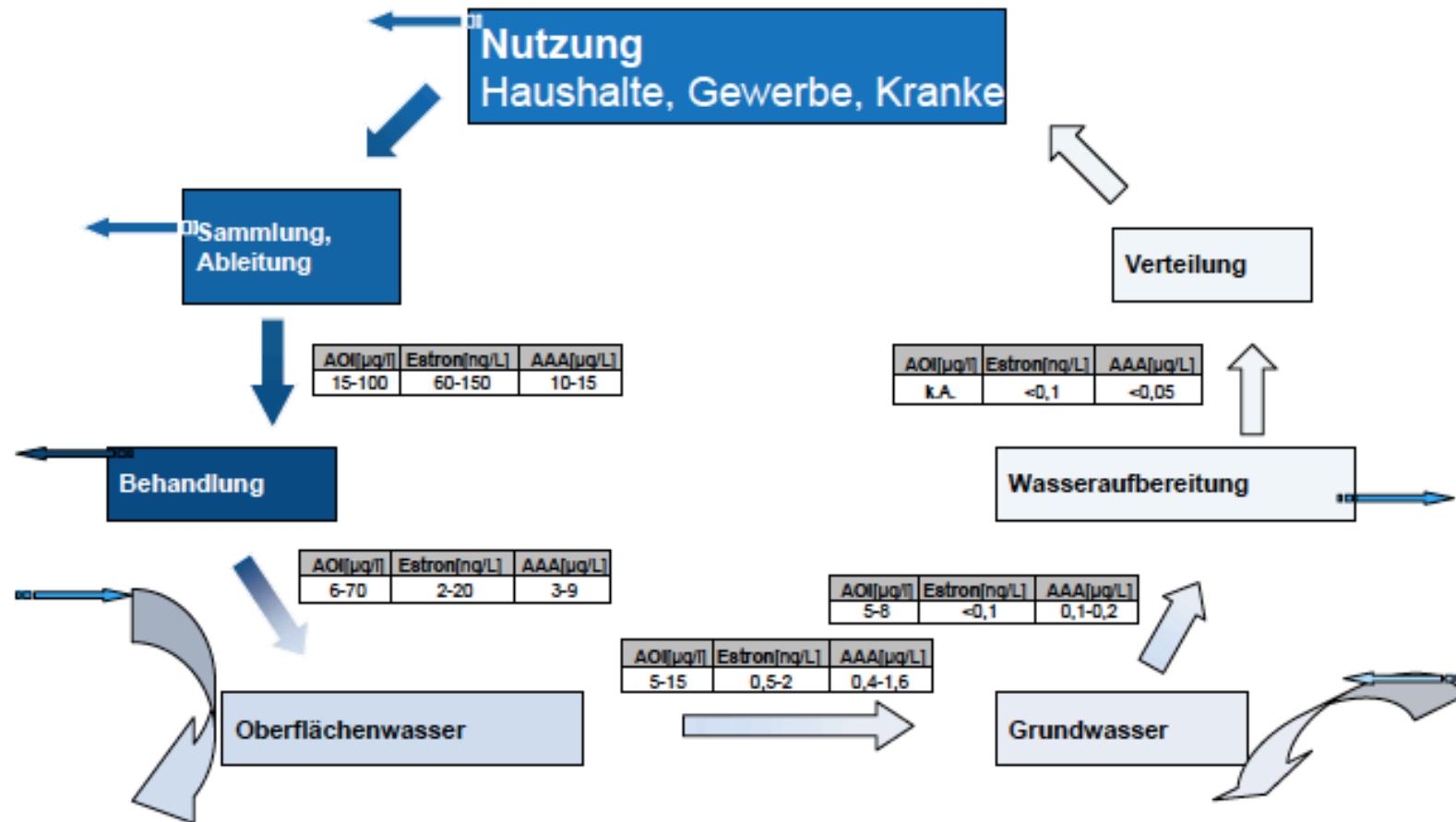
Groundwater quality in Germany



No “good status” until 2015

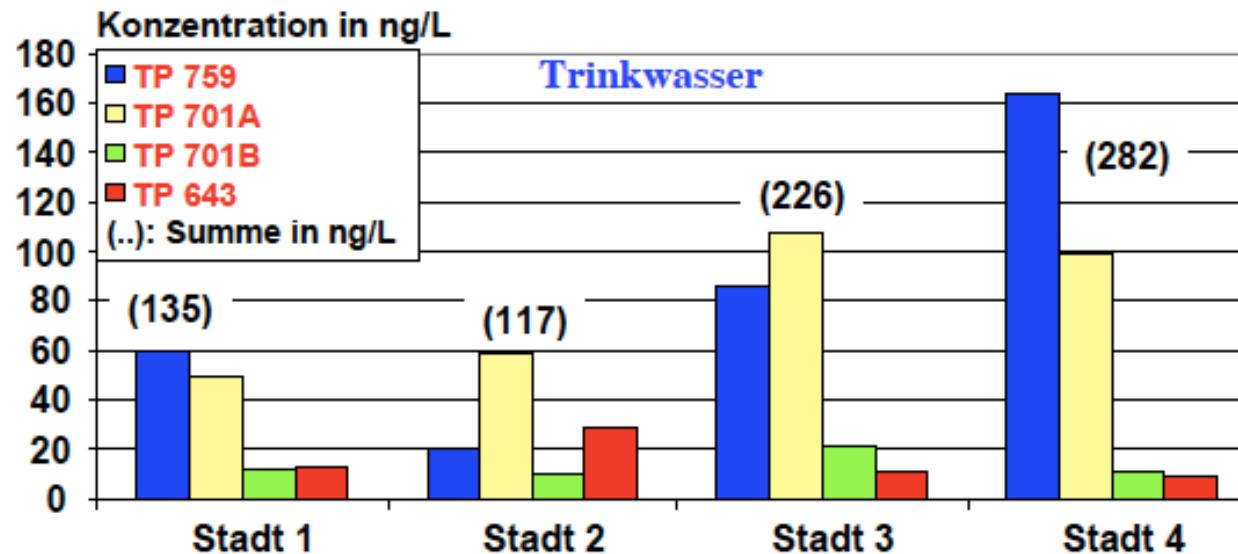


Wasserkreislauf Berlins

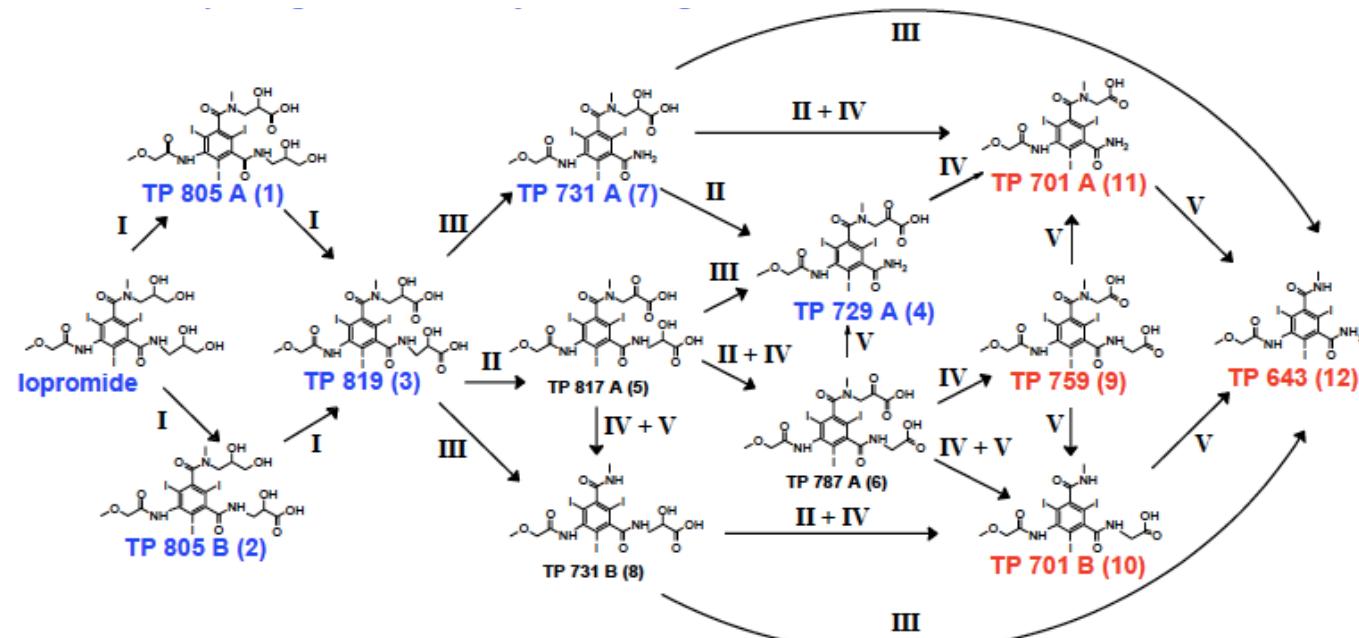




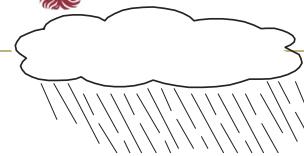
Multiple cycles: Higher concentrations in tap water in downgradient cities



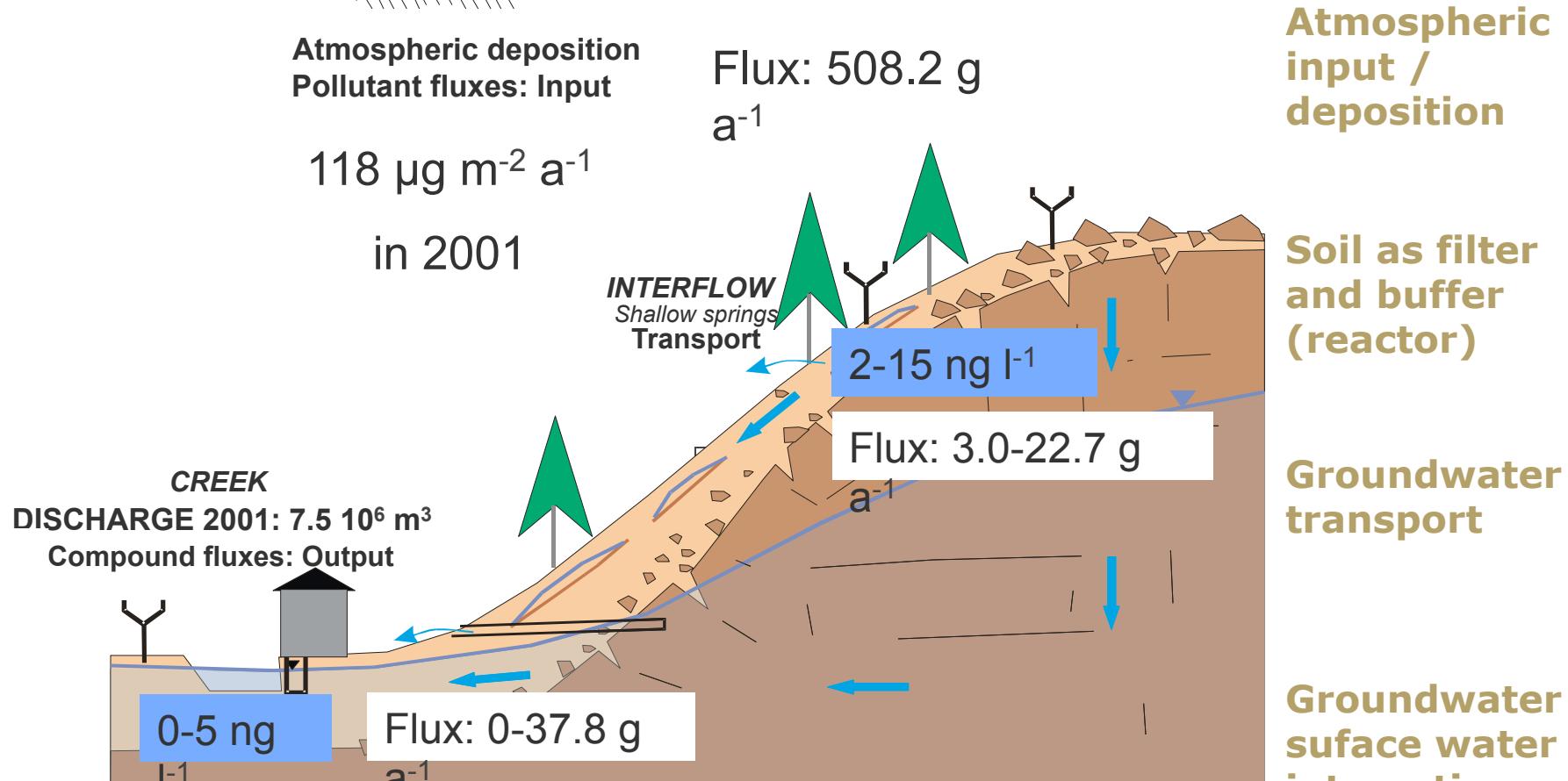
Quelle: Schulz et al., ES&T,



Quelle: Schulz et al., ES&T, im Druck



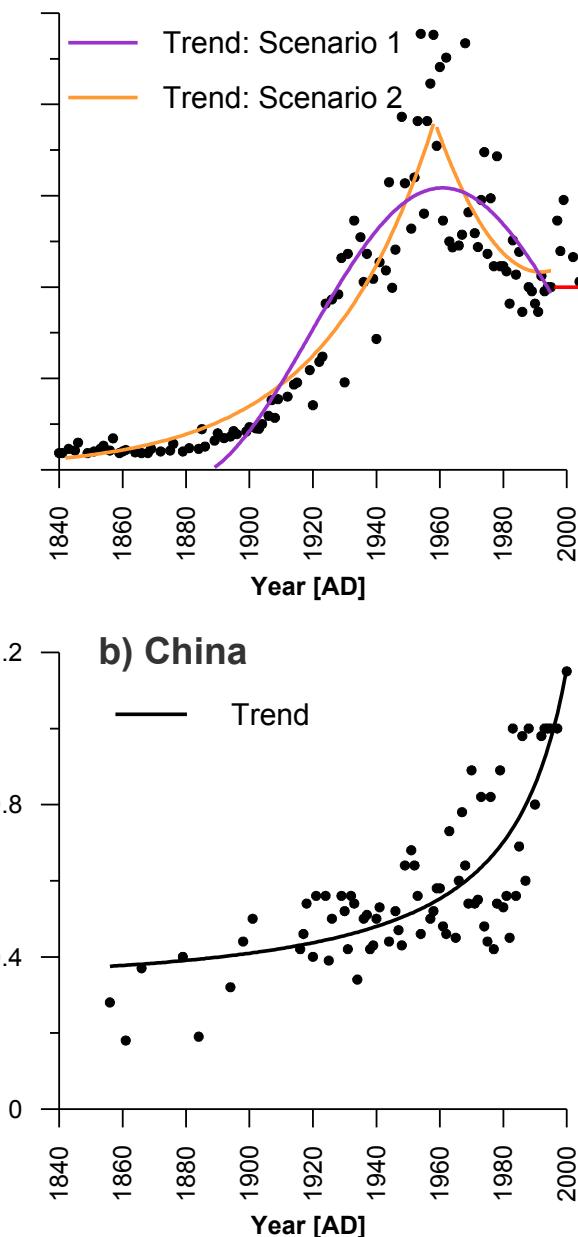
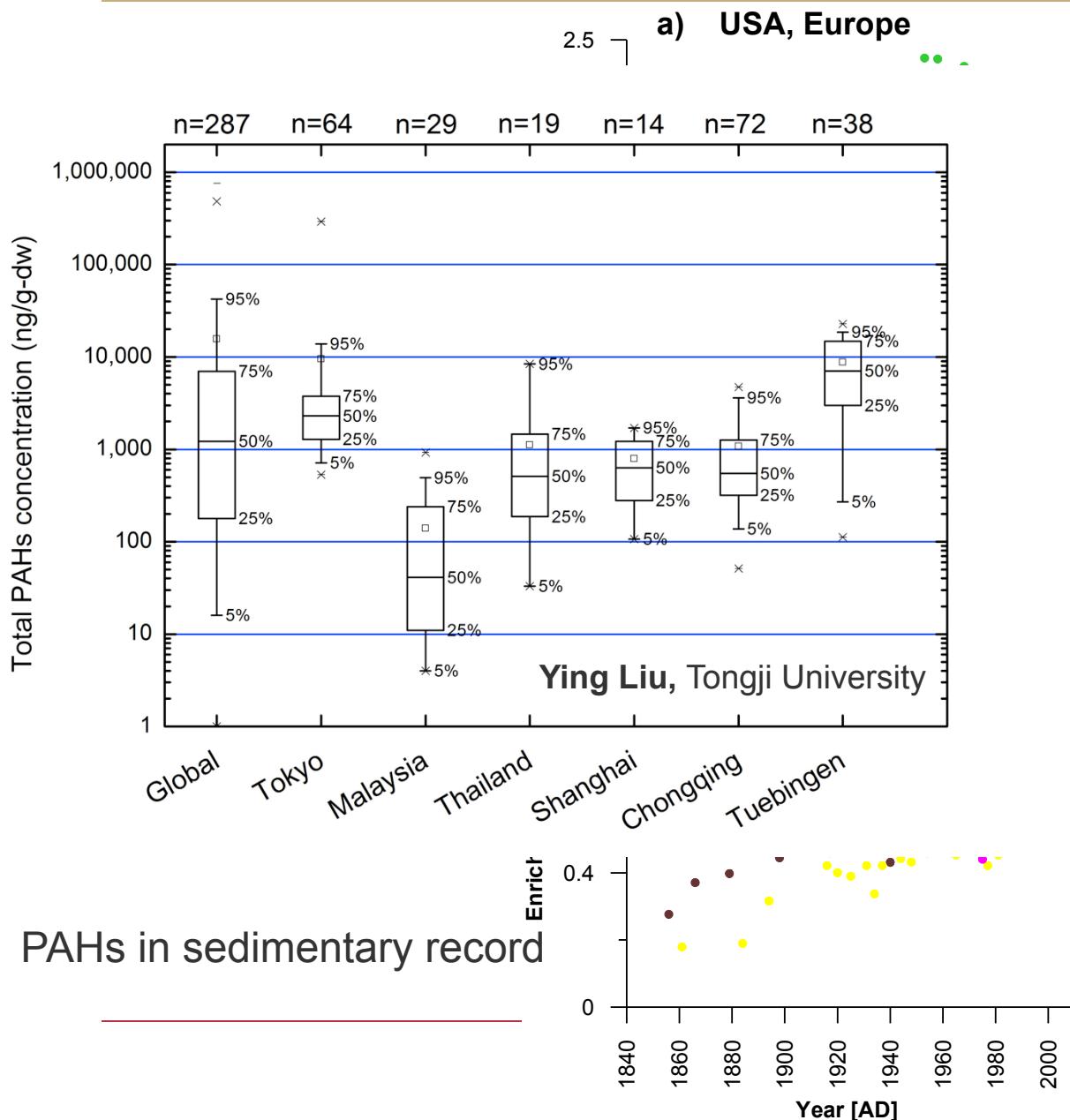
Legacy compounds: POPs



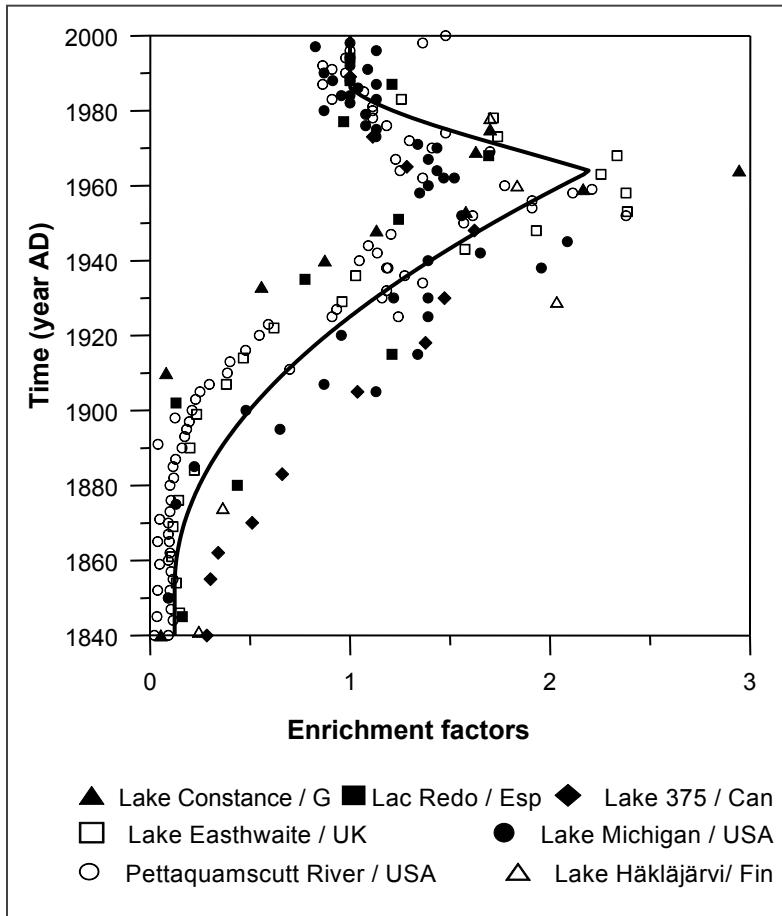
More than 90% of incoming PAHs accumulate in the soils!
Good news for groundwater – bad news for soils



Historical and recent pollution



Stable (secondary) sources: soils



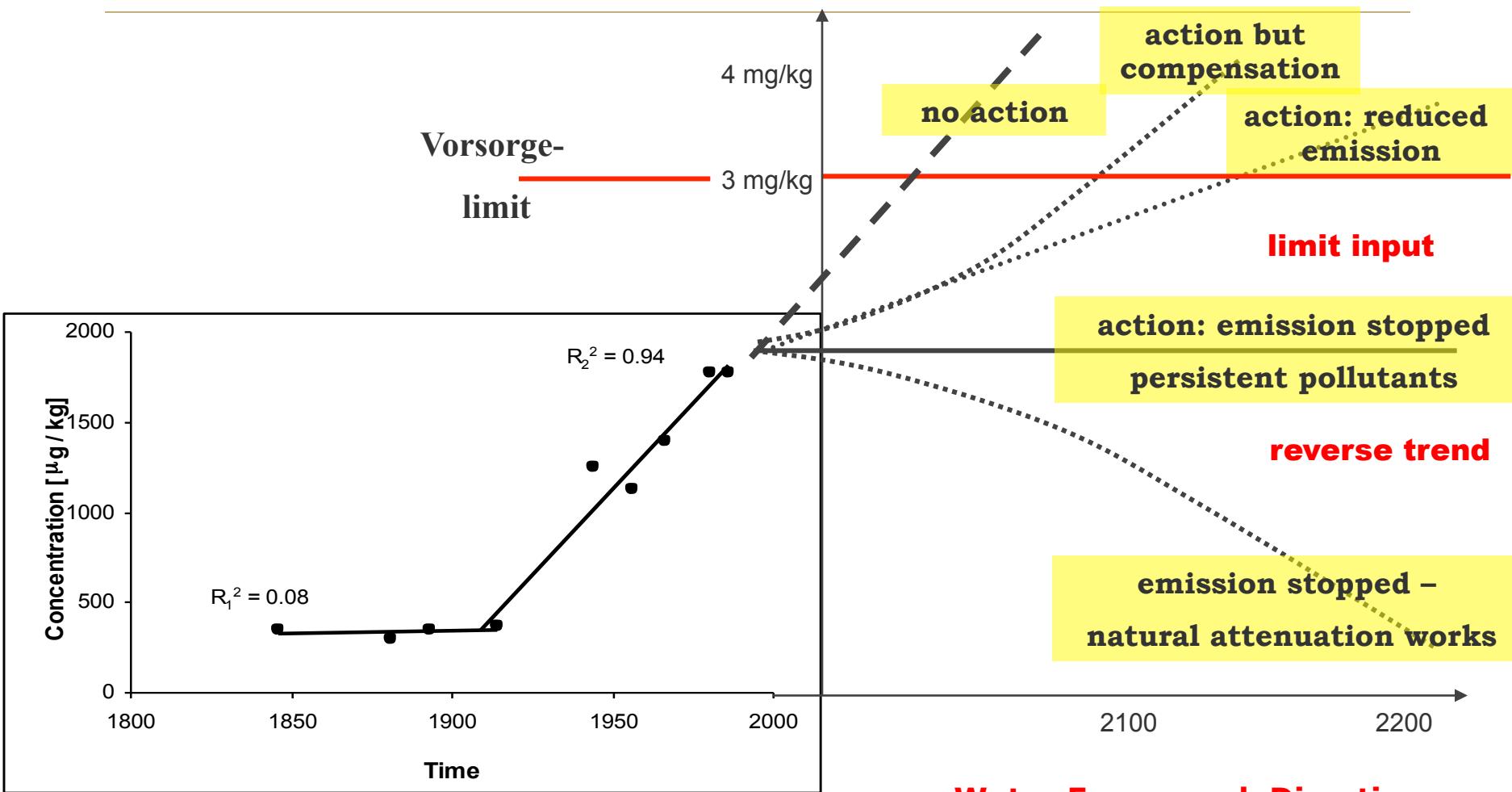
$$S = \sum_{i=1}^n C_s \rho M$$

$$S(t) = \int_{t_1}^{t_2} D E f(t) dt$$

EPA PAHs "State Wide"

Baden-Württemberg [$\mu\text{g m}^{-2}$]		Atmospheric deposition [$\mu\text{g m}^{-2}$]
Soils	Forest soils	
Humic horizons	2 500	200 (actual, per year)
Topsoils	57 350	
Sum	59 850	26 000
Bavaria [$\mu\text{g m}^{-2}$]		
Soils	Forest soils	
Humic horizons	6 500	200 (actual, per year)
Topsoils	27 800	
Sum	34 300	26 000
Sum	10 000	6 500
Sum	71 000	68 250
		17 000

Todays inventory 3-8 larger than expected! PAHs are stable and/or unknown sources



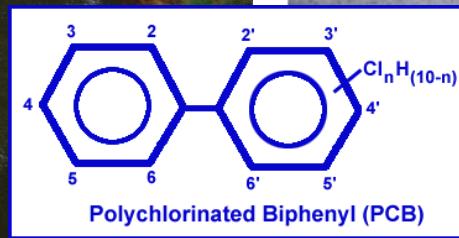
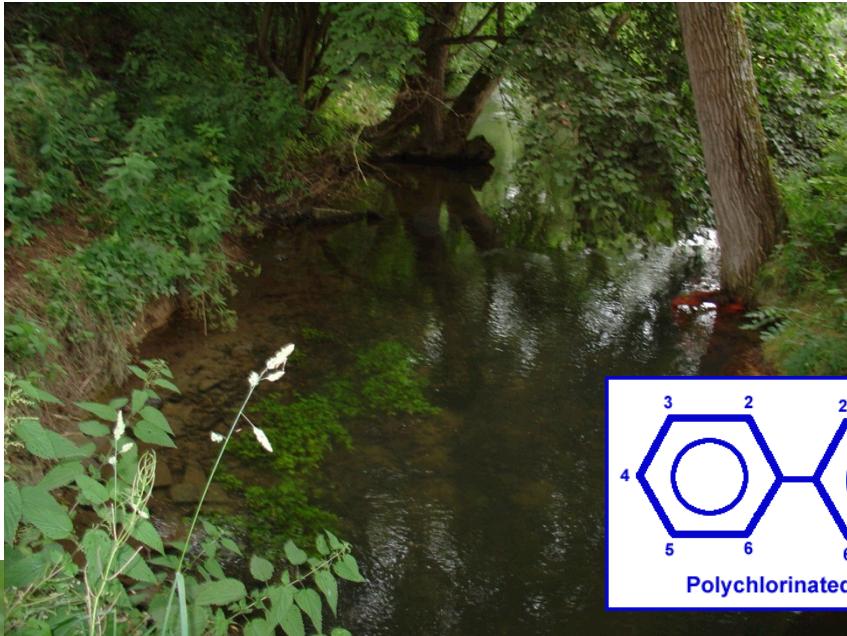
Jones, K. C.; Stratford, J. A.; Waterhouse, K. S.; Furlong, E. T.; Giger, W.; Hites, R. A.; Schaffner, C.; Johnston, A. E. (1989): Increases in the polynuclear aromatic hydrocarbon content of an agricultural soil over the last century.- Environ. Sci. Technol., 23: 95

The average deposition rate from 1900 – 1980 is ca. $12 \mu\text{g m}^{-2} \text{ d}^{-1}$. Recent measurements in urban centres indicate deposition rates of PAHs up to $4 - 8 \mu\text{g m}^{-2} \text{ d}^{-1}$; in rural areas typically ca. $0.5 \mu\text{g m}^{-2} \text{ d}^{-1}$ are observed [Martin, H., Prüß, A., Grathwohl, P. (2002). Bestimmung der Depositionsraten für Polzyklische Aromatische Kohlenwasserstoffe an verschiedenen Standorten nach DIN 19739-2 (Entwurf).- Bodenschutz, 2/02]

Water Framework Directive
Groundwater Directive
Thematic Strategy on Soil Protection
REACH!!!



Legacy compounds in the food web

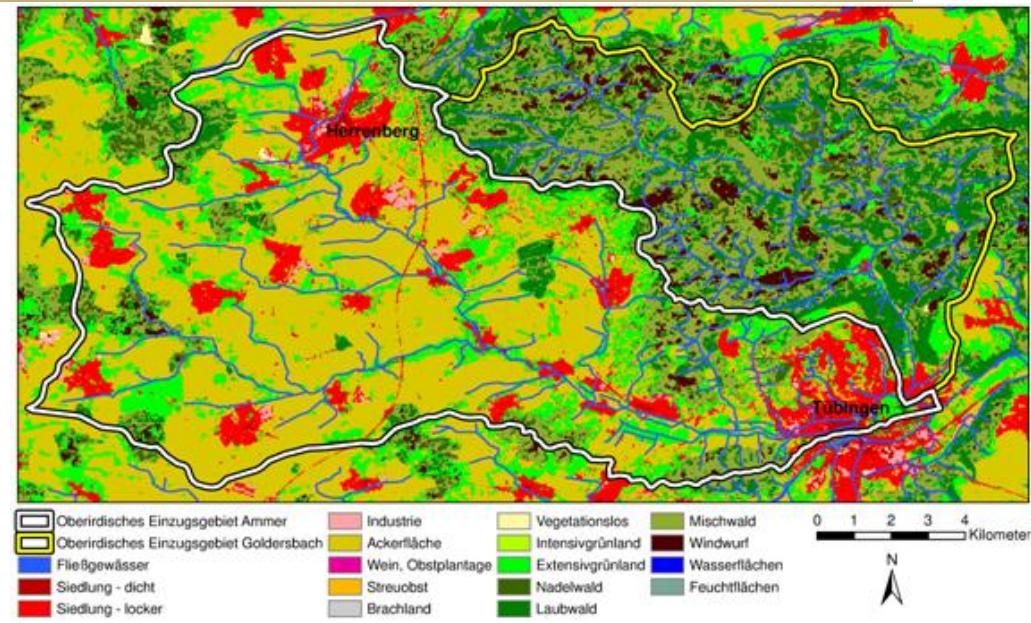
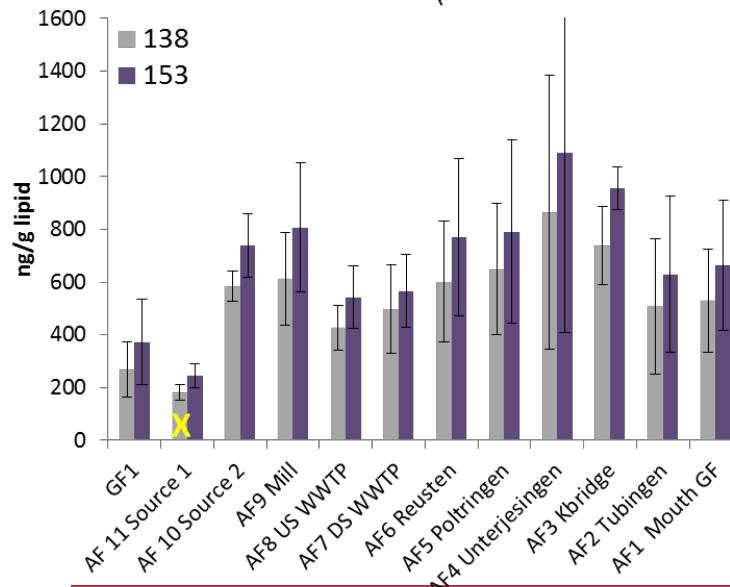
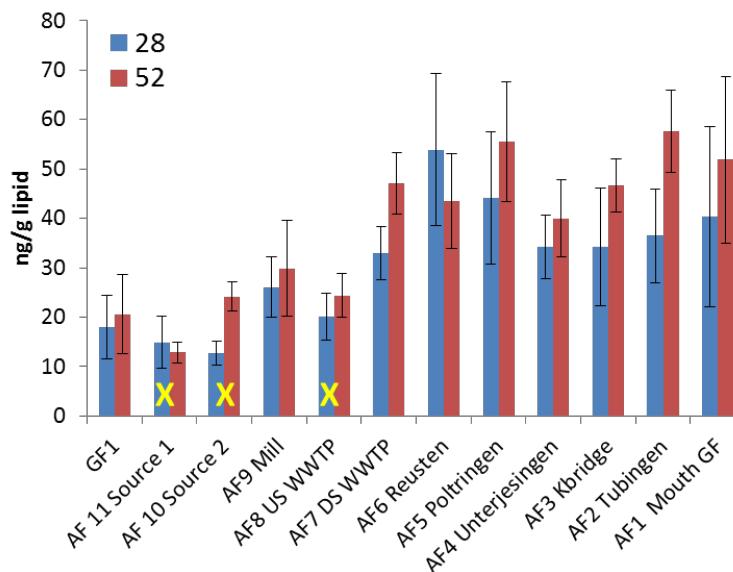


WESS is supported by the Ministry of Science, Research and Arts Baden-Württemberg (AZ Zu 33-721.3-2) and the Helmholtz Centre for Environmental Research, Leipzig (UFZ).

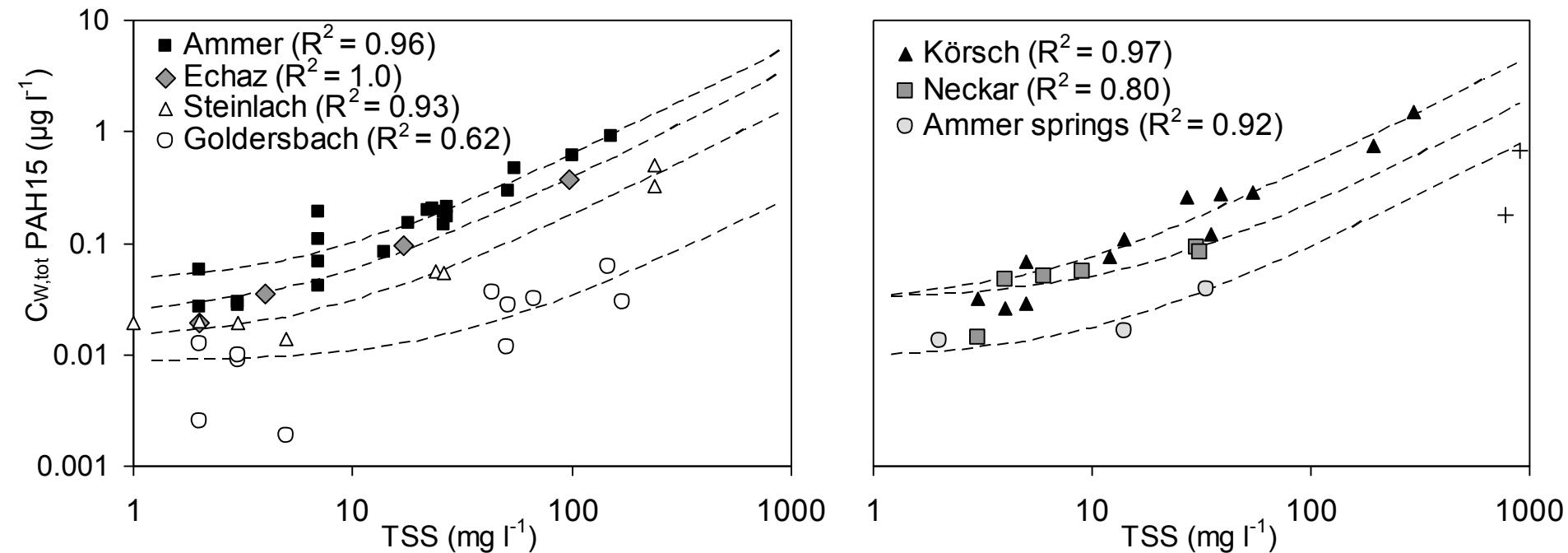
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PCB in fish: Sources?



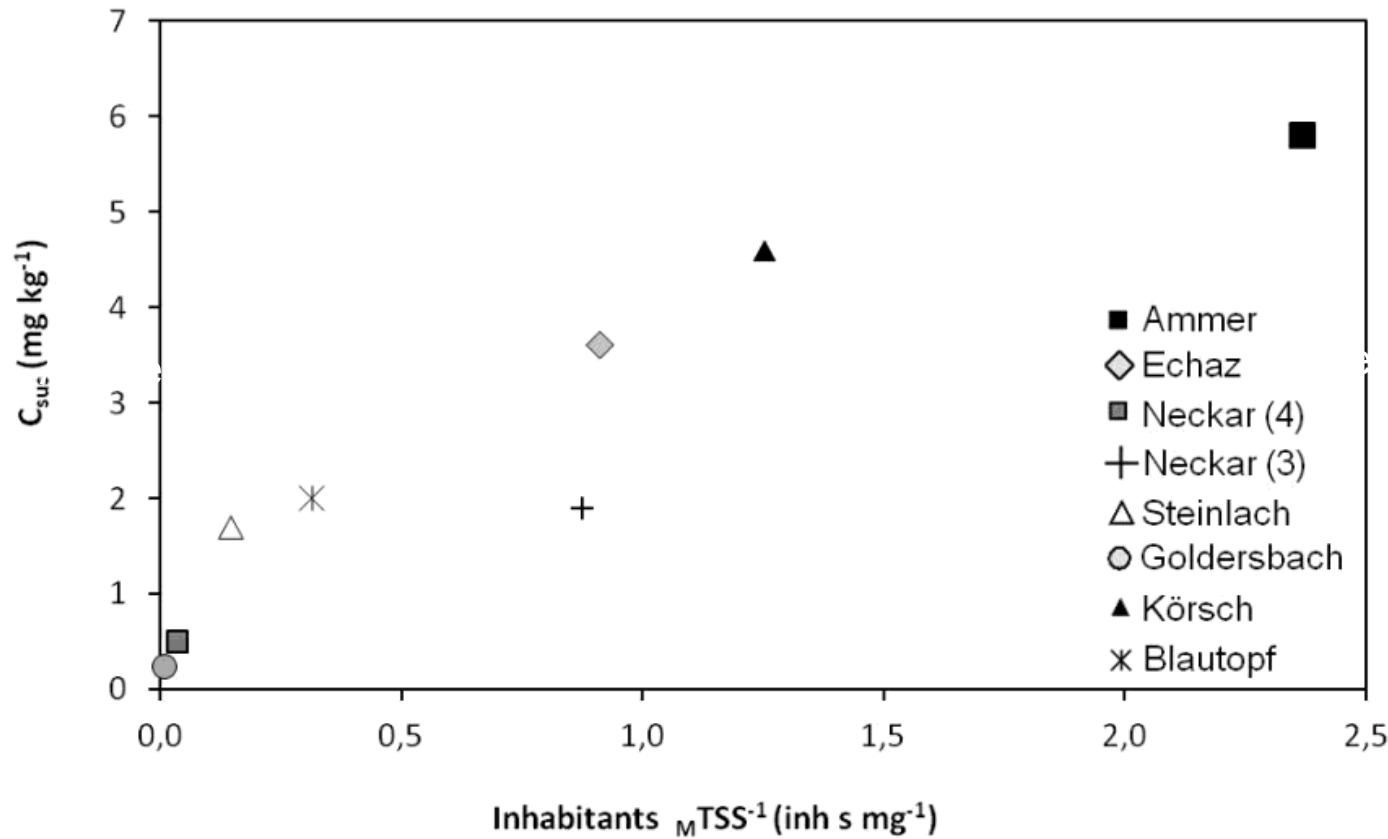
Loadings of POPs on suspended solids → different in different catchments



Catchment	Ammer	Körsch	Echaz	Neckar	Steinlach	Ammer springs	Goldersbach
$C_{sus}\text{PAH15}$ (mg kg^{-1})	5.8 ± 0.3	4.6 ± 0.3	3.6 ± 0.1	1.9 ± 0.5	1.7 ± 0.2	0.84 ± 0.2	0.25 ± 0.1



Source of PCB: Diffuse Pollution

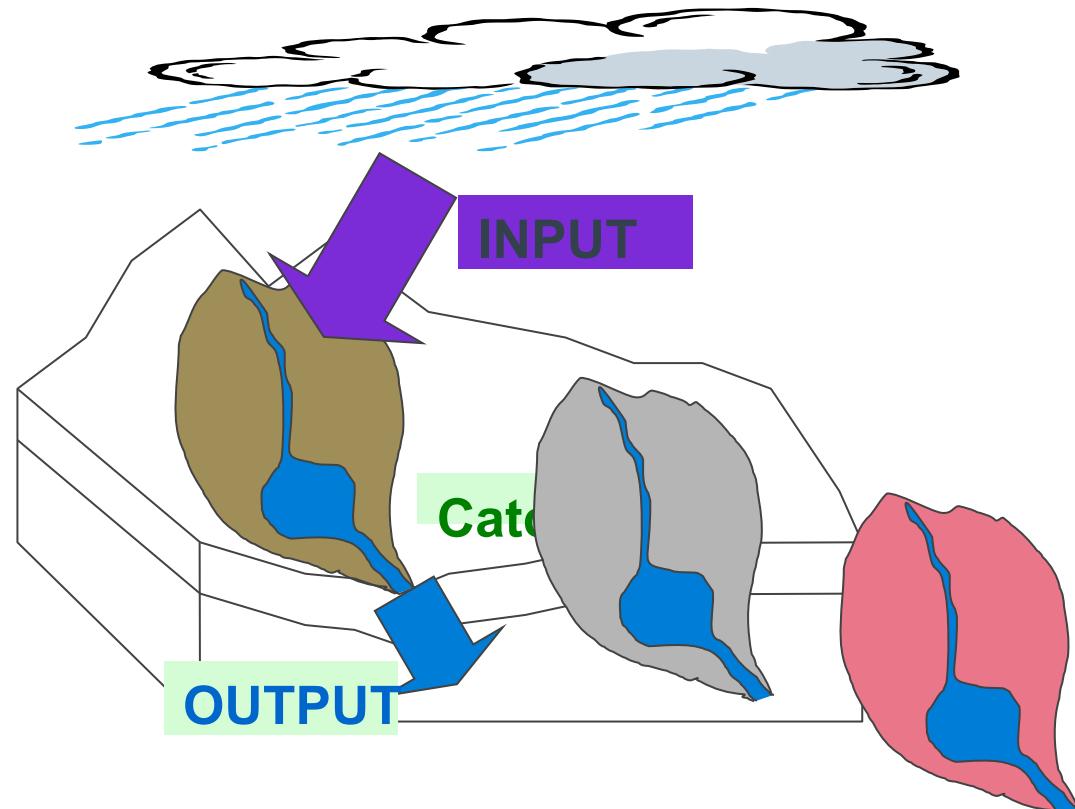


C_{sus} : a representative average correlating well with population density per mass flux of suspended particles in the catchment ($Inh/MTSS$).

(Grathwohl et al., 2012, submitted)

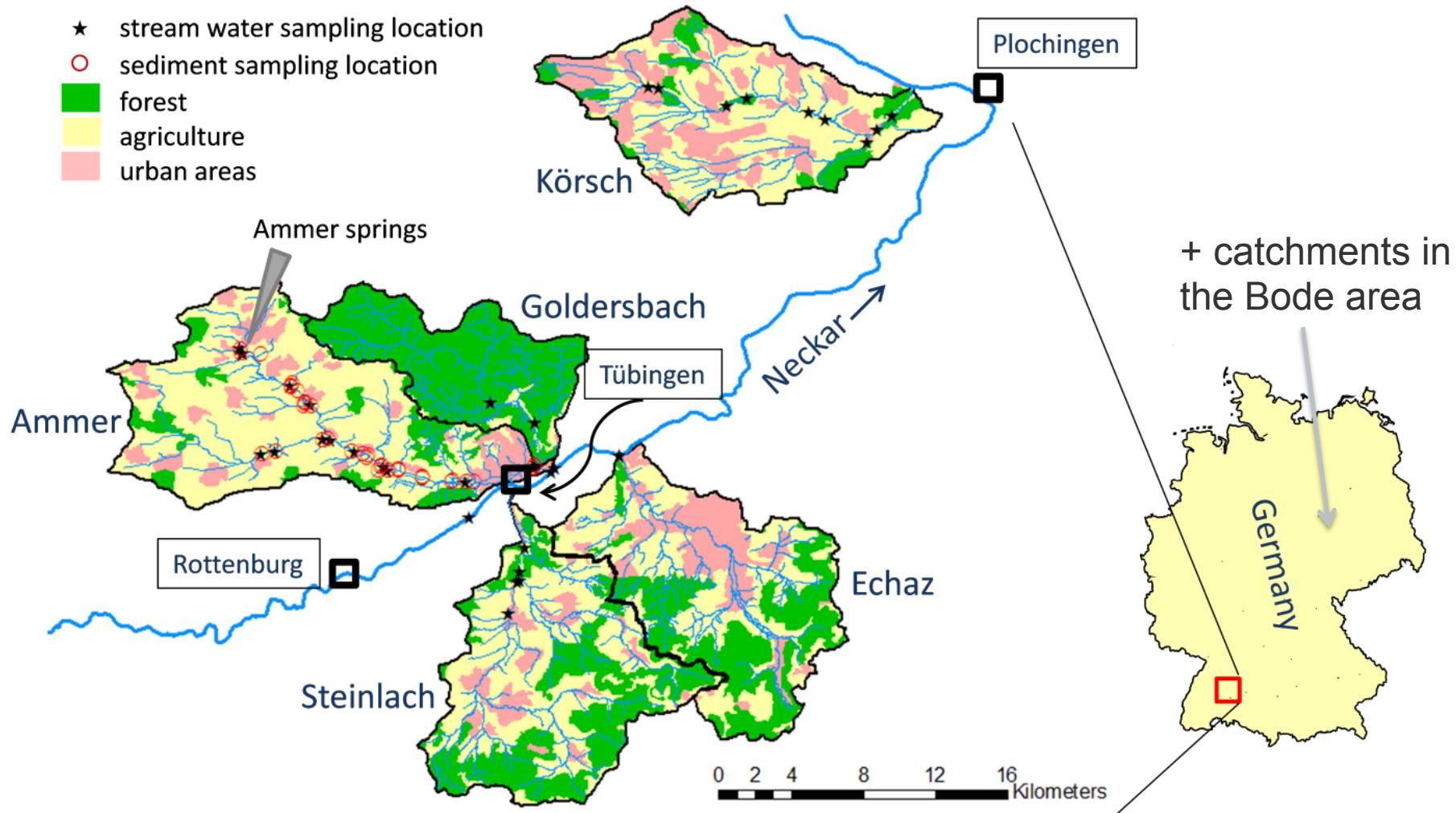


Contrasting catchments





Contrasting catchments





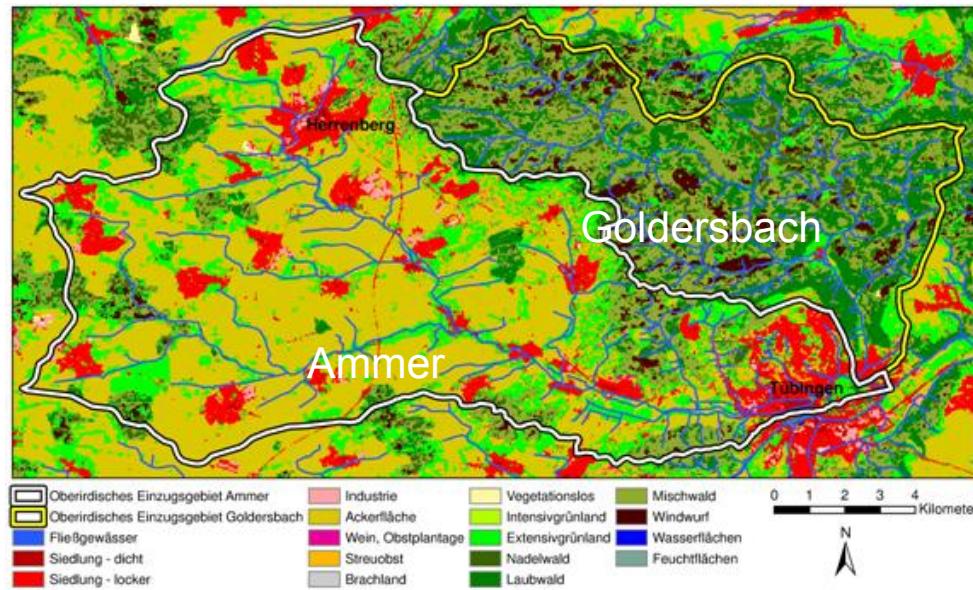
Large scale and long term catchment monitoring

Question to be answered

- How do landscapes process contaminants?
- What is the filter, buffer and transformation capacity of soils, vadose zone and aquifers

Understand catchments as reactors

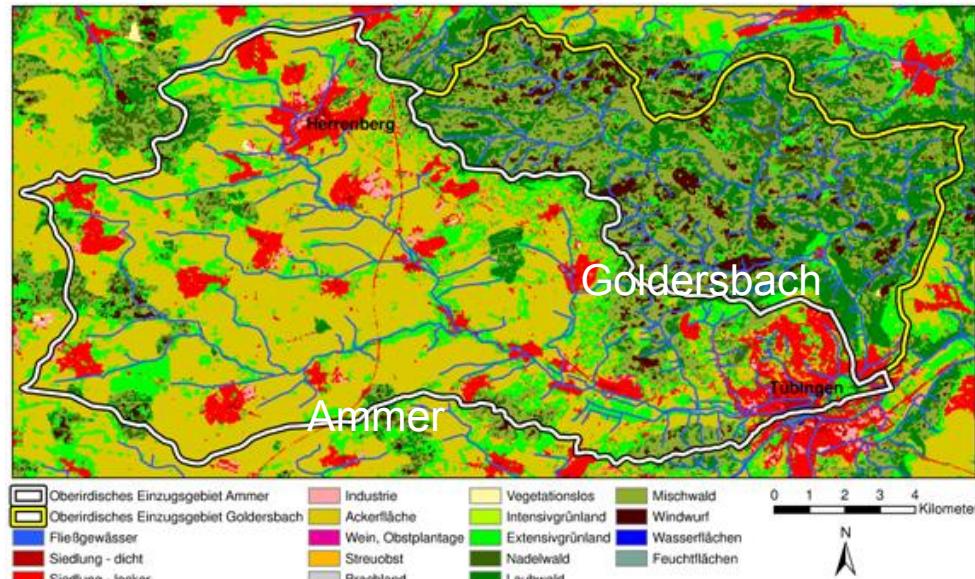
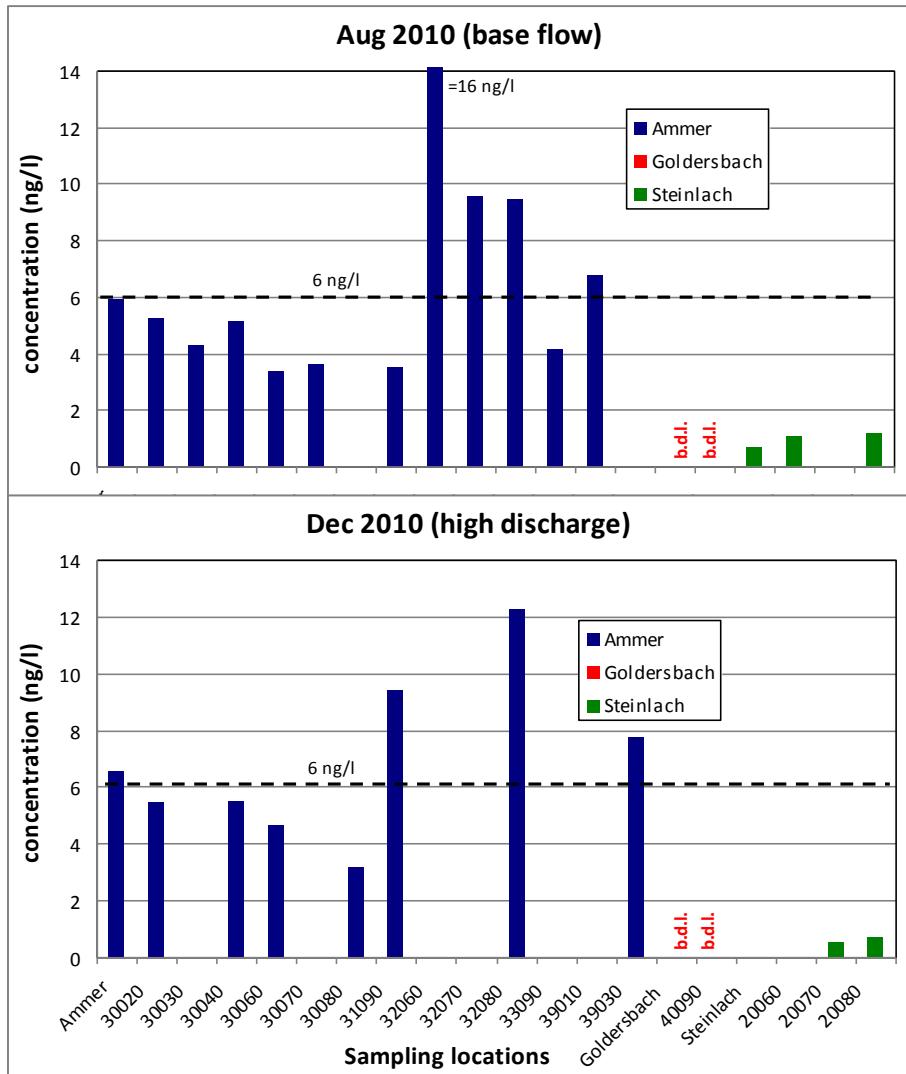
- Input-output mass balances
- High frequency sensor based monitoring of indicators
- Time-integrated passive sampling of specific target compounds
- Reconcile remote sensing with hydrological, physical and chemical data (satellites, aircraft...)
- Develop double coupled numerical models: Reactive flow and transport + saturated and unsaturated zone (+ atmosphere)





Space integrated monitoring

Atrazine (banned since 20 years) in Ammer vs. Goldersbach vs. Steinlach

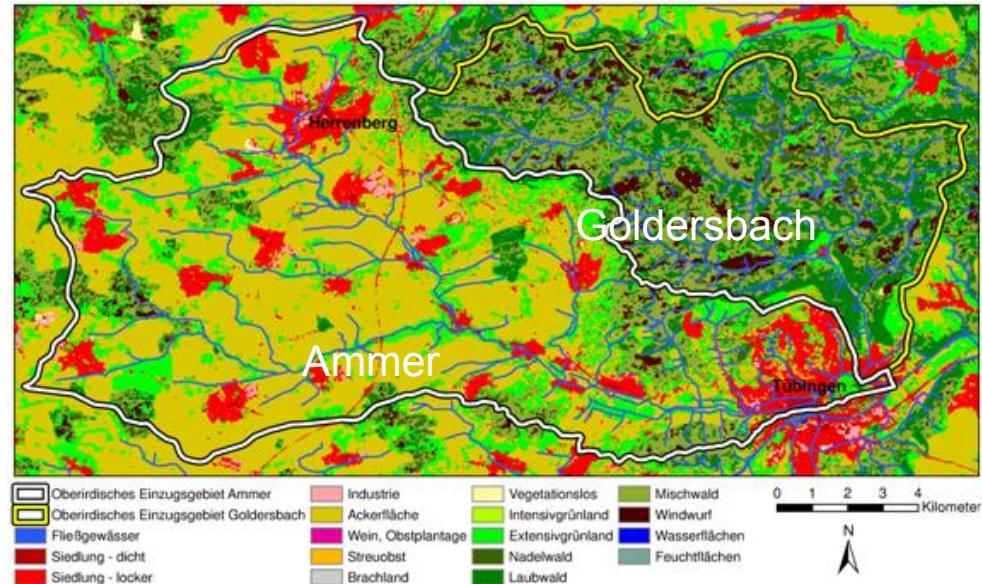
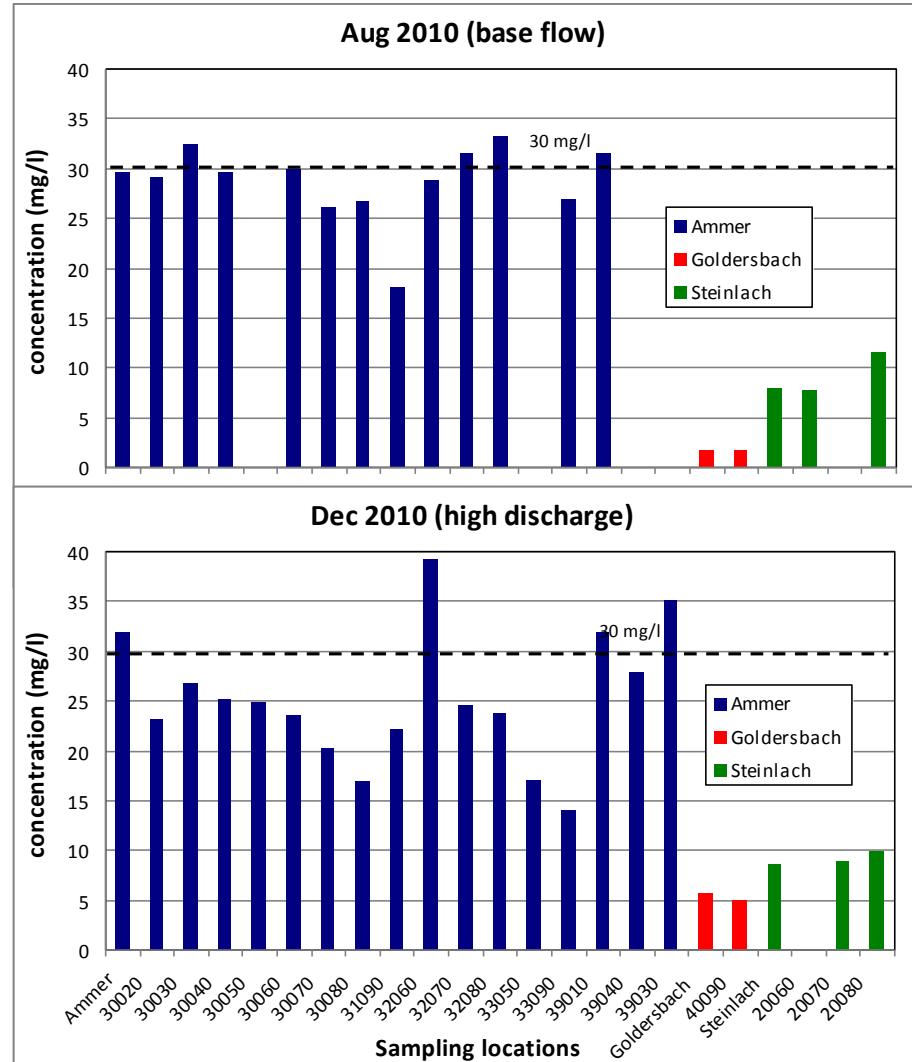


→ same concentrations in base flow and high discharge, different in catchments



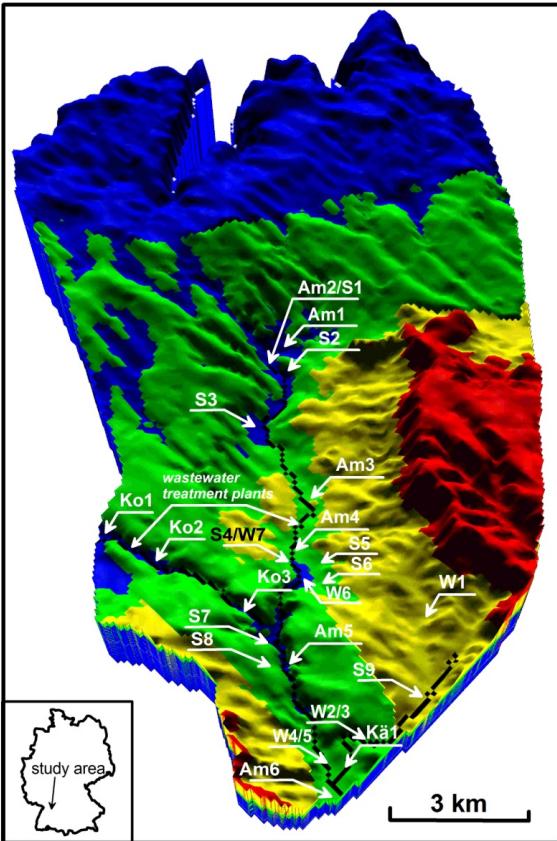
Space integrated monitoring

Nitrate in Ammer vs. Goldersbach vs. Steinlach catchment:
→ same concentrations in managed land, different in catchments



Catchment	Area [km ²]	agricultural land [%]	Mean discharge [l/s]	Mean nitrate concentration [mg/l]	Annual nitrate load [tons]
Ammer	134	50	1,080	32	1.090
Steinlach	138	20	1,750	9	497
Goldersbach	73	0	425	3	40

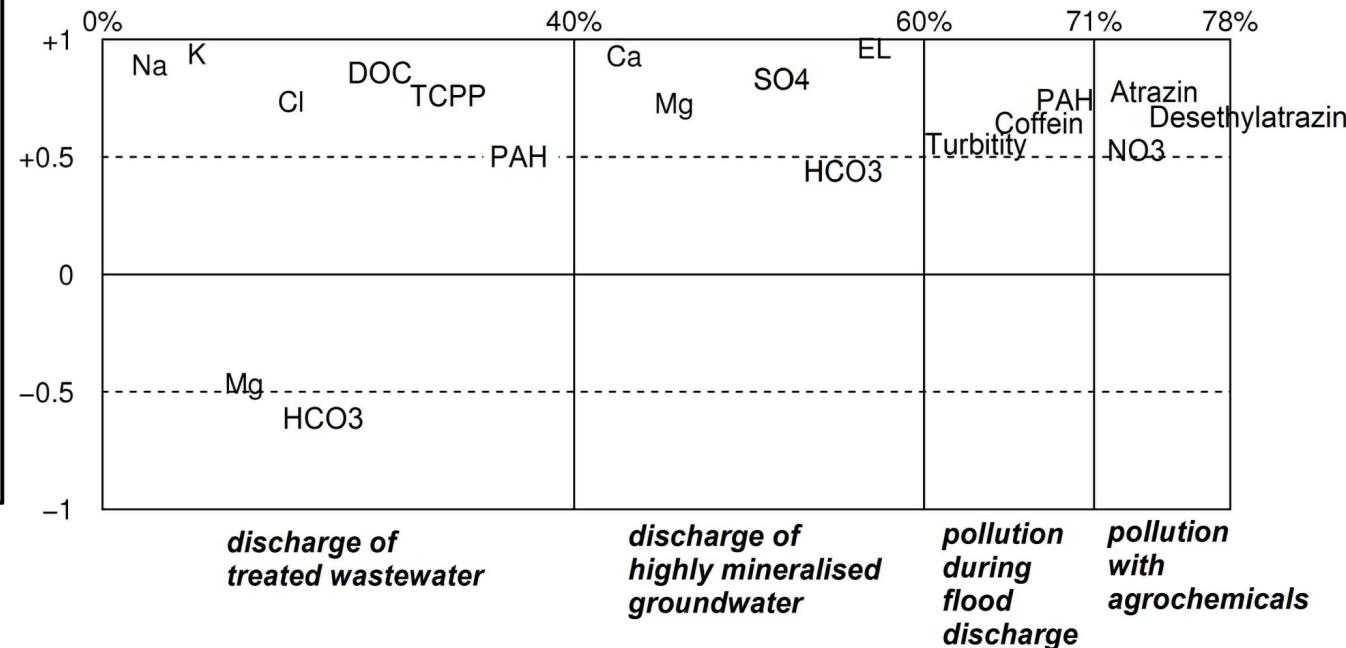
Basu, N.B., Rinaldo, A., Rao, P.S.C., Destouni, G., Jawitz, J.W., Thompson, S.E., Loukinova, N.V., Sivapalan, M.(2010): Nutrient loads exported from managed catchments reveal emergent biogeochemical stationarity. Geophysical Research Letters, 37 (23), art. no. L23404.



PCA: Heterogeneous data sets contain valuable information on catchment scale processes:

> 150 chemical samples (monthly samples, 11 locations) from River Ammer were used for principal component analysis).

--> Origin/composition of river water





The “vision”: A systems approach for solute fluxes

Disciplines:

Meteorology, Soil physics
Soil chemistry, Geophysics
Freshwater ecology
Hydrology, Hydrogeology
Environmental chemistry
Geomicrobiology
Analytical chemistry
Remote sensing

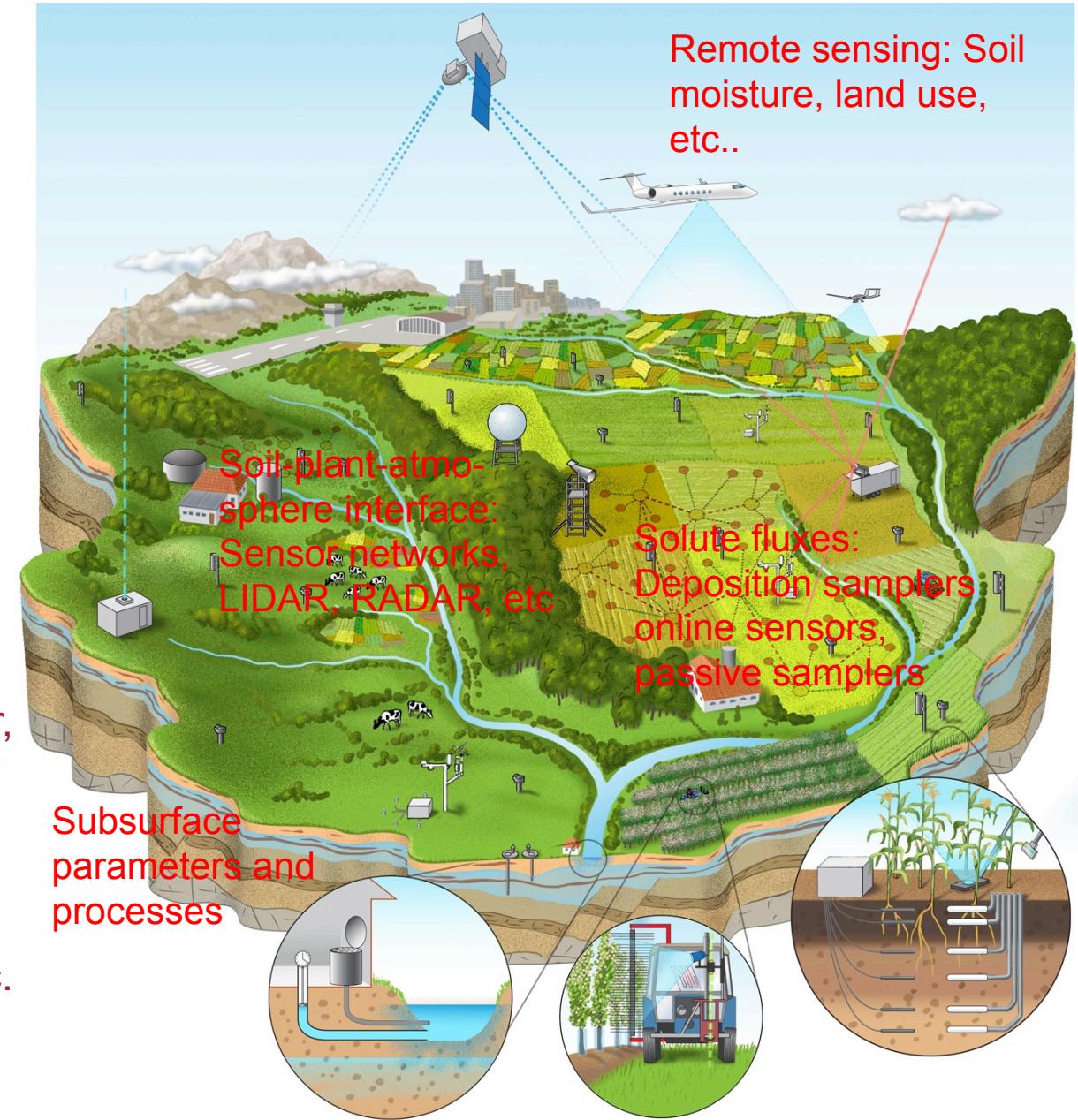
Numerical modeling
Software engineering, etc.

Compartments:

Atmosphere – plant – soil –
groundwater – surface water,
etc..

Processes:

Flow + transport + reaction
(biotransformation,
dissolution/precipitation), etc.



- **Assess the quality of water resources in a comprehensive way:** Catchment scale monitoring, long term data series (early identification of deteriorating trends), cross compartment data (land use, water content, evapotranspiration from satellites, aircrafts, cosmic ray probes, sensor networks, passive samplers, etc.), indicator monitoring (sensors, passive samplers, etc.)
 - **Develop scenarios of future development for economical evaluation of management options:** Requires 3D numerical models coupling flow + transport / transport + reaction and compartments soil/ vadose zone + groundwater for water balances and solute transport)
 - **Consider new water management activities:** Water reuse, recycling activities, new waste streams from emerging technologies (biofuel, - char, fertilization of new crops, etc...)
 - Obtain and maintain data in a way that others can use it
 - Take advantage of solute data (nitrate, DOC, etc.), on line sensors with high temporal resolution and time integrated passive samplers
-

Acknowledgements

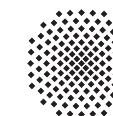


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(Water Alliance)

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applied-geosciences.html](http://www.geo.uni-tuebingen.de/en/work-groups/applied-geosciences.html)