Improving monitoring strategies and process understanding using novel continues water quality sensor technologies

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## Motivation: Patterns in hydrochemical and biological time series may help to clarify catchment and instream processes



#### **Solutes matter:**

- (a) in their own right
  - -contaminants
  - -nutrients
- (b) as keys to hydrological and chemical processes

(c) constrain model parameters and define process description



## What is really new?

We are able to measure water quality constituents in the same frequency than discharge

Temporal variability of chemical and biological data can be evaluated every hour or even every minute

# Diurnal cycles reflect many different mechanisms, including

Photosynthesis & respiration: -> O<sub>2</sub> & CO<sub>2</sub> -> pH & Eh -> reactions, redox, speciation Temperature effects: -> reaction rates & biotic activity Evapotranspiration: -> streamflow cycles & source mixing

**Biotic uptake and release:** 

-> macro- & micro-nutrients, DOC



Heffernan and Cohen (2010) - L&O



## Hydrological Observatory Bode Catchment (TERENO) Helmholtz Centre for Environmental Research-UFZ



## **River metabolism and biotic nitrate uptake**

- Stream ecosystem metabolism
  - Impact of environmental factors on Gross Primary Production
  - Land use-riparian vegetation
- Nitrate retention due to GPP
- Assess the value of new UV sensors





## Online Water Quality Measurement Stations River stations







## **Measurement Sensors and Automatic Samplers**



TRIOS UV sensors

YSI Sensors

### **Online-Data**



2,5

2

1,5

1

0,5

190

Absorption [AU]

### **Study sites**

#### Forest stream, Selke Station Meisdorf



- mean discharge =  $1,5 \text{ m}^3/\text{s}$
- mean NO<sub>3</sub>-N=1,5 mg/l
- reparian vegetation

## Agricultural stream, Selke Station Hausneindorf



- mean discharge = 1,7 m<sup>3</sup>/s
- mean  $NO_3$ -N = 3,3 mg/l
- spars reparian vegetation



### **Continues sensor data offer new insights into Ecosystem metabolism (Selke river)**



- T

# Diurnal variability of selected constituents in the forest stream reach (Selke river)



- Clear diurnal oxygen amplitudes in spring
- Nitrate amplitudes show maximum at dawn
- pH shows high correlation with oxygen
- Nitrate minimum shows hysteresis with oxygen maximum



## **Ecosystem metabolism in the Selke River**

### (agricultural stream, Selke)



- One station diel DO method (Roberts et al. 2007) and energy dissipation method
- Gross Primary Production (GPP) clearly follows seasonal variation
- NEP was mostly positive during vegetation period
- Clear regression between ER and GPP

>strong contribution of autotrophic respirtion on ER



## Impact of temperature on GPP (forest stream reach, Meisdorf)



- High GPP during spring
- Much lower GPP than in agricultural stream
- Clear temperature effect only in spring
- Light is the controlling factor of GPP
- Autumn peak during leave litter fall

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# Impact of discharge on Gross Primary Production (agricultural stream, Hausneindorf)





## Nitrogen cycling in streams.





## Diel Method for Inferring Nitrogen Retention Mechanisms



Heffernan and Cohen 2010

## NO<sub>3</sub> uptake rate related to GPP, Selke River

Forest stream (Meisdorf), April 2011

Agricultural stream (Hausneindorf), 2011



- Low flow conditions
- Lower GPP in forest stream
- Similar slopes of regression functions



## N assimilatory uptake rate, forest and agricultural stream reach, Selke

#### based on regression between U and GPP



# Ranges of NO<sub>3</sub> assimilatory uptake rates on a yearly basis (2011-2012)

### comparison of different stream systems



- Forest stream shows lowest assimilatory NO<sub>3</sub>-N uptake
- Light availability controls areal NO<sub>3</sub>-N uptake



## Stream network characteristics of the Selke river



- Stream order
- Stream bottom area

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Stream order	Mean area (km²)	Stream length (km)	Mean length (km)	Mean direct drainage (km²)	Numbers	Direct Drain to Order (Proportion)
1	0.95	168	0.74	0.95	226	0.50
2	5.22	114	1.99	1.48	57	0.19
3	23.9	41.4	2.96	2.71	14	0.09
4	224	68.4	34.2	42.8	2	0.20
5	446	3.15	3.15	6.76	1	0.02

# River network assimilatory NO3-N uptake, whole catchment (2011-2012)



- Percentage network uptake up to 40% in agricultural and forset streams
- Total yearly Ua uptake up to 13% of total load NO<sub>3</sub>



## Inferring DOC mobilisation processes from UV-vis spectral data



Funded by BMBF TALKO Project

## Bode Catchment (TERENO)



## Instrumentation

- Measuring period: 2 years
- Measurement interval : 15 minutes
  - UV-vis sensor (S::CAN)
  - 220-730nm wavelength
  - Self contained deployment







## Sampling interval and DOC load





## **Seasonality**

- Large [DOC] variation during discharge events
- Temperature controlled seasonal [DOC] variation



# DOC~Q hysteresis gives information on transport mechanisms

- Hysteresis slope (correlation between DOC and discharge)
  - Log [DOC]=log a + b x log Q
  - steeper slope in spring and summer
- Hysteresis rotation
  - clockwise > surface runoff
  - Counter clockwise> interflow



## Seasonality – DOM quality -using spectral slope ratios



## Slope ration (Sr) as proxy for DOM quality

- Sr = S275-295 / S350-400
- decreasing Sr → increasing molecular weight
- Spring: enrichment in higher molecular weight
- Autumn: reduced molecular weight
- Sr converges with increasing dicharge

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## Rappbode Reservoir Observatory Station map





## Warme Bode June/July 2012





## Königshütte Reservoir June/July 2012



## Rappbode Pre-dam Automated vertical profiler measurments





## **2D Water quality monitoring**

### **BATHYMETRY of the Rappbode Reservoir**





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### Hydrodynamic Simulation (3D)





# Modelling NO<sub>3</sub>-N concentration and loading with high frequency data



#### Nitrate-N concentration at daily time step



#### Nitrate-N load at daily time step



- Same density of hydrological and NO<sub>3</sub>-N data
- High data density support model parametrization
- Improvement of model performances

# Reduction of model parameter uncertainties compared to fortnightly data





### Markov Chain Monte Carlo approach

- Improved model identification
- Reduced parameter uncertainty bounds
  - Parameter uncertainties
  - Total uncertainties



### Conclusions

- Continues measurements allow new continues insights into stream ecosystem metabolism and nutrient processing
- Assimilatory N uptake can be evaluated by continues nitrate measurements (diel NO<sub>3</sub> method)
- Spectral analysis of UV sensors reveal information on DOC composition
- New data streams can support dynamic modelling of freshwaters



# Thank you very much for your interest

# Miniaturized, monochromatic absorbance measurements in waters

Lead: Jan Bumberger (MET), Cooperation: MET, SEEFO , UFZ



## Lab-on-Chip Technology





- Still in development
- Currently used for marine systems HELMHOLTZ CENTRE FOR ENVIRONMENTAL RESEARCH - UFZ