

# Stable Isotopes in rivers - spatial and temporal variations

**Robert van Geldern**

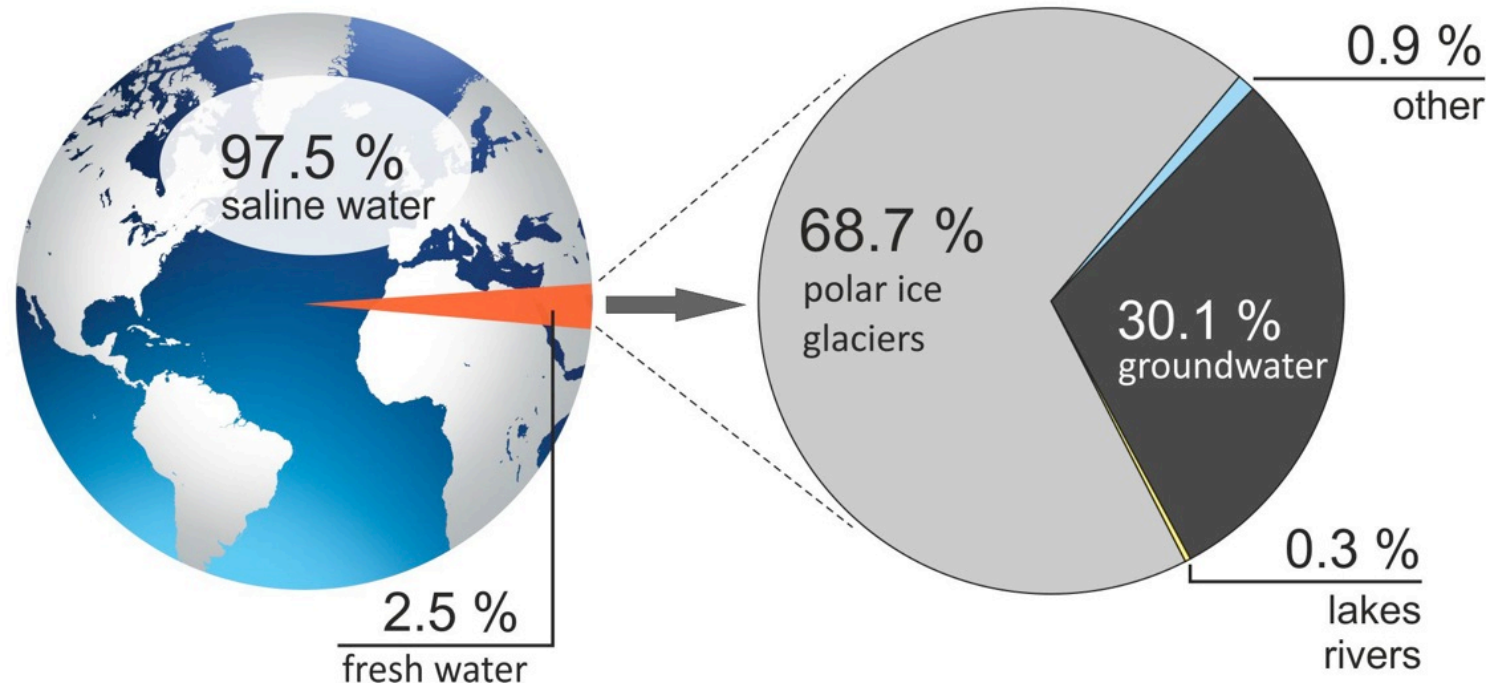
*Geozentrum Nordbayern*

*Hydrogeology Group*

*Friedrich-Alexander University Erlangen-Nuremberg*



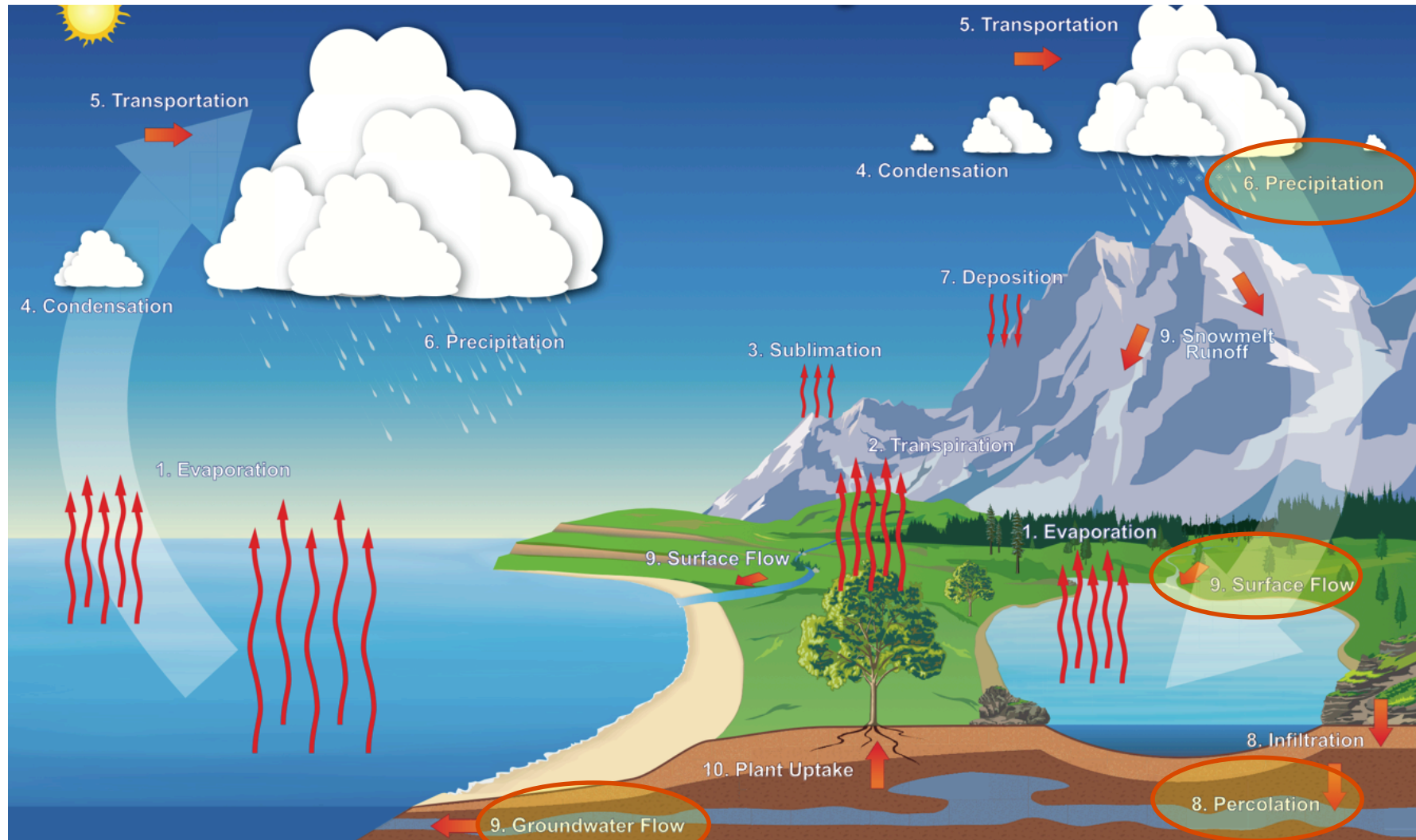
# Water on the Earth



numbers after Gleick (1996),  
NASA Earth Observatory

- Only a small fraction of Earth's water is directly accessible for daily use
- Today's need: 20 – 50 Liter clean water

# The hydrologic cycle



NOAA National Weather Service

# Outline

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- Stable isotopes in the hydrologic cycle
- Global isotope distribution maps
  - RCWIP – next generation water isoscapes
- Linking precipitation, rivers, and groundwater
  - Wiesent River (Germany)
  - Island of Corsica (France)
  - Nuremberg aquifers (Germany)
  - New Jersey Shelf (USA)
- River isotope monitoring programs
  - GNIR<sup>3</sup> – rivers worldwide
  - Global Rivers Observatory



Tasmania, Australia





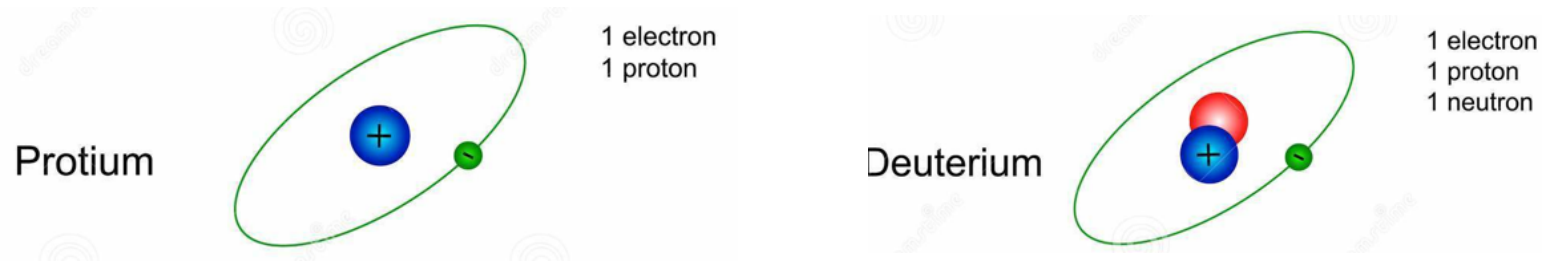
Zaragoza, Spain

Stable isotopes in the

# HYDROLOGIC CYCLE

# Stable isotopes and fractionation

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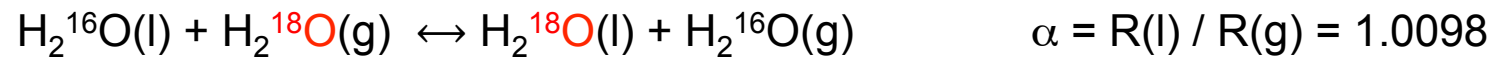
## ■ Fractionation

Change of an isotope ratio ( $\delta$ -value) due to chemical or physical processes

- equilibrium fractionation
- kinetic fractionation
- *mass-independent fractionation*

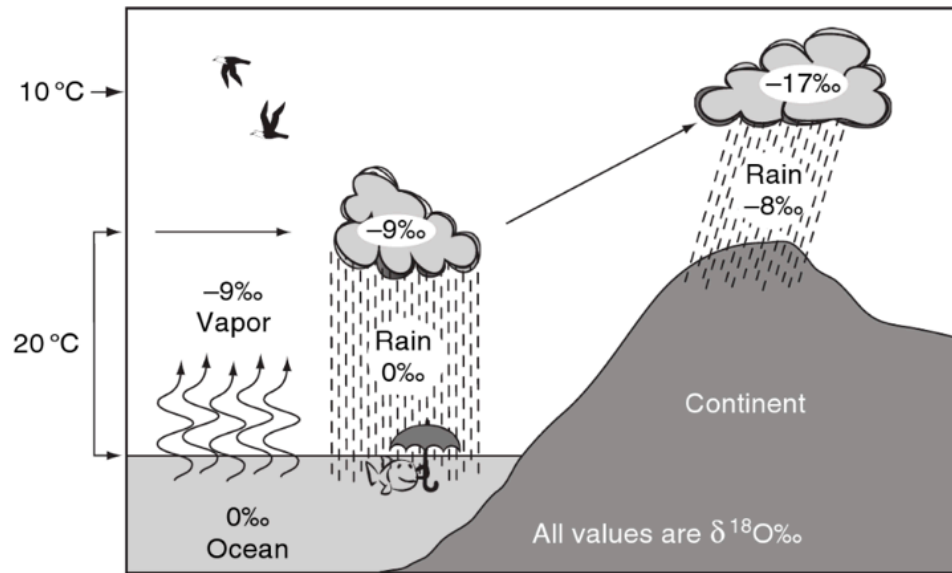
## ■ Fractionation factor $\alpha$

- Example: H<sub>2</sub>O liquid(l) – water vapor (g) ( $T = 20\text{ °C}$ )



# Isotopes in the hydrologic cycle

## Rayleigh distillation



Emerson and Hedges (2008)

- Water vapor is depleted in <sup>18</sup>O/<sup>2</sup>H (→ low δ<sup>18</sup>O/δ<sup>2</sup>H values)
- Rain is relatively enriched in <sup>18</sup>O/<sup>2</sup>H (→ higher δ<sup>18</sup>O/δ<sup>2</sup>H)
- Clouds and rain get continuously depleted along their journey (→ lower δ<sup>18</sup>O and δ<sup>2</sup>H values)

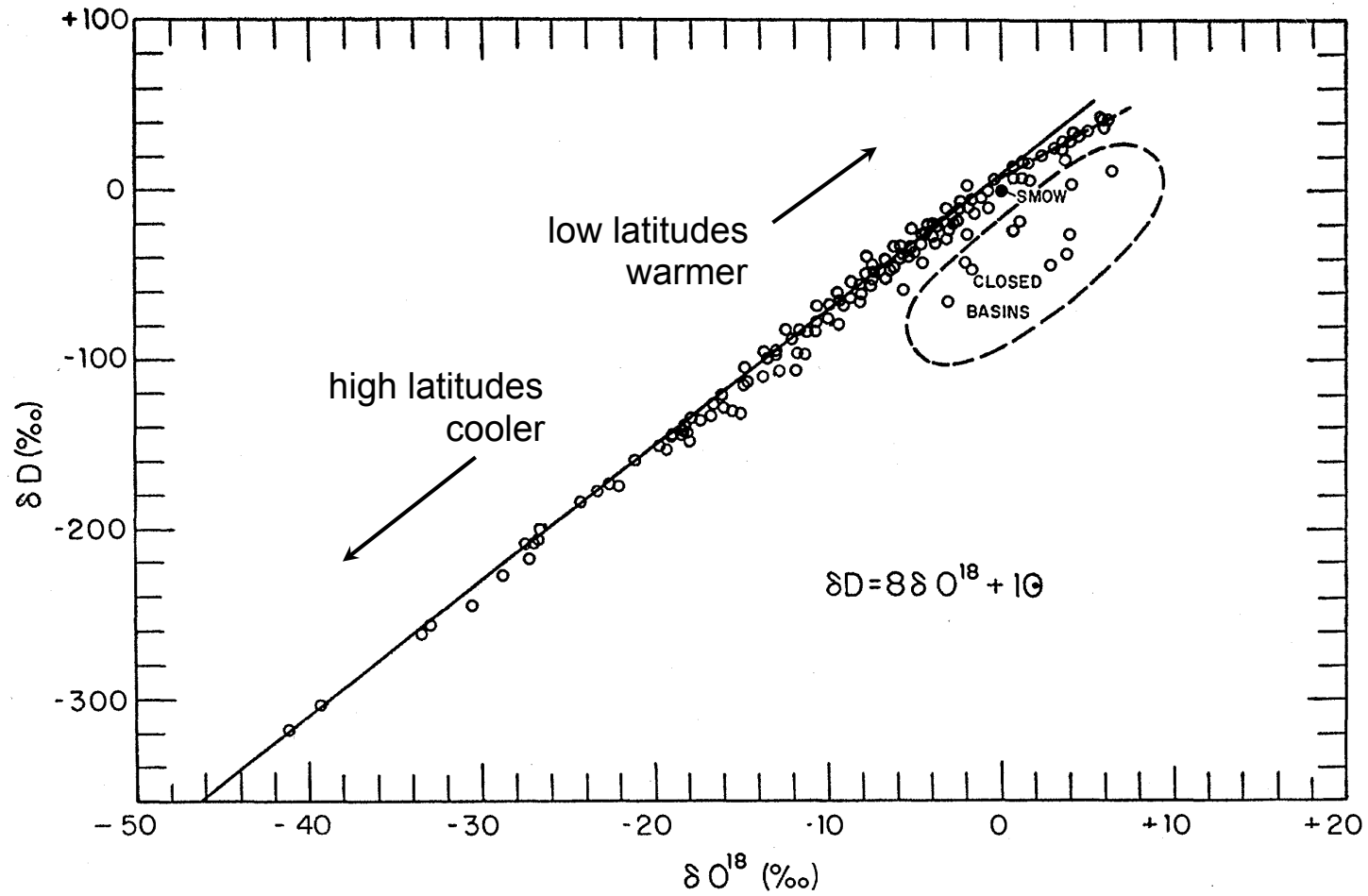
Standard „delta“ notation in per mil (‰) vs Standard Mean Ocean Water (VSMOW):

$$\delta = \left( \frac{R_{sample}}{R_{reference}} - 1 \right)$$



H<sub>2</sub>O → isotope fingerprint

# Global Meteoric Water Line (GWML)



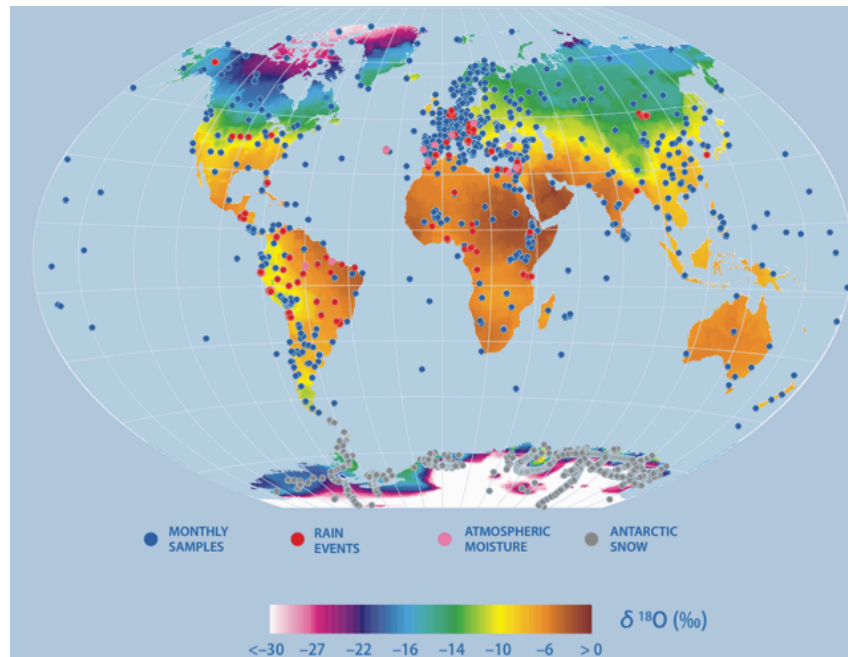
Craig (1961)



# GNIP network

## GNIP – Global Network of Isotopes in Precipitation

1961 – today



IAEA (Water Resources Programme)



Hydrology and  
Water Resources  
Programme  
(HWRP)



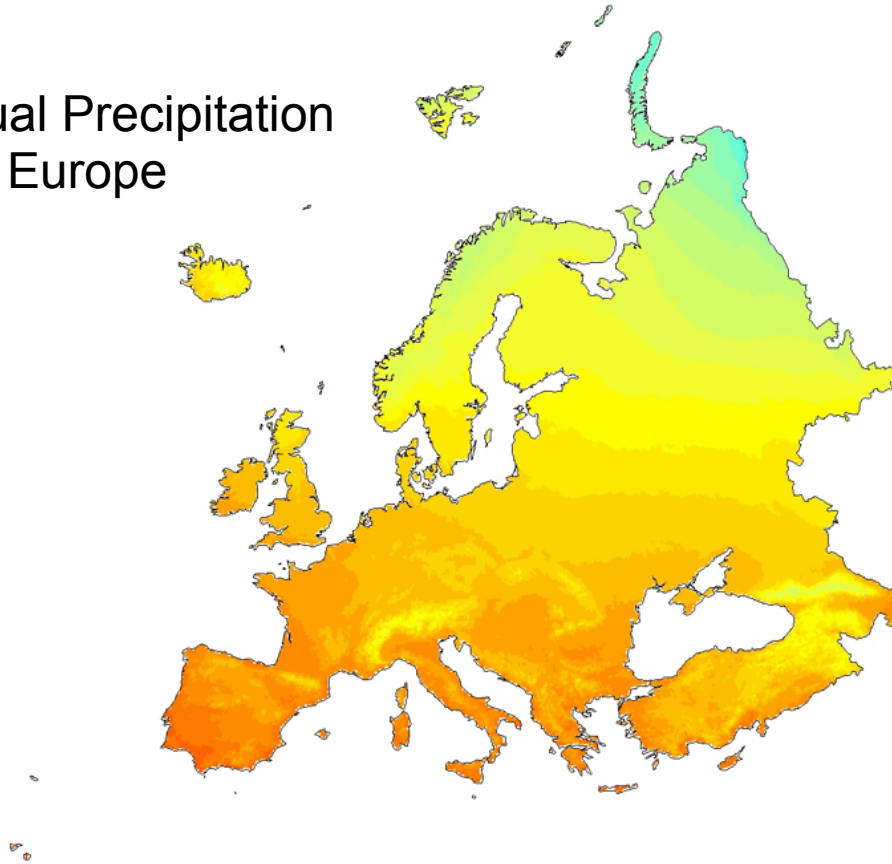
Water  
Resources  
Programme

- Global precipitation data of  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$ ,  $^3\text{H}$  (Tritium)
- about 900 stations in more than 100 countries
- 120.000 monthly data sets
- Applied in various research fields
  - Climate change
  - Water resources
  - Hydrogeology
  - Food authenticity
  - Paleoenvironmental studies (e.g. tooth enamel, tree rings, speleothemes)
  - Forensic sciences
  - ...
- One of the most important and successful monitoring programs in hydrology

# Global spatial distribution maps – ‘Isoscapes’

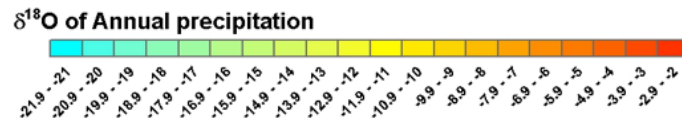
- Key publications: Bowen and Revenaugh (2003), WRR

Annual Precipitation  
 $\delta^{18}\text{O}$  Europe



Spatial means 3D:

- Latitude
- Longitude
- Elevation



[www.waterisotopes.org](http://www.waterisotopes.org)

# Interpolated isotope data



Main

**OIPC: THE ONLINE ISOTOPES IN PRECIPITATION CALCULATOR**

Information

[Citing the OIPC](#)

Data Products

Enter site coordinates:

Figures

Data Tables

Google Earth

OIPC

ArcGIS Grids

Web Resources

49.5942402

Latitude (decimal deg; North positive)

11.0292443

Longitude (decimal deg; East positive)

285

Elevation (meters)

Annual values

Monthly values

**Erlangen University Campus**



Do Confidence Intervals (computing intensive)

Submit

Reset Form



OIPC2.2

See version notes [here](#).



# Isoscape results versus local analytical data

## Isoscape results

[www.waterisotopes.org](http://www.waterisotopes.org)

### Data Products

Figures

Data Tables

Google Earth

OIPC

ArcGIS Grids

### Web Resources



### Estimates for latitude 49.5°

$\delta^2\text{H}$ (‰, V-SMOW)	-59
$\delta^2\text{H}$ 95% CI (‰)	3
$\delta^{18}\text{O}$ (‰, V-SMOW)	-8.7
$\delta^{18}\text{O}$ 95% CI (‰)	0.3

Measured data  
(weighted annual means)

$$\delta^2\text{H} = -66 \text{ ‰}$$
$$\delta^{18}\text{O} = -9.4 \text{ ‰}$$



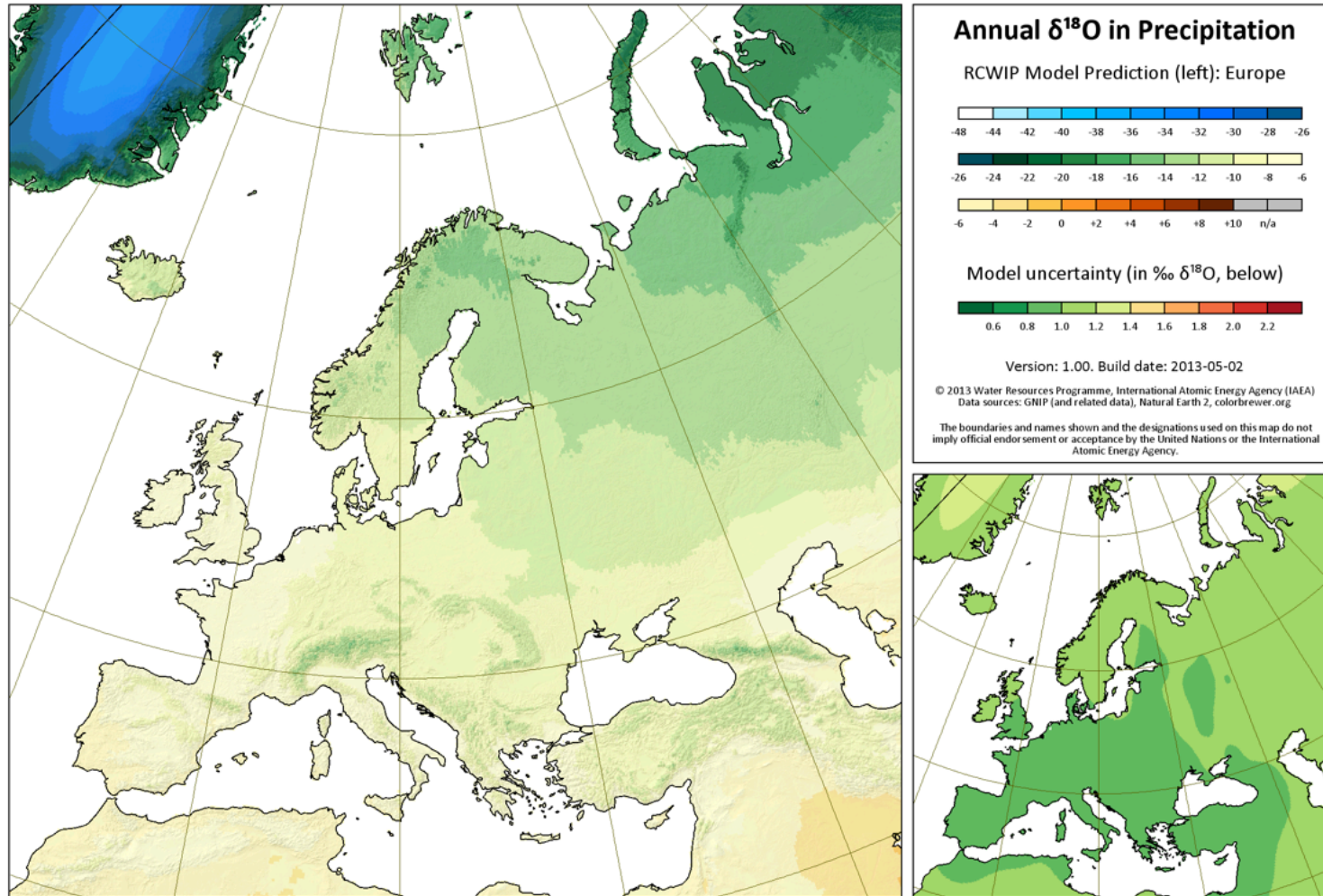
GeoZentrum GNIP sampler

→ Water isotope composition depend on local effects that cannot be reproduced precisely in global interpolation models



# RCWIP-next generation precipitation isoscapes

(regionalized cluster-based water isotope prediction)



Terzer et al. (2013), HESS, vol. 17

[www.iaea.org/water](http://www.iaea.org/water)



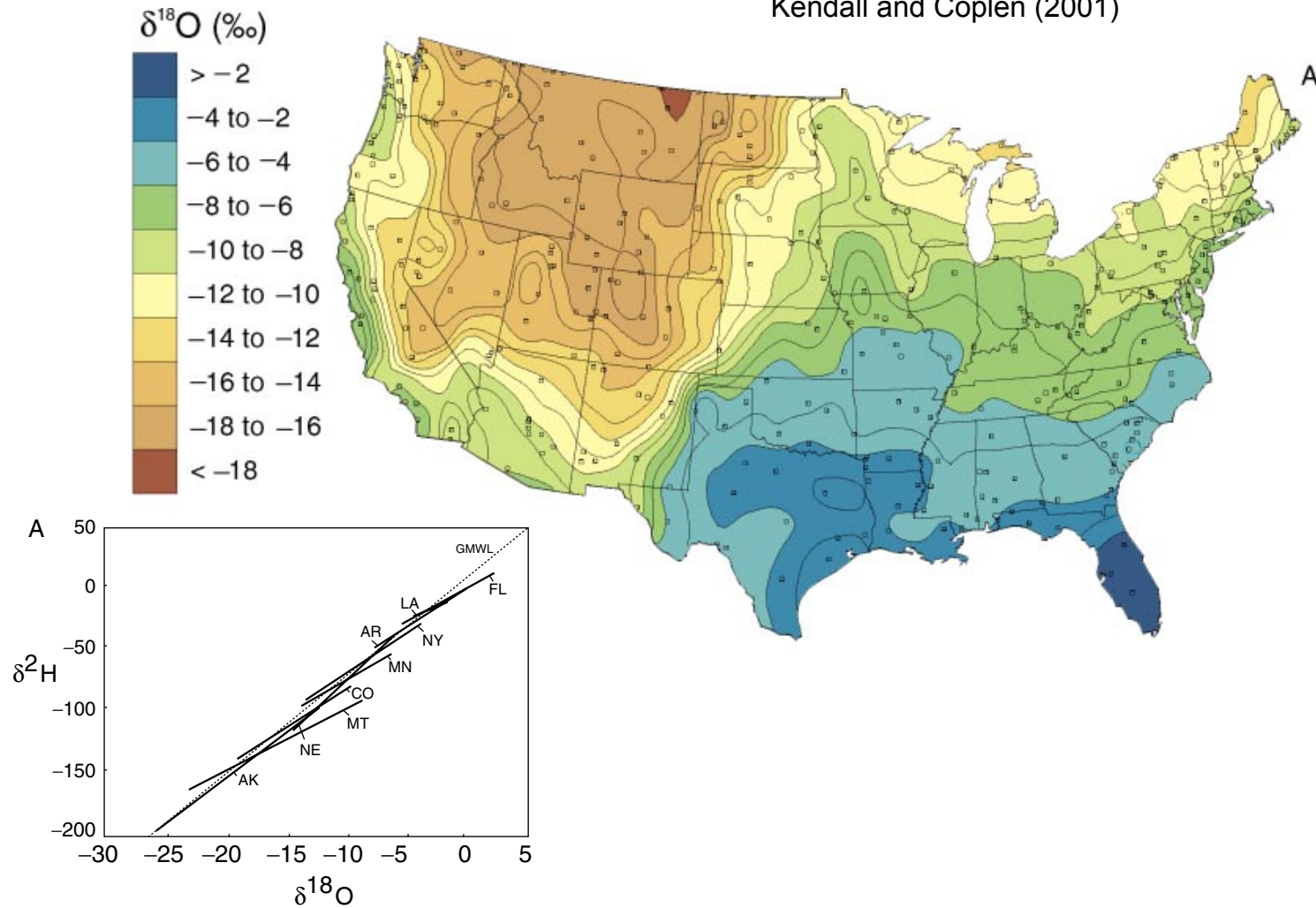
Tasmania, Australia

Linking

# PRECIPITATION, RIVERS AND GROUNDWATER

# Linking rivers and precipitation

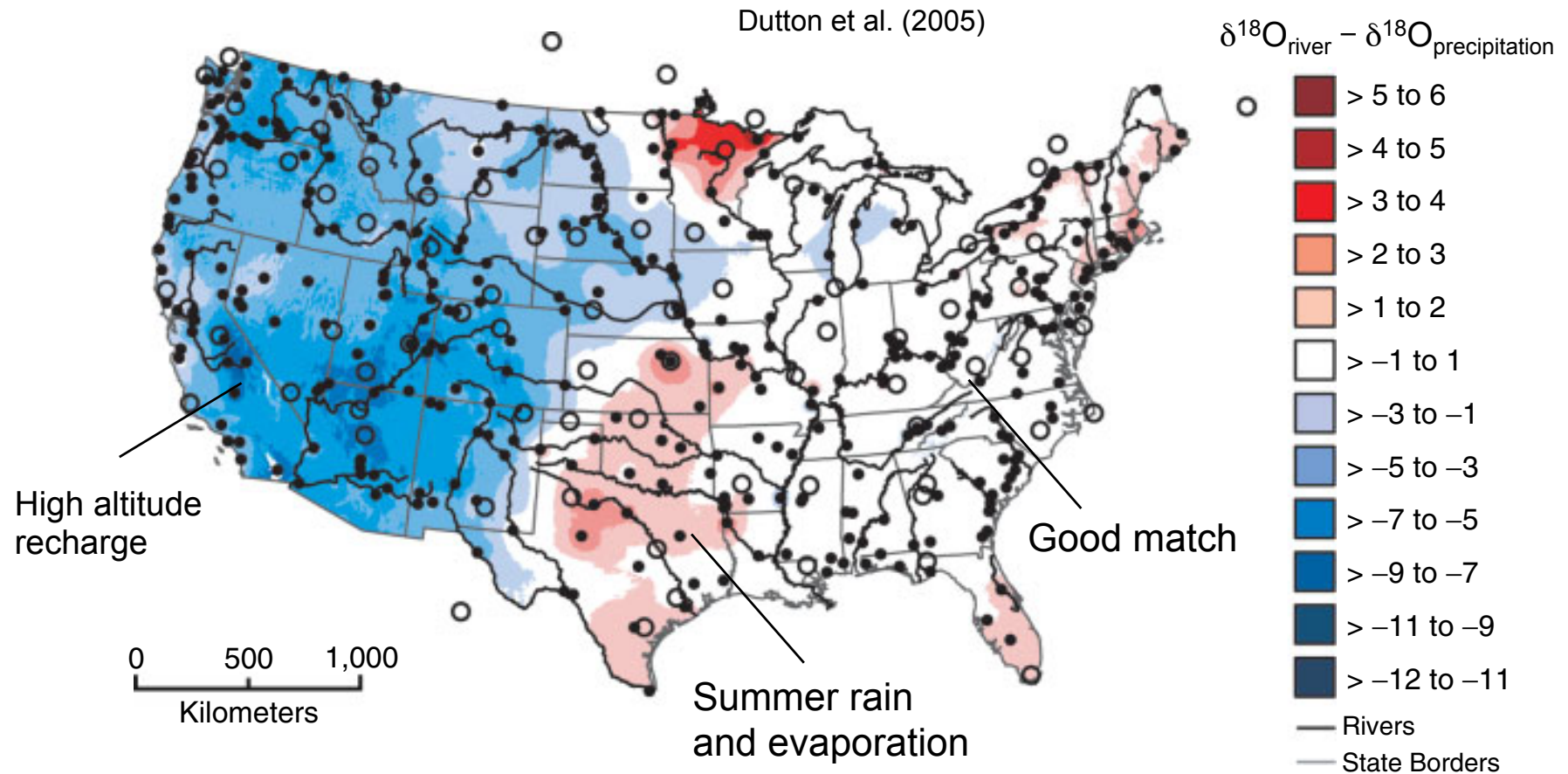
Kendall and Coplen (2001)



→ Local Meteoric Water Lines (LMWL) derived from river water data



# Catchment effect



→ Differences between  $\delta^{18}\text{O}_{\text{precipitation}}$  and  $\delta^{18}\text{O}_{\text{river}}$

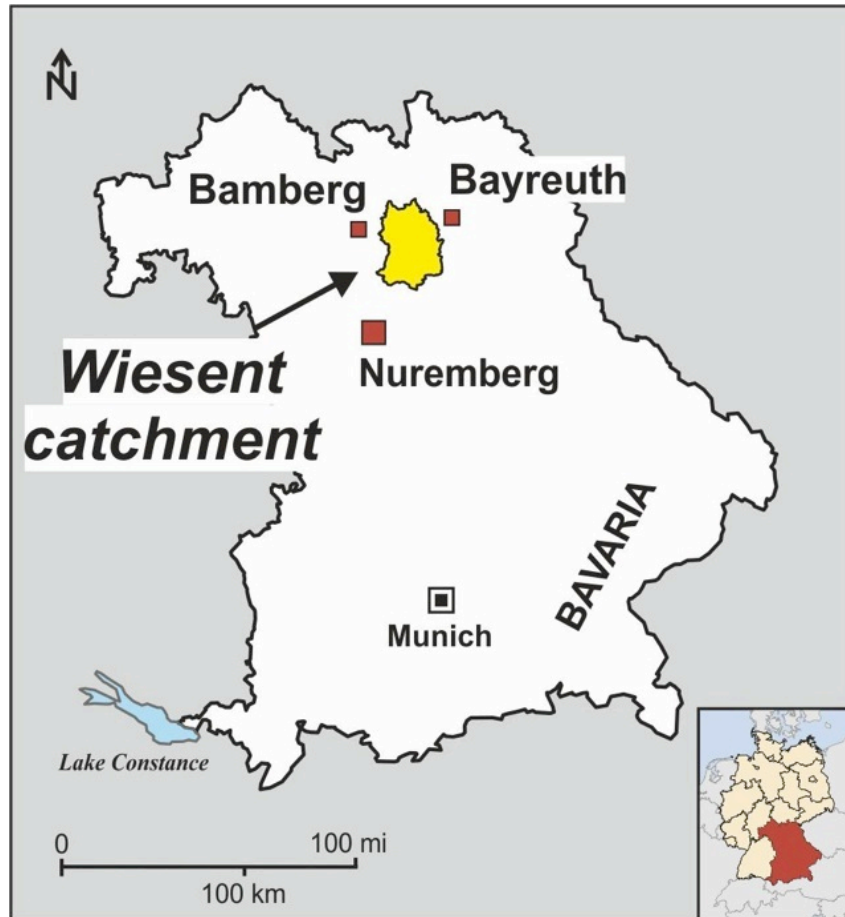




Wiesent River

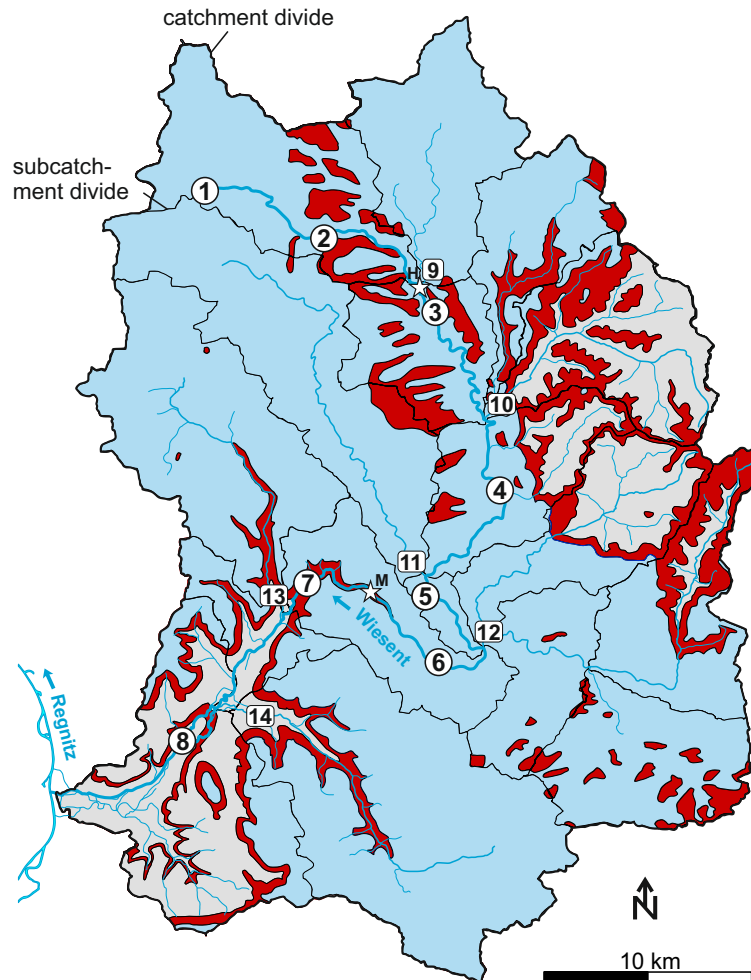
# WIESENT RIVER

# Wiesent River (southern Germany)



Wiesent spring at Steinfeld

# Wiesent catchment



## Lithology

- limestone
- sandstone (with clay layers)
- claystone

## Locations

- Wiesent samling location
- Tributary samling location
- Discharge gauge  
H-Holfeld, M-Muggendorf

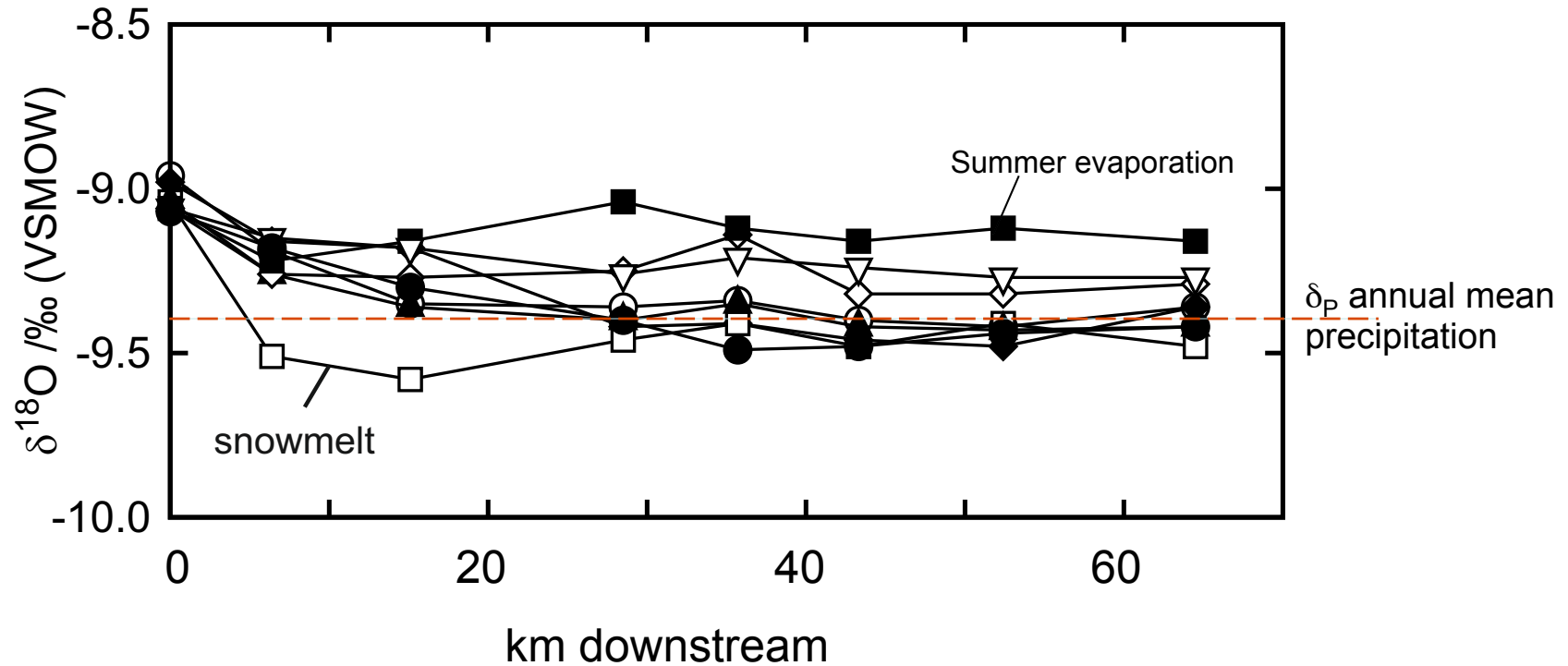
- Area: ~1040 km<sup>2</sup>
- River length: ~73km
- 8 sampling locations (6 tributaries)
- Sampled over one year to cover all seasons

## Lithology:

- Jurassic carbonates (67%), >100m thickness (deep karst)
- Sandstones (14%)
- Shale (15%)

van Geldern et al. (subm.)

# Water stable isotopes

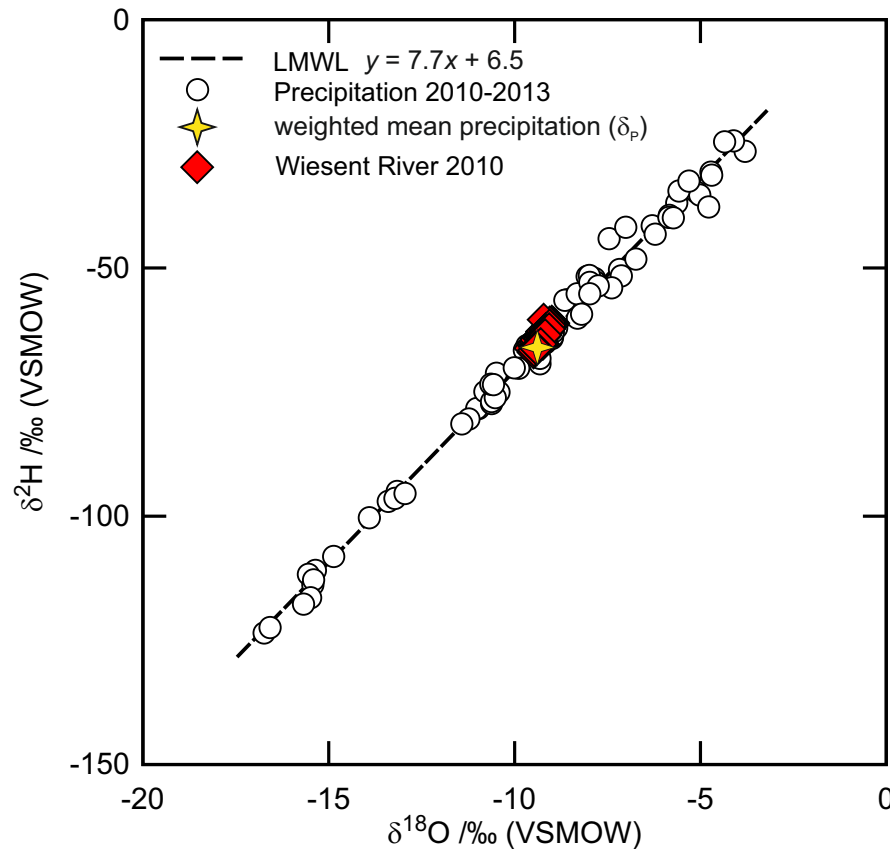


## Date 2010

- |   |        |   |        |   |        |   |        |
|---|--------|---|--------|---|--------|---|--------|
| ○ | 19 Feb | □ | 12 Apr | ◇ | 19 Jul | ▽ | 23 Sep |
| ◆ | 04 Mar | ▲ | 10 May | ■ | 09 Aug | ● | 08 Nov |



# River water and LMWL



## Stable isotopes

- Wiesent data plot on LMWL
- Stable source value
- No seasonal cycle in river

## Stream flow generation

- groundwater dominated river over entire course
- system buffered by deep karst groundwater body
- minor importance of surface run off

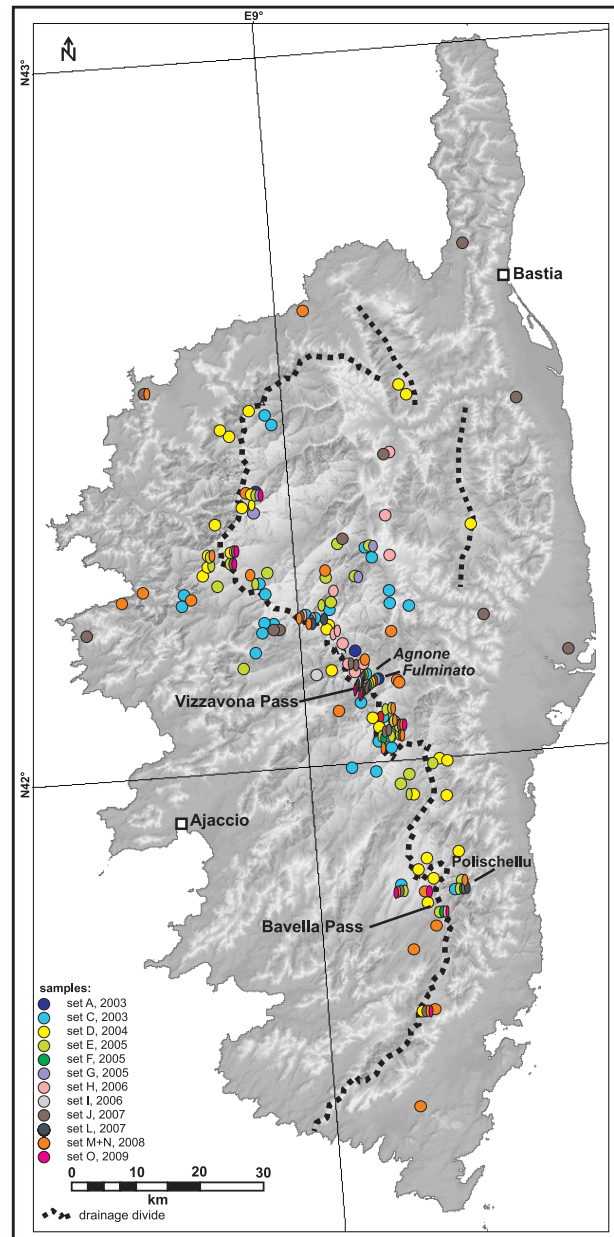


Solenzara River, Corsica

Isotope hydrology of the

# ISLAND OF CORSICA

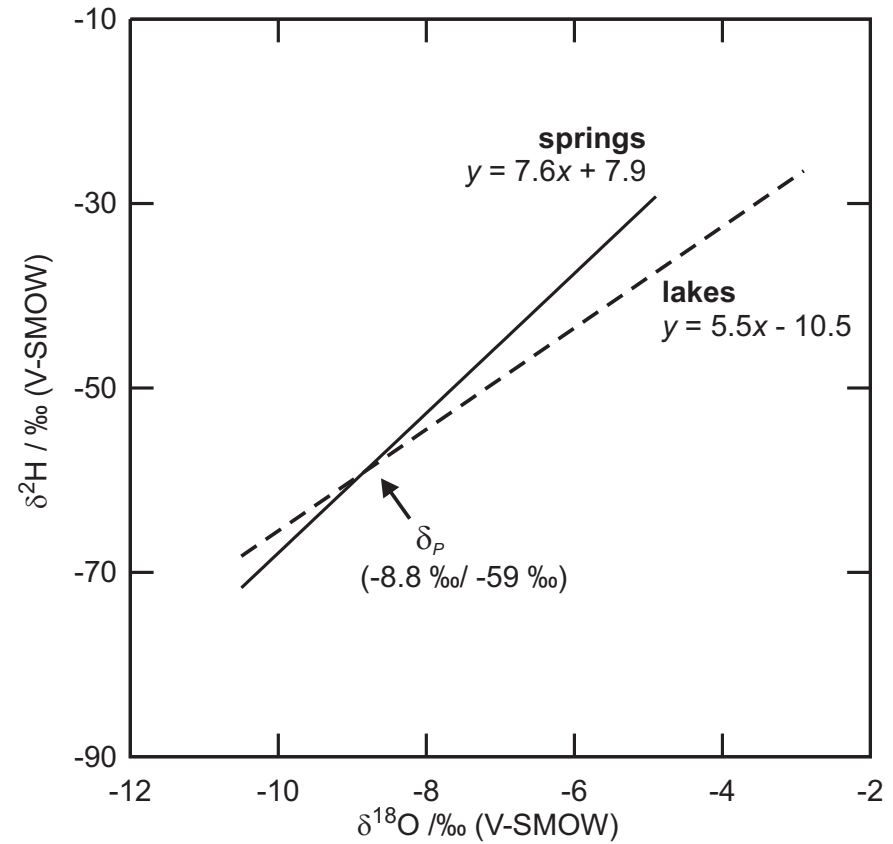
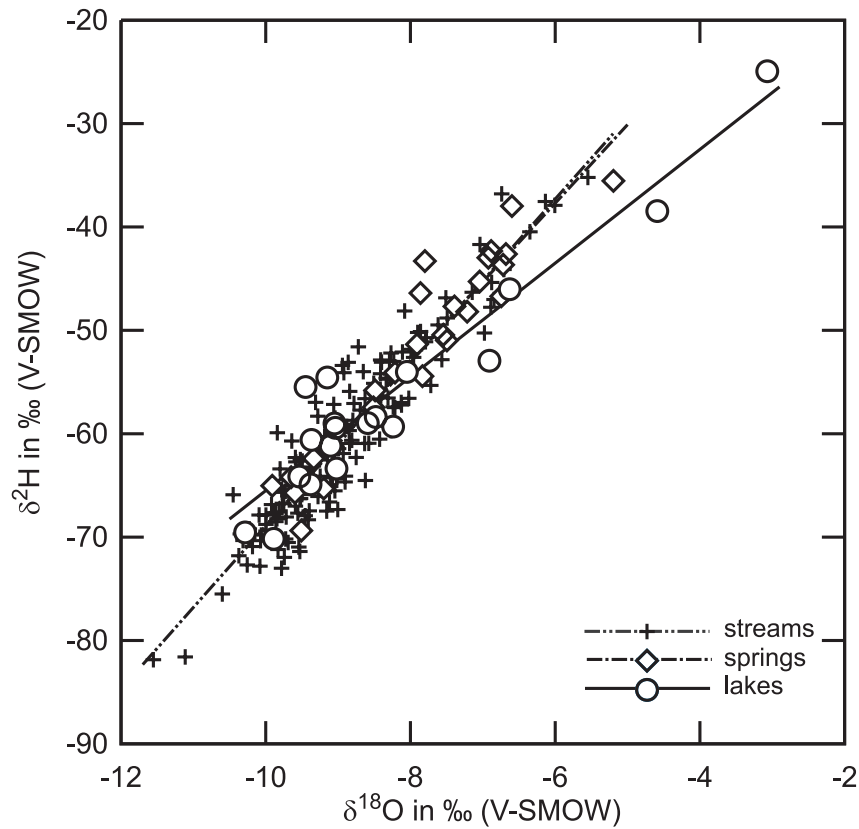
# Sampling locations



- Paleoclimate study on tree rings of our institute
- Accompanying water sampling from 2003 to 2009
- 210 surface water samples
- Isotope analysis performed at Tübingen, Erlangen and Hanover
- 3 different compartments:
  - (1) Lakes ( $n = 19$ )
  - (2) Springs (26)
  - (3) streams (166)

van Geldern et al. (2014)

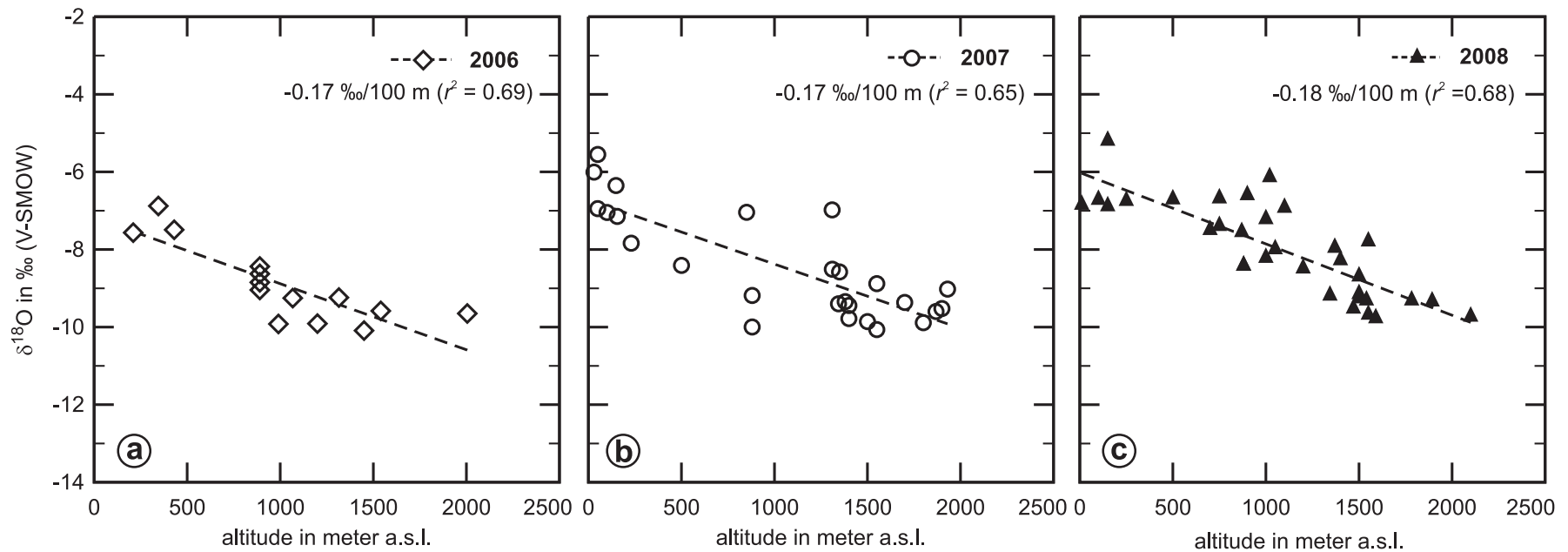
# From streams to the LMWL



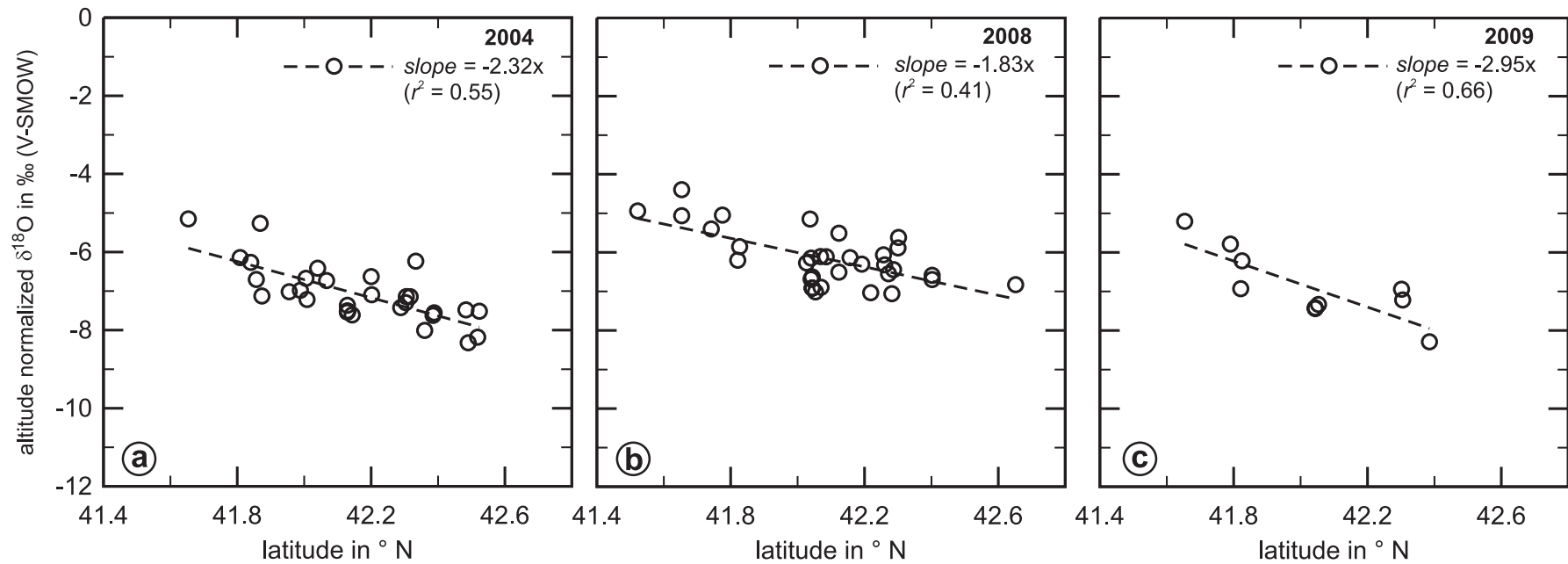
van Geldern et al. (2014)



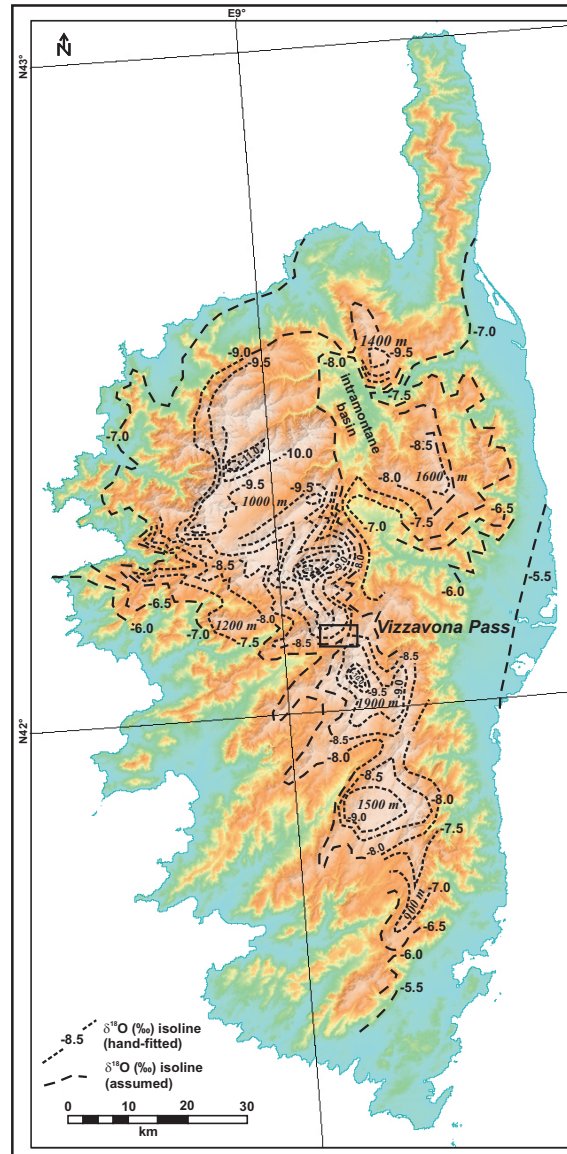
# Altitude effect



# Latitude and climatic effects



# Corsica isotope map from river water data





Klingengraben spring, Nuremberg

Stable isotopes and

# PALEOWATERS



# Nuremberg

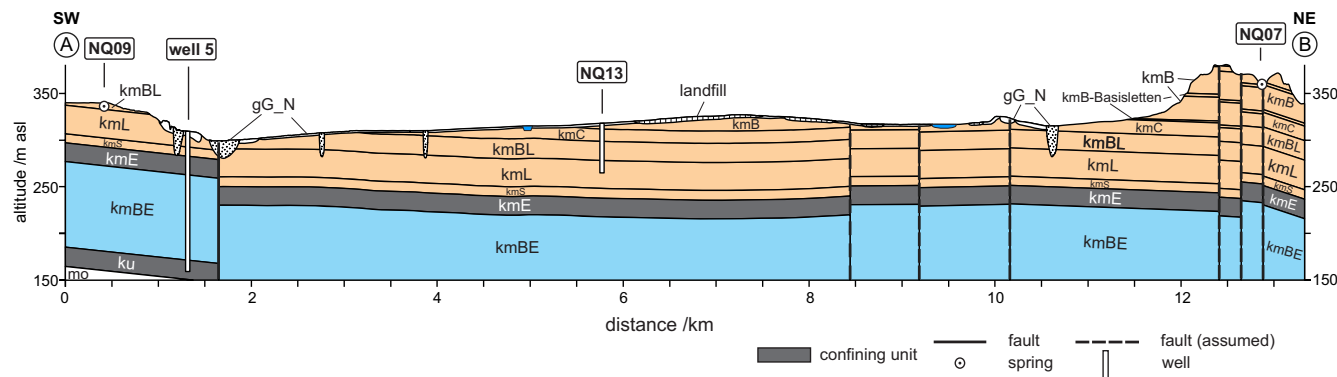


Tiefer Brunnen, Nuremberg Castle

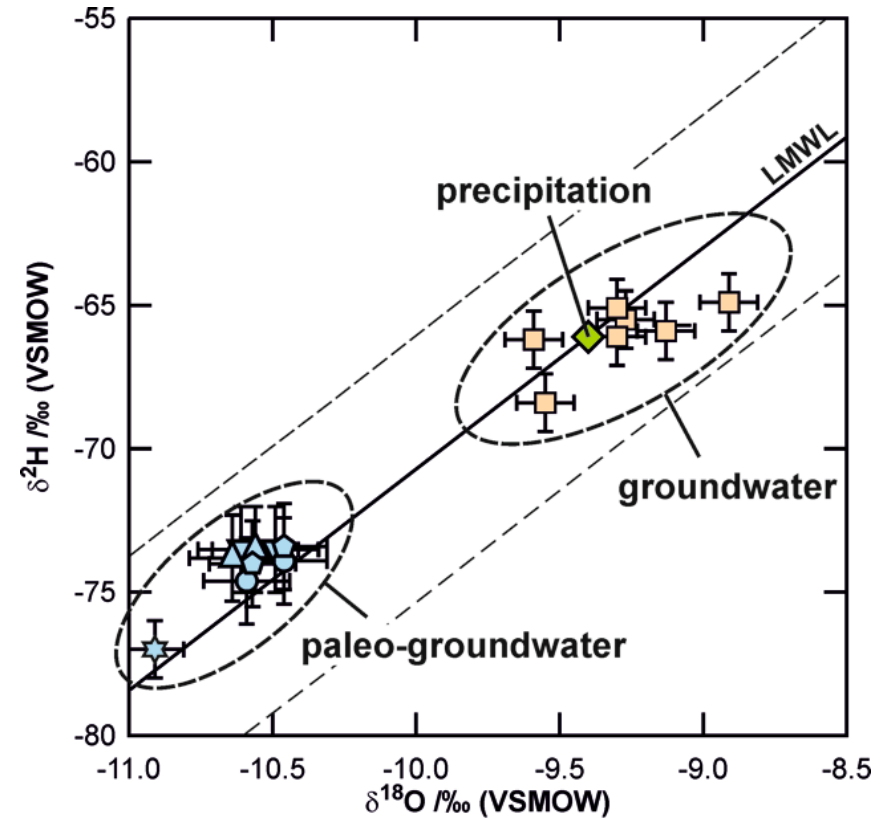
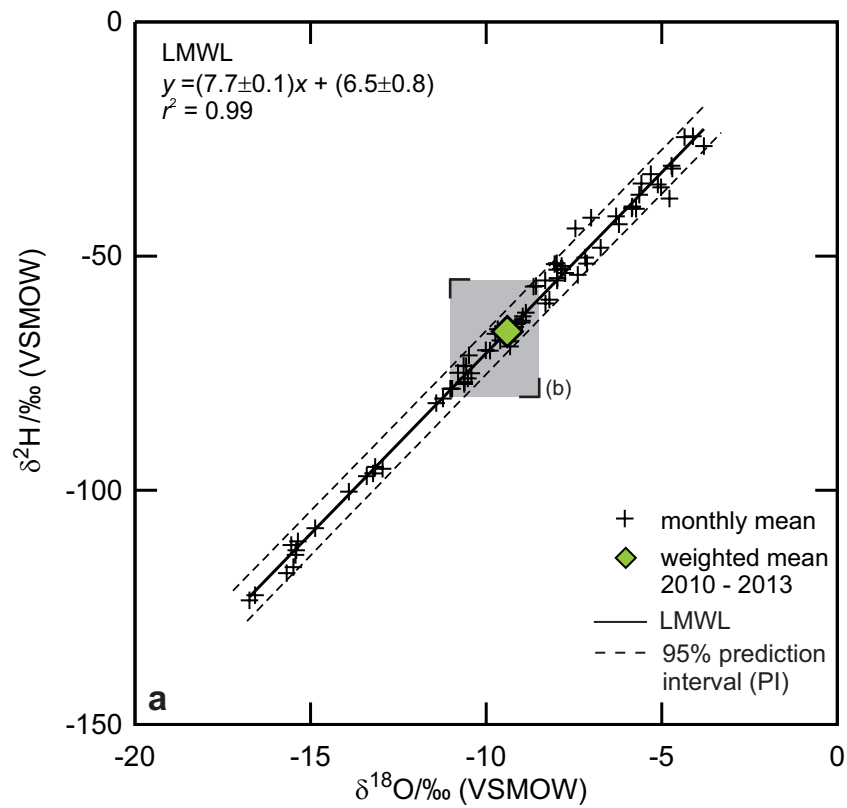
# Hydrogeology

SYSTEM	EUROPEAN LITHOSTRATIGRAPHY	GEOLOGIC UNIT	SYMBOL	THICKNESS [m]	HYDROGEOLOGIC UNIT
Quaternary	Pleistocene	sand and gravel	gG_N	0-30	Aquifer Ia
Triassic	Sandstein-keuper	Burgssandstein	kmB	~90	Aquifer Ib
		Coburger Sandstein	kmC	~15	
		Blasensandstein	kmBL	~25	
		Lehrbergschichten	kmL	~30	
	Keuper Group	Schilfsandstein	kmS	4-30	confining unit
		Estherienschichten	kmE	20-30	
		Gips-keuper	Benkersandstein	kmBE	
Lettenkohlenkeuper	ku		~20	confining unit	

van Geldern et al. (2014)



# Paleowaters



van Geldern et al. (2014)

# Radiocarbon dating of deep aquifer

**Table 3**

Radiocarbon ages for different correction models. Ages are in years BP rounded to 100 years.

	Well 4 (sampling A)	Well 4 (sampling B)
Uncorrected $^{14}\text{C}$ -years	26,000	27,500
Vogel (1970)	24,700	26,100
Pearson and Hanshaw (1970) <sup>a</sup>	21,200	23,400

<sup>a</sup>  $\text{pH} = 6.5$ ,  $p\text{CO}_2(\text{soil air}) = 10^{-2} \text{ atm}$ ,  $\delta^{13}\text{C}(\text{soil air}) = -23\text{‰}$ ,  
 $\delta^{13}\text{C}(\text{carbonate}) = 0\text{‰}$ .

- Stable isotopes of the deep aquifer are depleted in  $^{18}\text{O}/^2\text{H}$
- Radiocarbon age suggests that water is  $> \sim 21,000$  years
- No tritium found
- → Paleowaters recharged before the end of the LGM under **cooler climatic conditions.**
- GeoZentrum, LfU, and Helmholtz Munich will start to measure groundwater samples systematically in 2015



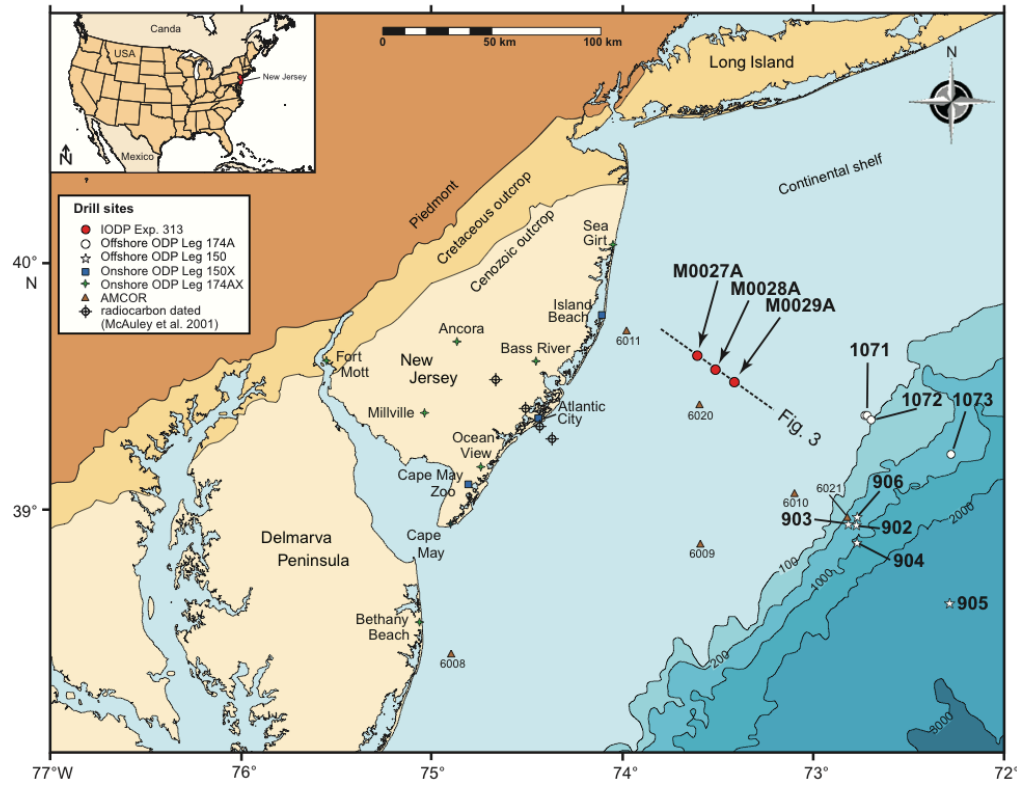


45 km offshore Atlantic City, NJ

New Jersey Shallow Shelf

# COASTAL AQUIFERS

# IODP 313 Drilling Site

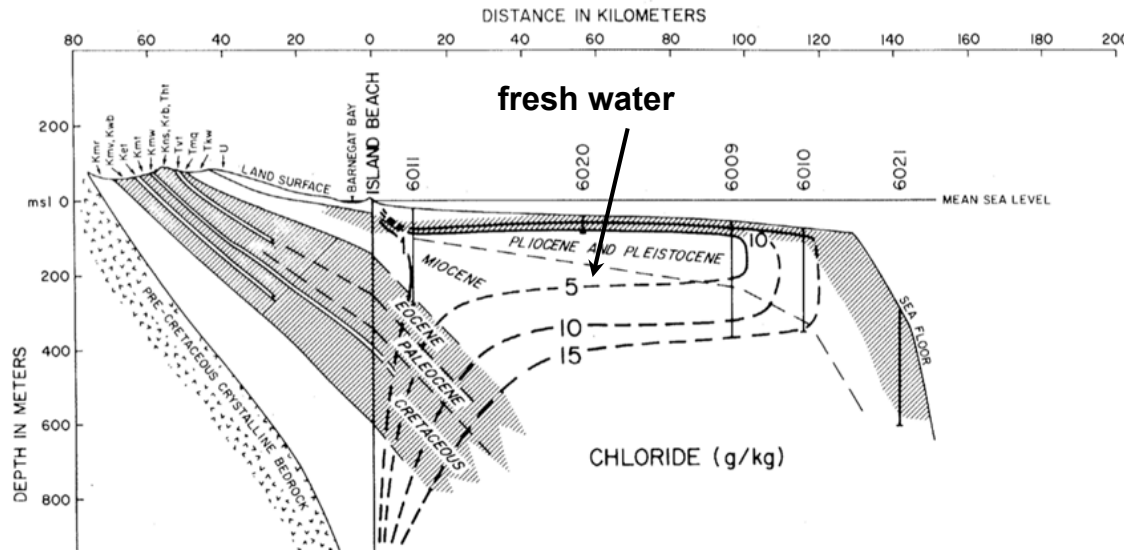


van Geldern et al. (2013)



Photo: ECORD

# Submarine fresh water

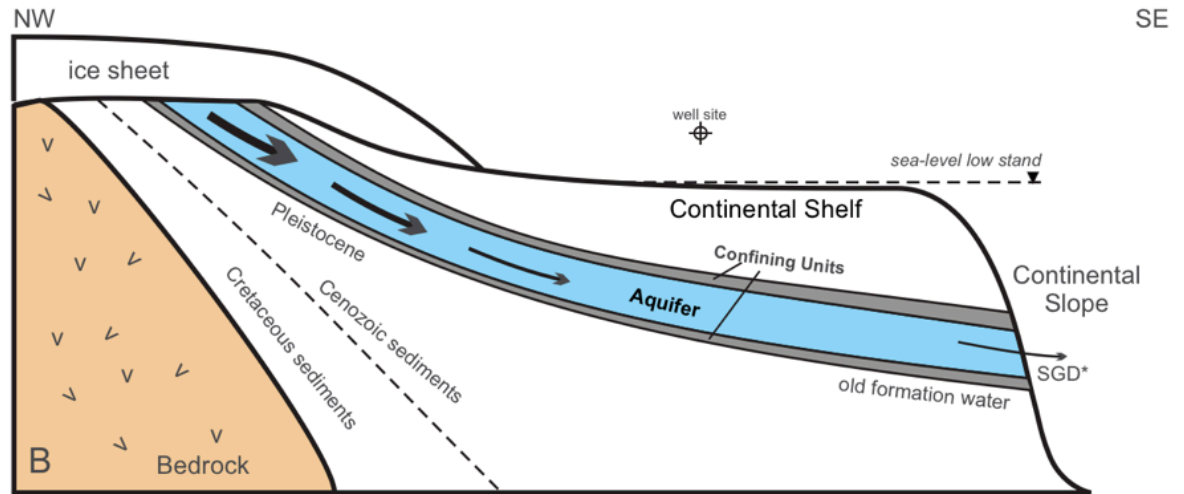


Hathaway et al. (1979)

- Fresh water lens known since 1970s
- Simple geometry assumed
- All hydrogeological models base on these assumptions

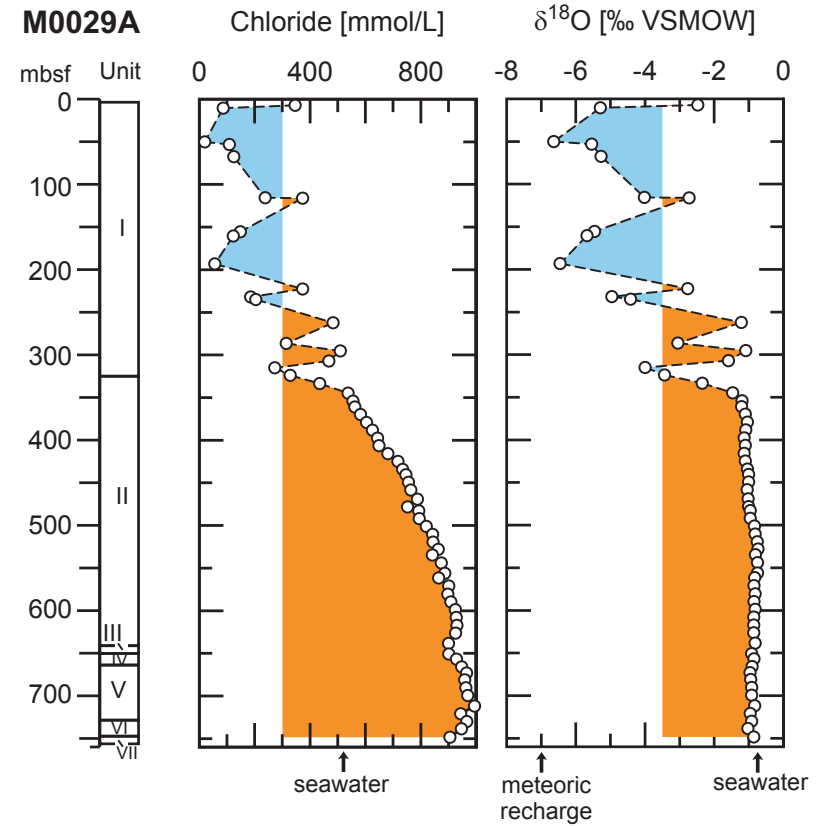
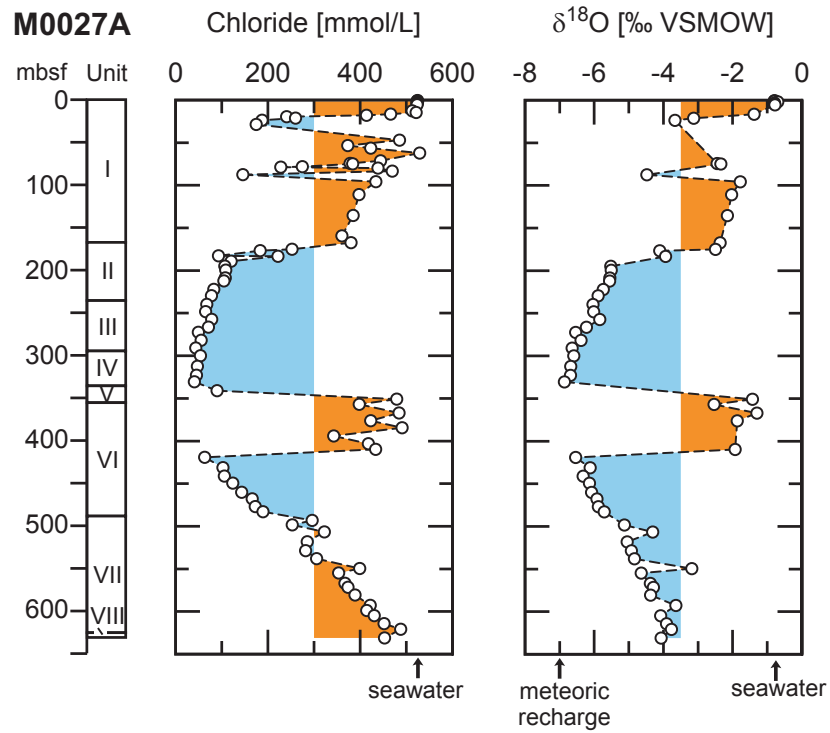
## before IODP 313

- Paelowater recharged during the Pleistocene
- from melt waters below ice sheets (LGM)



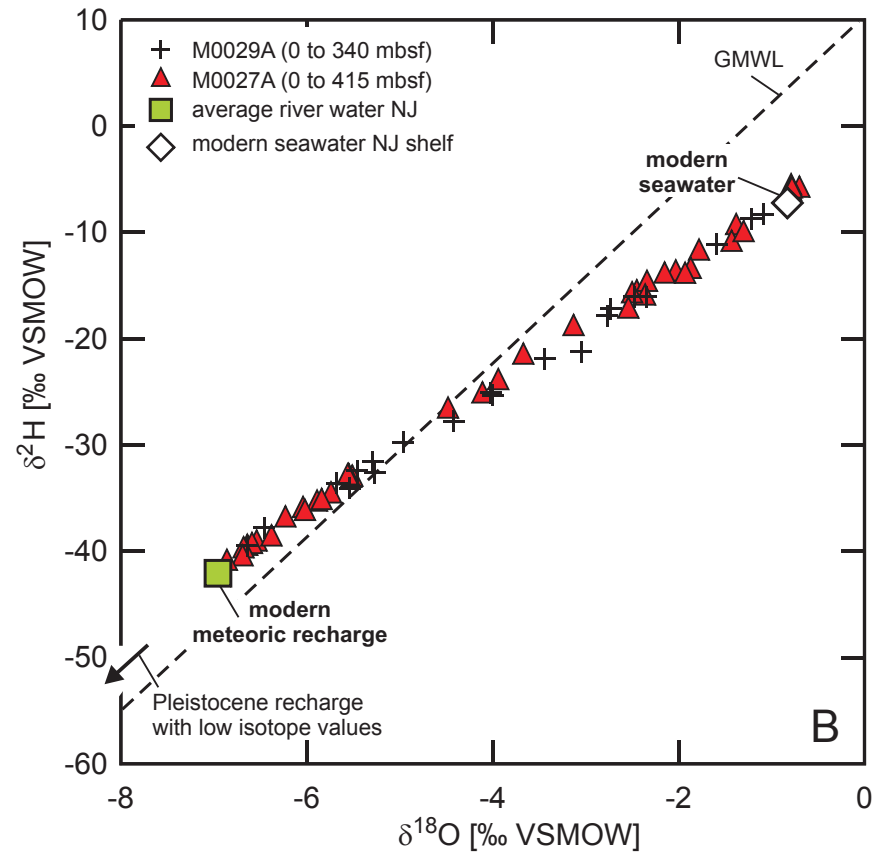
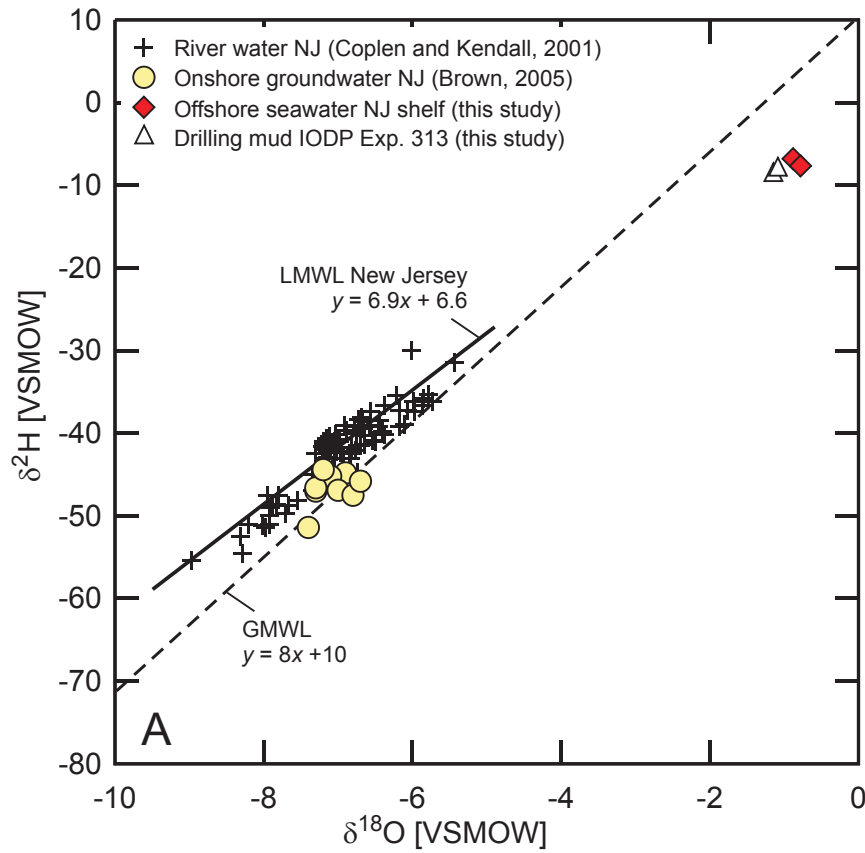
van Geldern et al. (2013)

# Stable isotopes



van Geldern et al. (2013)

# Water origin

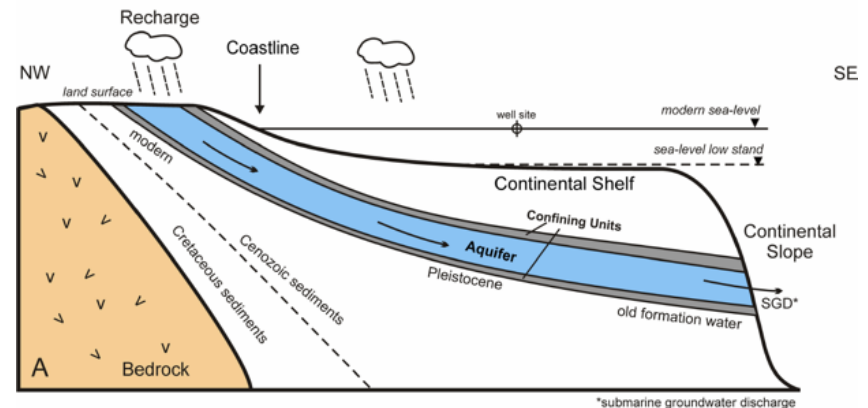


van Geldern et al. (2013)

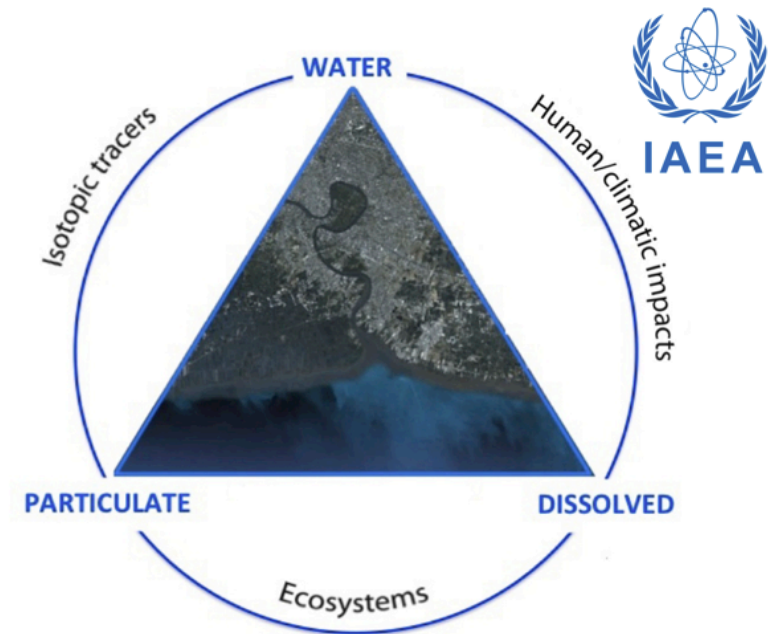


# Paleoclimatic implications

- Today's onshore recharge is characterized by stable isotope analyses from river water
- Stable isotopes of fresh water below the shelf is identical to today's onshore recharge
- No indications for cooler recharge conditions or recharge during the last glacial maximum
  - Isotope hydrology was identical to modern conditions during the LGM?
  - Water is older (millions of years?) and was recharged during similar conditions that today
  - Water is younger (<20,000 years) and is actively recharged



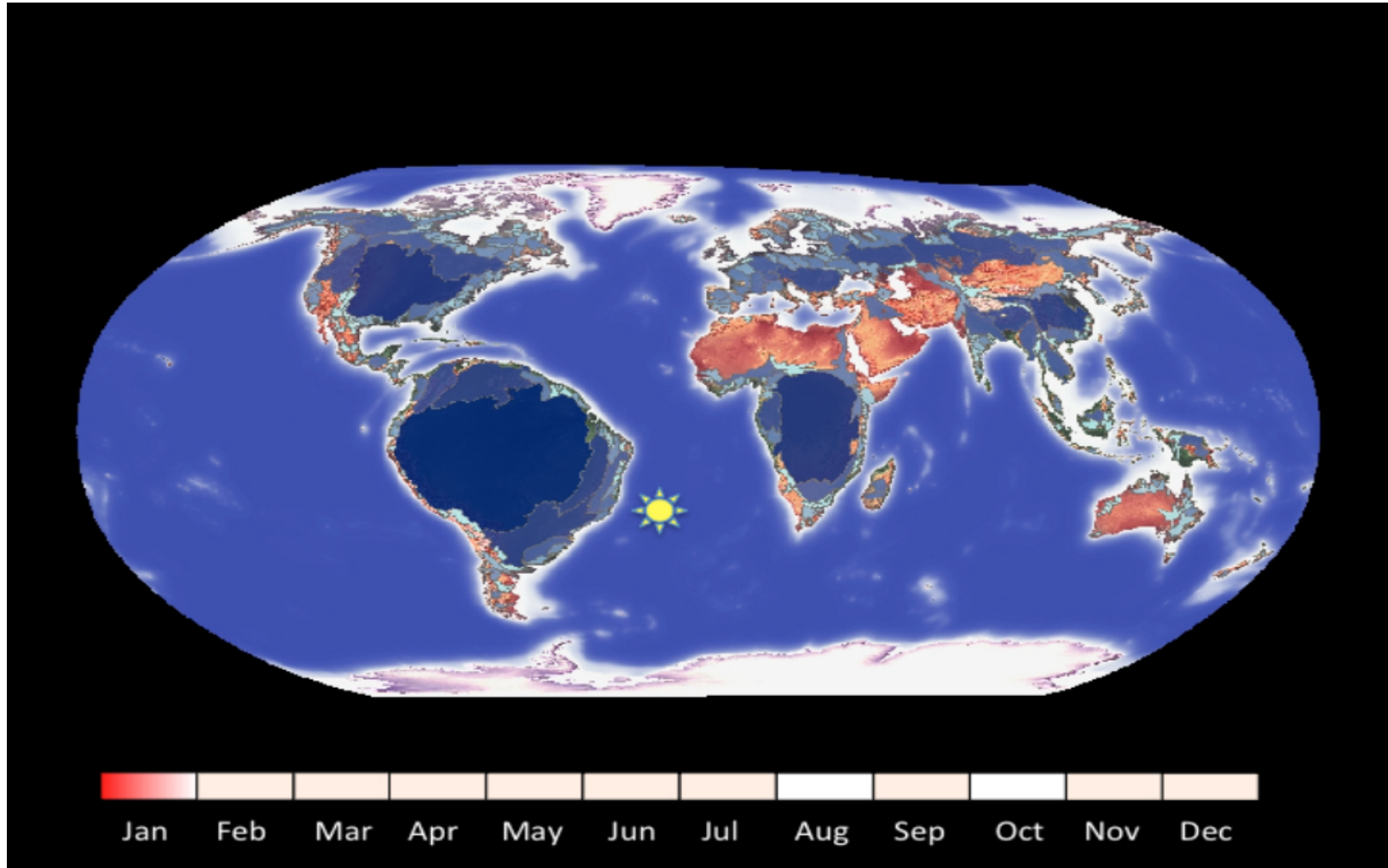
van Geldern et al. (2013)



Global Network of Isotopes in Rivers

# GNIR<sup>3</sup> AND GLOBAL RIVERS OBSERVATORY

# Global discharge data



Data from GRDC (BfG Koblenz)  
Animation: B. Peucker-Ehrenbrink (WHOI)

# GNIR<sup>3</sup> – Rivers worldwide

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- **GNIP** is one the most successful isotope monitoring programs
  - numerous applications that were not initially thought
  - radically improved our understanding of recharge mechanisms
  - rivers are less understood and not systematically investigated
  
- **Rivers** transport valuable information about
  - climate change and mankind adaption to it
  - changes in land use
  
- **GNIR** should change this
  - Pilot GNIR 2002 – 2006 as IAEA Coordinated Research Project (CRP)
  - New IAEA-CRP launched in 2014 (2014 – 2018)
  - Focus on worlds largest rivers

# Summary

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## **Stable isotopes** in hydrology

- are the geochemical fingerprint of the water molecule
- allows to trace water along its journey from precipitation to the sea
  - rivers integrate signals from an entire region and transport them
- carry information about the impact
  - of climate change
  - of anthropogenic induced changes of ecosystems
- help to monitor these changes and investigate the reasons
- identify paleo-climatic conditions through preserved paleowaters



## **Isoscapes** derived from precipitation or river water data

- are helpful tool in identifying potential regions of origin
- **must not be used** as a 'black box'
- do not account for every isotope effect
- try to understand the regional hydro(geo)logical system for reliable results



# Acknowledgments

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- Irene Wein, Lars Wunder, Silke Meyer, Christian Hanke (GZN laboratory)
- Sonja Konrad (GZN/LGL)
- Alfons Baier (GZN)
- Laura Balk, Markus Lehner, Hannah Subert (BSc Students)

Isotope ratio mass spectrometer (IRMS)

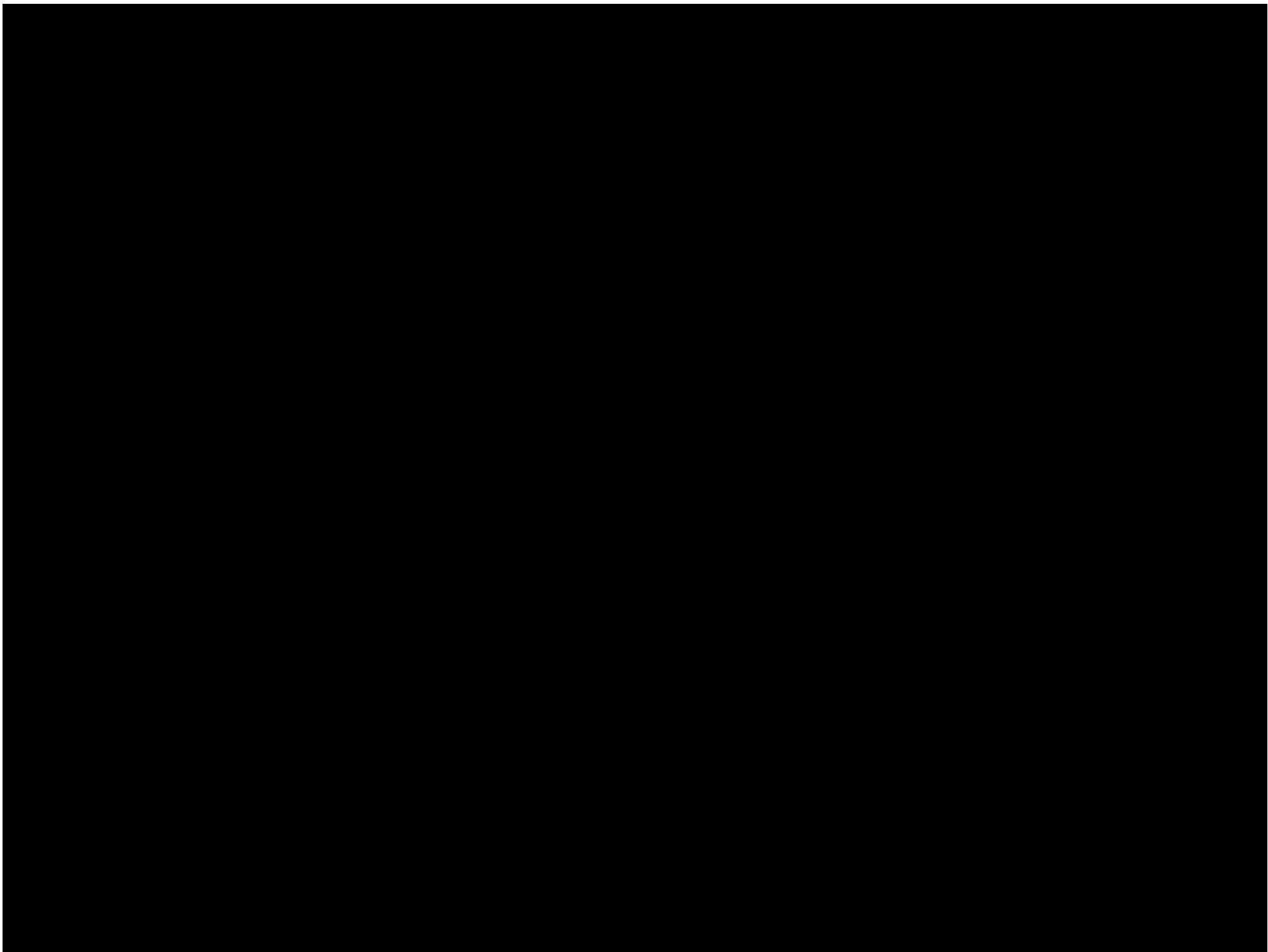


GeoZentrum Nordbayern

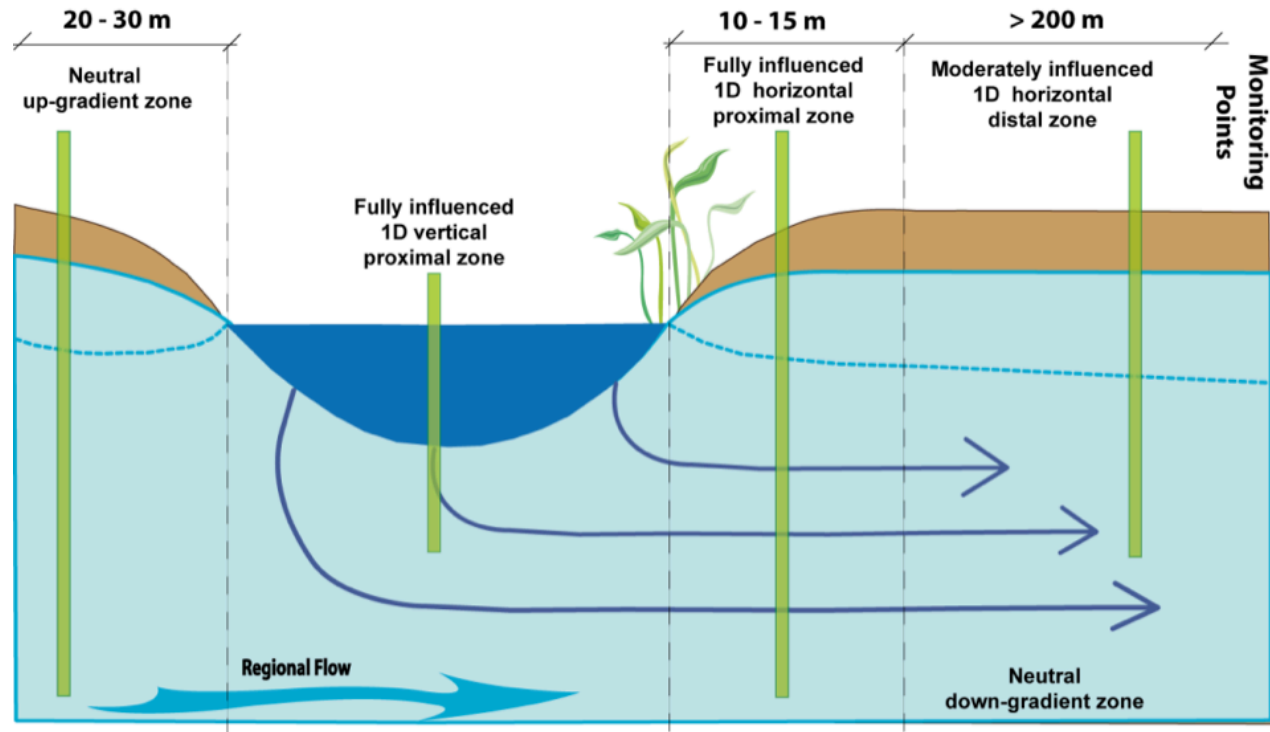
Laser spectroscopy (IRIS)



GeoZentrum Nordbayern

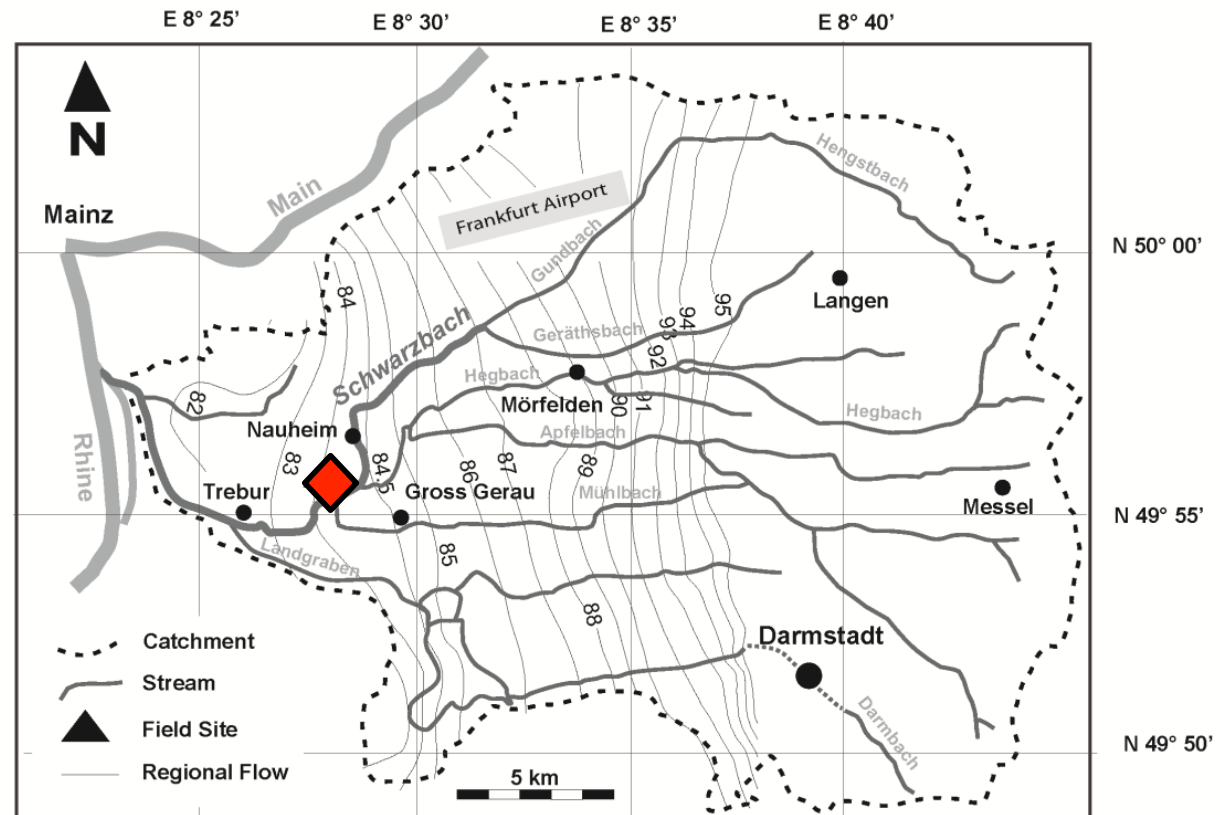


# Surface water – groundwater interaction



- Principle hydraulic conditions
  - Infiltration of stream water into groundwater → losing stream
  - Exfiltration of groundwater into stream → gaining stream
- Potential threat
  - Infiltration of sewage into drinking water wells *via* surface water – groundwater interaction

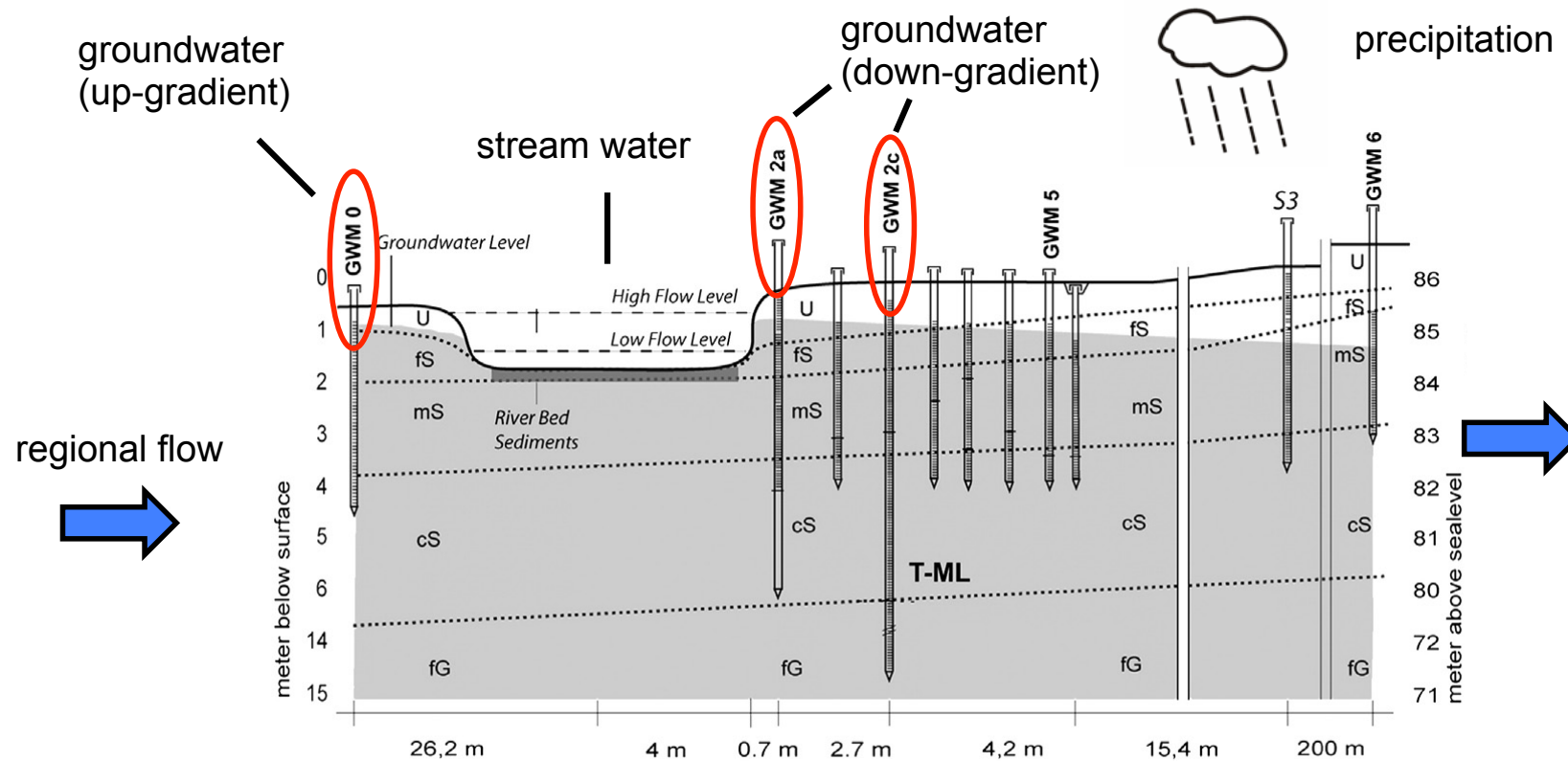
# Study Site



## Schwarzbach

- 7 km upstream of the river Rhine
- Intensive agricultural and industrial land use
- Mean discharge with about 50% waste water from sewage water treatment plants (SWTP; municipal and Frankfurt airport)

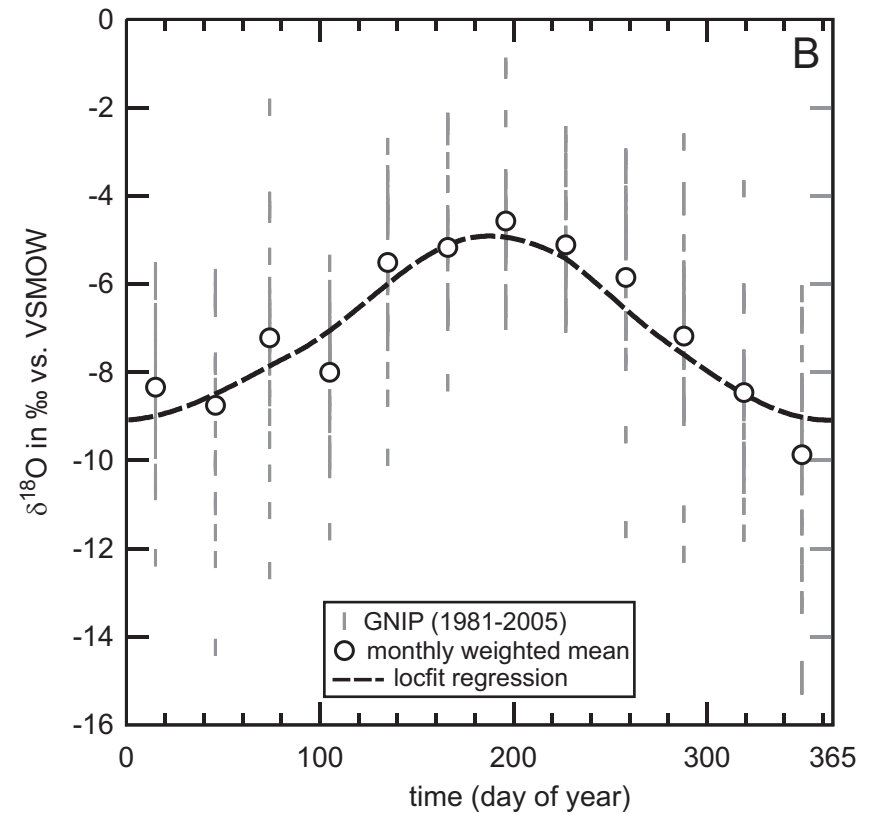
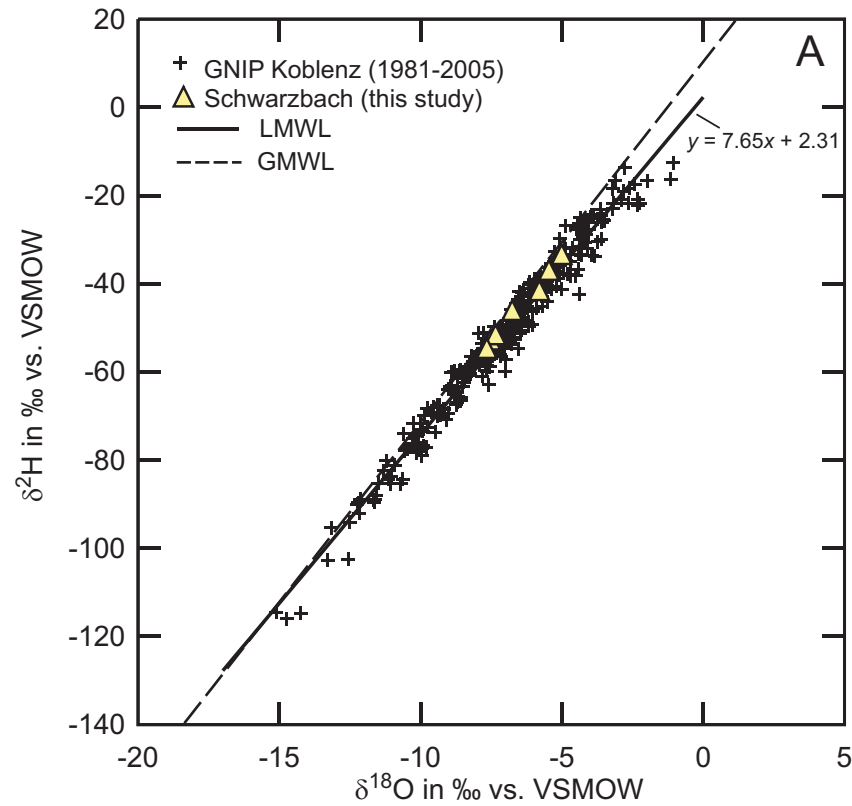
# 2D transect parallel to flow lines



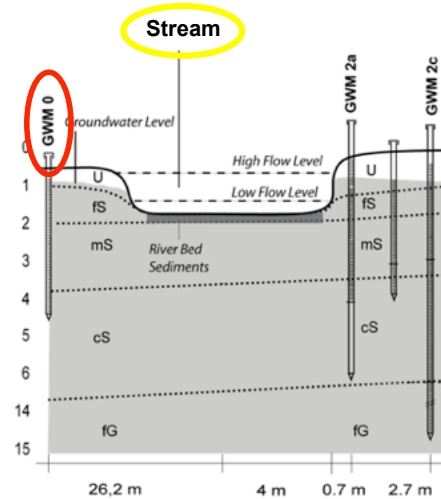
- Comparative geochemical tracer analyses over 5 months
  - **Stable isotopes** ( $\delta^2\text{H}$  and  $\delta^{18}\text{O}$ )
  - **Artificial sweetener Acesulfam K** ( $\text{C}_8\text{H}_8\text{KN}_2\text{O}_8\text{S}_2$ )
  - (X-ray contrast media (Iomeprol) and metabolites)
- Numerical flow (MODFLOW) and transport (MT3DMS) simulation



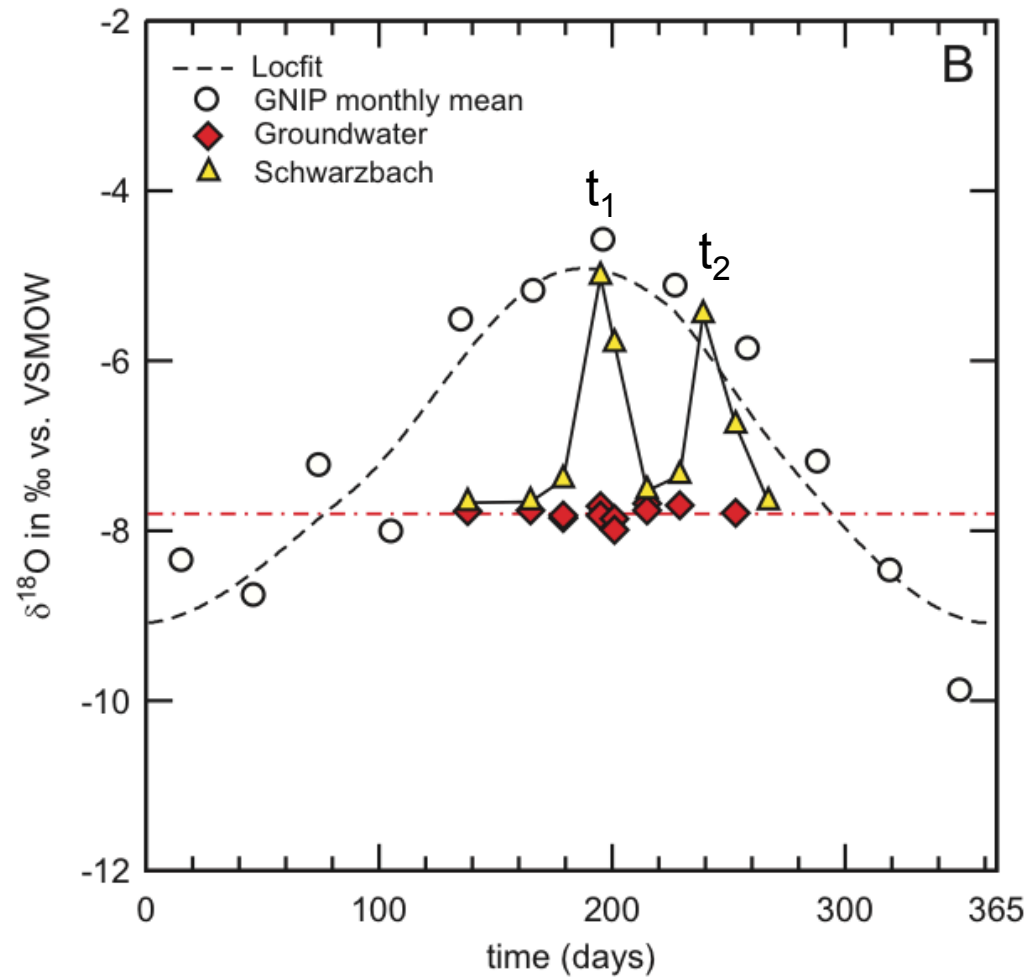
# Stable isotopes in precipitation



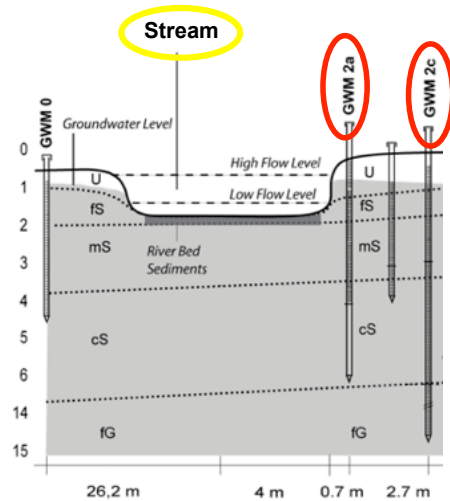
# Stable isotopes events



- Stable  $\delta^{18}\text{O}$  value in groundwater
- Precipitation events traced in stream water



# Stable isotopes



- Stable  $\delta^{18}\text{O}$  value in groundwater
- Precipitation events traced in stream water

