

## Selected groundwater studies of EU project AquaTerra leading to large-scale basin considerations

J.A.C. Barth<sup>1\*</sup>, E. Kalbus<sup>2</sup>, C. Schmidt<sup>2</sup>, M. Bayer-Raich<sup>2</sup>, F. Reinstorf<sup>2</sup>, M. Schirmer<sup>2</sup>, D. Thiéry<sup>3</sup>, I.G. Dubus<sup>3</sup>, A. Gutierrez<sup>3</sup>, N. Baran<sup>3</sup>, C. Mouvet<sup>3</sup>, E. Petelet-Giraud<sup>3</sup>, Ph. Négrel<sup>3</sup>, O. Banton<sup>4</sup>, J. Battle Aguilar<sup>5</sup>, S. Brouyère<sup>5</sup>, P. Goderniaux<sup>5</sup>, Ph. Orban<sup>5</sup>, J.C. Rozemeijer<sup>6</sup>, A. Visser<sup>6</sup>, M.F.P. Bierkens<sup>6</sup>, B. Van der Grift<sup>7</sup>, H.P. Broers<sup>7</sup>, A. Marsman<sup>7</sup>, G. Klaver<sup>7</sup>, J. Slobodnik, P. Grathwohl<sup>1</sup>

<sup>1\*</sup> Corresponding Author: Eberhard Karls Universität Tübingen, Center for Applied Geoscience, Sigwartstr. 10, D 72076 Tübingen. [Johannes.barth@uni-tuebingen.de](mailto:Johannes.barth@uni-tuebingen.de)

<sup>2</sup> Helmholtz Centre for Environmental Research - UFZ, Department of Hydrogeology, Permoserstr. 15, 04318 Leipzig, Germany

<sup>3</sup> BRGM, Avenue C. Guillemin, BP 6009, 45060 Orléans Cedex 2 France

<sup>4</sup> Université d'Avignon, Laboratoire d'Hydrogéologie d'Avignon, 33 rue Louis Pasteur, 84000 Avignon, France

<sup>5</sup> Group of Hydrogeology and Environmental Geology, <sup>2</sup>Aquapôle ULg University of Liège, Building B52/3, 4000 Sart Tilman, Belgium

<sup>6</sup> Department of Physical Geography, Utrecht University, Heidelberglaan 2, P.O. Box 80115, 3508 TC Utrecht, The Netherlands

<sup>7</sup> TNO Built Environment and Geosciences, Geological Survey of the Netherlands, Princetonlaan 6, P.O. Box 80015, 3508 TA, Utrecht, The Netherlands

<sup>8</sup> Environmental Institute, Okružna 784/42, 97241 Kos, Slovak Republic

**Abstract** Several local groundwater studies within the EU project AquaTerra in the Basins of the Meuse, Elbe point at significant influences of groundwater on surface water, while the Brévilles Catchment shows a distinct problematic of pesticide loading to groundwater. Further modeling studies are currently being developed. In the Danube Basin no specific groundwater studies were carried out in the framework of AquaTerra. However on larger scales geochemical proxies such as strontium isotope ratios can give an insight into groundwater contributions to the river that reflects an integral signal of the environmental status of the Basin. Future local groundwater studies should be further correlated to the environmental status of rivers nearby.

### INTRODUCTION

As one of the key compartments for future water resources, groundwater does not only constitute a highly valuable resource, but also lies between the soil and the river-sediment- and floodplain system. Groundwater thus constitutes a transitional reservoir that receives pollutant fluxes and passes them on to the surface system. Furthermore, turnover of material is possible, particularly over longer time periods with low flow velocities. This particular position in the environmental system renders groundwater a highly interesting and important compartment. Groundwater therefore deserves detailed study on a variety of scales.

Within the EU project AquaTerra several local groundwater studies are being carried out in the Basins of the Meuse, the Elbe and the small French catchment of the Brévilles spring (Fig. 1). In the Ebro a few groundwater samples have been collected and environmental studies on the Danube do not specifically include groundwater monitoring. However, some conclusions about groundwater surface water interaction can be drawn from investigations of the river itself. This relies for instance on methods of strontium isotope ratios that allow deciphering interactions between groundwater and the aquifer matrix system.

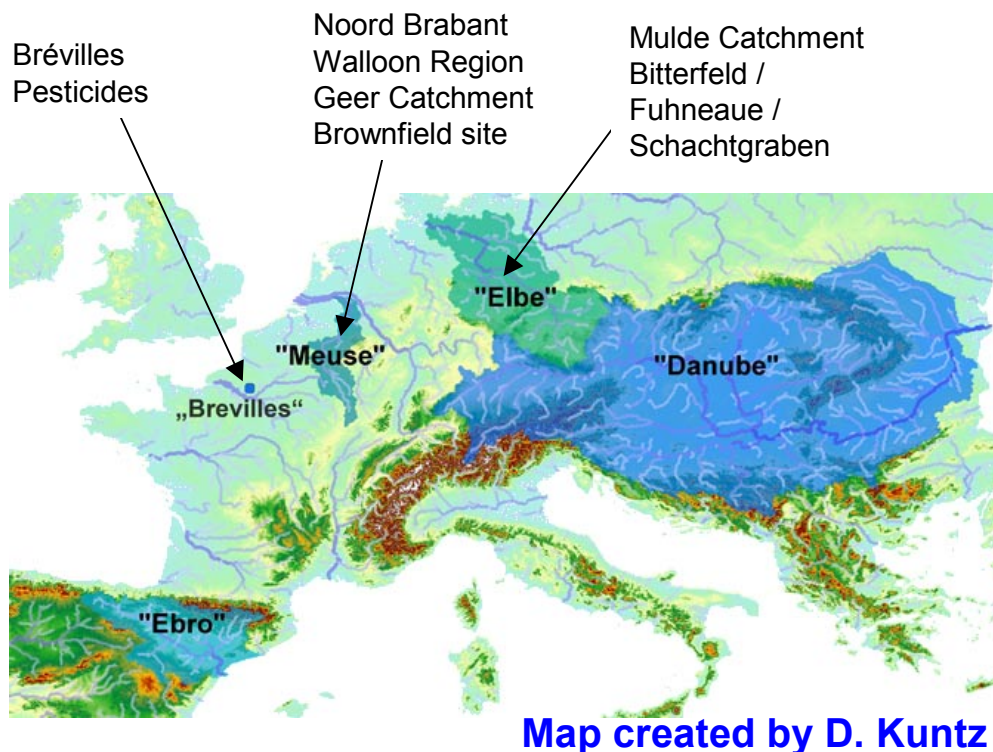


Fig. 1. Overview of the AquaTerra Basins and locations of groundwater studies

In the following, selected groundwater studies of AquaTerra are briefly presented to provide an overview of groundwater monitoring and management techniques. AquaTerra also produces a growing body of literature specific groundwater studies (Baran et al., 2007; Barth et al., 2007; Batlle Aguilar et al., 2007; Kalbus et al., 2006; Kalbus et al., 2007; Petelet-Giraud et al., 2007; Rozemeijer and Broers, 2007; Schmidt et al., 2006; Visser et al., 2007). Further information about the project as a whole is available on the AquaTerra website (<http://www.eu-aquaterra.de/>).

### GROUNDWATER STUDIES IN THE MEUSE BASIN

Several groundwater investigations exist in the Meuse Basin within the framework of AquaTerra. This includes a study on groundwater contribution to surface water contamination in a region with intensive agricultural land use (Noord-Brabant, The Netherlands). Work in this area involves the development of a conceptual model that outlines how stream water quality at different discharges results in different mixing ratios of groundwater from different depths. Available data from the regional monitoring networks are being fed into this study and show that that groundwater is a dominant source of surface water contamination. In many cases the poor chemical condition of upper and shallow groundwater exceeds the quality standards such as nitrate fertilizers in receiving surface waters. This is particularly observed during quick flow periods.

In addition to this, a three-dimensional reactive transport model is used for the trend detection an extrapolation of groundwater and surface water quality. The purpose of this model is to establish groundwater flow and reactive transport modeling in the Dutch part of the Meuse

Basin with focus on Zn and Cd loading to the soil and their subsequent leaching to the groundwater.

Another groundwater flow and reactive transport model in the Geer Catchment of the Meuse Basin treats the problematic of nitrate pollution that is particularly pronounced in this area due to traditionally intensive agriculture as given by thick and fertile loess layer in the area. It is known that at least since 1960, nitrate concentrations have risen dramatically and have approached the drinking water limit of  $50 \text{ mg L}^{-1}$ . More recently, pesticides (mainly atrazine) have also been detected in some observations and pumping wells. This outlines the need for future scenario estimation of present and future groundwater quality trends in the area. Such work is of primary importance to support future decisions in terms of land use.

On the other hand, tritium isotopes enabled to demonstrate trend reversal of groundwater quality in relation to time of recharge. This is particularly important because recent EU legislations direct towards reversal of pollutant concentrations in groundwater. So far, uncertainty of the travel time towards the screens of the groundwater quality monitoring networks complicated clear demonstration of such trend reversal. The local study in the Netherlands treated pollutant trend reversal by relating concentrations of pollutants in groundwater to the time of recharge, instead of the time of sampling. This was arranged by establishing the travel time to monitoring screens in sandy agricultural areas via  $^3\text{H}/^3\text{He}$  groundwater dating. Results indicate that concentrations of fertilizers increased in groundwater recharged before 1985 and subsequently decreased after 1990. This shows that dating techniques can facilitate (re)interpretation of existing groundwater quality data. By investigating a large number of time-series, the method could be shown to be robust and insensitive to outliers, subsurface heterogeneity, and spatial and temporal variation in inputs. This approach is widely applicable in areas with unconsolidated granular aquifers.

A further new groundwater study in a contaminated former gaswork cookery site in the alluvial plain of the Meuse River, in the vicinity of Liège city (Belgium), quantified river-aquifer interactions to outline possible release of contaminants to the river. This included detailed mapping of the groundwater and river levels, tracer and pumping tests. Additionally, various sources of data were consulted to obtain records on the Meuse River and rainfall, and groundwater monitoring campaigns were performed on the above mentioned brownfield. Findings led to a model that relates fluctuating groundwater levels to changes in neighbouring Meuse River. The established model carefully indicates that the effective porosity of the alluvial aquifer is low when assuming radially symmetric distribution of groundwater fluxes and effective velocities. This condition is not always met and some tracer experiments revealed groundwater being fed by water from the Meuse River. It is likely that the hypothesis of homogeneity leads to strong underestimation of groundwater fluxes. In a next step, established hydrodynamic parameters of the site will be used in a transport model for heavy metals and organic compounds.

### **GROUNDWATER STUDIES IN THE BRÉVILLES CATCHMENT**

The  $3 \text{ Km}^2$  catchment of the Brévilles Spring near Paris in France has been investigated for pesticide pollution since 1999 starting already with the Pegase Project. Formerly used for water supply, the spring was disconnected from the distribution network in August 2001 because pesticide and nitrate concentrations exceeded water quality criteria. Atrazine was the most studied herbicide and was detected on numerous occasions at the spring that is fed from the local groundwater even years after its application stopped. Various activities helped to characterise the system including:

- The history of atrazine applications through farmer interviews
- Drilling campaigns: to establish a total of 19 piezometers
- Gamma Ray logging in existing wells to reveal information about position of low permeability marly and clayey layers
- 12 pumping tests to yield information about the transmissivity of the sandy aquifer
- Geophysical electric profiles to enable the mapping of electrical resistivity of the geological layer in a cross section
- Geophysical Magnetic Nuclear Resonance (MNR) campaigns to indicate saturated areas in the underground with an investigation depth of ~ 60 m
- Tracer tests to reveal stratification of groundwater flow and thus indicating that mostly the upper aquifer is drained by the Brévilles Spring with most solutes following an almost horizontal path. The lower part of the aquifer is drained downstream from the source but is not completely isolated from the lower aquifer with a progressive transfer of solutes from the lower, less permeable sandy layer, to the upper sandy layer.
- Routine measurements including monthly monitoring of piezometers as well as precipitation and discharge measurements
- Geochemical measurements and tritium dating showing the importance of the stratification of the sandy saturated zone and the buffer function of the unsaturated limestone.

With the above, the monitoring of the Brévilles agricultural catchment over five and a half years revealed considerable spatial and temporal variability in the concentrations of atrazine and its metabolite deethylatrazine with maximum 0.97 and 2.72  $\mu\text{g L}^{-1}$ , mean 0.19 and 0.59  $\mu\text{g L}^{-1}$ , respectively. The variabilities remained high even though atrazine has not been used for six years. On the other hand, isoproturon, the pesticide applied in the greatest amount, was detected in only 10 of the 133 samples. Further laboratory analyses were performed to estimate the sorption of atrazine on selected soils. Results were added to a 1D soil leaching model (MACRO) and also fed into a 3D saturated zone model (MARTHE, (Thiéry, 1993)). The running of MACRO and the extraction of relevant data to be used as inputs in MARTHE were fully automated to allow a smooth sequential running of the two models.

### **GROUNDWATER STUDIES IN THE ELBE BASIN**

Most groundwater investigations within the Elbe Basin focussed on the Wolfen/Bitterfeld Megasite in the Mulde subcatchment within Germany. This site has multiple contaminant sources from more than a century of industrial activity. At present, the contaminated groundwater covers an area of about 25 km<sup>2</sup> and poses a threat for the surrounding aquifers and the Mulde River. The groundwater contamination was mostly caused by the former Bitterfeld chemical works and was released through damages in the production facilities and pipelines and inappropriate and unsecured storage and wastewater treatment. Key contaminants include chlorinated benzenes as intermediate products in the manufacture of dyes and plant protecting agents with monochlorobenzene (MCB) being the major contaminant of the Quaternary aquifer. A number of small streams within the Bitterfeld

Megasite potentially interact with the Quaternary aquifer. These streams are gaining groundwater and therefore a considerable amount of contaminant discharges into the surface water. Investigations are mainly focused on the Schachtgraben, a man-made channel in the Mulde floodplain that collects the effluents of the industrial area.

One of these studies aimed to characterise the relationship between surface- and groundwater in the northern part of the Bitterfeld/Wolfen Megasite. Due to the long industrial and mining use of this region the hydrologic situation was largely disturbed. The geochemical and isotopic analysis provided insight into the interconnection between different surface- and groundwater bodies. Moreover, it was possible to show industrial influences on the different water bodies within the megasite. Waters were found to be of Ca-SO<sub>4</sub>-type with total dissolved solids reaching 3.8 g L<sup>-1</sup> in the industrial area. Stable isotopes of the water ( $\delta^{18}\text{O}$ ,  $\delta^2\text{H}$ ) showed that recharge occurs mainly through groundwater. The Schachtgraben Channel was found to be distinct compared to local groundwater but also to other waters from the center of the industrial area.

Other studies focused on the determination of the magnitude and spatial distribution of mass fluxes at the stream-aquifer interface. Investigations were performed in the different compartments of the stream-aquifer system and at various spatial and temporal scales.

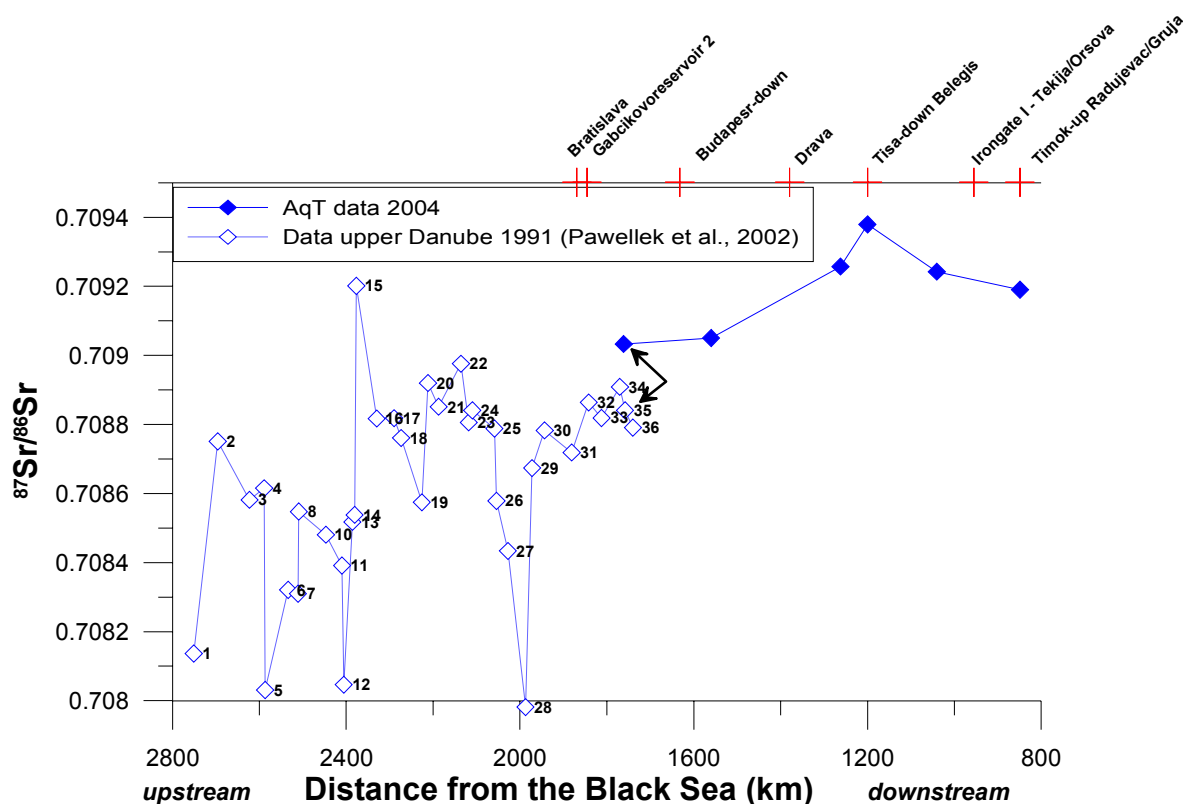
In the groundwater compartment, direct-push hydrostratigraphic profiles with electrical conductivity logs, injection logs, and slug tests were established to characterize the spatial heterogeneity of the subsurface and obtain input parameters for a flow and transport model. Furthermore, integral pumping tests (IPT) were performed at four wells located at a control plane parallel to the stream to determine average contaminant concentrations and mass flow rates in the groundwater approaching the stream. Overall average concentrations were computed at each well using a new analytical solution (Bayer-Raich et al., 2004; Bayer-Raich et al., 2006). It was found that the pumping wells were located within a wide plume with an insignificantly varying contaminant concentration. Average mass fluxes of MCB in the aquifer ranged from 1705 to 3138  $\mu\text{g m}^{-2} \text{d}^{-1}$  at the control plane (Kalbus et al., 2007).

In the streambed, temperature profiles were measured to determine the spatial heterogeneity of groundwater discharge and to calculate groundwater fluxes to the stream. At an 280 m long stream reach, streambed temperatures were measured at intervals of  $\sim 3$  m simultaneously at five depths between 0.10 and 0.50 m below the streambed surface. Water fluxes between aquifer and stream were quantified by solving the heat transport equation at each measurement location. The groundwater fluxes varied between  $-10 \text{ L m}^{-2} \text{d}^{-1}$  (stream water exfiltration) and  $+455 \text{ L m}^{-2} \text{d}^{-1}$  (groundwater discharge) with a mean of  $58.2 \text{ L m}^{-2} \text{d}^{-1}$  (Schmidt et al., 2006).

A combination of the contaminant concentrations obtained from the IPT and the groundwater fluxes calculated from the temperature measurements allowed an estimation of the potential contaminant mass fluxes from the aquifer to the stream. It was found that approximately 7 g MCB are released daily through the entire streambed (Kalbus et al., 2007).

Time integrating passive samplers and streambed sediment samples were used to determine contaminant concentrations and distributions in the streambed. A total of 20 ceramic dosimeters were deployed in the surface water, in the streambed sediment and in groundwater monitoring wells adjacent to the stream. Sampling locations in the streambed were selected according to zones of high and low groundwater discharge to the stream as identified from the

streambed temperature observations mentioned above. The contamination levels of the streambed were higher than in the local groundwater along the investigated reach. For



**Fig. 2** Sr isotope profile along the Danube River from the source of the Danube to the rkm 849 (upstream of the Timok River). The  $^{87}\text{Sr}/^{86}\text{Sr}$  signatures in the dissolved load fluctuate between 0.707982 and 0.709379. These values are close for input of Carbonates formed in Mesozoic of Seawater with endmember values ranging around 0.708 thus reflecting significant dissolution of carbonates by local groundwater. Data of upstream sampling by (Pawellek et al., 2002). Similar techniques were applied in a study on suspended sediments on the Danube (Klaver et al., 2007).

example, pore water concentrations of MCB reached  $\sim 100 \mu\text{g L}^{-1}$ , while groundwater concentrations ranged around  $12 \mu\text{g L}^{-1}$ . Moreover, groundwater discharge had a major influence on the contaminant distribution in the streambed. High discharge locations were characterized by lower pore water concentrations and reduced contaminant load of the sediments. This indicates that at these locations contaminants were already released into the stream.

### LARGE SCALE CONSIDERATIONS ON THE DANUBE

No local groundwater investigations were carried out in the Danube Basin within AquaTerra. On the other hand, a detailed AquaTerra Danube River Survey was conducted in August and September of 2004. It covered an 1147-km stretch of the Danube with 30 stations in 6 different countries and revealed a series of pollutant impacts in waters and sediments of the main river. Results range from a large variety of new findings in ecotoxicity and bioavailability, heavy metal, nutrient and organic pollution. Resulting data in water,

suspended, bottom sediments and fish were also made available to the International Commission for the Protection of the Danube River (ICPDR, <http://www.icpdr.org/> Surveys Database).

The origin of pollutants found in this survey is often difficult to discern. Various sources include urban and industrial direct inputs or atmospheric deposition. Nevertheless, a significant groundwater input of pollutants is very likely. This was also shown by many of the above-mentioned local AquaTerra groundwater studies that indicate significant pollutant transferral from ground- to surface waters. Such input avenues can become particularly important for readily soluble materials including nutrients and pesticides.

The river water chemistry can in many cases be taken as a proxy for groundwater. Indeed, a perennial stream can be thought of as a constantly running integral pumping test. As an example, a technique with Sr isotope ratios ( $^{87}\text{Sr}/^{86}\text{Sr}$ ) indicates groundwater input or can demonstrate interaction between various water bodies ((Brenot et al., 2007)). Fig. 2 shows a typical Sr isotope signal for carbonate dissolution found in the Danube. Since the Danube flows to large parts through Mesozoic sediments containing carbonates, this finding also reflects significant input of local groundwater. While the Sr isotope findings reflect natural inputs from the background geology, future studies should investigate which local groundwater sources could also contribute contaminants to River.

## References

- Baran, N., Mouvet, C. and Négrel, P. (2007). Hydrodynamic and geochemical constraints on pesticide concentrations in the groundwater of an agricultural catchment (Brévilles, France). *Environmental Pollution*. **148**, 729-738.
- Barth, J.A.C., Grathwohl, P. and Jones, K.C. (2007). Introduction to AquaTerra special Issue "AquaTerra: Pollutant behavior in the soil, sediment, ground, and surface water system". *Environmental Pollution*. **148**, 693-694.
- Batlle Aguilar, J., Orban, P., Dassargues, A. and Brouyère, S. (2007). Identification of groundwater quality trends in a chalky aquifer threatened by intensive agriculture. *Hydrogeology Journal*. accepted.
- Bayer-Raich, M., Jarsjo, J., Liedl, R., Ptak, T. and Teutsch, G. (2004). Average contaminant concentration and mass flow in aquifers from time-dependent pumping well data: Analytical framework. *Water Resources Research*. **40**, W083031
- Bayer-Raich, M., Jarsjo, J., Liedl, R., Ptak, T. and Teutsch, G. (2006). Integral pumping test analyses of linearly sorbed groundwater contaminants using multiple wells: Inferring mass flows and natural attenuation rates. *Water Resources Research*. **42**, W08411.
- Brenot, A., Baran, N., Petelket-Giraud, E. and Négrel, P. (2007). Interaction between different water bodies in a small catchment area in the Paris basin (France): Sr isotopic tracing of multiple Sr sources. *Applied Geochemistry*. submitted.
- Kalbus, E., Reinstorf, F. and Schirmer, M. (2006). Measuring methods for groundwater - surface water interactions: a review. *Hydrology and Earth System Sciences*. **10**, 873-887.
- Kalbus, E., Schmidt, C., Bayer-Raich, M., Leschik, S., Reinstorf, F., Balcke, G.U. and Schirmer, M. (2007). New Methodology to Investigate Potential Contaminant Mass Fluxes at the Stream-Aquifer-Interface by Combining Integral Pumping Tests and Streambed Temperatures. *Environmental Pollution*. **148**, 808-816.
- Klaver, G., van Os, B., Négrel, P. and Petelet-Giraud, E. (2007). Influence of Hydropower Dams on the Composition of the Suspended and River-bank Sediments in the Danube *Environmental Pollution*. **148**, 718-728.

- Pawellek, F., Frauenstein, F. and Veizer, J. (2002). Hydrochemistry and isotope geochemistry of the upper Danube River. *Geochimica et Cosmochimica Acta*. **66**, 3839-3853.
- Petelet-Giraud, E., Négrel, P., Gourcy, L., Schmidt, C. and Schirmer, M. (2007). Geochemical and isotopic constraints on groundwater – surface water interactions in a highly anthropized site. The Wolfen/Bitterfeld Megasite (Mulde sub-catchment, Germany) *Environmental Pollution*. **148**, 707-717.
- Rozemeijer, J.C. and Broers, H.P. (2007). The groundwater contribution to surface water contamination in a region with intensive agricultural land use (Noord-Brabant, The Netherlands). *Environmental Pollution*. **148**, 695-706.
- Schmidt, C., Bayer-Raich, M. and Schirmer, M. (2006). Characterization of spatial heterogeneity of groundwater-stream water interactions using multiple depth streambed temperature measurements at the reach scale. *Hydrology and Earth System Sciences*. **10**, 849-859.
- Thiéry, D. (1993). Modélisation des aquifères complexes - Prise en compte de la zone non saturée et de la salinité. Calcul des intervalles de confiance. *Revue Hydrogéologie*. **4**, 325-336.
- Visser, A., Broers, H.P., van der Grift, B. and Bierkens, M.F.P. (2007). Demonstrating Trend Reversal of Groundwater Quality in Relation to Time of Recharge determined by  $3\text{H}/3\text{He}$ . *Environmental Pollution*. **148**, 797-807.