

Lecture session: G.3 (Harbours/Waterfronts)

## HYDRODYNAMIC CHARACTERISATION OF A GROUNDWATER-SURFACE WATER SYSTEM AND EVALUATION OF BTEX, PAHs DECAY AND HEAVY METAL FATE

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### INTRODUCTION

As many other industrialized regions in the World, the Walloon Region in Belgium, now has to face problems related to former heavy industrial activities, such as metallurgy and chemistry, that were and are still generally located nearby navigable rivers to facilitate transport operations of industrial manufacturing. This has resulted in the existence of numerous contaminated sites close to rivers and in relatively urbanised areas, posing a major risk of contaminant dispersion in the environment, particularly by possible migration to surface water through groundwater discharge. Because of that and in order to develop new economic activities in these areas, such sites often need detailed investigations aiming at defining the actual risk posed by the presence of contaminants and defining which remediation measures have to be taken. Referring to that, one of the first aspects to assess is to evaluate if natural attenuation processes are likely to contribute to reducing the level of risk. Natural attenuation in groundwater is only effective when contaminant degrading microorganisms are present and/or when hydrogeochemical conditions of the system are favourable. To evaluate this effectiveness, many site specific factors have to be considered, among which the dynamics of groundwater fluxes and groundwater – surface water interactions and biogeochemical processes.

In the scope of the EU FP6 Integrated Project AquaTerra, several advanced field and laboratory investigations were performed, including the characterisation and quantification of groundwater – surface water interactions, the assessment of benzene and PAH degradation by isotopic fractionation and the conditions under which bioprecipitation of heavy metals is likely to occur. Based on the detailed dataset obtained for the site, all the information is integrated to discuss the natural attenuation capacity of existing contaminants with respect to the risk of contamination of the neighbouring river by groundwater discharge.

## **FIELD SETTINGS**

The site of concern for this research is a brownfield of 7.3 ha corresponding to a former coke factory (Flémalle cokery site), on the North bank of the Meuse River, upstream of the city of Liège, in Belgium. The site was occupied by a coke and gaswork plant, from 1922 to 1984. At present, the site is dismantled and unused in an industrial environment where urban cores have developed around during the last century.

The aquifer is located in the alluvial gravel sediments deposited by the Meuse River on the low permeability shale and sandstone carboniferous substratum, from 7 m depth from the soil surface, with a mean saturated thickness of 8 m. Topography is very flat, the general groundwater flow direction is towards the Meuse River and the mean hydraulic gradient is low, with a value approximatively equal to 0.3 %. The brownfield is located close to the Meuse River, at a distance of 25 m.

The level of water in the river section corresponding to the brownfield is controlled by dams at around 59.4 meters a.s.l. (above sea level) in order to ensure navigation as well as to prevent floods downstream. However, river water level fluctuates continuously with amplitude varying from few centimetres in normal conditions to up to 2 meters during winter-spring seasons.

## **GROUNDWATER HYDRODYNAMICS CHARACTERISATION**

In order to improve the knowledge on the hydrodynamic and transport parameters of the gravel aquifer and to study the possible interaction between the Meuse River and the adjacent alluvial aquifer, detailed monitoring campaign of the groundwater level fluctuation was performed, as well as several pumping tests and tracer injections.

### **Groundwater – surface water interactions**

#### *Monitoring data*

The study of groundwater – river interactions needs detailed sets of data concerning both aquifer and river system, as well as rainfall series. Different sources of data were consulted to obtain records on the Meuse River level fluctuations (from an hydroelectric plant located in the opposite river bank in front of the site, where river level is recorded hourly) and rainfall (from a dam located 1 km upstream of the site, where rainfall is daily recorded). Detailed monitoring of groundwater level fluctuations was performed using pressiometric TrollLevel<sup>®</sup> probes at time step of 1 hour. Two pressiometric probes were permanently placed in observation wells located near and far along an orthogonal section to the river (wells U5 and U3). In addition, two more pressiometric probes were used at pairs of observation wells (near and far from the river) for short periods of time (1 month). Altogether 16 observation wells spatially distributed in the field were monitored during 2 years (Figure 1). An example of river-stage and groundwater hydrographs at selected characteristic observation wells, as well as daily rainfall, is presented in Figure 2.

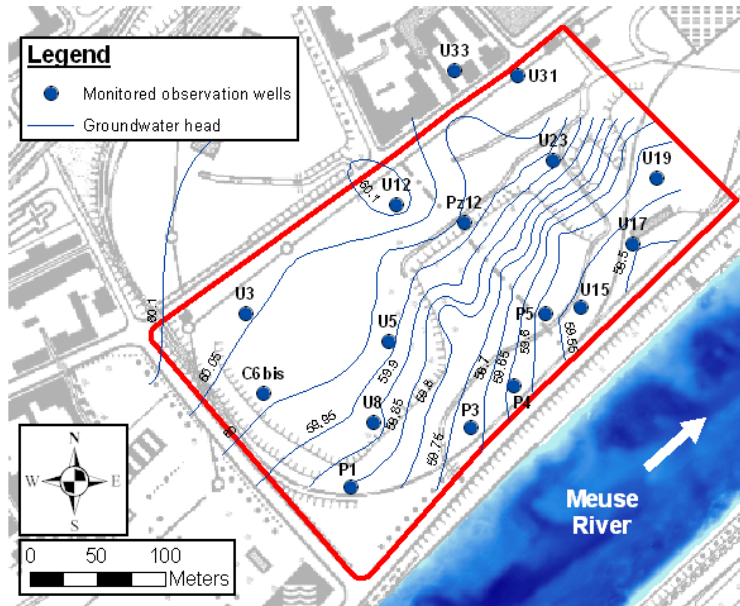


Figure 1. Location of 16 observation wells monitored with pressiometric probes TrollLevel®. Piezometric lines correspond to the monthly groundwater survey campaign performed in June 2005.

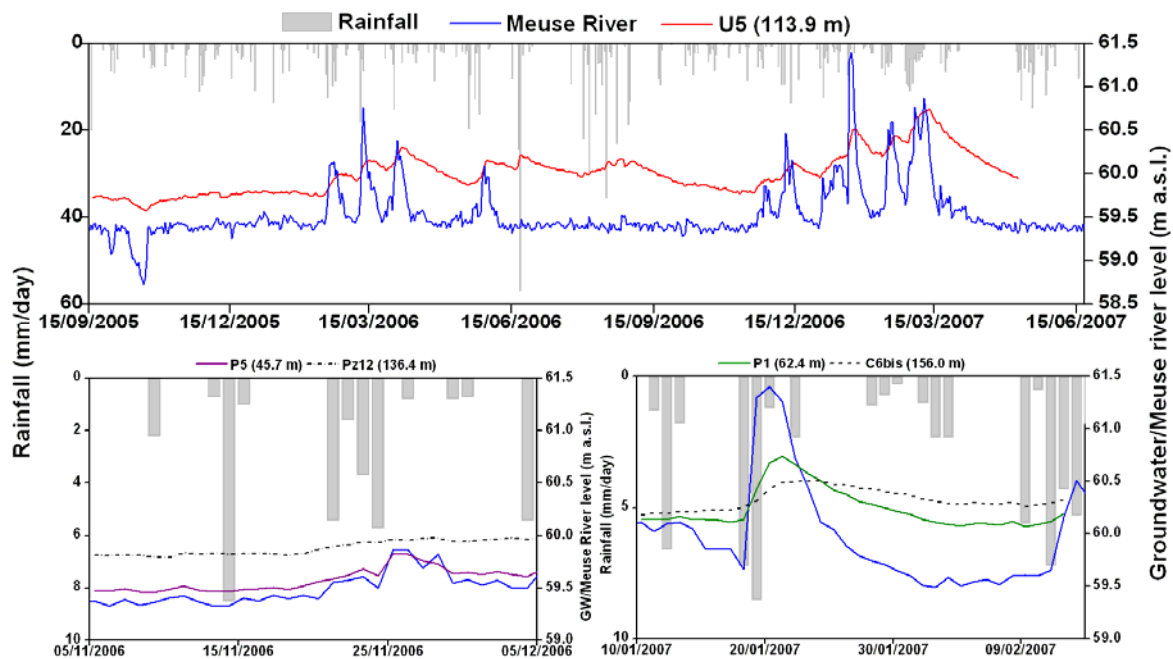


Figure 2. Fluctuations of ground- and surface water of the Meuse River and selected observation wells monitored from September 2005 to May 2007. Rainfall recorded 1-km upstream of the site is also depicted. Distances of the wells to the aquifer-river interface are indicated in brackets.

Because dams in the Meuse River are operated in function of observed/predicted rainfall, the effect of rainfall on the river water level is smoothed. From June to November 2006, important rainfalls were recorded, while water river level was permanently established at around 59.4 meters a.s.l. (above sea level). Contrary to this, from November 2006 to March 2007, no important rainfalls affected the region, while river level rose up to 2 meters from its normal level. In fact, groundwater levels fluctuate mostly in response to river-stage variations rather than to rainfall, causing frequent inversions of groundwater hydraulic gradient in the vicinity of the river essentially during winter and spring seasons.

## *Analysis of monitoring data*

Monitored groundwater head, river stage levels and rainfall were analysed applying cross-correlation time-series analysis. This technique not only relates the inputs and outputs of a system, but furthermore it aims to know the time-response between the input (river stage fluctuation and/or rainfall) and the output (groundwater level fluctuation) of the system. Cross-correlation analyses were performed with the BRGM TEMPO<sup>®</sup> software (Pinault, 2001), designed to treat and model hydrogeological and hydrogeochemical time series. Regression analysis between groundwater levels and river-stage was also done in order to compare and corroborate results of the cross-correlation analysis.

Cross-correlation coefficients (CCC) and coefficient of determination ( $R^2$ ) from regression analysis are in good agreement, with values for wells located nearby the river ranging between 0.8 and 0.98. As expected, CCC and  $R^2$  decrease as the distance to the river increase inland, while time lag response increases. This can be conceptualised in the form of a wave propagation into the aquifer, which amplitude is progressively attenuated and time lag increased (Jha *et al.*, 2004; Ha *et al.*, 2007). The same cross-correlation analysis shows that rainfall plays a secondary role in groundwater level fluctuations, with maximum CCC values of 0.3. The heterogeneity of the gravel aquifer highlighted within this analysis, since wells located at similar distances to the river presents significantly different time response.

## **Gravel aquifer properties**

Pumping tests were carried out in 6 piezometers close to the Meuse River. During each pumping test, between 7 and 10 observation wells/piezometers were monitored at different distances and depths. In the most contaminated zone of the site (source of the main organic pollutants) pumping tests were not carried out because of difficulties in managing polluted groundwater pumped from the aquifer. To get an idea of hydraulic conductivity values in this zone, 5 slug permeability tests were carried out. Estimated hydraulic conductivity ( $K$ ) values from pumping and slug tests range from  $1 \times 10^{-3}$  to  $5 \times 10^{-5}$  m s<sup>-1</sup>. Such values are lower than expected for an alluvial aquifer, and the spatial variability highlights the important heterogeneity of the aquifer. These values displayed a large uncertainty, attributed mainly to the fact that most of the observation wells are partially penetrating in the gravel aquifer, which may lead to an underestimation of  $K$  values (Alcolea *et al.*, 2007).

Radially converging flow and single-well tracer tests were carried out in order to 1) identify and quantify transport and retardation processes in the gravel aquifer and, 2) obtain estimates of groundwater flux at the border of the contaminated site close to the river. A semi-analytical solution considering homogeneous radially converging flow and transport conditions, using CATTI –Computer Aided Tracer Test Interpretation- (Sauty *et al.*, 1992), was applied to obtain values of effective porosity ( $\theta_m$ ) and longitudinal dispersivity ( $\alpha_L$ ).  $\theta_m$  ranged from 1.5 to 2.9 % and  $\alpha_L$  between 1.4 and 3.4 m, respectively. Although effective porosity is low, one has to remember that the analytical solution CATTI assumes a radially symmetric distribution of groundwater fluxes and effective velocities. Since the medium is very heterogeneous, the hypothesis of homogeneity may lead to erroneous estimation of groundwater fluxes. Longitudinal dispersion coefficient is low, as expected for gravels deposits.

Single-well tracer tests (Finite Volume Point Dilution Method, -FVPDM-) (Brouyère *et al.*, 2008) applied in the field have given Darcy fluxes from  $3 \times 10^{-6}$  to  $3 \times 10^{-4}$  m s<sup>-1</sup> from the North-West (well P1) to South-East (well U15). The calculated variability of Darcy fluxes is in good agreement with values obtained from the hydraulic gradient observed during monthly groundwater monitoring campaigns. These gradients are higher in the South-East (0.45 %) than the North-West (0.15 %).

## CONTAMINANTS BEHAVIOUR

Degradation of benzene and PAH was investigated using two different methods, measurement of carbon isotope ratios of these compounds in field samples and laboratory incubation studies with <sup>13</sup>C-labelled substances. The field method is based on the occurrence of shifts in the isotopic composition of organic compound during biodegradation because molecules with light isotopes degrade faster than molecules with heavy isotopes. The method is well adapted for small molecules such as BTEX. However, for PAH, the isotope discrimination by microorganisms is small and thus the method is not very sensitive to assess biodegradation. Therefore, for these compounds, laboratory incubation experiments were carried out as well.

### Organic pollutants

#### *Microcosm set up*

During the drilling campaign performed on March 2005, fresh sediment material was sampled for microcosm studies, directly filled into brown-glass bottles of 250 mL with teflon-sealed caps (Infochroma AG, Zug, Switzerland), cooled immediately, and stored at 5 °C until usage. Microcosms consisted of 25 g of sediment that was transferred into 50 mL-culture bottles (Ochs, Bovenden, Germany) working under an atmosphere of N<sub>2</sub> in a glove bag (Sigma-Aldrich, Buchs, Switzerland). Groundwater from the site was sterile filtrated using disposable syringe filters (0.22 µm; Schleicher & Schüll, Dassel, Germany) and diluted 5-fold with sterile nanopure water to result in concentrations of NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup> of 6 and 140 mg L<sup>-1</sup>, respectively. The diluted groundwater was purged with N<sub>2</sub> for 0.5 h to remove dissolved O<sub>2</sub> and was filled into 250 mL-glass bottles (Infochroma AG). Benzene, naphthalene, or acenaphthene labeled with <sup>13</sup>C at 6 positions (99 % purity; Cambridge Isotope Laboratories, Andover, MA) were added into these bottles. The microcosms, which contained 15 mL of the anoxic substrate solution, were incubated at a temperature of 16 °C. Details on these experiments were published previously (Morasch *et al.*, 2007).

Groundwater samples from 18 piezometers were analyzed for mono- and polyaromatic hydrocarbons (by SPME extraction and gas chromatography), and the stable carbon isotope ratios in the respective compounds (using a TRACE™ gas chromatograph (GC) coupled to an ThermoFinnigan™ Delta Plus XP isotope-ratio mass spectrometer (IRMS) via a ThermoFinnigan™ GC combustion III interface).

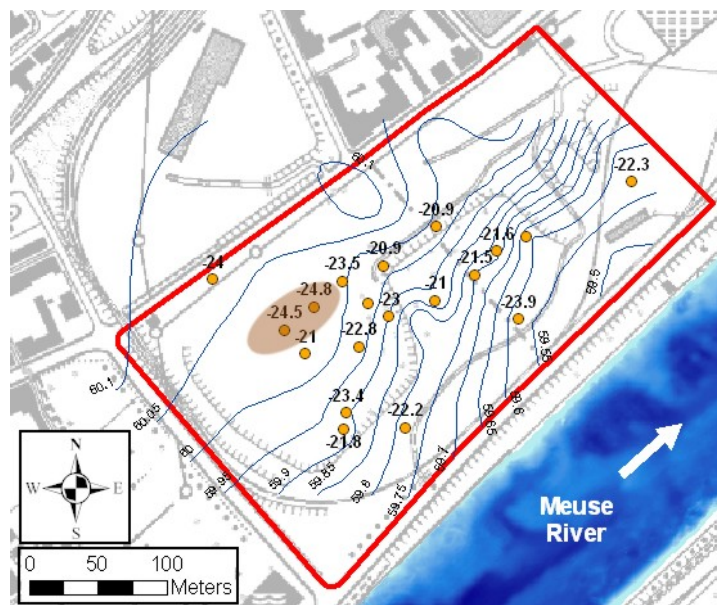
The carbon isotope ratios are reported relative to the VPDB standard using the δ-notation according to:

$$\delta^{13}\text{C}[\text{‰}] = \left( \frac{{}^{13}\text{C}_{\text{sample}} / {}^{12}\text{C}_{\text{sample}}}{{}^{13}\text{C}_{\text{reference}} / {}^{12}\text{C}_{\text{reference}}} - 1 \right) \times 1000$$

A shift in positive direction corresponds to an enrichment in  $^{13}\text{C}$ .

### *Stable isotope field data*

For benzene, toluene and naphthalene a significant enrichment in  $^{13}\text{C}$  could be detected along in the flow direction. These findings are direct evidence for microbial mineralization of aromatic hydrocarbons under in situ conditions. The  $\delta^{13}\text{C}$  of benzene increased by 3 ‰ between the source zone (-24.8 ‰) and piezometers further downgradient (mainly around -21.5 ‰) (Figure 3). Contaminant degradation at the field site was quantitatively assessed with the following equation:  $k = -\Delta\delta^{13}\text{C}/(\epsilon \times t)$ . Assuming a mean groundwater flow velocity of  $1.04 \times 10^{-5} \text{ m s}^{-1}$ , and taking an average isotope enrichment factor of  $\epsilon = -2.4 \text{ ‰}$  from the literature (Meckenstock *et al.*, 2004), a first-order rate constant  $k$  of 0.017/d was obtained corresponding to a half-life of 41 days. The half-life can also be expressed in terms of flow distance necessary for a mass reduction by a factor of two, which correspond in this case to 36m.



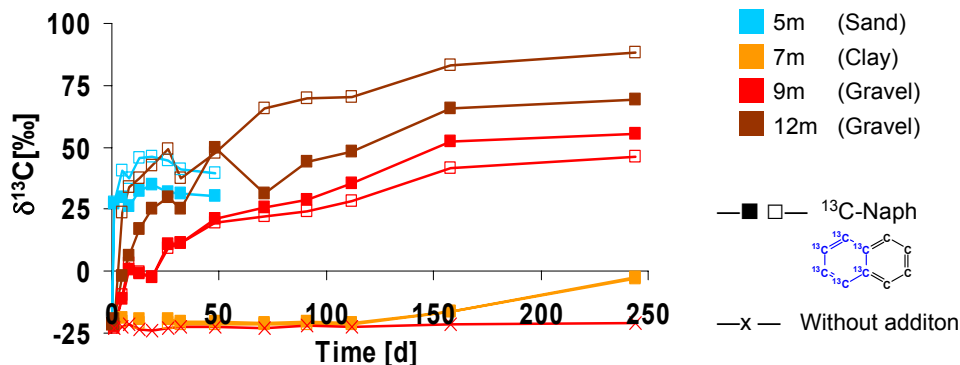
**Figure 3.  $\delta^{13}\text{C}$  isotope ratios of residual benzene in groundwater samples from the field site. The major source zone is highlighted in brown ellipse.**

To apply this quantitative evaluation of field stable isotope analysis, redox conditions and hydrology have to be well characterized, and the respective isotope enrichment factor  $\epsilon$  has to be available in a database.

### *$^{13}\text{C}$ -labelled compounds in microcosms*

By adding a  $^{13}\text{C}$ -labelled substrate into microcosm bottles, it was possible to prove mineralization of the compound of interest in the presence of other unknown organic substances of the sediment material based on the evolution of  $^{13}\text{C}\text{-CO}_2$ . This new approach provided evidence for the intrinsic biodegradation potential for benzene, naphthalene, and acenaphthene under oxic and under anoxic

conditions. In Figure 4, we illustrate the mineralization of  $^{13}\text{C}$ -naphthalene in microcosms with sediments from drilling location U13.



**Figure 4. Mineralization of  $^{13}\text{C}$ -labelled naphthalene in microcosm experiments with sediments from four different depth layers under in situ-like oxic (5 m) and anoxic (7 m, 9 m, 12 m) conditions.**

Using a mass balance for  $^{13}\text{C}$  and  $^{12}\text{C}$  in the microcosm bottles and assuming first-order kinetics, rate constants for  $^{13}\text{C}$ -labelled pollutants could be determined. The average rate constants  $k$  for benzene were 0.12/d and 0.06/d for microcosms with sediments from drilling location U13 under oxic and anoxic conditions, respectively. With increasing molecular size, rate constants were found to decrease significantly (0.005/d and 0.0005/d for naphthalene and acenaphthene in aerobic microcosms).

### *Comparison on field and laboratory approaches based on stable isotopes*

The rate constants obtained for anaerobic benzene degradation in microcosm experiments and by the field approach were in good agreement suggesting that both stable isotope-based methods might be useful and appropriate for the quantification of in situ contaminant degradation. The first order biodegradation rate were in the upper range or higher than values reported in previous studies which ranged from  $k = 0.01/\text{d}$  to  $k = 0.0001/\text{d}$  at different field sites with a mean value of  $k = 0.002/\text{d}$  (Chapelle *et al.*, 1996; Wiedemeier *et al.*, 1999; Suarez and Rifai, 2002). In sections of the field site of Flémalle which had small hydraulic gradient (South-East), flow velocities of  $2.3 \times 10^{-7} \text{ m s}^{-1}$  were reported, the corresponding first order rate constant for this scenario would be  $k = 0.0004/\text{d}$ .

## **Inorganic pollutants**

### *Sediment and groundwater sampling*

Groundwater and sediment were sampled between 8 and 12 m below ground in well U15 (Figure 1). Undisturbed sediment samples were collected with a dual tube sampling system with a core drilling device (Geoprobe<sup>®</sup>, USA), homogenized under nitrogen atmosphere, and both sediment and groundwater samples were analyzed for the parameters listed in Table 1.

**Table 1. Aquifer sediment and groundwater properties at well U15.**

	T(°C)	pH	Eh (mV)	DO ( $\mu\text{M O}_2$ )	DOC ( $\text{mg C L}^{-1}$ )	$\text{SO}_4^{2-}$ (mM)	$\text{NO}_3^-$ (mM)	Zn ( $\mu\text{M}$ )	Cd ( $\mu\text{M}$ )	As ( $\mu\text{M}$ )	Fe ( $\mu\text{M}$ )
<b>Groundwater</b>	12.9	7.66	187	0.02	68	4.38	<0.04	0.63	<0.04	<0.03	<0.04

	pH	Dry mater (%)	Organic matter (%)	TOC (%C dm)	Zn ( $\text{mg Kg}^{-1}\text{dm}^{-1}$ )	Cd ( $\text{mg kg}^{-1}\text{dm}^{-1}$ )	As ( $\text{mg kg}^{-1}\text{dm}^{-1}$ )	Fe ( $\text{mg kg}^{-1}\text{dm}^{-1}$ )	Total S ( $\text{mg kg}^{-1}\text{dm}^{-1}$ )
<b>Sediment</b>	7.6	8.32	11.8	8.7	255	<0.5	34	38500	7400

### *Microcosm set up*

Microcosms were set up, in an anaerobic chamber at 20 °C containing aquifer material (10 g) sampled and homogenized as described above. Groundwater (25 ml) was added to all vials under a nitrogen atmosphere. Three different terminal electron acceptors (TEA, e-acceptors) at four different concentrations were examined (sulphate and nitrate at 2, 5, 10 and 20 mM respectively, and oxygen at 0, 62, 125 and 250  $\mu\text{M}$ ). Acetate (3.5 mM) was used as carbon source (e-donor). Both the e-acceptor and e-donor were added from stock solutions to the vials in the anaerobic chamber. A natural attenuation condition (AG) and one abiotic control were set up as controls. In the abiotic control, 3.5 mM acetate, 20 mM sulphate and 20 mM nitrate were added in addition to formaldehyde (0.175%) to inhibit the bacterial activity.

### *Behaviour of heavy metals under different redox conditions*

Significant impact on the turnover of Zn caused by microbial life was observed. However, only in the presence of acetate, Zn was removed from the aqueous phase under all TEA conditions with an efficiency of more than 95%. If no acetate was supplied, oxygen as TEA resulted in the least efficient Zn removal from the aqueous phase (<50%) while for both nitrate and sulphate as TEA up to 95% Zn removal was observed. Cd behaved very similar to Zn and was removed from the aqueous phase efficiently under all biotic acetate containing conditions. Regarding As behaviour, it was released in most of the conditions (Table 2) (Vanbroekhoven *et al.*, 2007).

### *Microbial population*

Dissimilatory iron reducing bacteria (DIRB, detected by PCR targeting the 16S rRNA gene of the geobacteracea family) and sulphate reducing bacteria (SRB, detected by PCR targeting part of the dissimilatory sulphate –*dsr*- gene) were originally detected. Despite the different TEA added, SRB were detected in all samples. Only a few conditions showed negative results, i.e., no denitrifiers were detected in the microcosm containing a low concentration of  $\text{NO}_3^-$  without acetate. Also, no DIRBs were found for the oxic conditions without acetate.



**Table 2. TEA and metals (Zn, Cd and As) measured in the groundwater samples after 211 days in the microcosm tests containing aquifer sediment (AG = sediment aquifer and groundwater without additional compounds; low TEA = 62  $\mu\text{M}$   $\text{O}_2$  and 2 mM for nitrate and sulphate; high TEA = 250  $\mu\text{M}$   $\text{O}_2$ , 20 mM for nitrate and 15 mM sulphate).**

Conc TEA	Without acetate			With acetate		
	$\text{O}_2$ ( $\mu\text{M}$ )	$\text{NO}_3^-$ (mM)	$\text{SO}_4^{2-}$ (mM)	$\text{O}_2$ ( $\mu\text{M}$ )	$\text{NO}_3^-$ (mM)	$\text{SO}_4^{2-}$ (mM)
AG	33	0.04	4.00	33	0.04	0.01
Abiotic	nd	nd	Nd	213	22.43	19.00
Low TEA	35	0.84	5.00	31	0.01	0.01
High TEA	164	22.43	18.00	32	0.01	5.00
Zn ( $\mu\text{M}$ )	Without acetate			With acetate		
	$\text{O}_2$	$\text{NO}_3^-$	$\text{SO}_4^{2-}$	$\text{O}_2$	$\text{NO}_3^-$	$\text{SO}_4^{2-}$
AG		100.00			0.49	
Abiotic	nd	nd	nd		400.77	
Low TEA	245.38	164.00	102.35	0.88	0.86	0.29
High TEA	323-69	184.15	116.71	0.31	12.23	0.32
Cd ( $\mu\text{M}$ )	Without acetate			With acetate		
	$\text{O}_2$	$\text{NO}_3^-$	$\text{SO}_4^{2-}$	$\text{O}_2$	$\text{NO}_3^-$	$\text{SO}_4^{2-}$
AG		6.74			0.48	
Abiotic	nd	nd	nd		23.94	
Low TEA	14.06	11.08	7.73	0.32	0.46	0.04
High TEA	11.95	11.39	8.41	0.61	0.16	0.02
As ( $\mu\text{M}$ )	Without acetate			With acetate		
	$\text{O}_2$	$\text{NO}_3^-$	$\text{SO}_4^{2-}$	$\text{O}_2$	$\text{NO}_3^-$	$\text{SO}_4^{2-}$
AG		1.13			26.67	
Abiotic	nd	nd	nd		1.00	
Low TEA	1.61	1.83	0.92	30.67	29.33	0.49
High TEA	1.13	1.37	1.37	19.20	4.53	1.73

	release		$50 < \text{removal}\% < 90$
	$> 95\%$ removal		$< 50\%$ removal

## CONCLUSIONS AND PERSPECTIVES

Field experiments provided hydraulic conductivity and gradient values ranged from  $1 \times 10^{-3}$  to  $5 \times 10^{-5}$   $\text{m s}^{-1}$  and from 0.15 to 0.45% respectively, delineating an important spatial heterogeneity of the gravel aquifer. Furthermore, detailed groundwater level monitoring and correlation analysis (groundwater level, river level, precipitation) revealed a strong link between groundwater and river level. Inversion of hydraulic gradient was also observed and reported during winter – spring season.

Biodegradation of benzene and PAH was investigated and biodegradation quantified using a field and laboratory method based on stable isotope analysis. A good agreement between field and laboratory rates was observed. For benzene, a half-life distance of 36 m was derived from field isotope data for the anaerobic zone of the aquifer. Given that the river is about 180 m away from the source zone in flow direction a significant reduction of the benzene mass flux is expected before the river is reached. Furthermore, in downgradient parts of the plume biodegradation might be accelerated due the fluctuation of the water table leading to dissolution of oxygen from entrapped air bubbles and due to the infiltration of oxygen-rich river water. The laboratory incubations studies have demonstrated that biodegradation is more rapid under aerobic than anaerobic conditions as expected. For PAH, the

biodegradation rates are smaller. However, these compounds likely migrate at lower velocities due to retardation by sorption to organic matter increasing the time available for biodegradation.

Results obtained from metals microcosm laboratory studies should allow predicting metal impact on the Meuse River. DOC seemed to most efficiently affect Zn and Cd removal from the groundwater towards the solid aquifer phase despite the predominant TEA. Combining this information with data on the stability of sorbed or precipitated metals, a through insight into the transfer, mobility and behaviour of these inorganic pollutants in the long term should be attained.

In order to better evaluate contaminants fate in the aquifer with the dynamics of groundwater – surface water interactions at the border of the site and the evidenced spatial heterogeneity, numerical modelling of the Flémalle site is on the way.

## ACKNOWLEDGEMENTS

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