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FINAL SCIENTIFIC REPORT

Flux-based Risk Assessment of the impact of Contaminants on Water resources and ECOsystems

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Annexe 1

Copy of the Publications


ELSEVIER
Volume 409 Number 4 • 15 January 2011 • ISSN 0048-9697
Published in 24 issues each year
Science of the Total Environment
An International Journal for Scientific Research into the Environment and its Relationship with Humankind

Science of the Total Environment 409 (2011) 800–809

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Improving surface–subsurface water budgeting using high resolution satellite imagery applied on a brownfield

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ARTICLE INFO

Article history:
Received 25 June 2010
Received in revised form 28 October 2010
Accepted 29 October 2010
Available online 26 November 2010

Keywords:
Urban recharge modeling
Object-oriented classification
Remote sensing
Brownfields

ABSTRACT

The estimation of surface–subsurface water interactions is complex and highly variable in space and time. It is even more complex when it has to be estimated in urban areas, because of the complex patterns of the land-cover in these areas. In this research a modeling approach with integrated remote sensing analysis has been developed for estimating water fluxes in urban environments. The methodology was developed with the aim to simulate fluxes of contaminants from polluted sites. Groundwater pollution in urban environments is linked to patterns of land use and hence it is essential to characterize the land cover in a detail. An object-oriented classification approach applied on high-resolution satellite data has been adopted. To assign the image objects to one of the land-cover classes a multiple layer perceptron approach was adopted (Kappa of 0.86). Groundwater recharge has been simulated using the spatially distributed WetSpass model and the subsurface water flow using MODFLOW in order to identify and budget water fluxes. The developed methodology is applied to a brownfield case site in Vilvoorde, Brussels (Belgium). The obtained land use map has a strong impact on the groundwater recharge, resulting in a high spatial variability. Simulated groundwater fluxes from brownfield to the receiving River Zenne were independently verified by measurements and simulation of groundwater-surface water interaction based on thermal gradients in the river bed. It is concluded that in order to better quantify total fluxes of contaminants from brownfields in the groundwater, remote sensing imagery can be operationally integrated in a modeling procedure.

1. Introduction

Land use is one of the main factors affecting the hydrological cycle and the protection of groundwater systems, especially discharge and recharge areas are consequently highly dependent on it (Boeye and Verheyen, 1992; Pucci and Pope, 1995). The estimation of groundwater recharge is complex and it has been repeatedly shown to be highly variable in time and space due to variability and changes in land use and climate (de Vries and Simmers, 2002). Estimating urban recharge is even more difficult, and little research has been done on methodologies or for particular cities over the last decades (Erickson and Stefan, 2009). Most cities have many paths, car parks, compacted soils, driveways, and other low permeability surfaces that do not have any storm drainage associated with them. Very likely significant localised recharge occurs, but little or no evidence exists for this, and no data are available to quantify the amounts (Lerner, 2002).

In urban and industrial areas there are several pathways for groundwater recharge and they are more complex than in rural environments (Lerner, 2002) and are difficult to quantify (Alley et al., 2002). Studies on the hydrogeological effects of urbanization demonstrate that there are significant alterations to rates of recharge and permeability distributions. These alterations affect groundwater pollution and its remediation (Sharp et al., 2003). The water quality of a drainage basin and its receiving streams is related to the contribution from groundwater but also from surface runoff, which is strongly related to imperviousness. Increase in impervious cover and runoff therefore directly impacts the transport of nonpoint source pollutants including pathogens, nutrients, toxic contaminants, and sediment (Hurd and Civco, 2004).

Worldwide large environmental pollution is related to contaminated sites, which resulted from economical and industrial development during the 19th and 20th century. Three hundred thousand sites across the EU have been identified as definitely or potentially contaminated (European Environment Agency, 2007). Since a few decades policy makers and stakeholders have become more and more aware of the risk posed by these sites because some of those sites present direct public health hazards. In terms of preventive

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doi:10.1016/j.scitotenv.2010.10.055

groundwater protection, knowledge of the sources and behaviour of pollutants in groundwater is required for an assessment of the potential risks for aquatic ecosystems and human health (Osenbrück et al., 2007; Sun et al., 2006).

Groundwater pollution in urban environments is linked to patterns of land use (Foster, 2001) and sources of potential contamination in these environments are numerous and change frequently (Morris et al., 2006). Groundwater recharge is a key parameter for the determination of the inputs of pollution components toward a groundwater body.

Water resources and regional pollution studies require areal totals of recharge, which are difficult to obtain in urban settings (Lerner, 2002). To identify the sources of contamination in urban environments with great accuracy it is essential to characterize the land cover in a detailed way. The use of high resolution spatial information is then required, because of the complexity of the urban land use.

The goal of this research is to develop a methodology to simulate in a detailed way the surface–subsurface water fluxes using high resolution satellite data to obtain detailed information on land cover. The obtained land cover information will be used as information for the estimation of the groundwater recharge and groundwater flow. Once the surface and subsurface water fluxes are characterized they can be used to simulate the transport of the sources of groundwater pollution from e.g. brownfields. The method will be illustrated for a case study located in Vilvoorde–Machelen, Belgium. This study site is selected because it is heavily contaminated with Chlorinated Aliphatic Hydrocarbons (CAHs) and is a typical example of a large complex urban brownfield.

2. Methods

2.1. High-resolution land cover mapping

In order to produce detailed land cover information for the study site, a land cover map is produced from very high-resolution (VHR) imagery. Ikonos satellite data is used having 1 m resolution for the panchromatic band and 4 m resolution for the multispectral bands (blue, green, red and near infrared). Because high-resolution sensors like Ikonos have limited spectral resolution (only 4 bands), they do not allow distinguishing well between some types of land cover that are important in the context of hydrological modelling. Bare soil, for example, is often difficult to distinguish from certain types of artificial sealed surfaces (Thomas et al., 2003). Hence, to obtain accurate information on land cover an object-oriented classification approach has been adopted. This approach allows using next to spectral information, geometric, textural and contextual information, defined at the level of homogeneous image objects.

2.1.1. Image segmentation

The delineation of homogeneous land cover objects was performed using the region-growing segmentation algorithm introduced by Baatz and Schäpe (2000) as implemented in Definiens® image processing software (Definiens Imaging, 2004). This algorithm is based on region-merging and was chosen for its low sensitivity to texture, which is strongly present in VHR data (Carleer et al., 2003). Each pixel is first considered as a separate object. Those objects are then iteratively merged in pairs to form larger objects. The merging decision is based on three criteria: colour, smoothness and compactness. These criteria are combined in numerous ways to obtain varying output results. The combination of these criteria describe the similarity between adjacent image-objects. The pairs of objects with the smallest increase in variance are merged. The process terminates when the smallest increase is above a user-defined threshold, the scale parameter (van der Sande et al., 2003; Definiens Imaging, 2004). The heterogeneity tolerance affects the relative size of output polygons: the boundary between different types of land cover and the delineation of the different segments became worse by increasing the heterogeneity threshold. Hence, a scale parameter of 40 for the segmentation was used for the final classification because of the better overall accuracy obtained with this segmentation result after testing several thresholds.

For each image object a range of features is calculated: spectral, textural and morphological features. In this study 39 features were selected as input data for a classification, including band-specific spectral features at object level, direction-independent texture measures and shape-related features (Table 1).

2.1.2. Neural network classification

After the segmentation process, image objects need to be assigned to different land cover classes. Cluster separability analysis and visual interpretation of the image objects belonging to each cluster resulted in the selection of eight land cover categories for image classification: water, bare soil, meadow, mixed forest, grey urban surfaces, red roofs, bright roofs, and shadow as an extra image class. To assign the image objects to one of the eight selected classes a multiple layer perceptron (MLP) approach was adopted, using the NeuralWorks Predict® software. MLP classification is a preferred technique for non-parametric classification, because next to spectral data other kinds of data with non-normal class frequency distributions, like textural data, can be used as an input for the classification process. Especially in urban areas, the technique is known to produce accurate results (Van de Voorde et al., 2007).

The key to build a robust MLP is to collect many examples or records of input values and corresponding output values for training. The neural network uses this training data to determine a mathematical relationship between the input data and the output data. The different steps for a MLP classification are collecting and pre-

Table 1
The 39 features used in the study. NIR: Near InfraRed; GLCM: Grey Level Co-occurrence Matrix.

Spectral features	Textural features	Morphological features
Mean of panchromatic band	St. Dev. of panchromatic band	Area
Mean of blue band	St. Dev. of blue band	Roundness
Mean of green band	St. Dev. of green band	Compactness
Mean of red band	St. Dev. of red band	Shape index
Mean of NIR band	St. Dev. of NIR band	Length
Brightness	Homogeneity on panchromatic band	Width
Brightness of panchromatic band	Contrast on panchromatic band	Length/Width
Brightness of blue band	Dissimilarity on panchromatic band	Density
Brightness of green band	Entropy on panchromatic band	Rectangular fit
Brightness of red band	Angular second moment on pan. band	Elliptic fit
Brightness of NIR band	Max. Difference on panchromatic band	Asymmetry
	GLCM Mean on panchromatic band	Border Length
	GLCM St. Dev. on panchromatic band	Number of neigbourgs
	GLCM Correlation on panchromatic band	Distance to border

Table 2
Overview of the context-based rules in the order they were applied.

Object	Enclosed by	Assigned to
Red roofs	Grey urban surfaces	Grey urban surfaces
Bare soil	Grey urban surfaces	Grey urban surfaces
Grey urban surfaces	Bare soil	Bare soil
Grey urban surfaces	Bright roofs	Bright roofs
Bright roofs	Bare soil	Bare soil
Grass	Water	Water
Bare soil	Water	Water

processing training data, constructing and training the network, and finally testing and validating it based on a set of proper validation data. For training the MLP model, 100 samples were randomly selected for each land cover class based on visual interpretation of the imagery. In order to evaluate the accuracy of the classification model it was validated on an independent validation set containing about 50 randomly sampled image objects per land cover class.

2.1.3. Post-classification Shadow Removal

Especially in urban areas, shadows caused by strong variations in elevation of buildings and trees affect the available information from remote sensing of land cover because all areas covered by shadow show similar spectral values, regardless the surface found underneath the shadow (Bianchin and Bravin, 2003). Thus large areas with useful information are lost because they are hidden by shadows. When they are not taken into account in the initial classification phase, shadowed areas are often classified as water or dark artificial surfaces. A separate class for shadow was therefore defined in our classification scheme (Dare, 2005; Van de Voorde et al., 2007; De Roeck et al., 2009). De Roeck et al. (2009) improved the overall accuracy of the land cover classification with an increase of the percentage correctly classified pixels (PCC) with 6% by using this post-classification shadow removal technique.

To reassign shadow objects to one of the seven land cover classes we made use of simple context-based rules. Every shadow object was reassigned to the land cover class of one of its neighbouring image objects according to the proportion of its border that is shared with the neighbouring objects. After trial and error, the proportion was set to 0.4 for the land cover classes bare soil, forest and water, to 0.35 for the class meadow, and to 0.3 for the class grey urban surfaces. We assumed that no shadow occurs on red or bright roofs because of their height, so the shadow objects that shared borders with those classes were reassigned to grey urban surfaces, because most of the time the red and bright roofs are surrounded by roads or grey artificial sealed surfaces. In this way every shadow object was attributed to one of the target land cover classes. The accuracy of the post-classification shadow removal was assessed with an independent validation data set containing 400 randomly sampled image objects.

2.1.4. Rule-based classification enhancement

Image objects can be misclassified due to spectral confusion between various urban surface types such as grey urban areas and bare soil. A set of context-based rules were designed to solve these problems of spectral confusion. Each rule assigns wrongly labelled objects to another land cover class, depending on the spatial context of the image object, like inclusion. Table 2 shows the seven context-based rules in the order they were applied on the image objects of the study area. All the rules change an object's label into the label of the region that completely surrounds it.

2.2. Recharge simulation

Groundwater recharge has strong spatial and temporal variability but is not directly measurable. Developments in GIS, remote sensing and availability of spatially variable land cover and soil data offer chances for a simulation approach. Such an approach can take into account the influence of the spatial variability of soil texture, land cover, slope and meteorological conditions, and hence improves the spatially distributed estimation of recharge. This will allow a better understanding of recharge–discharge systems, and leads to a more accurate calibration of groundwater flow models. It also will ensure a better management of groundwater quantity and quality.

The methodology used for the simulation of the recharge in this study is based on the spatially distributed seasonal WetSpass simulation model (Batelaan and De Smedt, 2007). WetSpass integrates a water balance in a geographical information system and simulates the temporal average and spatial differences of surface runoff, actual evapotranspiration, and groundwater recharge. The model treats a region as a regular pattern of raster cells, where every raster cell is further sub-divided in a vegetated, bare soil, open water and impervious surface fraction, for which independent water balances are maintained. The different processes in each cell are simulated seasonally. Since evapotranspiration from shallow groundwater can be significant, the position of the water table is taken into account in the estimation of the recharge. Therefore, WetSpass is iteratively connected to a groundwater model, which provides the position of the water table, while WetSpass returns a recharge estimate accordingly. The groundwater flow model is developed using MODFLOW (Harbaugh et al., 2000).

To use the obtained land cover map as an input for the WetSpass model the seven used land cover classes were combined to five classes; built-up or impervious (containing red roofs, bright roofs and grey surfaces), open water, bare soil, grassland and forest.

For validation of the groundwater flow model, use was made of estimates of groundwater discharges into a receiving river based on measured thermal gradients in the riverbed (Constantz, 2008). Given the fact that deeper groundwater temperatures are relatively stable throughout the year and stream temperatures vary on a seasonal and daily basis, heat can be used as a surrogate for hydraulic head measurements. Vertical fluxes of groundwater cause disturbances of the temperature–depth profile in a river bed permitting water temperature to be used as a tracer for vertical fluxes. A 1D vertical heat transport model (Anibas et al., 2009) as part of the STRIVE (Stream RIVer Ecosystem) (Buis et al., 2008) model was applied to calculate point estimates of the vertical groundwater flux.

3. Case study: the Vilvoorde–Machelen brownfield

3.1. Study area

This integrated methodology has been applied on a well-known Belgian brownfield. Several contaminated sources have been identified in this study area and the authorities aim to manage the complex plumes by reducing the flux of contaminants, which flow towards a receiving water body. The study area, the industrial area Vilvoorde–Machelen, is located about 10 km north-east of Brussels, Belgium (Fig. 1) and comprises 10 km^2. It is located in the Zenne catchment (about 600 km^2). The site lies between the Brussels–Scheldt Maritime Canal and the Zenne River on the west, which flows in NW direction, the R22 road on the east and the Trawool River on the north. The topography ranges from 10 to 50 m, with an average value of 16 m above sea level and with a mean slope of 1.3%. The dominant soil type is silty loam, in the northeastern part some clay-loam occurs. The average precipitation is 358 mm/y in the winter and 377 mm/y in summer (Dupriez and Sneyers, 1978,1979).

The long industrial history of the area has led to complex patterns of pollution from multiple sources. The Vilvoorde area has been a major industrial site since the completion of the first railroad on the European continent in 1835 until the 1960's, with considerable chemical activity. Due to more than a century of industrialisation the site has been polluted to the extent that in general individual plumes are not definable anymore. Field investigations on the study area indicate the presence of an extensive regional contaminant plume, which contains a mixture of BTEX (benzene, toluene, ethylbenzene and xylene), Polycyclic Aromatic Hydrocarbons (PAH) and Chlorinated Aliphatic Hydrocarbons (CAH). The detected contaminant plume covers an area of at least 72 ha (plume dimensions are 1.2 by 0.6 km) (Bronders et al., 2007). Fig. 2 presents 4 well-known contaminated sources in the study area (Malcorps, 2002; OVAM, 2003-2006).

Source area 1 is characterized by the presence of a LNAPL (light non-aqueous phase liquid) pool. At source area 2 and 3, both LNAPL (BTEX) and DNAPL (dense non-aqueous phase liquid) pure product were

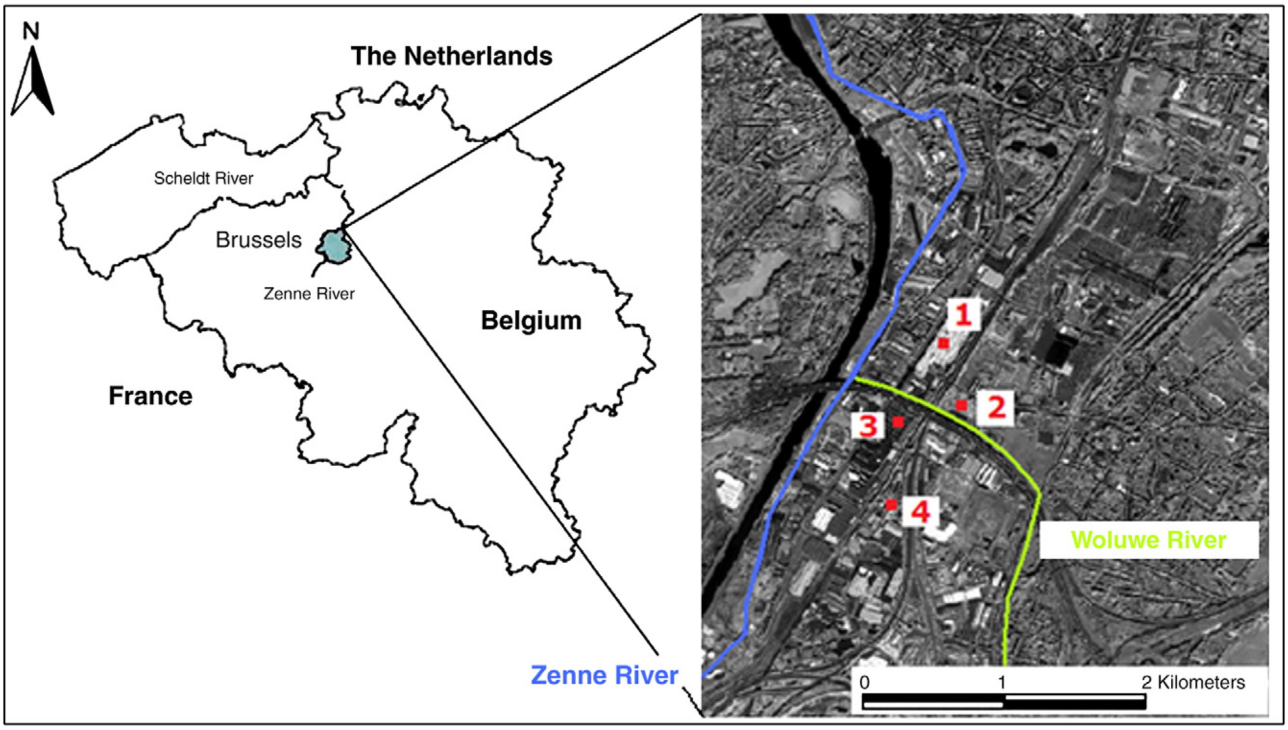

Fig. 1. Study area with the geographical position of the four major (known) contaminated sources.

identified. Source area 4 only contains high concentrations of DNAPL. Besides these identified sources several other volatile organic hydrocarbon (VOC) plumes were identified. However, no clear indication of the source zones could be given for these plumes (Bronders et al., 2007).

Geologically, the area is formed by an accumulation of several marine sand deposits. The top of the Tertiary clay-rich Kortrijk Formation is taken as the lower boundary of the hydrogeological model because of its low conductivity. It is overlain by a 25 m thick deposit of silty, glauconite-containing fine sands, known as the Tielt Formation (TiEg). The wedge-shaped Ghent Formation only appears in the northern part of the study area. It was deposited in a shallow gulf, whose southern edge roughly coincided with the location of the Woluwe River (Fig. 1). The Formation consists at the bottom of clay-containing silty sand (GeMe), followed by densely packed sand (GePi) and has a local thickness of about 4 m. The formation also contains glauconite. The lime and glauconite-containing sandy hills bordering

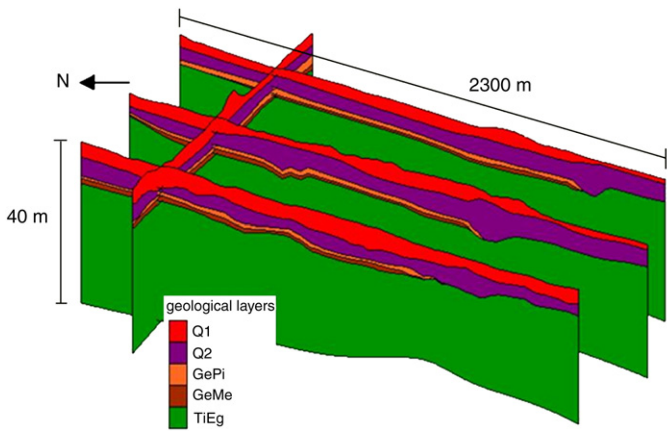

Fig. 2. N–S and E–W hydrogeological cross-sections of the subsurface of the study area (Q1: silty eolian sands; Q2: gravel; GePi –GeMe: Ghent Formation; TiEg: Tielt Formation).

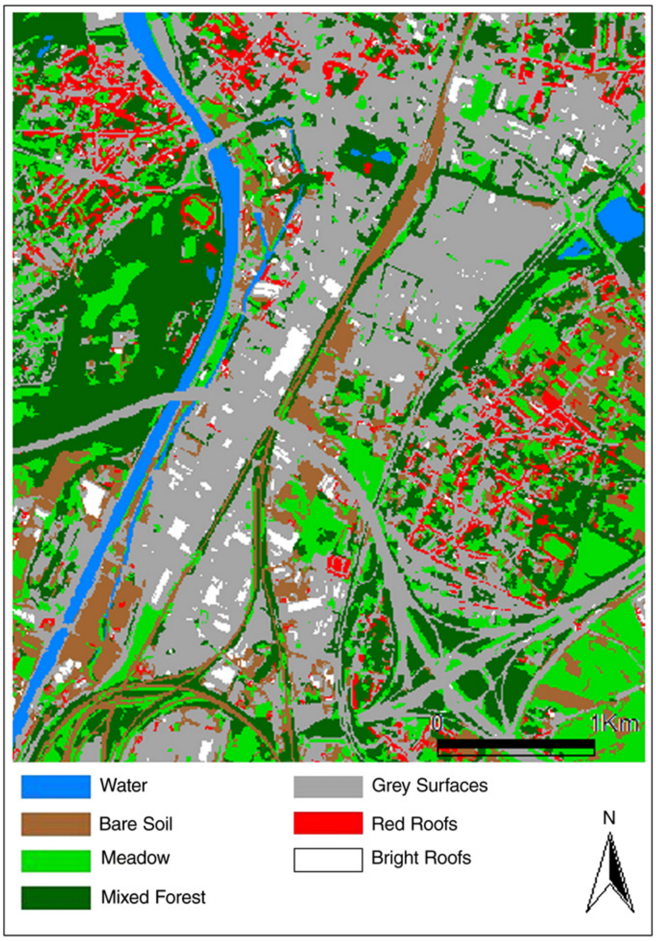

Fig. 3. Land-cover map of the study area obtained from the object-oriented classification approach of the 1 m resolution Ikonos image (2003).

the Zenne valley are deposits of the Brussels Formation, which do not occur in the valley itself.

During the Pleistocene, ice ages caused the sea level to drop as far as 130 m below the current level. Due to its steeper inclination, the Zenne River changed into a braided river. The resulting high stream gradient accelerated the erosion process. As a consequence, the Zenne River cut itself into and eroded the Brussels Formation, hereby creating the Zenne valley. The hills adjacent to the valley indicate the original relief. The sediments deposited by the braided river consist of gravel in a silty sand matrix, with a clay-containing organic base (Q2), having a thickness varying between 3 and 10 m. They are covered by fine, silty eolian sands (Q1), deposited by a permanent northern wind regime during the glacial periods (thickness between 2 and 12 m).

3.2. Groundwater modelling

The groundwater flow in the study area is in north–northwestern direction and is drained by the River Zenne, which is the main receptor of the pollutants. A steady-state groundwater model of the study area was developed by Touchant et al. (2007) to understand better the flow direction of the pollutants. The hydrogeological concept of this model was relatively simple because of limited geological information. A second model with an adaptation of the hydrogeological concept was created with the aim to obtain more accurate information on the groundwater flow and fluxes in the study area. Therefore the hydrostratigraphy was refined by interpreting new borehole loggings (68 instead of 16 boreholes used in the first model) and 179 cone penetration tests, available from the Geological Database for the Subsoil of Flanders (DOV, 2008). The interpreted data were imported in GMS Groundwater Modelling System 6.0. Fig. 2 shows a N–S and E–W hydrogeological cross-section of the subsurface of the study area.

Distributed recharge for the groundwater model is acquired from the described WetSpass methodology. Averages of measured groundwater level records for the period (1999–2006) were used for the calibration of the groundwater model. Continuously measured temperatures at three points in depth from three locations along the Zenne River were used as input for heat modelling for estimation of vertical groundwater fluxes to the river. With STRIVE we performed transient simulations based on Lapham's (1989) analytical solution of the vertical conductive and advective transport of heat and water. The model uses the measured river temperature and a constant groundwater temperature as boundary conditions, whereas the time series of a temperature-depth profile are used to calibrate the model over periods of one week or one month. This leads to results of vertical fluxes integrated over the simulation time. The median value of these simulations covering the time between April and November 2006 was used to validate the results of the MODFLOW model.

Remediation or contaminant containment efforts will be dependent on a proper understanding of the three-dimensional groundwater flow in the study area but also on the behaviour of the contaminants. In first instance is therefore advective transport simulated using the groundwater flow model, and flow paths and travel times by use of particle tracking in MODPATH (Pollock, 1994). The particle tracking analyses provide insight in the potential transport of pollutants from the four identified severely polluted sources towards the Zenne River.

Table 3
Error matrix for the classification before shadow removal and rule-based classification enhancement; b: Error matrix for the classification after shadow removal and rule-based classification enhancement.

			Reference Data								
		Water	Bare Soil	Meadow	Forest	Grey Surfaces	Red Roofs	Bright Roofs	Shadow	Total	U.A. (%)
a											
Land cover map	Water	28	1	0	0	6	0	0	8	43	65
	Bare Soil	0	34	2	1	7	4	1	0	49	69
	Meadow	0	8	52	3	1	0	1	1	66	79
	Forest	0	0	4	54	1	0	0	7	66	82
	Grey Surfaces	0	9	4	2	57	0	0	4	76	75
	Red Roofs	0	2	0	1	5	41	0	0	49	84
	Bright Roofs	0	0	0	0	0	0	49	0	49	100
	Shadow	4	0	4	5	6	0	0	30	49	61
	Total	32	54	66	66	83	45	51	50	447	
	P.A. (%)	88	63	79	82	69	91	96	60		
										OCC:	77%
										kappa:	0.73

		Water	Bare Soil	Meadow	Forest	Grey Surfaces	Red Roofs	Bright Roofs	Total	U.A. (%)
b										
Land cover map	Water	31	0	0	0	0	0	0	31	100
	Bare Soil	0	46	3	1	9	1	0	60	77
	Meadow	1	8	58	4	2	4	0	77	75
	Forest	0	0	6	86	2	1	0	95	91
	Grey Surfaces	1	4	3	2	84	2	0	96	88
	Red Roofs	0	0	0	0	0	37	0	37	100
	Bright Roofs	0	0	0	0	0	0	51	51	100
	Total	33	58	70	93	97	45	51	447	
	P.A. (%)	94	79	83	92	87	82	100		
									OCC:	88%
									kappa:	0.86

4. Results

4.1. High-resolution land cover mapping

In order to produce detailed land-cover information for the Vilvoorde study site, a land-cover map has been produced from a VHR Ikonos imagery (05/08/2003 and 04/09/2003). The obtained land-cover map is shown in Fig. 3. 47% of the area is covered by impervious surfaces (40% grey surfaces, 5% red roofs and 2% bright roofs). The second most present land-cover class is forest with 23% of the study area, followed by grass (15%) and bare soil (10%). Finally, water covers 5% of the study area.

The accuracy of the object-oriented classification, assessed with an independent validation data set but before shadow removal and rule-based classification enhancement, is presented in Table 3a. The percentage of correctly classified image objects is 77%. The kappa index of agreement is a measure of the overall classification accuracy and resulted in a value of 0.73. The producer's accuracy (PA) of the shadow objects (Table 3a) is rather low (60 percent) because quite some shadow objects from the validation set were assigned to other land cover classes such as water or forest. The confusion matrix shows also that shifts occur from one class to another caused by spectral confusion, especially from grey surfaces to bare soil.

Despite relatively high classification accuracy, some problems still occur. The presence of shadow causes a lack of information on land cover (17% of all the image objects are shadow objects), some image objects are wrongly classified due to spectral confusion and a salt-and-pepper effect appears on some parts of the classified image. The shadow objects are removed by reclassifying them with help of a shadow post-classification rule-set. In order to evaluate the accuracy of the shadow post-classification rules, it was validated on a randomly sampled set of 400 image objects. The percentage of correctly classified shadow objects is 81%. The kappa index of agreement resulted in a value of 0.71.To improve the classification accuracy and to remove salt-and-pepper effect, context-based rules have been applied to the original classification. Table 3b illustrates the confusion matrix for the land cover map after shadow removal and rule-based classification enhancement. Using the same validation set as before and the use of the post-classification rules, we obtained an overall classification accuracy of 88% and a kappa index of 0.86.

4.2. Recharge simulation

The resulting yearly groundwater recharge map obtained from the WetSpass simulation is presented in Fig. 4. The recharge ranges from 0 to 350 mm/y, with an average value of 159 mm/y and a standard deviation of 91 mm/y.

In order to analyze the influence of the land cover on groundwater recharge, the average recharge has been determined for each land cover class. Fig. 5 presents the average yearly groundwater recharge and its standard deviation as a function of land cover in the study area.

From Fig. 5 it is clear that the groundwater recharge depends strongly on land cover. The highest recharge values occur in the forested areas (275 ± 20 mm/y), followed by bare soil (230 ± 25 mm/y) and grassland (215 ± 30 mm/y). In Table 4 the average recharge values are presented for winter and summer season for the different land cover classes. The total average recharge in winter is 159 ± 85 mm/y and in summer 0 ± 20 mm/y.

4.3. Groundwater modelling

The model was calibrated using observed heads from 27 piezometers. The average error between the simulated and observed heads is 0.02 m, the average absolute error is 0.25 m and the root mean square error is 0.31 m.

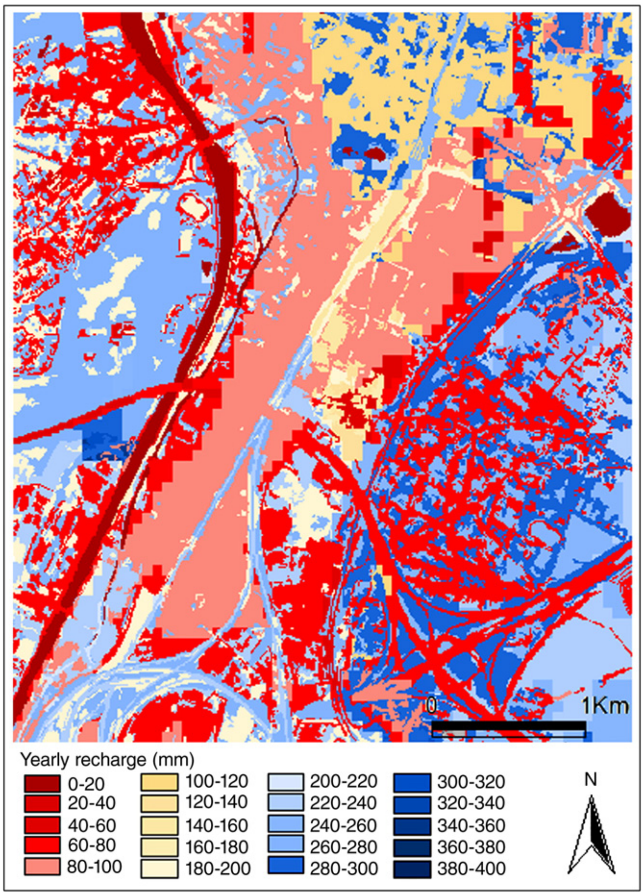

Fig. 4. Yearly simulated recharge map (mm) of the study area using the WetSpass model.

The validation of the steady-state groundwater model was performed via heat transport modelling, representing an independent estimate of the groundwater fluxes. Results of 75 simulations of one week covering data from April 2006 as well as October–November 2006 show a median groundwater discharge in the River Zenne of −34 mm/d. This median point estimate is compared with the simulated flux of −35 mm/d of the respective 50 by 50 m cell of the groundwater model. The small difference shows the good agreement between the measured and simulated groundwater fluxes to the receiving river.

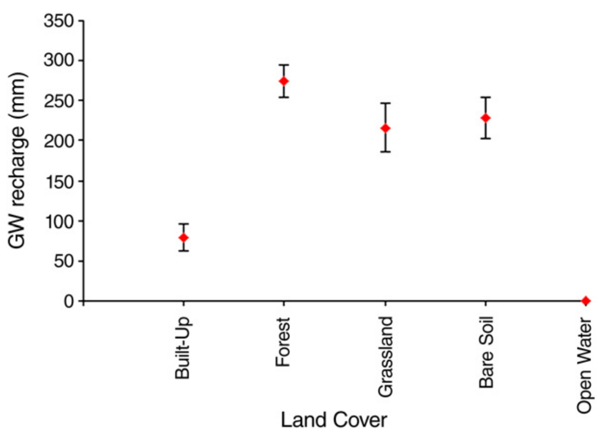

Fig. 5. Average yearly groundwater recharge (mm) with its standard deviation in function of the land cover.

Table 4
Simulated average recharge values (mm) and their standard deviation in winter and summer season for different object-oriented classified land cover classes for the Vilvoorde study area.

Land cover	Surface area (10^{-3} km²)	% Surface area	Average groundwater recharge in winter ± Std.dev.(mm)	Average groundwater recharge in summer ± Std.dev. (mm)
Built-up	5171	48	82 ± 15	−4 ± 5
Forest	2545	23	249 ± 14	26 ± 7
Grassland	1706	16	243 ± 8	−27 ± 25
Bare soil	1107	10	227 ± 22	1 ± 10
Open water	325	3	0 ± 0	0 ± 0
TOTAL	10854	100,00	159	0

Fig. 6a presents the simulated hydraulic heads for the upper geological layer. The highest heads (14.5 meter) occur in the south-western part of the study area, while the lowest heads occur in the north-eastern part (9.5 m).

Because of the high hydraulic conductivity of the upper three geological layers (Q1: silty eolian sands; Q2: gravel; GePi: Ghent Formation-Pittem Member) small hydraulic gradients are observed in these layers. The lower laying Member from Merelbeke (GeMe), which consists of clay-containing silty sand, has a lower conductivity. The layer is only present in the northern part of the model area where it forms a semi-confining layer between the Ghent and Tielt Formation.

Fig. 6b presents the simulated groundwater flow directions in the upper geological layer Q1. In the white zones in the figure the upper geological layer is absent. All flow vectors have the same length, and the colour of the arrows represent the flow fluxes. Most of the arrows are dark blue, what means that they are characterized by fluxes between 0 and 20 m^3/d. Just a few of the arrows from the north-western and western part of the study area have a higher flux varying from 30 to 60 m^3/d. The general groundwater flow direction is oriented to the north-western part of the study area, while in the western part the groundwater flow is oriented towards the east because of the draining influence of the Zenne River.

Particle tracking was used to find the flow paths starting at the contaminant source sites, the location of the receptor and to determine the time it takes to flow from the polluted site towards the receptor. Forward tracking was applied for the four contaminant sites (Fig. 7), Fig. 7b shows additionally the downward flux through the upper layer. The white zones in this figure are characterized by upward fluxes.

The advective transport of the pollutants from the polluted sites 1, 3 and 4 is similar, i.e. they infiltrate with the precipitation into the gravel layer, in which they are transported horizontally until the plume reaches the Zenne River. Assuming that the pollutants move purely by advection they will not reach lower geological layers, and will only affect the upper layers Q1 (eolian silty sands) and Q2 (gravels). The pollutants of site 1 will reach the Zenne after 10 to 16 years, for site 3 and 4 is this respectively 6 to 17 years and 8 to 11 years.

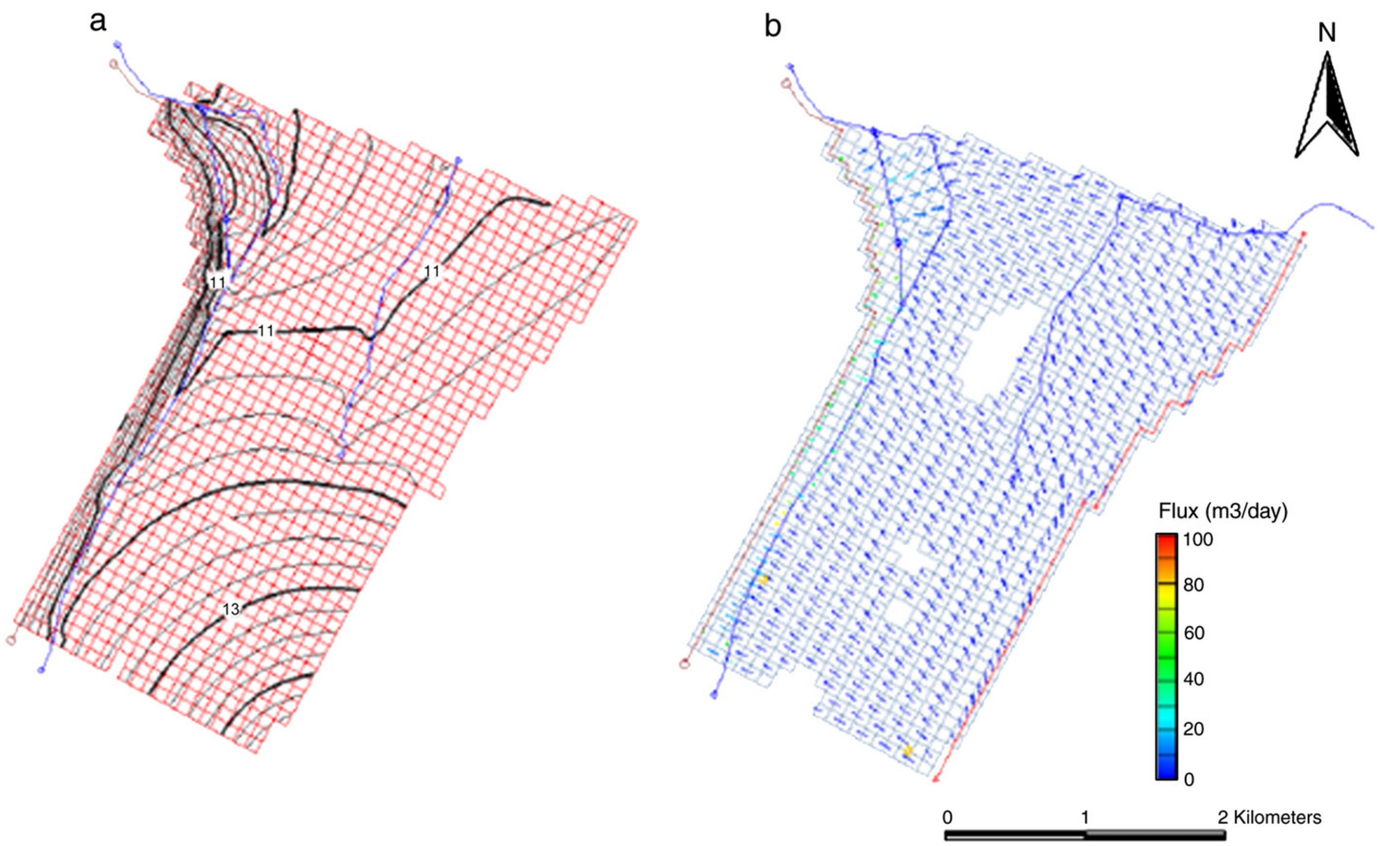

Fig. 6. a: Simulated hydraulic heads for the upper geological layer Q1 (Q1: silty eolian sands) indicated as isohypses (in m); b: Simulated groundwater flow directions and fluxes for the upper geological layer Q1 (silty eolian sands).

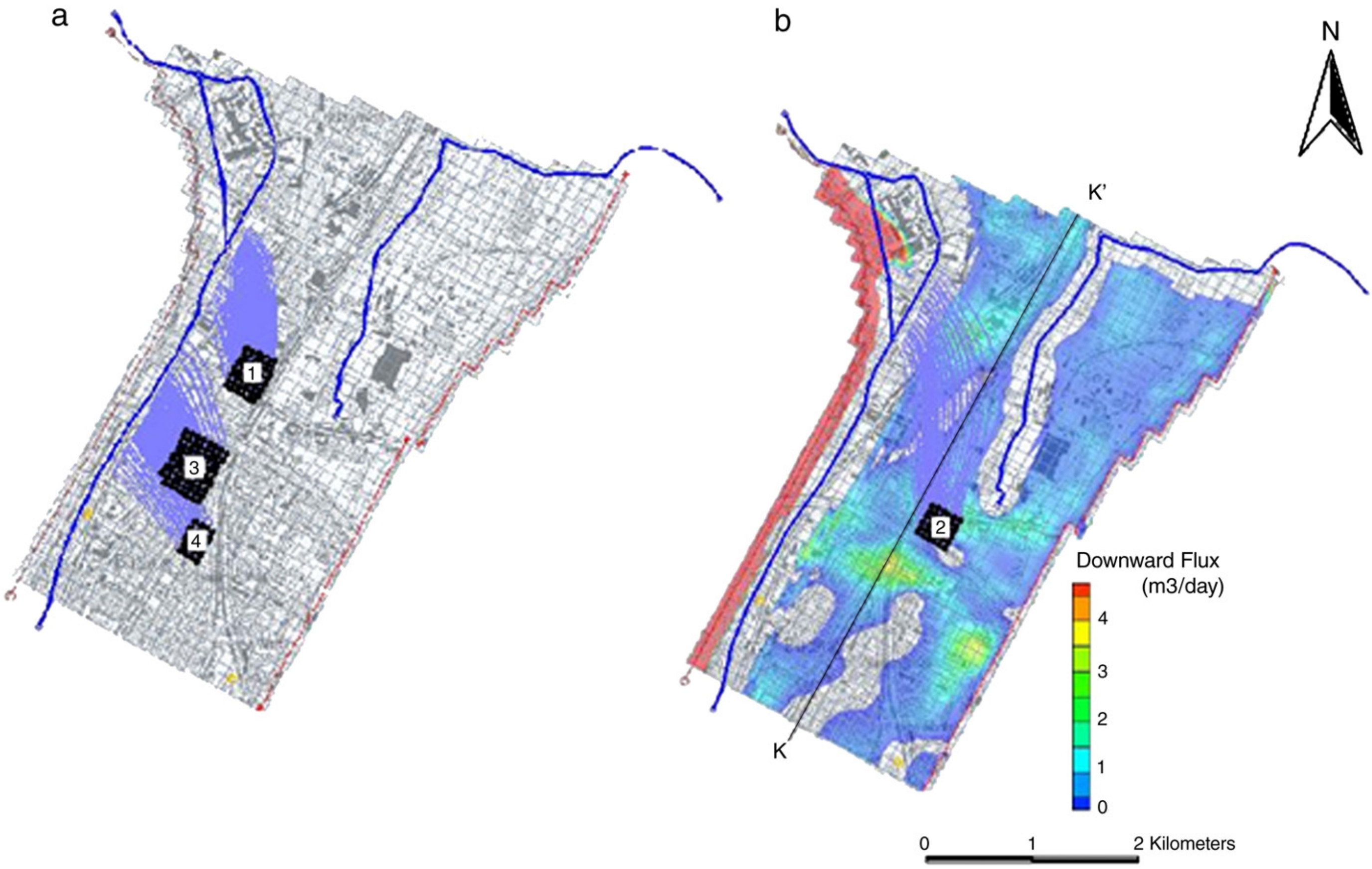

Fig. 7. a: Spread of contaminants by pure advective flow as simulated by particle tracking from the polluted sites 1, 3 and 4. b: Flow paths from contaminant site 2; on background downward fluxes in first layer; line KK' indicates the position of the vertical cross-section shown in Fig. 8.

The pollutants of site 2 take a much longer flow path and have a flow time of 15 to 45 years. Fig. 8 shows that the contaminants are moving downwards through the gravel layer Q2 and the Ghent Formation (GePi–GeMe) reaching the Tielt Formation (TiEg). In this case the lower geological layers are affected by the pollutants.

In all of the cases it can be concluded that the Zenne River is the final receptor of the pollution.

5. Discussion

The different outputs of the WetSpass simulation, surface runoff (not presented) and groundwater recharge, show a strong spatial distribution over the area. They clearly demonstrate the importance of having access to detailed information on land-cover types, especially on the distribution of impervious surfaces. These surfaces appear to have a determining impact on the surface runoff and groundwater recharge and are hence indispensible for obtaining reliable estimates of the urban recharge. Figs. 4, 5 and Table 4 reaffirm this strong spatial distribution of recharge over the area. The average recharge of 159 mm/y is considerably lower than the 220 mm/y being the average for the whole of Flanders as determined for the Flemish Groundwater Model using the same methodology but with less detailed land-cover data (Meyus et al., 2004). Also the model created by Touchant et al. (2007) used the average of 220 mm/y as recharge for whole the study

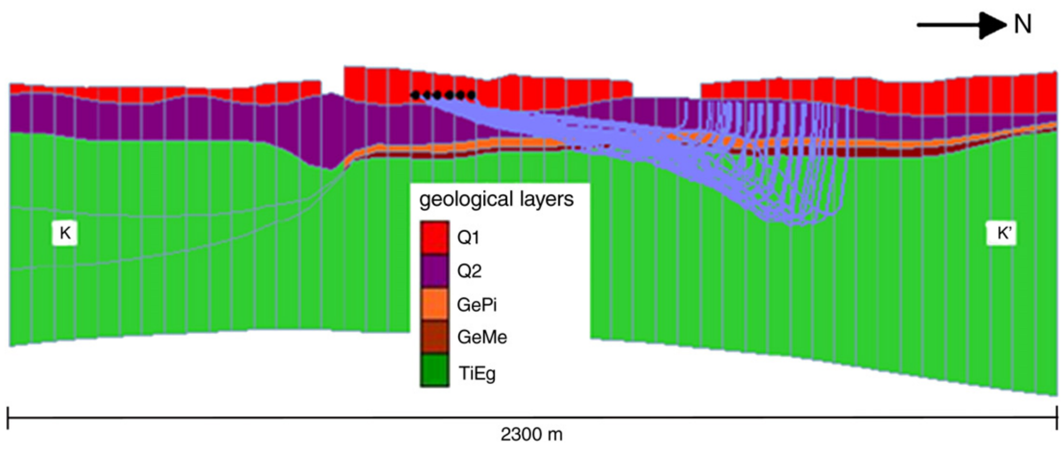

Fig. 8. Vertical cross-section of the flow paths and spread of contaminants by pure advective flow from the polluted site 2.

area. In their methodology no spatial variation of impervious areas was taken into account in the groundwater recharge simulation, and thus also in the transport of the contaminants from the polluted site. In the here presented approach the spatial variation in recharge as dependent on the type of land-cover is taken into account in the simulation of transport of the contaminants. Since there is no other flux of water than the recharge, which takes the contaminants along, this is an essential improvement.

Fig. 7 shows that the model area can be divided into two zones. From the particle tracking it can be concluded that most of the infiltrating rainwater does not reach the underlying aquifer and that hence the majority of groundwater flow occurs in the upper layer. The infiltrating rainwater moves through the gravel (Q2) and the advective transport of pollutants will therefore mainly be contained in this gravel layer. The water that infiltrates in the south-eastern part of the study area is characterized by much longer flow paths. Moreover, this infiltrating water flows over a considerable distance along areas with a downward flowing trend. This makes the infiltrating water flow into the Tielt Formation, hereby also contaminating the deeper layers. It is important to realize that the here presented spread of the contaminants should be regarded as a minimum since no account was taken of hydrodynamic dispersion of the contaminants.

The deeper regional groundwater flow is mainly through the Tielt Formation. It only comes in contact with the upper layers when there is discharge to a draining watercourse. This natural separation provides an initial protection against the penetration of advective pollutants. In the northern part of the study area, where the Gent Formation is present, a limited protection of the underlying Gent Formation is ensured by the clay rich Member of Merelbeke, characterized by a low conductivity. The penetration of any DNAPL (Dense Non Aquaous Phase Liquid) to the Tielt Formation will therefore be limited. Since this Member of Merelbeke does not occur in the southern part of the study area, the presence of any DNAPL will have a much higher risk.

6. Conclusions

The goal of this research was to develop a methodology to simulate surface–subsurface water fluxes in complex urban environments using high resolution satellite data. High resolution satellite data was needed to obtain detailed information on land cover in urban areas. The obtained land cover information was used as input to determine the groundwater recharge and flow. Once the flow and fluxes have been characterized they can be used for example to identify the flow direction and fluxes from pollution sources on brownfields. The different parts of the methodology are successfully combined into a coherent set of tools, which offer clear advantages for water budgeting in urban areas.

The developed groundwater modelling application highlights the fact that modelling tools not only require the ability to calculate reliable estimates of groundwater levels but also of water and contaminant fluxes. Only in that case these tools can be used for a flux-based risk assessment methodology, which is more appropriate than management based only on concentration levels of contaminants.

The work on the Vilvoorde test site also clearly demonstrates the importance of detailed information on complex urban land cover and on the spatial distribution of impervious surfaces, in order to obtain reliable estimates of runoff and groundwater recharge. Satellite data with a spatial resolution of 1 m like Ikonos are an interesting data source for obtaining such information and object-oriented image interpretation allows extracting reliable information on urban land-cover distribution from these data, which may then be used as an input for runoff and recharge modelling within urban catchments. Comparing recharge simulations, which were based on medium resolution remote sensing derived land-cover (standard land-cover product of the Flemish Agency for Geographical Information) with this high resolution land-cover data shows that the standard deviation of the recharge increases, indicating a stronger spatial variability in recharge values. Capturing the spatial recharge variability is of high importance for further pollution transport simulation. Increasing possibilities to sense spatially and temporally soil moisture conditions (Vereecken et al., 2008) will allow in the future further refinement of modelled processes and better calibration of the recharge estimates.

The new hydrogeological model was created to better understand the groundwater flow with a view to future management or remediation. Therefore the hydrostratigraphy of the model was refined by interpreting 68 borehole loggings and 179 cone penetration tests. With this new model increased understanding on determining factors as groundwater flow directions, fluxes and paths was obtained. The new model shows that most of the recharge will flow further as groundwater through the gravel to the river. The lower hydraulic conductivity of the Merelbeke (GeMe) Member in the north hinders the flow towards the deeper layers. The recharge in the south-eastern part of the study area has much longer flow paths than in the northern part of the area. Their pathways show a downward trend, so this water flows through the underlying Tielt Formation. Even without taking into account dispersion it appears that pollutants coming from this part of the study area will diffuse in the Tielt Formation.

The receptor of the pollutant flux is the draining Zenne River, the flow times to this receptor takes a few years to several decades. It also shows that future containment of the pollutants and safeguarding of the Zenne River has to focus on techniques for capturing the pollutant in the upper layer before they reach the receptor. The methodology can be extended by studying the spread of the pollutants through the area by use of a transport model, which takes into account the dispersion and the natural degradation of these pollutants.

Acknowledgements

Financial support for this research from the Belgian Science Policy Office in the framework of the Flux-based Risk Assessment of the impact of Contaminants on Water resources and ECOsystems (FRAC-WECO SD/TE/02) project is very appreciated.

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Journal of Hydrology 369 (2009) 305–317

Contents lists available at ScienceDirect

Journal of Hydrology

journal homepage: www.elsevier.com/locate/jhydrol

Benzene dispersion and natural attenuation in an alluvial aquifer with strong interactions with surface water

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ARTICLE INFO

Keywords:
Groundwater
Brownfield
Benzene
Stable isotope fractionation
Natural attenuation
Groundwater–surface water interaction

SUMMARY

Field and laboratory investigations have been conducted at a former coke plant, in order to assess pollutant attenuation in a contaminated alluvial aquifer, discharging to an adjacent river. Various organic (BTEX, PAHs, mineral oils) and inorganic (As, Zn, Cd) compounds were found in the aquifer in concentrations exceeding regulatory values. Due to redox conditions of the aquifer, heavy metals were almost immobile, thus not posing a major risk of dispersion off-site the brownfield. Field and laboratory investigations demonstrated that benzene, among organic pollutants, presented the major worry for off-site dispersion, mainly due to its mobility and high concentration, i.e. up to 750 mg L^{-1} in the source zone. However, benzene could never be detected near the river which is about 160 m downgradient the main source. Redox conditions together with benzene concentrations determined in the aquifer have suggested that degradation mainly occurred within 100 m distance from the contaminant source under anoxic conditions, and most probably with sulphate as main oxidant. A numerical groundwater flow and transport model, calibrated under transient conditions, was used to simulate benzene attenuation in the alluvial aquifer towards the Meuse River. The mean benzene degradation rate used in the model was quantified *in situ* along the groundwater flow path using compound-specific carbon isotope analysis (CSIA). The results of the solute transport simulations confirmed that benzene concentrations decreased almost five orders of magnitude 70 m downgradient the source. Simulated concentrations have been found to be below the detection limit in the zone adjacent to the river and consistent with the absence of benzene in downgradient piezometers located close to the river reported in groundwater sampling campaigns. In a transient model scenario including groundwater–surface water dynamics, benzene concentrations were observed to be inversely correlated to the river water levels, leading to the hypothesis that benzene dispersion is mainly controlled by natural attenuation.

Introduction

Sites of former industrial activities are often located near navigable rivers to facilitate the transport operations of industrial raw materials. This has resulted nowadays in the existence of numerous contaminated sites located in clusters close to rivers, in relatively urbanised areas. These sites often pose a major risk of dispersion in the environment and the exposure of human beings and ecosystems to contaminants, mainly by possible migration to surface water through groundwater discharge. This is particularly critical because of the possible cumulative effect of the different active pollution sources when several contaminated sites are located within the same water system(s). These sites, most of which could be defined as brownfield, are typically polluted by aromatic hydrocarbons such as benzene, toluene, ethylbenzene, xylene (BTEX), polycyclic aromatic hydrocarbons (PAHs) and heavy metals such as Zn, As or Cd, which belong to the major contaminants in groundwater (Lovley, 2000; Khan et al., 2005; Lee et al., 2006; Fischer et al., 2007). These compounds are of a particular environmental concern, since they represent a significant health risk because of their high recalcitrance and toxicity; several of these are

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doi:10.1016/j.jhydrol.2009.02.014

even known as human carcinogens (Burland and Edwards, 1999; Fischer et al., 2007). The concept of "natural attenuation" covers all physical, chemical and biological processes that help to reduce the mass of dissolved contaminants in a groundwater plume, such as dispersion, sorption, volatilisation, biological and chemical degradations (Wiedemeier et al., 1999).

Risks associated with dispersion of contaminants are intimately related to two main factors: the occurrence of water transfers between the various components of the soil–groundwater–surface water compartments as well as the mobility and persistence of identified contaminants through such compartments. At a single contaminated site scale, the first step is to characterise and quantify, as accurately as possible, water and contaminant fluxes.

Important insights have been gained in the study of biogeochemical and physical processes affecting the mobility and attenuation of contaminants in aquifers. Little attention, however, has been paid to the fate of contaminants and processes affecting the spatial distribution before they reach the river–aquifer interface of a polluted site with strong groundwater–surface water interactions. The determining factors for future evolution of these contaminants must still be defined. For example and at the aquifer level, heterogeneity is rarely addressed in studies on groundwater–surface water interactions and pollutant discharge (Wroblicky et al., 1998; Conant et al., 2004; Fleckenstein et al., 2006). Kao and Wang (2000) observed in a sandy–silty–loamy aquifer not subject to river interactions, an important drop in BTEX concentration 100 m downstream of the source area, which was related to iron and nitrate reduction; Lee et al. (2001) observed that hydrostratigraphy, seasonal recharge and biodegradation were the most important factors controlling the distribution of hydrocarbon contaminants within a sandy aquifer; and Fritz and Arntzen (2007) demonstrated a relation between hydraulic gradient changes due to river fluctuations and uranium fluxes discharging to the river.

This study focuses on the characterisation and quantification of water and contaminant fluxes in the groundwater–surface water system corresponding to the alluvial aquifer of the Meuse River, located in the brownfield of a former coke and gas factory in the Liège area, in Belgium. At first, a brief description of the study site as well as the investigations performed to assess groundwater hydrodynamic and hydrodispersive properties and groundwater–surface water interactions are presented. In a second step, we present the hydrogeochemical conditions together with the organic and inorganic pollutants fate in groundwater, which are analysed to identify which contaminants are of stronger concern with respect to off-site dispersion risks. Afterwards, a numerical groundwater flow and contaminant transport is presented, which is used to evaluate different scenarios of benzene dispersion in groundwater. Finally, results are discussed including all information gathered by means of laboratory, field studies and modelling approaches. Our objectives are reached by combining laboratory and field investigations as well as advanced numerical modelling of groundwater flow and contaminant transport in the alluvial aquifer.

General description of the study site

The study site is a brownfield of 400 m length and 250 m width, corresponding to the location of a former coke and gas factory. It is located at 25 m distance to the North bank of the Meuse River (Fig. 1), upstream the city of Liège (Belgium), in an industrial environment where urban cores developed during the last century. The facility was active from 1922 until 1984 when it was dismantled and abandoned.

The top–bottom geology of the site consists of 4 m backfill deposits, 2 m silt–sand–clay deposits and approximately 8 m alluvial gravels (mean thickness) deposited over a carboniferous shale bedrock, which is the impervious lower boundary for the alluvial aquifer. The main aquifer is located in the alluvial gravels, with a groundwater table fluctuating around 7 m typical mean depth. The topography is very flat with a general groundwater flow direction towards the Meuse River direction, with a low hydraulic gradient of 0.3% (Batlle-Aguilar and Brouyère, 2005, 2006).

In order to allow navigation and to prevent flooding of the alluvial plain, the river water level is controlled by dams (located 1.5 km upstream and 14 km downstream the brownfield, respectively), that keep the river water level at a 59.4 m a.s.l. (above sea level) baseline in that section of the river corresponding to the brownfield. River water levels fluctuate continuously with amplitudes varying from a few centimeters under its baseline and up to 2 m locally during winter–spring seasons.

Past characterisation campaigns evidenced important soil and groundwater contamination by organic compounds, mainly BTEX, PAHs and also by heavy metals. Benzene concentrations in groundwater were reported to be up to 750 mg L^{-1} in the source zone at the monitoring campaign in 2005 and up to 18 mg L^{-1} in 2006. Toluene and xylene were found at 77 and 15 mg L^{-1} (3 and 0.6 mg L^{-1} in 2006), respectively (SPAQUE, Sociétée Publique d'Aide à la Qualité de l'Environnement, internal report). Polycyclic aromatic hydrocarbons, like naphthalene, acenaphthene and fluoranthene, were present in the groundwater, at concentrations up to 3 mg L^{-1} (25 mg L^{-1} in 2006). Heavy metals were also found in groundwater at maximum concentrations of 5 μg L^{-1} for Cd, 10 μg L^{-1} for As and Pb, and 200 μg L^{-1} for Zn. In the source area, groundwater was anoxic with negative Eh values down to −300 mV and nitrate was found to be near-total depletion (ranging from 0 to 3 mg L^{-1}). Background nitrate concentrations of 190 mg L^{-1}, outside of the brownfield, were recorded upgradient. Downstream, towards the Meuse River, Eh values of +100 mV were observed and nitrate concentrations up to 15 mg L^{-1} were reported. Sulphate, that is also a by-product of coke manufacturing, was heterogeneously distributed over the totality of the aquifer, with concentrations typically ranging from 500 to 2100 mg L^{-1}. It is worth noting that all piezometers and monitoring wells were single screened, thus providing depth-integrated measurements.

Characterisation of groundwater flow and transport conditions in the alluvial aquifer interacting with the river

To improve the current knowledge on the hydrodynamic and hydrodispersive properties of the alluvial aquifer and the possible interactions with the Meuse River, groundwater level fluctuations were monitored and, pumping tests and tracer experiments were performed (Batlle-Aguilar and Brouyère, 2005, 2006).

Monitoring and analysis of interactions between rainfall, groundwater and surface water

Groundwater level fluctuations were monitored hourly using pressiometric–temperature LevelTroll® probes (time resolution: 1 h). Two of these probes were placed in observation wells located along an orthogonal section near and far from the river (wells U5 and U3) on an almost permanent basis over a 2 year period. Two more pressiometric probes were used by pairs in observation wells (near and far from the river) for shorter periods of time (1 month). Altogether, 16 observation wells were distributed all over the field and monitored during 2 years (Fig. 1). During that same period, the Meuse surface water level, temperature and discharge were continuously monitored at a hydroelectric plant located on the

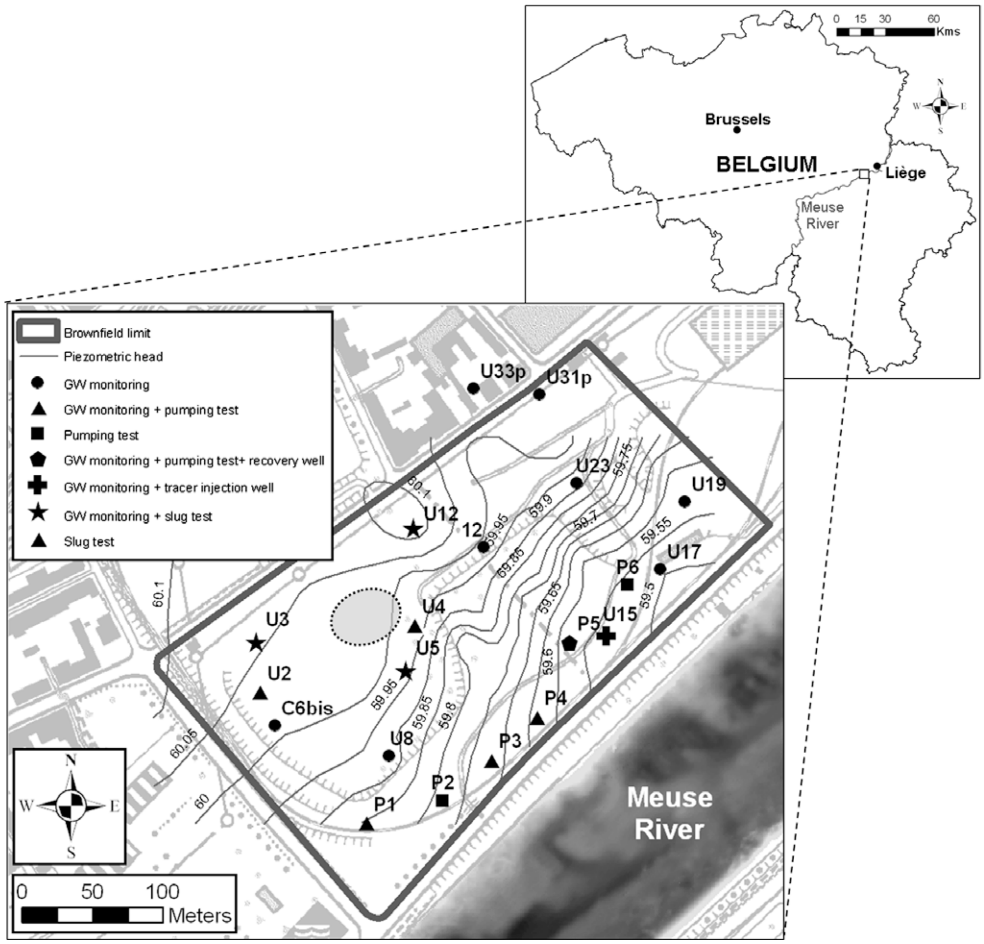

Fig. 1. Location of the studied brownfield. The main pollutant source is indicated with a dark ellipse, and the 16 wells monitored with pressiometric probes TrollLevel® are shown. Symbols of these wells agree to corresponding field works performed. Piezometric lines correspond to the monthly groundwater head survey in June 2005.

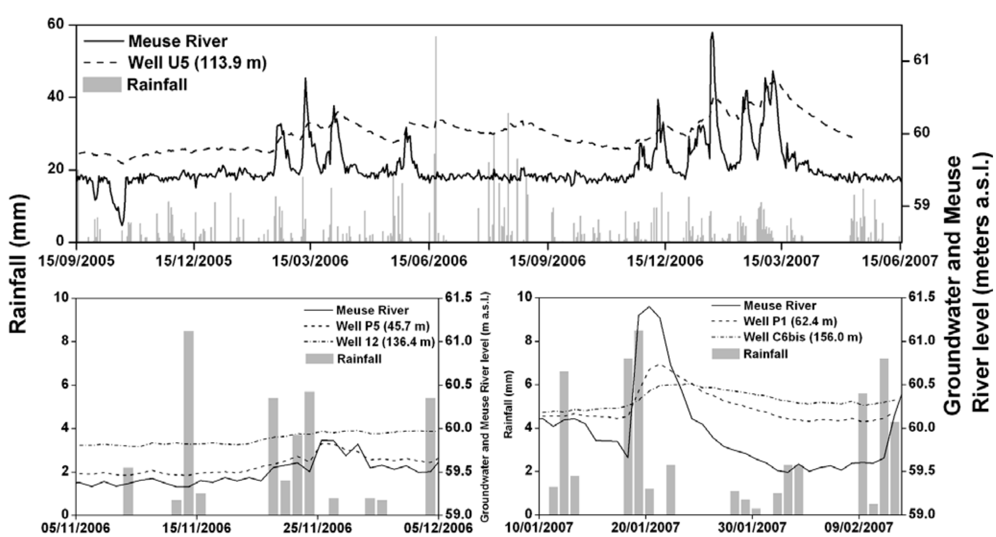

Fig. 2. Surface water level fluctuations of the Meuse River and groundwater heads at selected wells for different periods. Rainfall recorded 1.5 km upstream of the site is also depicted. Distance of the wells to the aquifer–river interface is indicated in brackets.

opposite river bank, in front of the brownfield. Daily rainfall data were available for the Ivoz–Ramet dam, located 1.5 km upstream the brownfield site.

Monitored groundwater heads, river levels and rainfall data (Fig. 2) were analysed for time cross-correlations using the BRGM TEMPO® software (Pinault, 2001) with hourly data, except for precipitation. For the latter, only daily data was available. Cross-correlation coefficients between river water levels and groundwater levels ranged from 0.8 to 0.98 for wells located close to the river. As expected, the correlation decreases as the distance to the river increases, while the time lag response increases. This can be conceptualised in the form of a wave propagation into the aquifer, which amplitude is progressively attenuated and the time lag is increased (Sophocleous, 1991; Jha et al., 2004; Ha et al., 2007). The same cross-correlation analyses showed that rainfall plays a secondary role in groundwater level fluctuations, with maximum cross-correlation coefficients of 0.3. Details on these correlation analyses can be found in Batlle-Aguilar (2008).

Hydrodynamic and hydrodispersive properties of the alluvial aquifer

Six pumping tests and five slug tests were performed in selected wells of the site (results not shown). Estimated saturated hydraulic conductivity (*Ks*) values resulting from both, pumping and slug tests, range from 1×10^{-5} to $1 \times 10^{-3}\ \mathrm{m\,s^{-1}}$. These values are lower than expected for an alluvial aquifer and their spatial variability reveals the heterogeneity of the alluvial deposits.

Radially convergent tracer experiments were performed in order to assess the hydrodispersive properties (mostly the effective porosity – θ_m and the longitudinal dispersivity – α_L), and to identify possible retardation, such as dual-porosity effects related to small-scale heterogeneities of the alluvial deposits that can be assimilated to immobile water (Herr et al., 1989; Li et al., 1994; Brouyère, 2001). Within the context of alluvial deposits, mobile water corresponds to that in the effective porosity, while immobile water (or less mobile) rather corresponds to water located in less pervious zones, mostly clay and silty sand with low saturated hydraulic conductivity than that of the gravels. Groundwater was pumped in well P5 until steady state radially convergent flow conditions were achieved. The tracers used for this experiment (eosin yellowish, uranin, naphtionate, sulforhodamine B, iodide and lithium) were instantaneously injected in well U15 (Fig. 1). The resulting breakthrough curves differed strongly from each other, mainly because of two factors: (1) the specific physico-chemical properties of each tracer and (2) changes of pumping rate at the recovery well to avoid dewatering the pumping well during lowering of groundwater levels. Measured breakthrough curves served subsequently to calibrate the groundwater transport model.

Redox conditions and contaminant distribution

From 1992, five groundwater monitoring campaigns have been performed by SPAQuE at the studied brownfield. Concentrations of various redox sensitive species in groundwater were determined in 2006 during a sampling campaign devoted to measurements of benzene concentrations and isotopic ratios (see “Assessment of benzene biodegradation using stable carbon isotope analysis” and “Natural attenuation of benzene” sections). Dissolved oxygen concentrations, temperature, electrical conductivity, and pH were recorded directly in the field, using specific field probes (WTW, Weilheim, Germany). Samples for the analysis of Fe^{2+} and Mn^{2+} were filtered (0.45 μm) and acidified with concentrated HNO_3^- directly in the field to prevent their oxidation. For colorimetric analysis, phenanthroline and 1-(2-pyridylazo)-2-naphthol were used (Goto et al., 1977; Stucki and Anderson, 1981). Samples for HS^- quantification were preserved in a Zn-acetate solution (2%) directly in the field and analysed by colorimetry following the procedure of Cline (1969). For CH_4 analyses, 40 mL VOC vials with Teflon–rubber septa were filled with 39 mL of a water sample and tightly sealed in the field. Back to the laboratory, head space samples were taken using a syringe through the septum and then analysed for CH_4 using a gas chromatograph equipped with flame ionisation detection (Platen and Schink, 1987).

Redox conditions in the aquifer were determined on the analyses of O_2, NO_3^-, Fe^{2+}, Mn^{2+}, SO_4^{2-}, HS^-, and CH_4 in groundwater sampled from 25 piezometers (Table 1). The results presented here focus on the most recent data from the campaign performed in 2006 (whenever helpful or complementary, data from 2005 campaign were used). The sampling points were located in the zone of major contamination with organic compounds and downgradient from this zone. Two reference wells (E6p and F4) were also sampled; these were located 92 and 74 m upgradient the major

Table 1
Benzene concentrations and corresponding stable isotope signatures in groundwater sampled from 25 different piezometers in 2006. Electron acceptors and products related to the degradation of organic compounds are also presented. Piezometer D2bis, located in the main source zone, was defined as contaminant source. E6p and F4 are reference wells upgradient from this contamination (n.a.: not analysed).

Well	Distance from source (m)	$\delta^{13}C$	Benzene (μg L^{-1})	CH_4 (μg L^{-1})	SO_4^{2-} (mg L^{-1})	HS^- (mg L^{-1})	NO_3^- (mg L^{-1})	Fe^{2+} (mg L^{-1})	Mn^{2+} (mg L^{-1})
E6p	−92	n.a.	<0.02	n.a.	737	0.1	16.3	<0.1	n.a.
F4	−74	−24.0	0.09	1.3	925	1.2	66	12.3	3.4
D2bis	0	−24.8	206	267.7	311	18.1	<0.1	0.3	1.4
C3bis	11	−21	20	0.6	863	0.4	0.3	11	6.8
D1p	22	−23.5	17,546	313	1112	2.9	<0.1	23.3	5
D3p	22	−24.5	4949	68	1329	1.9	0.4	2	0.7
U9	25	−21.8	0.47	8.1	1147	0.2	0.4	1.7	8
A3	26	n.a.	<0.02	0.9	930	<0.1	0.2	0.1	1.2
U5	34	n.a.	<0.02	12.1	1127	0.1	1.8	10.2	6.7
U4	39	−23.9	9763	156.2	21	13.9	<0.1	1.6	2.4
11	51	−20.9	1.2	22.2	570	0.8	<0.1	6.4	7.1
U6	54	−23.0	1319	0.9	1352	7.7	0.2	0.1	2.4
U10	68	−22.2	0.39	3.9	971	0.1	7.3	0.2	5
14	79	n.a.	29	31.6	540	1.1	0.3	0.2	1.4
U13	88	−21.0	0.38	1.1	728	0.2	19.7	0.1	3.8
12	89	−20.9	1	93.7	1103	0.2	<0.1	7.4	7.4
1	94	n.a.	<0.02	4.5	614	0.3	1.5	<0.1	1.1
7	117	−21.5	<0.02	5.6	801	0.1	9.1	<0.1	1.2
15	133	−21.6	1.5	24.3	925	1.2	<0.1	12.3	5.6
P5	149	−23.9	0.1	9.4	649	<0.1	3.3	0.1	1.4
8	155	−21.4	2	2.2	803	0.1	195.7	<0.1	4.4
U15	175	n.a.	<0.02	0.1	939	0.1	12	<0.1	1.8
U16	188	n.a.	<0.02	n.a.	786	<0.1	56.8	n.a.	n.a.
U17	213	n.a.	<0.02	3	710	<0.1	8.6	<0.1	0.7
U19	218	n.a.	<0.02	n.a.	721	0.2	45.5	<0.1	1.2

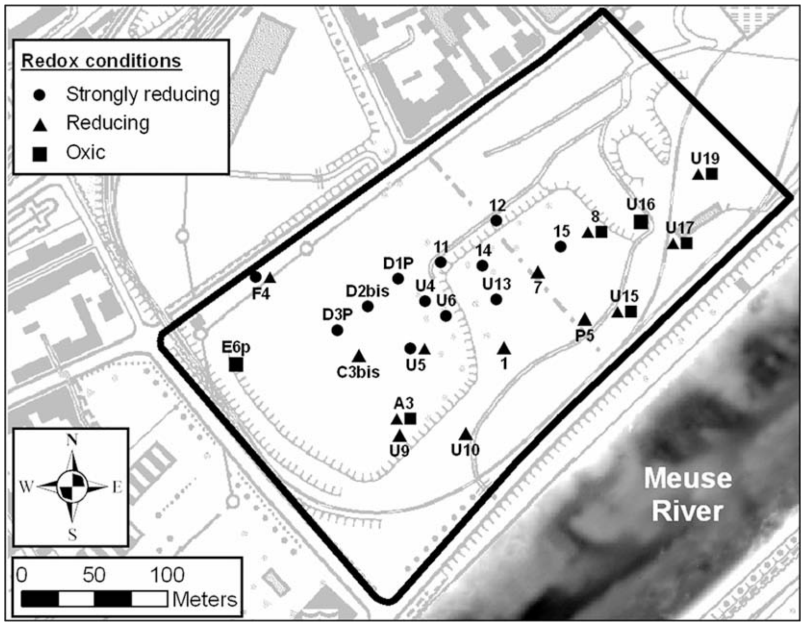

Fig. 3. Redox conditions at different locations shown for sampling campaign in 2006.

source of contamination. The data from these wells were divided into three categories (Fig. 3), "strongly reducing", "reducing" and "oxic" conditions. Wells were denoted as "strongly reducing" conditions when under sulphate-reducing and/or methanogenic conditions as indicated by $HS^- > 1\ mg\ L^{-1}$ and/or $CH_4 > 15\ \mu g\ L^{-1}$. Wells with "reducing" conditions were characterised by denitrifying (depletion of nitrate below the reference value at E6p), iron- or manganese-reducing (Fe^{2+} and/or $Mn^{2+} > 1\ mg\ L^{-1}$) conditions. Finally, wells with "oxic" conditions were characterised by the absence of CH_4, HS^-, Fe^{2+}, Mn^{2+}, presence of NO_3^- in concentrations comparable to the reference well E6p, and presence of O_2 in groundwater (data not shown). "Strongly reducing" conditions were mainly encountered in the source zone and in its immediate vicinity to the East and South-East (Fig. 3). Concentrations of $HS^- > 1\ mg\ L^{-1}$ in 8 out of 25 wells indicate that sulphate reduction is the predominant redox process at the site. Further to the East, conditions change to "moderately reducing" and finally "oxic" conditions.

In the 2006 sampling campaign, the highest benzene concentrations were found in D1p in the source area (17,550 $\mu g\ L^{-1}$, Table 1). In several other sampling points in the vicinity of the source area, benzene concentrations were >1000 $\mu g\ L^{-1}$, while concentrations rapidly decreased at locations further downgrading. At sampling wells located more than 80 m from D1p, benzene concentrations were $\leqslant 2\ \mu g\ L^{-1}$. In these monitoring wells, no other BTEX, naphthalene (detection limit 5 $\mu g\ L^{-1}$) or three-ring PAHs (detection limit 15 $\mu g\ L^{-1}$) were detected.

Fate of contaminants in the alluvial aquifer

Specific investigations were performed, in both the laboratory and the field, in order to characterise the specific behaviour of existing contaminants in the brownfield site (sorption, degradation, etc.). These investigations were aimed at identifying the most problematic contaminants with respect to the off-site dispersion risk toward the Meuse River, and at proposing adequate scenarios to be modelled using the numerical groundwater flow and transport model presented in the section "Groundwater flow and transport modelling". These investigations focused therefore on the potential degradation of organic mono- and polycyclic aromatic hydrocarbons as well as on the characterisation of redox conditions as they possibly affect the mobility of inorganic pollutants.

Fate of inorganic pollutants

To determine the mobility of heavy metals present in the aquifer, groundwater and sediment were sampled between 8 and 12 m below ground level in well U15 (Fig. 1), located downgradient from the source area, where no organic pollutants have been detected till now.

Microcosms were set up in an anaerobic chamber at 20 °C containing aquifer material (10 g) sampled and homogenised as described by Vanbroekhoven et al. (2007).

The soil–water distribution coefficients (K_d) were calculated from the measured equilibrium concentrations in the batch tests:

$$K_d = [(C_i - C_f)/C_f]L/S \tag{1}$$

where C_i and C_f are the initial and final metal concentrations in solution within the batches (mg m^{-3}), and L/S is the liquid to solid ratio ($m^3\ kg^{-1}$).

The distribution coefficient K_d expresses the ratio of the total amount of metals removed in the batches to the amount of metals in solution in equilibrium with the aquifer material. In the presence of a carbon source (i.e. acetate, which simulates organic contaminants as a carbon source), low available fractions were obtained for Zn (9%), Cd (14%), As (3%) and for Co (13%). Calculated K_d values range from 9.9 to 27.8 $m^3\ kg^{-1}$ for Zn, from 0.75 to 9.9 $m^3\ kg^{-1}$ for Cd, from 0.034 to 0.223 $m^3\ kg^{-1}$ for As, and from 0.66 to 1.30 $m^3\ kg^{-1}$ for Co. These high sorption constants suggest that heavy metals do not constitute a major risk in terms of off-site dispersion.

Assessment of benzene biodegradation using stable carbon isotope analysis

To determine residual concentrations of benzene in groundwater, samples were analysed with gas chromatography (Varian 3800) with a CP8410 autoinjector for solid phase microextraction

(SPME). Benzene was extracted from the headspace of half-filled 2 mL sample vials using polydimethylsiloxane fibers (100 μm film thickness, Supelco, Bellefonte, PA). Degradation of benzene along the groundwater flow path was assessed and quantified using compound-specific carbon isotope analyses of groundwater samples. As demonstrated in laboratory studies, during aerobic (Hunkeler et al., 2001; Fischer et al., 2008) and anaerobic (Mancini et al., 2003; Fischer et al., 2008) degradation of benzene, a significant carbon isotope fractionation occurs because molecules consisting of light ^{12}C isotopes are degraded faster than those containing a heavy ^{13}C isotope. The remaining benzene resulting from isotope fractionation becomes increasingly enriched in ^{13}C which can be used to track the progress of biodegradation.

Groundwater from 16 wells containing residual benzene sampled in 2006 was analysed for stable carbon isotope ratios (Table 1). Benzene was extracted from groundwater using a Tekmar Velocity Purge & Trap System and analysed using a Thermo Finnigan Trace gas chromatograph (GC) coupled to a Thermo Finnigan Delta Plus XP isotope ratio mass spectrometer (IRMS) via a GC combustion III interface.

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

$$\delta^{13}C[‰] = \left(\frac{^{13}C_{sample}/^{12}C_{sample}}{^{13}C_{reference}/^{12}C_{reference}} - 1\right) \times 1000 \tag{2}$$

where a $\delta^{13}C$ shift in positive direction corresponds to an enrichment in ^{13}C.

First-order biodegradation rates can be retrieved from isotope data using the following equation (Hunkeler et al., 2002; Blum et al., 2009):

$$\lambda = -\Delta\delta^{13}C/(\varepsilon \times t) \tag{3}$$

$\Delta\delta^{13}C$ is the shift in the carbon isotope ratio between the source and a downgradient monitoring point, ε is the isotope enrichment factor and t the travel time. Travel times were estimated based on the average groundwater flow velocity (1.04×10^{-5} m s^{-1}), itself calculated from the average hydraulic gradient, saturated hydraulic conductivity and effective porosity.

Natural attenuation of benzene

Sampling locations in the source area with benzene concentrations >10,000 μg L^{-1} were characterised by $\delta^{13}C$ values of −24.8‰ and −23.5‰, while locations with lower concentrations were generally enriched in ^{13}C. This clearly demonstrates the occurrence of biodegradation of benzene in the aquifer along the groundwater flow. The observed increase in $\delta^{13}C$ was in the same range as previously observed at a gaswork site in Germany (Griebler et al., 2004). All of the sampling points with ^{13}C enriched benzene were located in zones with "strongly to moderately reducing" conditions (Fig. 3). Furthermore, benzene was degraded to concentrations below the limit of detection before the contaminant plume turned oxic again, underlining that benzene degradation at this site mainly occurred under anoxic conditions. Consequently, for the determination of the biodegradation rate constant using Eq. (3), an average carbon isotope enrichment factor of ε = −2.4‰ for anaerobic benzene biodegradation was used. The isotope enrichment factor was determined in a laboratory study (Mancini et al., 2003). For benzene biodegradation, first-order rate constants were estimated for the section between the source zone and points located downgradient, taking into account only sampling points indicating "reducing" or "strongly reducing" conditions (D1p, U9, U4, U10, U13, 12, 7, or P5). Since the whole source zone (Fig. 4) was not only presenting irregular benzene concentrations but also different stable isotope signatures comprised between −23‰ and −24.8‰, we chose the piezometer D2bis ($\delta^{13}C$ = −24.8‰) located at the Eastern (upgradient) fringe of the source zone and oriented towards the groundwater flow direction, as a reference point. A mean first-order degradation rate of $1.7 \times 10^{-2}/d$ was obtained. This rate constant for benzene is slightly higher, but in the same range as rate constants in a previous study on fuel contaminated sites and former gas plants in the USA ($3.3 \times 10^{-4}/d$ to $4.4 \times 10^{-2}/d$; Lewandowski and Mortimer, 2004) and it is higher than values observed at six former manufactured gas plants in the US (3.3×10^{-4}/d to 4.1×10^{-3}/d; Lewandowski and Mortimer, 2004).

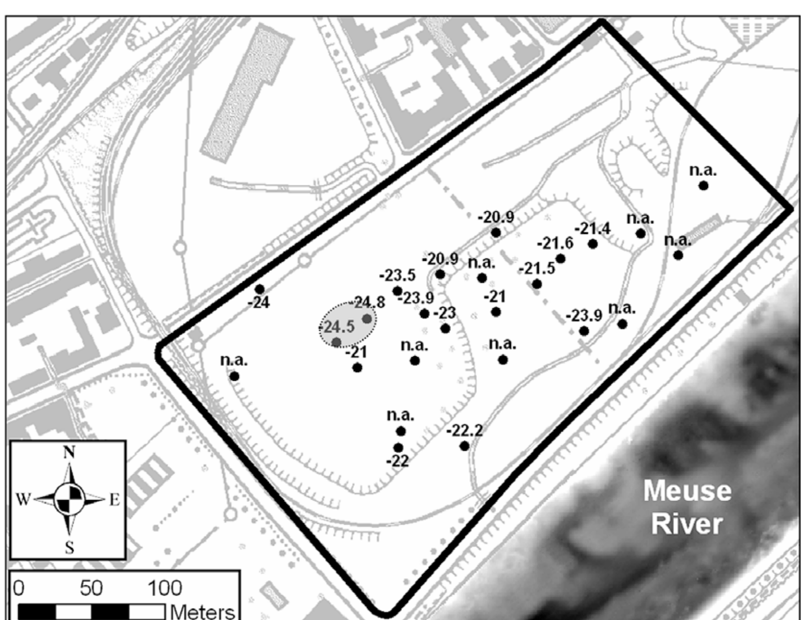

Fig. 4. $\delta^{13}C$ isotope ratios of residual benzene in the groundwater of the field site. Highlighted in dark ellipse is the major source zone (n.a.: not analysed).

Table 2
Heavy metals concentrations in groundwater sampled from three different piezometers in 2006 (concentrations are given in $\mu g\ L^{-1}$).

Well	Zn	Cd	Co	Fe	Cu	Pb	Hg	Ni	As	Cr
U15	41.7	4.0	18.0	<1.95	9.1	104.0	<0.1	8.0	1.0	2.0
U17	<1.52	<1.84	4.4	150.6	<2.65	<26.52	<0.1	4.0	1.0	0.5
U23	<1.52	1.84	11.5	6496	<2.65	19.0	<0.1	1.0	5.0	0.2

Summary on the fate of contaminants in the alluvial aquifer

Based on previous investigations performed on contaminants that were detected in the brownfield site, the following conclusions can be drawn. Redox conditions at the site favour immobilisation of heavy metals, as demonstrated by Vanbroekhoven et al. (2007). These findings are confirmed by the low concentrations of metals detected in the groundwater in the field (Table 2). For the organic contaminants, the conclusions are not as straightforward, as PAHs seem to be relatively stable (i.e. naphthalene half-life: 139 days; acenaphthene half-life: 1386 days; Batlle-Aguilar et al., 2008). At the same time, they are known as being relatively immobile (strong sorption). BTEX and particularly benzene, are present at large concentrations and are potentially mobile. However, they have been shown to degrade in the alluvial aquifer. The presence of oxidants at the site, particularly sulphate, is one factor which could have contributed to the slightly higher biodegradation rate constant. Although site specific and always prone to uncertainties and variations, biodegradation rate constants for one particular contaminant can be assumed to be in the same order of magnitude under related environmental conditions. Therefore, cautiously applied, rate constants which were determined at one site might give important insights into further field scenarios. The calculated rate constant of benzene corresponds to a half-life of 41 days. When the half-life time is converted to the flow distance necessary for a mass reduction by a factor of two, 36 m are obtained. Given that the river is about 160 m from the source area in flow direction, a significant reduction of the benzene mass flux is expected before the river is reached.

The risk of BTEX dispersion depends of the balance between mobility and degradation effects along the flow path, downstream the pollutant sources. Furthermore, in downgradient parts of the plume, close to the river, biodegradation might be accelerated due to the fluctuation of the water table and also the infiltration of oxygen-rich river water (Williams and Oostrom, 2000).

Considering the above, benzene (as a representative of BTEX compounds) has been identified as the most critical pollutant present in the brownfield for short and middle terms risk of off-site dispersion towards the river. Subsequent modelling efforts have consequently been focused on this particular compound.

Groundwater flow and transport modelling

A numerical groundwater flow and transport model was developed in order to run different scenarios of benzene pollution using calculated degradation rates and to determine the risk of benzene off-site dispersion.

Development and calibration of the groundwater flow and transport model

The numerical groundwater flow model was developed using MODFLOW-2000 (Harbaugh et al., 2000). The limits of the modelled zone were extended to a larger part of the alluvial plain than that occupied by the brownfield, in order to fit the "natural" boundary conditions and to avoid the influence of self-defined boundary on modelling results (Fig. 5). Upstream, along the Meuse River (SW-boundary), the model was extended up to the Ivoz–Ramet dam, where a difference of 3 m in the Meuse River water level is produced by the dam, inducing a lateral "bypass" of surface water through the alluvial plain. At this boundary, piezometric levels are prescribed (Dirichlet boundary) at a level equal to the water level in the Meuse River upstream of the dam, inducing thus the mentioned surface water lateral "bypass". Downstream, along the

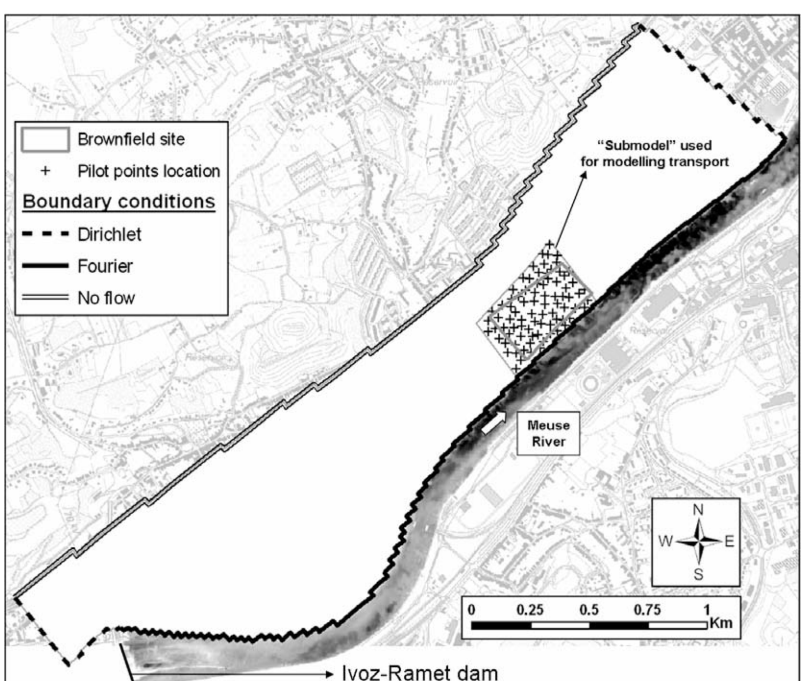

Fig. 5. Conceptual model of the groundwater flow and transport model.

Meuse River (NE-boundary), the model is extended to 1-km downstream the brownfield. At this boundary, piezometric levels are prescribed (Dirichlet boundary) because there is no reason to think that no-flow may occur across that specific limit. Laterally (NW-boundary), the modelled area is extended to the limit between the alluvial and the up-hill shaly bedrock. Because of the expected large difference in saturated hydraulic conductivity between the shaly bedrock and the alluvial deposits, a no-flow boundary condition was assumed. At the boundary between the Meuse River and the alluvial aquifer (SE-boundary), a third-type boundary condition (Fourier) is assumed to account for riverbank effect. The modelled domain is made of a single layer horizontally subdivided into 204 columns and 88 rows with variable grid refinement from 5 m × 5 m inside the brownfield to 25 m × 25 m at the edges of the regional modelled domain. More details on groundwater flow modelling can be found in Batlle-Aguilar and Brouyère (2008) and Batlle-Aguilar (2008).

The finite-difference groundwater flow model was calibrated and validated using the very detailed transient groundwater head dataset resulting from the monitoring performed with the pressiometric probes (see "Monitoring and analysis of interaction between rainfall, groundwater and surface water"). An innovative combined zonation–pilot point modelling approach automatically calibrated with Parameter Estimation Software – PEST (Doherty, 2003) was used. A classical zonation of saturated hydraulic conductivity values was used outside the brownfield, which was combined with the pilot points (de Marsily et al., 1984) distributed throughout the area corresponding to the brownfield. This combined approach, recently used by Doppler et al. (2007), allows an improved representation of the alluvial deposits heterogeneity within the brownfield. Daily groundwater heads monitored from 16 monitoring wells (Fig. 1) were used for the calibration of groundwater flow, applying a calibration target of 5 cm. A comparison between the observed and modelled groundwater heads in several wells is presented in Fig. 6 to illustrate the quality of calibration. Modelled groundwater heads match well with measured ones (see Fig. 7) and show an efficient correlation coefficient (R^2 = 0.967). Optimised values of saturated hydraulic conductivity ranged from 1×10^{-5} to 1×10^{-3} m s^{-1}, lower than expected for an alluvial aquifer but not unrealistic for the alluvial Meuse River deposits (Brouyère, 2001).

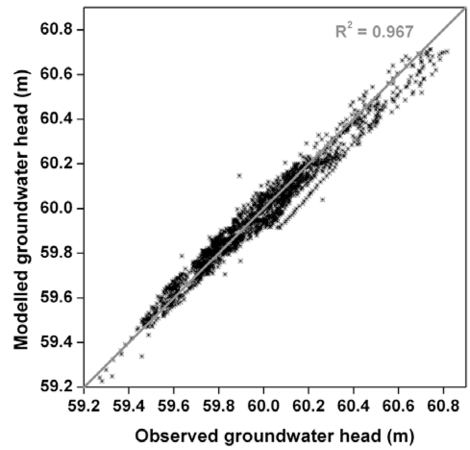

Fig. 7. Observed vs. modelled groundwater heads.

A transport model was developed using MT3DMS (Zheng and Wang, 1999). From the groundwater flow model developed using MODFLOW, a "submodel" of reduced dimensions corresponding almost to the studied brownfield was created for solute transport simulations (Fig. 5). This groundwater transport model has dimensions of 550 m × 380 m, with 159 columns and 113 rows and a variable grid refinement 0.5 m × 0.5 m in the benzene source to 10 m × 10 m at the limits of the model. Boundary conditions were considered as follows: a Fourier boundary condition in the contact area between the Meuse River and the aquifer (SE-boundary); prescribed time-varying piezometric head levels for the other boundaries (NE, NW and SW), which values come directly from the calibrated regional groundwater flow model. More details concerning the groundwater transport model are presented by Batlle-Aguilar and Brouyère (2008) and Batlle-Aguilar (2008).

The transport model was calibrated to fit measured breakthrough curves obtained in radially convergent tracer tests. To do so, the advection–dispersion equation (ADE) was considered, playing with longitudinal dispersion, dual-porosity effect and first-order transfer as fitting parameters to adjust observed to modelled tracer concentration and mass recovery at the pumping well (P5). Dual-porosity or mobile–immobile (MIM) water was consid-

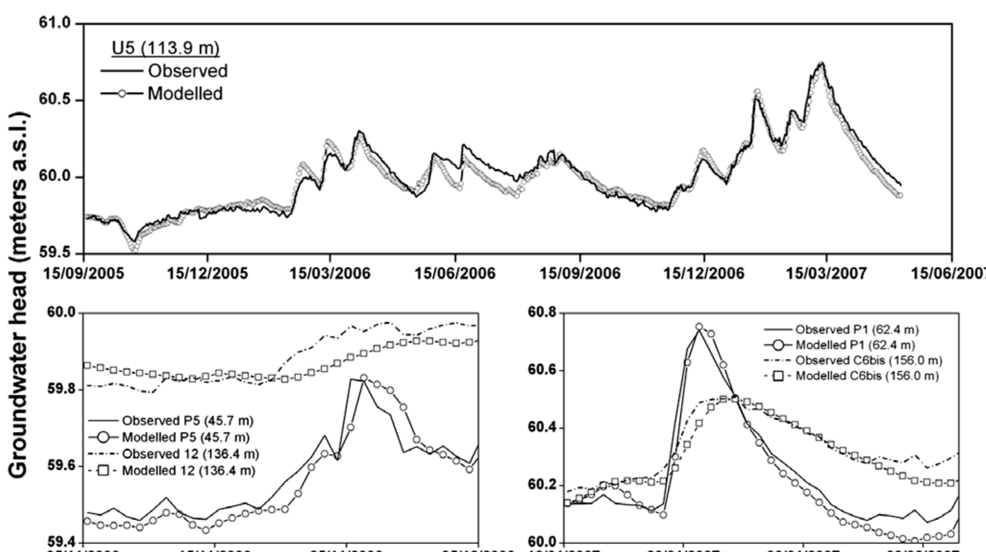

Fig. 6. Comparison between observed and measured groundwater heads at wells located near and far from the Meuse River for long and short modelled periods of time (distance between well and river is indicated in brackets).

Table 3
Hydrodispersive parameters used for the calibration of tracer tests (θ_m: mobile porosity; θ_{im}: immobile–or less mobile-porosity; α_L: longitudinal dispersivity; α: diffusion coefficient between mobile and immobile domains; K_d: distribution coefficient between sorbed and dissolved phases; p: fraction of sorption in contact with the immobile phase).

Tracer	θ_m (–)	θ_{im} (–)	α_L (m)	α (s^{-1})	K_d ($m^3\ kg^{-1}$)	p (–)
Iodide	0.041	0.10	1.4	4.50×10^{-8}	–	–
Eosin yellowish	0.060	0.05	3.0	1.60×10^{-7}	–	–
Lithium	0.068	0.70	4.5	1.05×10^{-7}	1.0×10^{-4}	0.91
Uranine	0.050	0.70	2.0	2.10×10^{-7}	1.0×10^{-4}	0.93
Sulforhodamine B	0.03	0.70	3.0	3.00×10^{-7}	7.6×10^{-3}	0.96
Naphtionate	0.047	0.10	2.2	2.10×10^{-8}	–	–

ered in order to avoid difficulties in modelling tracer concentration attenuation and tailing for conservative tracers, such as iodide and eosin yellowish. The hydrodispersive parameters obtained in transport model calibration are summarised in Table 3. Mobile or effective porosity (θ_m) is indeed somehow low, with values ranging between 0.04 and 0.07; such effective porosity could be considered as low for alluvial gravels. However, related to the heterogeneity of the aquifer, this is relatively common for the alluvial deposits of the Meuse River (e.g. Brouyère, 2001; Rentier, 2002).

Modelling benzene attenuation in the alluvial aquifer towards the Meuse River

Although five characterisation campaigns were performed by SPAQuE at the studied site between 1992 and 2006, these data acquired do provide neither a spatial nor time continuity since the site is so heterogeneous. Among the 100 piezometers drilled within the brownfield during these campaigns, none of them has been sampled on a regular basis through time. In the best case, one or two measurements of contaminants are available in some of them and there is not enough information for any comparison between benzene concentrations observed in the field and calculated with the groundwater transport model. The approach is therefore to model different pollution scenarios in order to evaluate benzene dispersion and attenuation in the alluvial aquifer using the previously calibrated groundwater transport model together with biodegradation rates as estimated in the field as well as estimates of retardation constants coming from the literature.

The transport of benzene was modelled while considering firstly the steady state flow conditions, with the Meuse River level at its baseline (59.4 m a.s.l.) and the alluvial aquifer discharging into the river. The source of benzene of 2 m × 2 m, was placed at 165 m from the Meuse River and was modelled as a constant concentration equal to 750 mg L^{-1}, which corresponds to the maximum benzene concentration measured in groundwater in the source area. Because piezometers in the brownfield are single screened, the vertical distribution of the benzene is not known and, thus, depth-average conditions were assumed. The different scenarios are compared on the basis of the maximum concentration evolutions calculated at five control planes (A, B, C, D and E) defined in the model between the source and the river, at respective distances of 25, 50, 80, 115 and 160 m from the source area (Fig. 8).

A total of five scenarios were modelled to study benzene transport in the aquifer (Table 4). Scenarios 1, 2 and 3 consider steady state groundwater flow conditions, starting from the worst contaminant scenario where only advection–dispersion and dual-porosity processes are considered without sorption or degradation (scenario 1). Benzene retardation processes are then considered (scenario 2) assuming linear sorption. Then, benzene degradation is considered (scenario 3) assuming a first-order degradation model with degradation constants as estimated in the field using

Table 4
Benzene transport scenarios (ADE: advection–dispersion equation; MIM: mobile–immobile water; ✓: process considered in modelling tasks; ×: process not considered in modelling tasks).

Scenario	ADE	MIM	Sorption	Biodegradation	Steady state	Transient
1	✓	✓	×	×	✓	×
2	✓	✓	✓	×	✓	×
3	✓	✓	✓	✓	✓	×
4	✓	✓	✓	✓	×	✓
5	✓	✓	×	×	×	✓

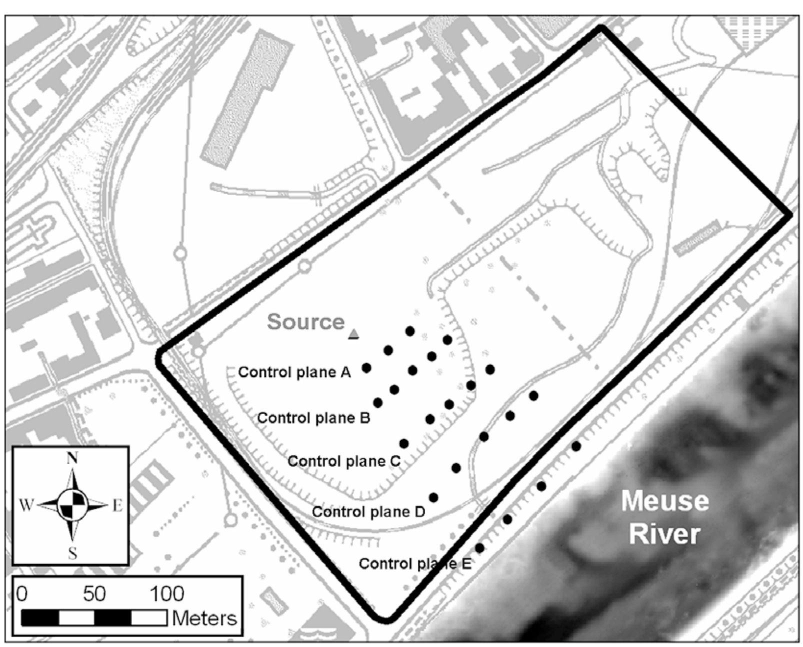

Fig. 8. Location of the main pollution source in the model and five control planes defined towards the river for modelling benzene transport in the aquifer.

the isotopic fractionation. In order to evaluate the influence of groundwater–surface water dynamics on benzene dispersion and attenuation in the alluvial aquifer, the model was run under transient conditions for 2 years (scenario 4), corresponding to the period when Meuse river levels and groundwater levels were monitored (from April 2005 to June 2007). Finally, an evaluation of the river fluctuations on benzene migration was performed in scenario 5. This scenario is quite similar to scenario 4 but without considering benzene biodegradation and sorption. As initial conditions for scenarios 1–3, benzene concentration was zero everywhere except in the source area. For scenario 4, initial conditions correspond to the stabilised benzene plume of scenario 3. Finally, the stabilised plume of scenario 1 was considered as initial condition in scenario 5.

Mean values of hydrodispersive and retardation parameters obtained from the calibration of radially convergent tracer tests are used for the five scenarios (Table 5) and, where required, the linear distribution coefficient (K_d) was calculated as follows:

$$K_d = K_{oc} f_{oc} \tag{4}$$

where K_{oc} is the soil sorption coefficient for soil organic carbon ($L^3\,M^{-1}$), and f_{oc} is the fraction of soil organic carbon (–). For K_{oc} and f_{oc} characteristic values of alluvial aquifers were considered (Alvarez and Illman, 2006). The resulting K_d value ($4.15 \times 10^{-5}\,m^3\,kg^{-1}$) is in good agreement with values proposed by Fetter (1993) and used by van den Brink and Zaadnoordijk (1997) within a similar context.

The retardation factor R was determined as follows:

$$R = 1 + (\rho_b K_d / \theta_m) \tag{5}$$

where ρ_b is the bulk density ($M\,L^{-3}$), K_d the distribution coefficient ($L^3\,M^{-1}$) and θ_m the mobile porosity.

The first-order biodegradation rate constant for benzene biodegradation's estimation was based on the carbon isotope data using Eq. (3) (see details in "Assessment of benzene biodegradation using stable carbon isotope analysis" and "Natural attenuation of benzene" sections).

Results on benzene transport modelling

Benzene concentrations at control planes A to E for scenarios 1 (no retardation), scenario 2 (retardation by physic-chemical attenuation) and scenario 3 (including all NA processes) using a logarithmic scale are illustrated in Fig. 9. Although the retardation and attenuation of benzene were expected to be away from the source because of sorption and degradation, it is interesting to observe that degradation alone can explain the very low benzene concentrations near the river. For scenario 3 and with a degradation rate of $3 \times 10^{-7}\,s^{-1}$, benzene concentrations stabilise much faster in comparison to scenarios 1 and 2, and concentrations are considerably reduced. Downgradient of control plane C (80 m), benzene concentrations are below $1 \times 10^{-6}\,mg\,L^{-1}$. Results of transient modelling of groundwater flow and transport are presented in Fig. 10. Benzene concentrations are presented at control plane B (50 m to the source area), together with the Meuse River levels and the groundwater levels for the same period. Benzene concentrations change over time inversely to river fluctuations. When the river water level fluctuates gently around its baseline (i.e. 59.4 m a.s.l.), the benzene concentration is at its maximum while when the river water level rises up to 61 m (hydraulic gradient inversion; e.g. January 2007), benzene concentration decreases to its minimum. This is due to the fact that the benzene plume moves backs as a consequence of the hydraulic gradient inversion between the river and the aquifer. When the river water level returns to its baseline, the benzene plume moves forward; this is translated in an increase of the benzene concentration. During the modelled period, benzene concentrations calculated in the zone adjacent to the river remain under the detection limit ($\mu g\,L^{-1}$), which is in good agreement with sampling results obtained in 2005 and in 2006.

The impact of river fluctuations on benzene migration was studied by running the model for scenario 5, where benzene degradation and sorption were not considered any longer. From Fig. 11 it is to observe that the benzene concentrations, being the same at the beginning of the simulation as those corresponding to scenario 1, are higher than concentrations presented in Fig. 10 for scenario 4. This further demonstrates that biodegradation is the main process controlling benzene migration in the aquifer. From a purely hydraulic point of view, the reversal of the groundwater flow direction is not efficient enough to prevent benzene migration off-site to the Meuse River.

Table 5
Hydrodispersive and retardation parameters used for benzene transport simulations (θ_m: mobile porosity; θ_{im}: immobile–or less mobile-porosity; α_L: longitudinal dispersivity; α_T: transversal dispersivity; α: diffusion coefficient between mobile and immobile domains; p: fraction of sorption in contact with the immobile phase; R: retardation factor; K_d: distribution coefficient between sorbed and dissolved phases; K_{oc}: soil sorption coefficient for soil organic carbon; f_{oc}: fraction of soil organic carbon; ρ_b: bulk density; λ: first-order degradation rate constant).

Hydrodispersive and retardation parameters	
θ_m (–)	0.04
θ_{im} (–)	0.1
α_L (m)	2.5
α_T (m)	0.5
α (s^{-1})	1×10^{-7}
p (–)	0.95
R (–)	3
K_d ($m^3\,kg^{-1}$)	4.15×10^{-5}
K_{oc} ($m^3\,kg^{-1}$)	0.083
f_{oc} (%)	0.05
ρ_b ($kg\,m^{-3}$)	2000
λ (s^{-1})	3×10^{-7}

Discussion

It was observed in the field that benzene was present at concentrations on the order of $mg\,L^{-1}$ in the source zone and also that these concentrations decreased of several orders of magnitude within a relatively short distance downstream from the source. As an example, benzene concentrations on the order of $\mu g\,L^{-1}$ have been reported in piezometer U10, located 115 m downgradient the source and located at a distance of about 50 m from the Meuse River (corresponding to control plane D). The numerical model demonstrated that a plume formed more than 25 years ago (i.e. at least around 1984, at which time industrial activities in the brownfield were stopped definitively and installations were demolished) would extend much further the downgradient source, in the absence of biodegradation and under the assumption of a constant benzene source of $750\,mg\,L^{-1}$. Consequently, high concentrations of benzene should be observed in groundwater close to the river. However, benzene was never detected in the different sampling points located in shorter distance to the Meuse River (U15, U17, P4). The strong decrease in the benzene concentrations over such a short distance can be attributed to biodegradation under strongly reducing conditions, as confirmed by the enrichment of ^{13}C in benzene with increasing distance from the source. When biodegradation is considered in the model, concentrations below $10\,\mu g\,L^{-1}$ are predicted at locations downgradient control plane B, which matches well with the measured data (Table 1). This conclusion is in agreement with a recent field study that used a stable isotope-based first-order decay model to investigate the natural attenuation of BTEX and naphthalene (Blum et al., 2009).

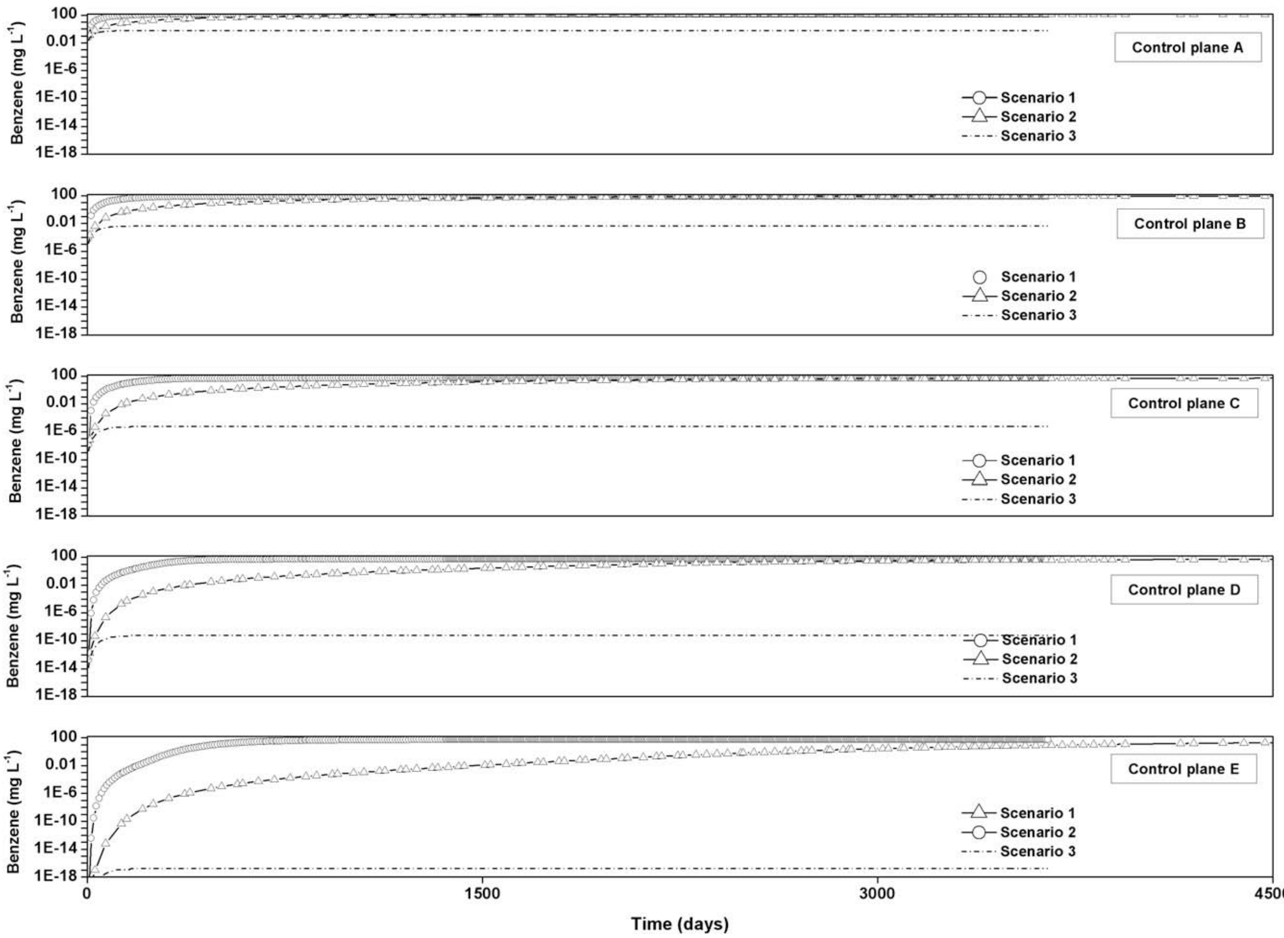

Fig. 9. Steady state benzene concentrations (logarithmic scale) at control planes A, B, C, D and E for scenarios 1 (no sorption), 2 ($R = 3$) and 3 ($\lambda = 3 \times 10^{-7}\ s^{-1}$) (see Table 4 for details).

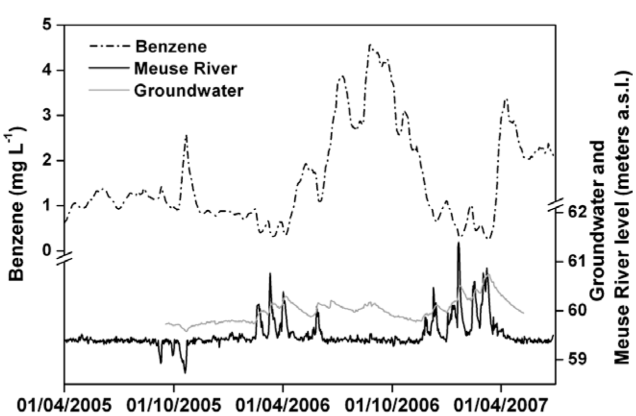

Fig. 10. Modelled transient benzene concentrations at control plane B (50 m to the source area) for a period of 2 years (scenario 4; see Table 4 for details).

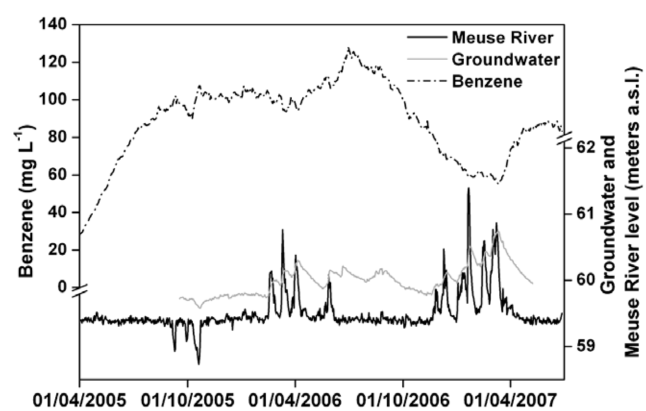

Fig. 11. Modelled transient benzene concentrations at control plane B (50 m. to the source area) for a period of 2 years (scenario 5; see Table 4 for details).

Considering the redox map of the site (Fig. 3), it becomes evident that benzene is mainly biodegraded under sulphate-reducing conditions. In particular, HS^- concentrations higher than 1 mg L^{-1} are observed in zones where benzene concentrations are larger than 1 mg L^{-1} in groundwater, therefore confirming this assumption. The potential for anaerobic biodegradation of benzene in the aquifer material from the site was also confirmed by a laboratory microcosm study, under *in situ* like conditions, using ^{13}C labeled substances. In these microcosms, 140 mg L^{-1} of sulphate as main electron acceptor were initially added to groundwater from the field site and mineralisation of benzene was observed (Morasch et al., 2007). A complementary batch study with aquifer material and groundwater from the site was performed to investigate the fate of heavy metals (Vanbroekhoven et al., 2007). The decrease in sulphate was monitored during degradation of acetate as an easily available carbon source and the effect of sulphide on heavy metal concentrations in the water phase was followed over time.

Based on these two microcosm approaches, it can be assumed that the immobilisation of divalent metals like Zn and Cd as metalsulphides is likely to take place in the aquifer and might be linked to the degradation of organic contaminants. The hypothesis could also explain the low concentrations of divalent Zn and Cd in the groundwater sampled from piezometers U15 (Vanbroekhoven et al., 2007). On the contrary, reducing conditions are expected to lead to a mobilisation of As(III).

Biodegradation processes have proved to be the main factor preventing benzene migration off-site. However, near the river, the fate of benzene or other organic contaminants could still be influenced by groundwater–surface water interaction as follows. Firstly, contaminants might be diluted by infiltrating river water which would decrease measured concentrations without removing the benzene out of the system. Secondly, infiltrating river water might stimulate biodegradation by supplying oxidants or nutrients. For PAHs such as naphthalene and acenaphthene, which can be biodegraded in the aquifer under anoxic conditions but at relatively low rates (Morasch et al., 2007), biodegradation by infiltrating river water might be even more pronounced. Finally, in areas where organic pollutants have not been reported (e.g. around piezometers U15 and U17), oxic conditions still prevail. In this case, As(III) might be converted to As(V) and immobilised; on the contrary, Zn and Cd would be released.

Conclusions and perspectives

Under prevailing conditions, the risk of contaminant dispersion to the Meuse River through groundwater discharge seems low. The largest fraction of benzene, and possibly also of other monoaromatic contaminants, is predominantly degraded under sulphate-reducing conditions. The sulphide that is released by contaminant degrading bacteria can lead to the precipitation of divalent cations Zn and Cd as their metalsulphides. Further downgradient source and closer to the river, a natural attenuation of more persistent organic contaminants could probably be enhanced by groundwater–surface water interactions. That is, groundwater level being influenced by river water level fluctuations, because surface water infiltration can induce the possible dilution of the front of the plume and supply oxidants, enhancing thus benzene biodegradation. As long as sulphate remains available at elevated levels, one can expect an efficient attenuation of organic compounds and a subsequent immobilisation of heavy metals such as Zn and Cd in the strongly reduced zone of the aquifer. It would be helpful firstly, to gain more insight into the long term availability of sulphate and secondly, to evaluate the temporal evolution of contaminant concentrations under the influence of fluctuating river levels in further details. Finally, there is a need for batch experiments directly linking the degradation of organic contaminants with the precipitation and dissolution of metal cations, under various reduced conditions. The use of a more advanced reactive transport modelling that incorporates geochemical processes would also provide additional understanding and knowledge on contaminant dispersion in the studied site, in particular or their possible interactions.

Acknowledgements

This work was supported by the European Union FP6 Integrated Project AquaTerra (Project No. 505428) under the thematic priority, sustainable development, global change and ecosystems, by the Belgian BELSPO through the SSD FRAC-WECO project no. SD/TE/02A and by ULg Aquapôle research funds. Thanks to SPAQuE, especially H. Halen and A. Lox, for access to data and to the brownfield. Thanks are also due to P. Theunissen (SPE-TGV) for his gracious contribution on Meuse data time series. Florian Châtelain is thanked for his assistance during benzene degradation field campaigns and for helping with the groundwater analysis. Authors gratefully thank Marie Sudki for editing and polishing of the English writing.

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GQ10: Groundwater Quality Management in a Rapidly Changing World (Proc. 7th International Groundwater Quality Conference held in Zurich, Switzerland, 13–18 June 2010).

A regional flux-based risk assessment approach for multiple contaminated sites on groundwater bodies

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Abstract In the context of the Water Framework Directive, management plans have to be set up to monitor/maintain water quality in surface and groundwater bodies in the EU. In heavily industrialised and urbanised areas, the cumulative effect of multiple contaminant sources is likely, and presents a challenge which has to be evaluated. In order to propose adequate measures, the calculated risk should be based on criteria reflecting the risk of water quality deterioration, in a cumulative manner and at the scale of the entire surface water or groundwater body. An integrated GIS- and flux-based risk assessment approach for groundwater and surface water bodies is described herein, with a regional scale indicator for evaluating the quality status of the groundwater body. It is based on the SEQ-ESO currently used in the Walloon Region of Belgium which defines, for different water uses and for a detailed list of groundwater contaminants, a set of threshold values reflecting the levels of water quality and degradation with respect to each contaminant. The methodology is illustrated with its first real-scale application on a groundwater body:a contaminated alluvial aquifer which has been classified at risk of not reaching a good quality status by 2015.

Key words regional risk assessment, groundwater body, groundwater quality, industrial contaminants, Water Framework Directive, multiple contaminant sources

INTRODUCTION

The EU Water Framework Directive requires management plans to maintain the quality of surface and groundwater bodies. These plans cannot be defined without considering industrial sites potentially harmful to water resources. In some instances, a single site does not necessarily constitute a threat to the whole aquifer or groundwater body. By contrast, in heavily industrialised and urbanised areas, because of the spatial extent of groundwater bodies, many contaminant sources may need to be considered, with complex groundwater vectors for contaminant dispersion. In such a context, a meaningful regional risk assessment approach has to be developed (e.g. Critto & Sutter, 2009) that considers the cumulative effect of multiple contaminant sources. In addition, the spatially distributed data require GIS databases and decision tools.

METHODOLOGY FOR REGIONAL RISK ASSESSMENT

The regional risk assessment tool is structured as follows: a geodatabase, organised according to the Source-Pathway-Receptor schema, has been developed under MS Access environment to store and manage all of the spatially distributed information required for regional risk assessment. An activity-matrix tool has also been incorporated to provide a list of pollutants potentially released by given industrial activities and inversely. Seventy five relevant contaminants are included with their physical and chemical properties (solubility, Koc, etc.). In the groundwater body, the various potential sources of pollution are identified and geo-referenced into the geospatial database (Fig. 1a). For each of the selected contaminant sources, the migration of contaminants within the aquifer is calculated using a numerical groundwater flow and transport model developed for that groundwater body. Repeating the same procedure for all identified sources of contamination provides a map of contaminants' plumes in the studied groundwater body (Fig. 1b). At each time step, the generated plumes are classified in terms of groundwater quality classes on a normalized scale between 100 (high quality) and 0 (degraded) that accounts for the threshold values defined specifically for each contaminant, using the SEQ-ESO evaluation system used in the Walloon Region (Rentier et al., 2006). This gives a global picture of the quality status of the groundwater body (Fig. 1c). Finally, a global quality index (I_{global}) is calculated for the groundwater body at each time step, using a weighting-average formula (Fig. 1d).

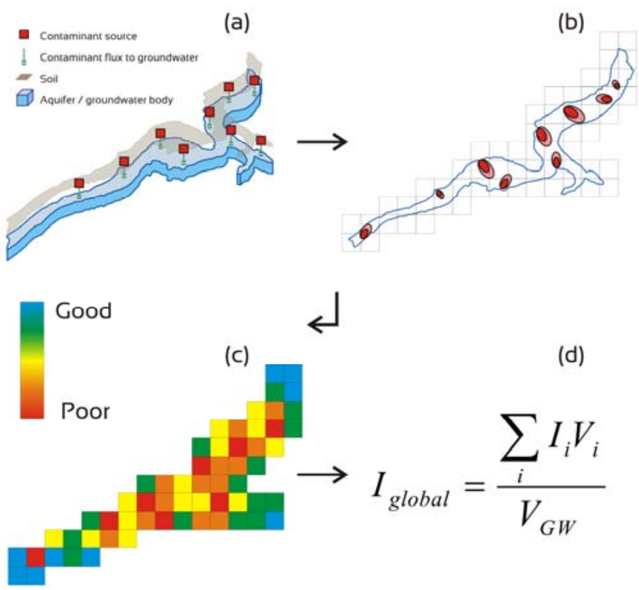

Fig. 1 Regional risk assessment methodology applied to a groundwater body. I_{global}: global quality index for the whole groundwater body at time t [-], V_{GW}: volume of groundwater comprised in the zone where the risk is assessed [V], V_i: volume of water into the cell *i* [V], I_i: quality index for the cell i[-].

The proposed methodology offers several advantages. First of all, it is compliant with the ongoing legislation in the Walloon region, based on the SEQ-ESO and it fits very well with the guidelines of the EU Water Directive which promotes the use of aggregated indicators able to reflect trends in groundwater quality. , This aggregation of different types of contaminants into a single ranking system is achieved by considering various water uses and their respective threshold values. The indicator can also be used for risk assessment by comparing the global spatially aggregated indicator to corresponding threshold values.

ILLUSTRATION AND CASE STUDY

As a first example illustrating the utility of this tool, a fictional groundwater flow and transport model has been developed. The model represents an aquifer with lateral no-flow boundaries conditions except a draining river boundary condition to the East, to model the pollution of an alluvial aquifer by industrial contaminants with contrasted physico-chemical properties (benzene, benzo(a)pyrene and TCE). Fig. 2 shows maps of SEQ-ESO indicators for the 3 pollutants after one and twenty years and the evolution with time of the groundwater global quality index which diminishes as the pollutants spread through the aquifer.

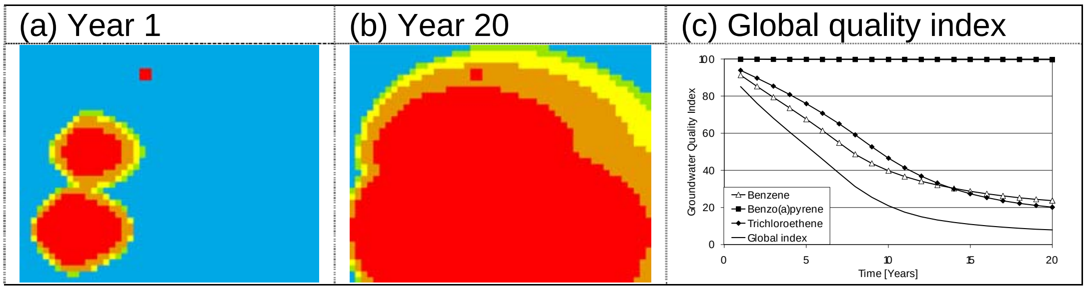

Fig. 2 SEQ-ESO indicator maps for the three contaminants after (a) 1 year and (b) 20 years and (c) evolution with time of the global quality index using SEQ-ESO after spatial integration.

The first application of the model to field data occurred for Groundwater Body RWM073, which corresponds to the alluvial deposits of the Meuse river in the region of Liège (Fig.3a). This site has the potential risk of not reaching the "good" chemical status required by the EU Water Framework Directive for 2015, because of numerous contaminated sites along its length, resulting from past heavy industrial use in this area. For this example, industrial plants lying within the category “mining”, “gas station” and “metallurgy”, with a spatial extent larger than 100 m² are considered and benzene as the sole contaminant. Groundwater flow and transport simulations are performed using Modflow and MT3D over a 20 years period. The groundwater flow model is calibrated using piezometric head measurements available in the area (Fig.3b). Transport parameters are defined based on experiments in the Meuse alluvial aquifer (Batlle-Aguilar et al., 2009). A worst case scenario is modelled assuming that all potential sources of benzene are active and that benzene does not degrade in the alluvial aquifer. Fig. 3c shows the resulting map of benzene concentrations in the alluvial aquifer after 20 years. Fig. 3d shows the evolution of the global groundwater quality index at this groundwater body as affected by benzene dispersion alone.

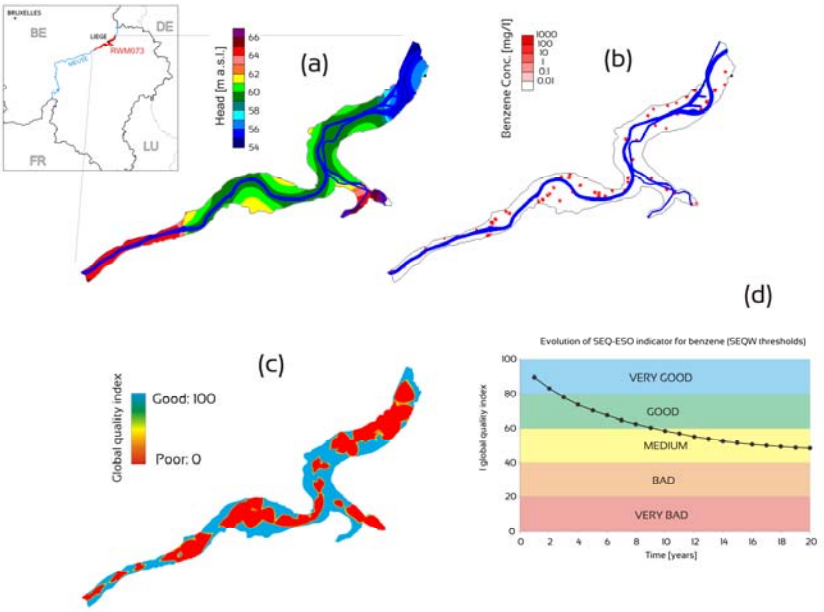

Fig. 3 Preliminary results of regional risk assessment on groundwater body RWM073 considering industrial activities releasing benzene into the groundwater. The resulting SEQ-ESO indicator suggests a "medium" quality status of the groundwater body.

CONCLUSIONS AND PERSPECTIVES

The regional scale risk assessment for groundwater bodies presented here is a flexible approach for evaluating the pressure of various sources of contamination on a regional groundwater body. It aggregates various cumulative sources of contaminants of different chemical natures, properties and toxicities into a single, easy to use and to report indicator. The indicator may be particularly useful for identifying and reporting trends in groundwater quality in the complex scenarios of urbanized and industrialized catchments. A key next step will be to incorporate a statistical approach for handling all the uncertainties that remain at regional scale, as they relate to contaminant sources, properties, hydrogeological conditions etc. This analysis is also now used as a referential for costs and benefits assessment of total or partial remediation of the contaminated groundwater body, according to different management scenarios.

Acknowledgements The FRAC-WECO project is financed by the Belgian Federal Science Policy Programme BELSPO (Project Nb SD/TE/02A). Thanks to the two anonymous reviewers of the original manuscript.

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Journal of Contaminant Hydrology 127 (2012) 65–75

Contents lists available at ScienceDirect

Journal of Contaminant Hydrology

journal homepage: www.elsevier.com/locate/jconhyd

A regional flux-based risk assessment approach for multiple contaminated sites on groundwater bodies ☆

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ARTICLE INFO

Article history:
Received 12 November 2010
Received in revised form 14 June 2011
Accepted 1 July 2011
Available online 27 July 2011

Keywords:
Regional risk assessment
Groundwater body
Groundwater quality
Groundwater modeling
Industrial contaminants
Water Framework Directive
Multiple contaminant sources

ABSTRACT

In the context of the Water Framework Directive (EP and CEU, 2000), management plans have to be set up to monitor and to maintain water quality in groundwater bodies in the EU. In heavily industrialized and urbanized areas, the cumulative effect of multiple contaminant sources is likely and has to be evaluated. In order to propose adequate measures, the calculated risk should be based on criteria reflecting the risk of groundwater quality deterioration, in a cumulative manner and at the scale of the entire groundwater body. An integrated GIS- and flux-based risk assessment approach for groundwater bodies is described, with a regional scale indicator for evaluating the quality status of the groundwater body. It is based on the SEQ-ESO currently used in the Walloon Region of Belgium which defines, for different water uses and for a detailed list of groundwater contaminants, a set of threshold values reflecting the levels of water quality and degradation with respect to each contaminant. The methodology is illustrated with first results at a regional scale on a groundwater body-scale application to a contaminated alluvial aquifer which has been classified to be at risk of not reaching a good quality status by 2015. These first results show that contaminants resulting from old industrial activities in that area are likely to contribute significantly to the degradation of groundwater quality. However, further investigations are required on the evaluation of the actual polluting pressures before any definitive conclusion be established.

1. Introduction

The EU Water Framework Directive (EP and CEU, 2000) requires management plans to monitor, to maintain and, if required, to restore the quality of surface water and groundwater bodies. In very urbanized and industrialized regions, water resources, and particularly groundwater, are subject to many pollution pressures related to different kinds of socio-economic activities and contaminants (UNEP/ADEME, 2005; European Environment Agency, 2006). These plans cannot be defined without considering industrial sites potentially harmful to groundwater resources and, in this context, different questions arise. How can we take into consideration all these potential and actual sources of pollution in evaluating the risk of deterioration of groundwater quality and the efficiency of programs of measures defined to restore this quality? And, as a consequence of this, how can we evaluate groundwater quality at the regional scale of the groundwater body and the evolution with time of groundwater quality?

Classical risk assessment and management concepts for contaminated sites are usually based on a univocal relationship between a source of pollution and a potentially exposed receptor, commonly referred to as the source–pathway–

☆ Revised manuscript prepared for submission to the GQ2010 special issue of the Journal of Contaminant Hydrology.

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doi:10.1016/j.jconhyd.2011.07.001

receptor approach, with an evaluation of the receptor's exposure level and a comparison to environmental and health regulations (e.g. Ferguson et al., 1998; Fairman et al., 1999). This conceptual approach is convenient for pollution sources and receptors well located in space, such as local pollution “hotspots” and pumping wells nearby. By contrast, in heavily industrialized and urbanized areas, because of the spatial extent of groundwater bodies, many point or diffuse pollution sources may need to be considered in the analysis, with complex groundwater vectors for contaminant dispersion, and a meaningful regional risk assessment approach has to be considered (Gay and Korre, 2006; Critto and Sutter, 2009).

Several projects have been dedicated recently to the development of methodologies for contaminated megasite management, such as CLARINET (2002), NICOLE (2003), WELCOME (2004), INCORE (Ptak et al., 2003; Jarsjo et al., 2005), DESYRE (Carlon et al., 2007; 2008), and SAFIRA II (Schädler et al., 2007; Morio et al., 2008). These projects propose concepts and tools for a regional analysis of environmental issues related to contaminated sites, for regional risk assessment, for prioritization of investment and rehabilitation on industrial land parcels and brownfields or for cost–benefit socioeconomic analyses. Beside these megasite-oriented projects, other decision support systems have been developed (Béranger et al., 2006), based on GIS systems, e.g. SMARTe (Vega et al., 2009) or DECERNS (Sullivan et al., 2009) for data management and cartography and for regional scale risk assessment for contaminated sites, SADA (Purucker et al., 2009) or ERAMANIA (Semenzin et al., 2009) for ecological risk assessment, BOS (Tait et al., 2004; 2008; Chisala et al., 2007) for the management of groundwater in urban areas and BASINS (Kinerson et al., 2009), RISKBASE (Brils and Harris, 2009) or CatchRisk (Troldborg et al., 2008) for water pollution risk assessment and management at catchment scale. However, these projects do not really propose specific indicators for the quality of groundwater seen as a regional resource (Caterina et al., 2009). The objective here is to fill this gap by proposing a flux-based methodology to calculate a groundwater quality indicator that considers the cumulative effect of multiple, spatially-distributed pollution sources with multiple types of contaminants. This approach can be used for groundwater quality trend assessment and for groundwater pollution risk assessment on groundwater bodies.

The methodology and related tools are described in details and illustrated using a synthetic example and a first real scale application to a deteriorated groundwater body in Belgium.

2. Methodology for regional risk assessment

The methodology for regional risk assessment is summarized in Fig. 1. The scale of application corresponds to the groundwater body defined in the context of the EU water framework directive as the groundwater management unit for aquifers in Europe. The approach can also straightforwardly be limited and applied to parts of groundwater bodies where stronger deterioration of water quality is observed or to specific areas such as contaminated megasites. In the groundwater body of interest, the various potential sources of pollution are identified and geo-referenced into a specific geospatial database (Fig. 1a). For each of the selected contaminant sources, the migration of contaminants within the aquifer is calculated using a numerical groundwater flow and transport model developed at the scale of the groundwater body. Repeating the same procedure for all identified sources of contamination provides a map of contaminants' plumes in the studied groundwater body (Fig. 1b) at different times. The generated plumes are classified in terms of groundwater quality classes on a normalized scale that accounts for threshold values defined specifically for each contaminant, using the SEQ-ESO evaluation system used in the Walloon Region (Rentier et al., 2006). This gives a global picture of the quality status of the groundwater body (Fig. 1c). Finally, a global quality index (Iglobal) is calculated for the groundwater body at each time step, using a weighting-average formula (Fig. 1d). The different modules composing the regional risk assessment system are described in details hereafter.

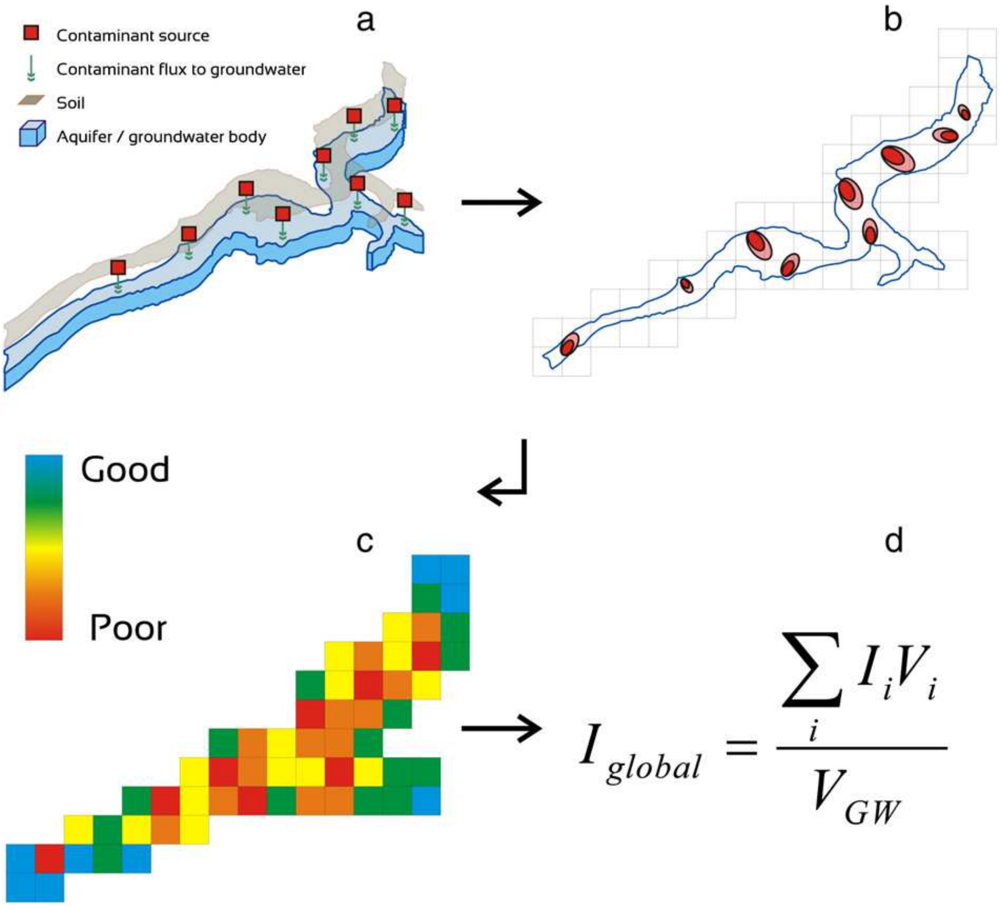
2.1. Geospatial database for regional groundwater quality and pollution risk assessment

A geodatabase, organized according to the Source–Pathway–Receptor schema, has been developed to store and manage the important quantity of spatially distributed data required by the regional approach. This geodatabase has been developed under ArcMAP environment, with a specific menu in the graphical user interface, based on Visual Basic scripts and routines, and using shapefiles and attributes tables for handling environmental data. The conceptual schema of the geodatabase is shown in Fig. 2. The “Source” module gathers the information on potential contaminated sites. It is used to characterize the nature, size and location of industrial sites. The “Pathway” module organizes the information needed to characterize the physical environment, such as geology, hydrogeology, soils or land-use. The “Receptor” module gathers the information on potentially exposed receptors, which are first the groundwater resource but possibly also other receptors such as streams, pumping wells or springs.

At such a regional scale, it is unlikely to obtain all the information on existing pollution sources because all the contaminated sites are not necessarily known or characterized in details. The selection of pollutant sources considered in the analysis can also be based on registered industrial activities using a matrix “activity-pollutant” presented as two Microsoft Access-type linked tables connected with a shapefile listing all industrial plants. The first table is a dictionary of seventy-five selected pollutants with their main physico-chemical properties (e.g. solubility, octanol–water partitioning coefficients, Henry's constants …) and contaminant threshold values used in the Walloon regulation (Walloon Soil Decree, 2008). The second table relates classified industrial activities and associated pollutants, based on previous similar works (e.g. MATE, 2000; SITErem, 2002). The “Industry” shapefile and the pollutant-activity matrix are linked using an activity code defined according to the European industrial activity classification NACE (European Commission, 2008) to create a shapefile of potential contaminant sources.

2.2. Groundwater flow and transport modeling concepts

In order to evaluate the impact of pollution sources on the quality of the groundwater resource, it is necessary to evaluate, at regional scale, how much and to which extent



$$I_{global} = \frac{\sum_i I_i V_i}{V_{GW}}$$

Fig. 1. Regional risk assessment methodology applied to a groundwater body. I_{global}: global quality index for the whole groundwater body at time t [−], V_{GW}: volume of groundwater comprised in the zone where the risk is assessed [L³], V_i: volume of water into the cell *i* [L³], I_i: quality index for the cell i[−].

groundwater is degraded from these sources. This requires quantifying contaminant mass fluxes to and through groundwater in order to determine the volumes of degraded groundwater and the severity of this degradation, *i.e.* the spatial extent of the contaminated plumes and concentrations of contaminants. Existing monitoring networks, usually based on piezometers, are unlikely to provide extensive and exhaustive information on groundwater pollution because they are very often limited to the neighborhood of identified polluted sites. The alternative is to use groundwater flow and transport models to calculate contaminant mass fluxes from the pollution sources to and through groundwater. The objectives of the groundwater flow and transport model is first to calculate the dispersion plumes of contaminants in the saturated zone, but also to evaluate the relative importance of specific pollutant sources within a regional contamination (*i.e.* site prioritization) and to test programs of measures defined for the restoration of groundwater quality for groundwater body management.

The extent and the boundaries of the concerned area (*i.e.* the model) have to be clearly defined before any other consideration. This step should be achieved with decision makers and stakeholders at the beginning of the risk assessment process. The most logical choice is to consider the whole groundwater body as defined by the EU Water Framework Directive, delineated according to geological, hydraulic and administrative factors and included into every EU member state legislations.

A comprehensive modeling approach requires calculating first the vertical leaching of contaminants from the pollution source to the groundwater table, then the horizontal dispersion of contaminants in the saturated zone. However, the pollution sources considered correspond mostly to historical contaminations having occurred when environmental regulations were less restrictive. Accordingly, it is assumed, as a first approximation, that contaminants have already reached the groundwater table and that the leaching of contaminants to groundwater can be modeled as a specified mass flux considering the recharge rate and the effective solubility of each contaminant.

The groundwater flow and transport model consists of a transient transport model based on a steady-state groundwater flow model. It serves to calculate groundwater fluxes and groundwater flow directions in order to route contaminants from the pollution sources through the groundwater body and, subsequently, to run transport simulations. Steady state simulations for groundwater flow are sufficient because the objective is to delineate contamination plumes over long time periods, and not to consider the influence of groundwater dynamics on these plumes.

Aquifer hydraulic conductivity defined in the regional model are essentially based on lithological entities using orders of magnitudes resulting from field measurements (pumping tests …) for similar materials. Realistic estimates of groundwater recharge are important because it is the driver of

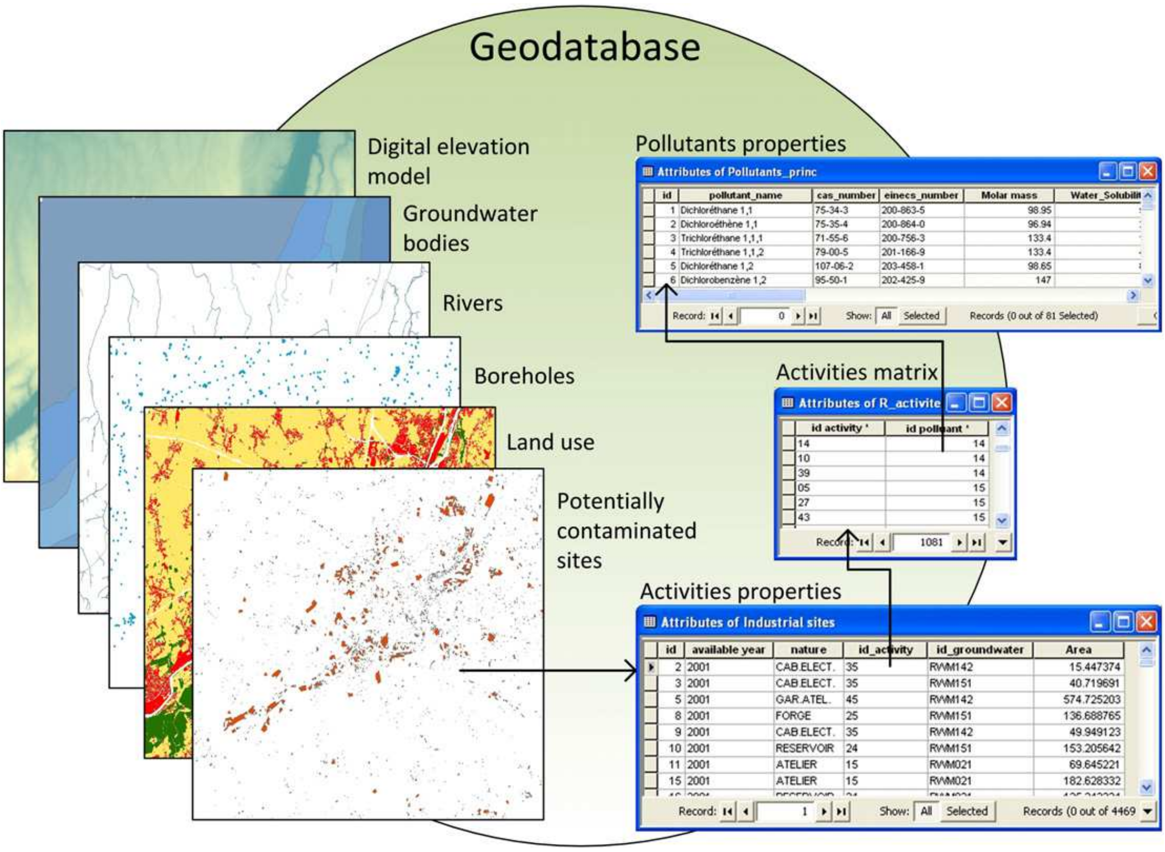


Fig. 2. General organization of the Geodatabase.

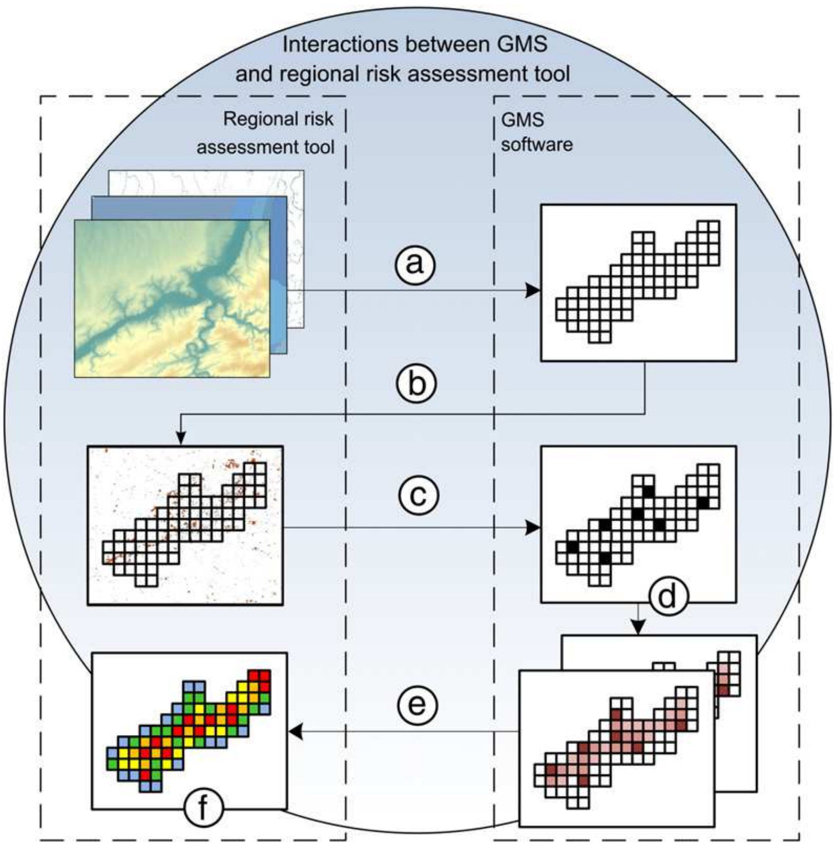


Fig. 3. Interactions between GMS and regional risk assessment tool.

contaminant fluxes to and in groundwater. In this context, a land cover mapping classification methodology has been developed from high resolution satellite data in order to distribute in space the recharge as a function of the land-use and soil imperviousness (Dujardin et al., 2009).

Practically, MODFLOW (Harbaugh et al., 2000) and MT3D (Zheng and Wang, 1999) numerical simulations are performed under GMS (Groundwater Modeling System) environment. Data and information exchanges between the modeling application and the regional risk assessment system are managed through specific communication modules developed in the GIS interface. The communication procedure is described in Fig. 3. The different shapefiles required for the hydrogeological conceptual model are prepared within the GIS system using data from the geodatabase and imported in GMS (Fig. 3a) using the 'GIS and Map Module'. Based on that, a regional finite difference grid is created and exported back to the GIS interface (Fig. 3b) where it is used to clip the pollution sources and related information (contaminant types and properties …) to be again further exported in the appropriate GMS grid format (Fig. 3c) for contaminant transport simulations (Fig. 3d). Currently, the considered contaminant transport processes are advection, hydrodynamic dispersion, linear sorption and degradation (Eq. 1).

$$R\frac{\partial C}{\partial t} = div\left(\underline{\underline{D}}\ \underline{grad}\ C - \underline{v_e}C\right) - \lambda RC + C^* \frac{q'}{n_e} \quad (1)$$

where C is the concentration [M L^{-3}], t: time [T], $\underline{\underline{D}}$ is the hydrodynamic dispersion tensor [L^{2}T^{-1}], v_e is the groundwater effective velocity [L T^{-1}], λ is the first-order degradation constant (T^{-1}), q': a source-sink term [T^{-1}], $C^*=C$ if $q'<0$ (sink) and $C^*=C_{in}$ if $q'>0$ (source), n_e is the effective (transport) porosity [−], R is the retardation factor equal to $1+\frac{\rho_b K_d}{n_e}$ with ρ_b is the bulk density of the porous media [M L^{-3}] and K_d the distribution coefficient between aqueous and solid phase (linear sorption) [L^{3}M^{-1}].

Once simulations are performed, modeling results (piezometric heads and contaminant concentrations at different time steps, one data set per contaminant) are imported into the GIS interface (Fig. 3e) for the calculation of the groundwater quality indicators (Fig. 3f), as described in the next section.

2.3. Groundwater quality assessment using the SEQ-ESO indicator

The transport model provides concentrations of contaminants in groundwater at different times. However, these contaminants are of different nature, with specific physico-chemical properties and harmfulness for health or environment. To evaluate objectively the overall quality of groundwater and its level of degradation, it is necessary to normalize the concentrations of contaminants using a uniform classification procedure with classes that consistently reflect equivalent levels of degradation for the different contaminants considered (e.g. drinking water limit). To reach that objective, the SEQ-ESO indicator ('Système d'Evaluation de la Qualité des Eaux Souterraines', i.e. Groundwater Quality Evaluation System) used by the Walloon Region of Belgium to report on the Water Framework Directive groundwater quality monitoring network (Rentier et al., 2004a; 2004b) has been selected and adapted. It is based on the SEQ-Eau ranking system initially developed by the French water agencies (Agences de l'Eau, 2002). The SEQ-ESO provides an interpretation grid for a complete protocol analysis related to a single water sampling point. Conversion from contaminant concentrations to a normalized non-dimensional index is based on interpolation functions between different threshold values that depend on the water uses. The final quality index, ranging from 100 (good quality) to 0 (very degraded) corresponds to the index of the most problematic compound (Rentier et al., 2006).

The calculation the SEQ-ESO quality index is performed in two steps. First, contaminant concentrations are normalized on a [0 = poor, 100 = good] scale considering different contaminant specific threshold values, as illustrated for benzene in Fig. 4. The threshold values are defined for each kind of contaminant with respect to different water uses. Three different water uses have been defined originally for the SEQ-ESO: patrimonial status (PS), drinking water use (DWU) and, biological impact on water courses (BIO). A global groundwater quality status, called SEQW, is also evaluated using a combination of PS and DWU thresholds (see example for benzene in Table 1). Four threshold values are defined for each pollutant with linear interpolation for the three first intervals (S0–S1, S1–S2 and S2–S3), antilogarithmic interpolation for the S3–S4 interval and negative exponential interpolation above the S4 threshold. In a second step, the quality index is set equal to the lowest quality index corresponding to the most degrading contaminant. In the regional risk assessment approach described here, the SEQ-ESO threshold values have been incorporated into the pollutant library of the database considering the different water uses (PS, DWU, BIO and SEQW). However, the SEQW indicator, which is assumed to better reflect the global quality of water, independently of any use, is effectively considered for the calculation of the regional indicator for groundwater quality. A specific SEQ-ESO module has been developed in the ArcMAP environment for calculation of the regional indicator of groundwater quality based on the SEQ-ESO methodology (Fig. 3d).

Results imported from the groundwater flow and transport simulations provide concentrations for each contaminant in each grid cell and at each time step. The SEQ-ESO procedure is applied in each cell of the grid to normalize the concentrations of contaminants and to convert them into groundwater quality indexes by considering the specific threshold values of each contaminant.

This provides, at each time step, a map of distributed groundwater quality indexes at the level of the grid. Finally, an overall indicator can be obtained at each time step, by spatial aggregation of the grid indicators weighted by the volumes of groundwater present in each cell (Eq. 2).

$$I_{global} = \frac{\sum_i I_i V_i}{V_{GW}} \quad (2)$$

where I_{global} is the global quality index for the whole groundwater body at time t [−], V_{GW}: the volume of groundwater comprised in the zone where the risk is assessed [L^3], V_i: volume of groundwater into the cell i [L^3] and I_i: quality index for the cell i[−].

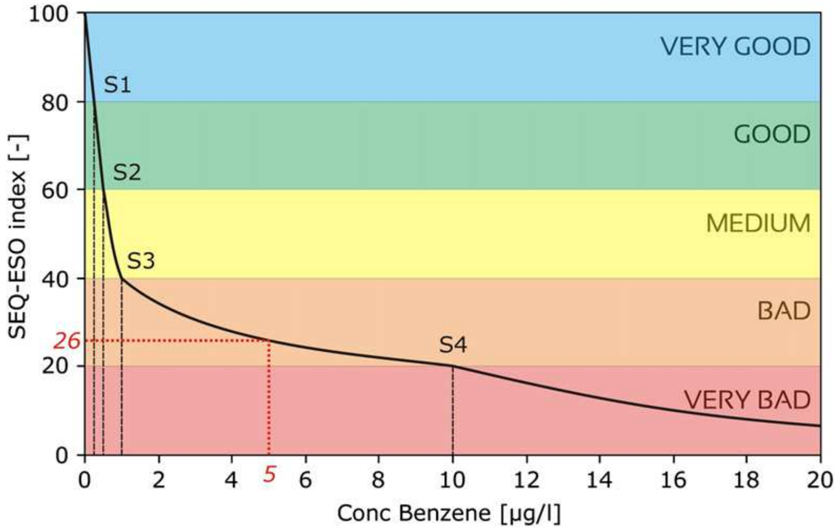


Fig. 4. Normalization from benzene concentration in groundwater to groundwater quality index according to SEQ-ESO method and SEQW thresholds (for example, groundwater contaminated at 5 µg/l of benzene corresponds to a quality index of 26).

The results of the SEQ-ESO application can be used in different ways. The maps of indicators can be used to identify most problematic sectors (contamination hot spots) with heavily contaminated groundwater volumes within a more generalized contamination. At the grid cell level, one can examine the global evolution with time of groundwater quality. Finally, the aggregated indicator can be used to report on the groundwater quality status of the groundwater body and for groundwater quality trend assessment. In this context, the indicator can be used as a referential for evaluating the risk of not reaching a good status and to test the efficiency of programs of measures defined to restore groundwater quality.

3. Illustrations

Two examples are proposed to illustrate the methodology and to show its usefulness for groundwater management in urbanized and industrialized areas: a synthetic example and the first results of a large scale application on a deteriorated groundwater body in Belgium.

3.1. Synthetic illustrative example

This simplified example reproduces the relatively frequent case of pollution of an alluvial aquifer by industrial contaminants emitted from an industrial plant located nearby a river (e.g. Batlle-Aguilar et al., 2009). The studied domain corresponds to a polluted area of 500 by 400 m. The alluvial aquifer has a thickness of 15 m The mean hydraulic conductivity of the alluvial sediments is 1×10^{-5} m/s. Groundwater is recharged by infiltration from rainfall (135 mm/y $=4.3\times10^{-9}$ m/s). The alluvial aquifer is drained laterally by the river. No-flow boundaries conditions are assumed at the external lateral boundaries (north, south, west) of the model, except at the riverbank (east) where a draining river boundary condition is defined (river stage: 55 m, hydraulic conductance of the riverbed: 2.5×10^{-4} m²/s). The pollution sources defined at three different locations in the contaminated land parcel are assumed to emit three different pollutants with contrasted physico-chemical properties representative of common contaminants in such contexts: a PAH-like pollutant (low mobility, moderate degradation), a BTEX-like pollutant (high mobility, high degradation) and a VOCl-like pollutant (high mobility, low degradation) (Table 2). Contaminants are assumed to leach into the aquifer at their maximum solubility in the recharge water for a period of 15 years, after which the sources are assumed to be removed and contaminant leaching is stopped. The contaminant transport model is run for 45 years from the beginning of the leaching of contaminants.

Fig. 5a shows the three contaminants plumes in terms of concentrations after 15 years. As expected, these plumes reflect the specific properties of the contaminants (solubility, sorptiv-

Table 1
Illustration of the combination of PS and DWU thresholds for the definition of SEQW threshold and origin of thresholds for benzene (example).

Benzene	Patrimonial status (PS)		Drinking water use (DWU)		SEQW
Threshold	µg/l	Origin	µg/l	Origin	µg/l
S1	0.25	Reference value for natural groundwater quality including geochemical background.	0.5	Guidance value of the 80/778/CEE EU Directive concerning drinking water (CEU 1980).	0.25
S2	0.5	Linear interpolation between S1 and S3	1	Walloon drinking water standard	0.5
S3	0.75	Threshold value as defined in the Walloon Soil Decree	–	*Does not exist*	1
S4	4	Intervention value for cleaning as defined in the Walloon Soil Decree	10	Guidance value of the 75/440/CEE EU Directive concerning quality water before treatment of surface abstracted for drinking water (CEU 1975).	10

Table 2
Contaminants parameters used for the synthetic test case.

Parameters	Units	Benzene-like species	PAH-like species	VOCl-like species
Concentration in recharge	mg/l	1830	10	1100
Kd	m³/mg	4.15×10^{-11}	4.77×10^{-7}	3.50×10^{-11}
Degradation	s^{-1}	1×10^{-7}	1×10^{-9}	1×10^{-9}

ity and degradability). PAHs are almost immobile and do not disperse into groundwater. VOCl are very mobile and BTEX are mobile but their plume extent is reduced because of degradation processes. However, these pictures do not give any clear insight on the actual degradation level of the groundwater resource in the area. Fig. 5b shows the SEQ-ESO map of indicators for the three contaminants concentrations scaled into in a single groundwater quality index. This shows that most of the groundwater is heavily contaminated in the plumes. Finally, Fig. 5c shows the evolution of the spatially aggregated groundwater quality index for each contaminant considered separately and the global SEQ-ESO indicator for the whole aquifer. During the period of contaminant leaching, groundwater quality is progressively degraded with time, the VOCl contaminant being the most significant contributor (approximately 40%) to this degradation. The BTEX contaminant contributes to a subsequent degradation of groundwater (approximately 10%) during the first 25 years. After 25 years, the contribution of BTEX to groundwater quality degradation becomes negligible because of the progressive removal of the remaining quantity of BTEX by biodegradation in contrast with VOCl that does not degrade and keep a strong impact on groundwater quality after 45 years. The PAH contaminant is very sorptive and insoluble and it remains captured near the source from where it never effectively contaminates groundwater.

3.2. Real-scale application in the alluvial aquifer of the River Meuse

The Meuse River flows in the Walloon Region of Belgium along 128 km from the French to the Dutch borders. The alluvial aquifer located in the deposits of the river contains an important groundwater resource which is exploited for water distribution and industry thanks to many water catchments located in the alluvial plain (Haddouchi, 1987; Brouyères et al., 2006). In the region of Liège, heavy industries related to coal extraction, metallurgy and chemistry have been developed for more than two centuries. These industries were preferentially settled in the alluvial plain, near the river, for facilitating transportation by boat of primary and final products. This, together with a growth in the urbanization, has resulted nowadays in the existence of numerous potentially contaminated sites and a generalized contamination of groundwater in the alluvial aquifer.

The portion of alluvial aquifer corresponding to the industrial area, located North-East of the Meuse Belgian stream (Fig. 6a), has been explicitly defined by regulators as a distinct groundwater body (named RWM073) from the rest of the alluvial aquifer to allow defining specific measures related to the issue of deterioration in groundwater quality in this part of the alluvial aquifer.

The problem of regional groundwater contamination is known and documented through water analyses at different locations, but important questions remain. There is no real global estimation of the actual level of water quality degradation at the scale of the groundwater body and of the actual contribution of industrial activities to this degradation as compared to other possible contamination sources, such as groundwater rebound after coal mine closure or diffuse atmospheric pollution. There is also no integrated referential for land cleanup prioritization and cost-efficiency assessment. To answer these questions, a referential for groundwater quality at the scale of the groundwater body is essential. An application of the regional-scale risk assessment approach has been initiated on this groundwater body. At the following, the first steps and results are described. At this step of the analysis, the objective of the real-scale application is not to provide a definitive value of the indicator of groundwater quality for the investigated groundwater body but to test and validate the concepts at real scale and to identify the priorities for further investigations.

The Meuse river alluvial gravel groundwater body RWM073 stretches on 40 km. The alluvial plain has a mean width of 3 km. The usual top–bottom geology consist of 2 to 4 m of backfill deposits, 1 to 4 m of silt sand clay deposits and approximately 8 m of alluvial gravels lying on a shaly bedrock that constitutes the impervious lower boundary of the aquifer. A data mining on the hydraulic properties of the aquifer has revealed hydraulic conductivity values ranging from 10^{-3} to 10^{-6} m/s with a mean value of 8×10^{-5} m/s. Along most of the river course, groundwater is drained by the Meuse River and it flows more or less perpendicularly to the river bank with a mean hydraulic gradient of 0.003 m/m. The aquifer recharge has been calculated using remote sensing imagery integrated in a modeling procedure. From medium resolution satellite imagery, the land-cover mapping is drawn and serves, along with soil type, topography and other physical parameters, in a hydrologic model to produce a high resolution spatially distributed groundwater recharge (Dujardin et al., 2011). Groundwater abstraction in the alluvial aquifer is limited to few industrial pumping wells which do not significantly affect regional groundwater patterns. As a first approximation, these pumping wells have been disregarded.

Groundwater flow and transport simulations are performed using MODFLOW (Harbaugh et al., 2000) and MT3D (Zheng and Wang, 1999). The model is developed using the finite difference method with a constant cell size of 20 by 20 m. The top of the model is given by a DTM and the cell thickness is assumed constant (15 m). The external boundary conditions are represented by specified fluxes at the lateral limits of the alluvial plain to consider groundwater flowing from the hill slope of the valley, by the infiltration recharge and by the River Meuse acting as regional drain of the aquifer. The groundwater flow model is calibrated in steady state mode using piezometric head measurements available in the area (Fig. 6b). Transport parameters are defined based on previous experiments and scientific works in the Meuse alluvial aquifer (Derouane and Dassargues, 1994; Brouyère, 2001; Batlle-Aguilar, 2008; Batlle-Aguilar et al., 2009). Transport simulations are run over a 20 years period.

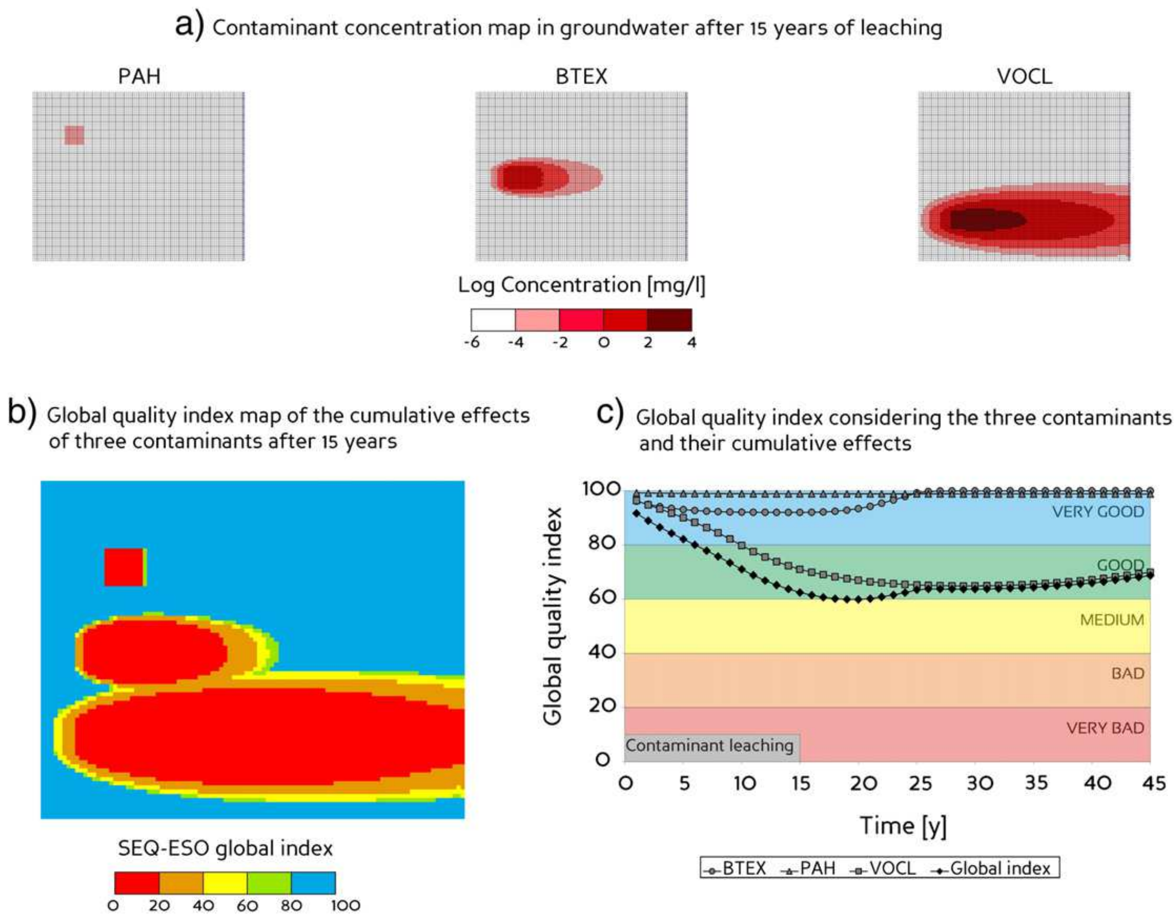


Fig. 5. (a) Contaminants concentration after 15 years, (b) map of groundwater quality index after 15 years and (c) evolution with time of the global quality index using SEQ-ESO after spatial integration.

The GIS-based regional risk assessment application has been used to extract the most common industrial activities recovered on the groundwater body, *i.e.* industrial plants included in the categories "mining", "gas station" and "metallurgy". Only important plants with a spatial extent larger than 5000 m² have been considered. In this example, benzene is the only contaminant taken into consideration, with a worst case scenario assuming that all potential sources are active. The sources of contaminant are assumed to leach continuously in the recharge to the aquifer at their maximum solubility and contaminant spreading in groundwater is modeled considering advection, dispersion, sorption and degradation processes (Table 3). In the reality, the different sources have certainly started to leach at different times and with different discharge rates and the contamination history should be reconstructed in order to produce a more representative sketch of the time evolution of groundwater contamination (e.g. Troldborg et al., 2008).

Once the simulation is performed in GMS, results files are exported to the GIS application to calculate maps of the SEQ-ESO indicators and the global quality index at each time step.

Fig. 6b shows the map of benzene concentrations in the alluvial aquifer and Fig. 6c a map of the global quality index, both after 10 years. This map highlights highly contaminated zones.

The last graph (Fig. 6d) shows the evolution with time of the SEQ-ESO global quality index for the whole groundwater body. Contaminant plumes reach steady state and equilibrium between source leaching and contaminant dispersion, attenuation and drainage to surface water after approximately 5 years. All the simulations performed here show that, a single polluted site does not have a significant effect on the overall quality of that whole groundwater body but that, with reasonable assumption and despite the turnover of groundwater and the degradation of pollutants, multiplication of industrial contaminated sites can have a strong effect on groundwater quality at the scale of the groundwater body.

However, simulations were run considering strong assumptions that constitute a worst case scenario for benzene for which a large amount of contaminant is probably released into the groundwater body. A real case is for sure much more complex. Many different contaminants with different physico-chemical properties (sorption, degradation) are usually released to groundwater at different times and for different durations. Source strengths are usually smaller because the contaminated soils are usually restricted to some parts of extents of the industrial sites. However, leaching can be greater in case of non-aqueous phase liquids. Based on these considerations, it can be concluded from the first simulations that the industrial pressure on the Meuse alluvial aquifer is likely to be important but no definitive and quantitative conclusions can be drawn at this level of the analysis. Further data on contaminated sites characterization remain necessary for refining the regional risk assessment.

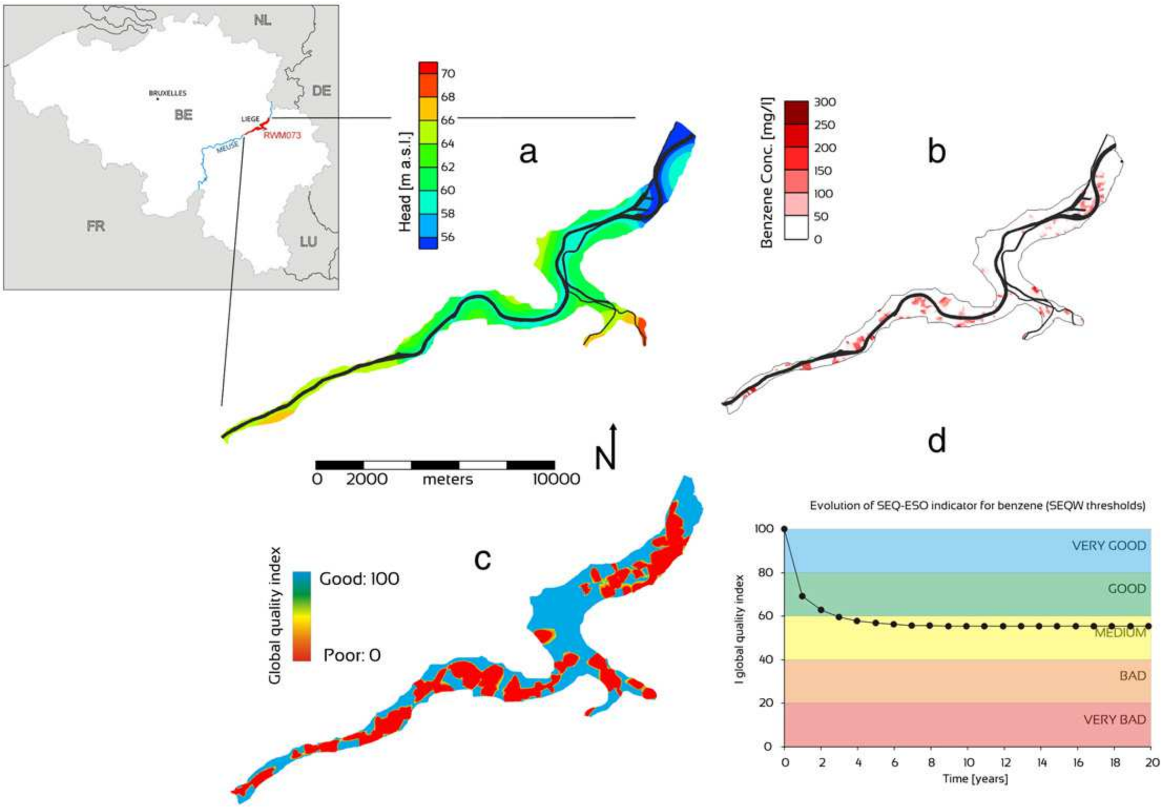


Fig. 6. Preliminary results of regional risk assessment on groundwater body RWM073 considering industrial activities releasing benzene into the groundwater. The resulting SEQ-ESO indicator suggests a "medium" quality status of the groundwater body.

Table 3
Contaminants parameters used for real application case.

Parameters	Units	Benzene
Concentration in recharge	mg/l	1830
Kd	m^3/mg	4.15×10^{-11}
Degradation	s^{-1}	1×10^{-7}
Longitudinal dispersivity	m	5
Transversal dispersivity	m	0.5
Effective porosity	–	0.05

3.3. Conclusions and perspectives

A regional scale risk assessment methodology for groundwater bodies is proposed as a flexible approach for evaluating the pressure exerted by various sources of contamination of groundwater resources. The methodology is based on the aggregation of various cumulative sources of contaminants of different chemical natures, properties and toxicities into a set of "easy to use" spatially distributed or aggregated indicators.

The spatially-distributed indicators (maps of indicators) can be used to identify most problematic sectors (hot contamination spots) with larger volumes of heavily contaminated groundwater and the evolution with time of groundwater quality at different locations in the catchment. The spatially-aggregated indicator can be used to report on the global status of groundwater quality in the groundwater body, for groundwater quality trend assessment and as a referential for site prioritization and for the evaluation of programs of measures aiming at restoring groundwater quality in the groundwater body, using cost-efficiency approaches.

Thanks to these capabilities, the regional risk assessment methodology is compliant with the ongoing legislation in the Walloon region, based on the SEQ-ESO and it fits very well with the guidelines of the EU Water Directive which promotes the use of aggregated indicators able to reflect status and trends in groundwater quality and to evaluate in a rigorous way the risk of not reaching a good status by specific milestones such as 2015.

A synthetic example and a first illustrative application have been developed for the alluvial aquifer of the Meuse River in the region of Liège (Belgium). These examples confirm that the approach provides a useful referential for decision-making in relation with regional contamination of groundwater. The synthetic test case demonstrate that the approach is able to turn a complex multiple contamination into a simple global quality index, evolving with time and easily incorporated or compared to a risk index.

The application on the RWM073 allows also defining the weakest points and drawbacks of such a regional approach and the priorities for further developments. First, the approach is data demanding. However, this is the case for all these regional scale approaches that require relatively important preparatory works for data acquisition, organization and processing. This drawback is partly overcome by the use of a geospatial database and specific interfacing tools between the GIS system, the groundwater flow and transport modeling application and the regional SEQ-ESO calculation module. In this context, further work is ongoing on developing customized user-interfaces for a better integration of the whole procedure.

Secondly, there are many sources of uncertainties in the different data feeding the approach. In particular, the pollution sources are not always perfectly identified and characterized and hydrogeological parameters and contaminant properties remain difficult to identify and to quantify at the regional scale. Further investigations are required on the reconstruction of the history of contamination of the groundwater body and on a better evaluation of source strengths. A key next step will be to implement a statistical approach for handling all the uncertainties that remain at regional scale. More particularly, it is expected to obtain, in a near future, statistics on contaminant leaching in relation with different industrial and environmental factors such as characterization of contaminated site (industrial activity, area, land use) and properties of the soil (groundwater flow, lithology). To reach that objective, information on contaminated sites available in the French database ADES (Chery et al., 2008) developed and managed by BRGM, will be used. This database contains analyses for contaminants in groundwater for most industrial plants in France as requested by the regional environmental agencies.

Finally, the regional flux-based risk assessment approach is now used as a referential for a cost–benefit assessment of total or partial remediation of the contaminated groundwater body, according to different management scenarios. This analysis starts from the actual groundwater body quality state for which groundwater restoration scenarios (based on natural attenuation or active remediation) are suggested. The regional risk assessment method is then applied on these scenarios to evaluate the improvement of the groundwater quality index when management plans are applied. This allows evaluating, in monetary terms, the costs for given improvements in the groundwater body quality status.

Acknowledgments

This research has been performed in the scope of the FRAC-WECO project financed by the Belgian Federal Science Policy Programme BELSPO (Project Nb SD/TE/02A). Thanks to all public partners that provided us with data on contaminated sites (SPW-OWD, SPW-Groundwater Division, SPAQuE), to all FRAC-WECO project partners (ULg-LEAE, BRGM, VUB, VITO) and members of the follow-up committee for the fruitful discussions on the subject and to the two anonymous reviewers of the original manuscript.

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FINAL SCIENTIFIC REPORT

Flux-based Risk Assessment of the impact of Contaminants on Water resources and ECOsystems
-
FRAC-WECO

SCIENCE FOR A SUSTAINABLE DEVELOPMENT

Annexe 2

Minutes of The Follow Up Committee Meetings

Project FRAC-WECO

Minutes of the meeting

Author : M. Haberman, D. Caterina	
Project : FRAC-WECO	
Objectives: **Presentation of the research activities progress of each project partner for the follow-up committee**	
Date : 11 December 2007	Location : **Liège (Belgium)**
TIMETABLE ***Afternoon session:*** 13.30 - 14.00: Project progress (Prof. A. Dassargues ULg) 14.00 - 14.20: Integration Methodology for FRAC-WECO (S. Brouyère, ULg) 14.20 - 14.40: Object Oriented Land Cover Mapping (J. Dujardin, VUB) 14.40 - 15.00: Ecotoxicological Results (S. Crèvecoeur, ULg) 15.20 - 15.40: Degradation of Chlorinated Aliphatic Hydrocarbons in the aquifer at three locations at the Zenne site (W. Dejonghe, VITO) 15.40 - 16.00: Economic analysis applied to Groundwater Degradation due to Contaminated Sites (C.Hérivaux, Brgm) 16.00 - 16.20: Field Investigations, Modelling & Selection of RA tools (M. Haberman, ULg) 16.20 - 17.30: Open discussion with the follow-up committee meeting	
Notice: The presentation of C. Hérivaux from Brgm was canceled the day before due to personal reasons.	

1. Participants

ULg-HG: S. Brouyère, A. Dassargues, D. Caterina, M. Haberman

ULg-LEAE: JP. Thomé, V. Debacker, S. Crevecoeur

VITO: L. Diels, W. Dejonghe

VUB: O. Batelaan, F. Canters, J. Dujardin

Follow-up committee: H. Halen (SPAQuE), C. Popescu (Ministère de la Région Wallonne), L. Lagadic (Institut National de la Recherche Agronomique), R. Therrien (Université de Laval), J. Barth (Eberhard Karls Universität Tubingen), M. Chevreuil (Université de Paris VI), D. Harmegnies (BELSPO)

Notice: There were some absences during the meeting: C. Hérivaux (Brgm), K. Van de Wiele (OVAM), D. Springael (KUL), E. Haubruge (Faculté Universitaire des Sciences Agronomiques), F. Onclincx (IBGE), L. Hoffmann (Centre de Recherche Lippmann)

2. Objectives of the day

The objectives of the meeting were to present the research activities of each project partner to the follow-up committee.

3. Project progress

A. Dassargues presented the planning of the meeting with the different presentations expected of each research team. He also reminded to participants the main purpose of the FRAC-WECO project and mentioned the previous meetings that took place. This consisted to show the constant interactions between all the partners. After this brief introduction, he summarized key points of research activities of each partner during the year 2007 and enunciated the activities planned for the next year 2008:

2007

- *ULg-HG*
    - Data collection for the test sites
    - First field investigations
    - Development of integration methodology
    - Review of risk assessment tools
    - Model development for the Morlanwelz test site

- *VUB*
    - Image selection and preprocessing
    - Object –oriented land cover mapping
    - Image segmentation and classification
    - Validation of the classification results

- *VITO*
    - Batch tests to study CAH potential degradation at three locations on the Vilvoorde study site

- *ULg – LEAE*
    - Sampling water and invertebrates
    - Analysis of contaminants
    - Ecotoxicological tests and risk assessment

- *Brgm*
    - Integration methodology
    - Consultation of end-users
    - Literature review
    - Typology of environmental damage

- Data collection for the 2 case studies to be carried out in 2008

The works of Brgm was not presented in detail due to the absence of C. Herivaux.

2008
- *ULg – HG*
  - Field investigations for flux quantification
  - RA tools: tests & validation
  - Modelling for test sites

- *VUB*
  - Spatially distributed recharge mapping
  - Spatially distributed runoff mapping
  - Intermediate report surface water budgeting

- *VITO*
  - Determination of degradation coefficients from batch tests
  - First attempt of integration of these coefficients in the models of the other partners

- *ULg-LEAE*
  - Analysis of chemical (PAH, heavy metals, PCB, pesticides)
  - Comparison of accute toxicity tests using NIPHARGUS and GAMMARUS PULEX
  - Comparison of all results according to spatial and temporal variations

- *Brgm*
  - Assessment of environmental damage related to groundwater contamination for 2 case studies

To finish, a progress state of deliverable reports were discussed. A. Dassargues asked to the person in charge of BELSPO an extension of one or two months for the submission of the deliverable. That was accepted.

4. Integration methodology for FRAC-WECO

S. Brouyère exposed the methodology of integration for the FRAC-WECO project by reminding its originality that relies mainly on two aspects: (1) the risk assessment based on the contaminants fluxes calculation between the source and the receptors and (2) the use of the DPSIR approach as a general framework for coupling the physical and socio-economic components of the analysis. To develop this methodology, various skills, tools and concepts are provided and developed by the different research groups involved in the project and it is the sum and the integration of these components that will allow reaching the final objectives. The integration methodology is described in detail in the deliverable D.1.2.

5. Object Oriented Land Cover Mapping

J. Dujardin presented an analysis method based on the object oriented land cover mapping. This study consists to develop a tool for spatially detailed mapping of land cover in urbanised areas and to understand the impacts of complex land-cover patterns on infiltration, run-off and groundwater recharge. This object-oriented approach consists to classify a satellite image (from IKONOS data) in many categories according to the soils use. From this, it will be possible to build a model (via WetSpass) and to validate it.

6. Ecotoxicological Results

Many samplings of groundwater, surface water and invertebrate organisms were collected at the three selected sites (Morlanwelz, Chimeuse and Vilvoorde sites) and analyzed to evaluate the parameters LC_{50} and EC_{50} according to the presence of different contaminants at various dilution levels. The results confirmed ecological risks on Chimeuse site are mainly caused by heavy metals compared to Morlanwelz and Vilvoorde site where the risks are mainly caused by chlorinated solvents.

7. Degradation of Chlorinated Aliphatic Hydrocarbons in the aquifer at three locations at the Vilvoorde site

Some batch tests were carried out to well understand and evaluate the degradation phenomenon of CAH contaminants. For this experiment, groundwater and soil samplings from the Vilvoorde site at three different locations were taken to represent the site medium in laboratory. The results showed the contaminants degradation was more or less fast as a function of additives responsible of the degradation. Some tests have not given responses yet but are still in process.

8. Field Investigations, Modelling & Selection of RA tools

A first model was realized on the Morlanwelz site to simulate the groundwater flow and the transport of pollutants dissolved in the subsoil. The modelling tools used are MODFLOW (for the flow) and MT3D (for the solute transport). The results of the model allowed for the moment to reproduce the groundwater flow trend which seems linked to the topography of site. A simulation of migration of contaminants (supposed totally dissolved) was also realized taking into account theoretically of adsorption and degradation phenomena. Nevertheless, the model can not be considered as calibrated and validated because it takes into account a limited number of observations. Moreover, a list of different decision support tools and risk assessment was listed, classified and will be chosen to complete the modelling tool according to different criteria such as the type of risk aimed, the input parameters, the complexity of the model, the calculation of uncertainty, etc.

9. Suggestions and propositions of the following committee

Some notices were proposed to each partner to better progress in the future and to facilitate the interactions:

- *VUB*

According to O. Batelaan, the technique using satellite mapping is effective for any sites. Even if the contrast of soil is less marked, the process should be relatively reliable. It is the reason why it would be a real challenge to use this mapping technique for the Morlanwelz site because it does not constitute a contrasted area like the Vilvoorde site.

- *ULg-LEAE*

Some questions were asked to understand the perspectives of research works concerning the analyses of groundwater and surface water. Indeed, is a comparison of the results from groundwater and surface water possible being given the oxygen concentration is totally different at the surface and in the soil? This notice was notably mentioned for the Morlanwelz case where samples were taken in boreholes as well as in the "Haine" river. Moreover, the collection of samples was not realised effectively because it was performed at a specific time during the year. It would be better to take more samples in different moments of the year when the surface water is mainly fed by the basic flow to avoid the dilution phenomenon with run-off water.

- *VITO*

The degradation kinetic depends strongly of many conditions and so it will be difficult to obtain a unique degradation constant in order to be integrated in the models.

- *ULg-HG*

S. Brouyère confirmed the model presented for Morlanwlez site is a first draft and it is necessary to calibrate and develop it more in detail. Moreover, a wide dataset would be very interesting not to work only in a steady state but also in a transient state. Finally, H. Halen did not understand the real purpose of the decision support tools. A. Dassargues answered him the main goal of these softwares is to develop a tool able to give some information about impacts and potential receptors to facilitate the understanding of the contamination risks, to complete the modelling results and to serve for the decision taking for the rehabilitation phase by the end-users.

- *Follow-up committee*

The follow-up committee will be led up to write a report to give his opinion about the research activities of the first year.

Project FRAC-WECO

Minutes of the meeting

Author : D. Caterina	
Project : FRAC-WECO	
Flux-based Risk Assessment of impact of Contaminants on Water resources and ECOsystems	
Date : 12 June 2008	Location : **Liège (Belgium)**

TIMETABLE

13.30 - 13.40:	Work progress	(A. Dassargue, ULg-HG)
13.40 - 14.00:	Ecotoxicological Risk Assessment	(S. Crèvecoeur, ULg-LEAE)
14.00 - 14.20:	Comparison and validation of risk assessment tools+ Field results	(D.Caterina, ULg)
14.20 - 14.40:	Mapping land cover, modelling recharge and runoff	(O. Batelaan, VUB)
14.40 - 15.00:	Economic analysis of groundwater degradation due to brownfields: methodological framework and key issues	(C.Hérivaux, Brgm)
15.00 - 15.20:	Quantification and stimulation of the degradation of Chlorinated Aliphatic Hydrocarbons in the aquifer at three locations at the Zenne site in Vilvoorde-Machelen	(W. Dejonghe, VITO)
15.20 – 16.00:	Orientation of the project for the second phase	(S. Brouyère, ULg-HG)
16.00 - 16.20:	**Coffee break**	
16.20 - 17.30:	Open discussion with the follow-up committee meeting	

Participants:

Project partners:

ULg-HG: A. Dassargues (AD), S. Brouyère (SB), D. Caterina (DC)

ULg-LEAE: S. Crevecoeur (SC)

VITO: W. Dejonghe (WD)

VUB: O. Batelaan (OB), F.Canters (FC)

Brgm: C. Hérivaux (CH)

Follow-up Committee:

L. Lagadic (*Institut National de la Recherche Agronomique - France*), R. Therrien (*Université de Laval - Canada*), M. Chevreuil (*Université de Paris VI - France*), H.Halen (SPAQuE).

Belspo:

D.Harmegnies (DH)

Absents: L. Diels (VITO), J-P. Thomé (ULg-LEAE), J. Barth (Eberhard Karls Universität Tubingen - Germany), E. Haubruge (Faculté Universitaire des Sciences Agronomiques de Gembloux), L. Hoffmann (Centre de Recherche Lippmann), F. Onclincx (IBGE), C. Popescu (Ministère de la Région Wallonne), K. Van de Wiele (OVAM), D. Springael (KUL).

1. Objectives of the meeting

- Presentation to the follow-up committee and to Belspo of research progress.
- Presentation of perspectives for the second part of the project

2. Subjects discussed

2.1. Research progress

General work progress (A. Dassargues, ULg-HG)

The presentation was an introduction to the FUC meeting. It was focused on 3 points:

- overview of meetings held during the first six months of 2008;
- brief description of works performed by each team (with the list of deliverable due for the end of June 2008);
- planning for the end of the year 2008.

Ecotoxicological Risk Assessment (S. Crèvecoeur, ULg-LEAE)

The presentation was focused on the following points:

- *Sampling water and invertebrates*

  Groundwater was sampled at the different industrial polluted sites: Morlanwelz, Zenne and Chimeuse. Boreholes at each polluted site were selected according to the groundwater flow direction.

  Studied sites were sampled for typical groundwater invertebrates (family *Niphargidae*) by the scientific team of Dr. P. Martin from IRScNB (Royal Belgian Institute of Natural Sciences). These organisms were absent at each site

- *Analysis of contaminants*

Samples of ground- and surface water were analyzed for different pollutants: PCBs and organochlorinated pesticides, heavy metals, Polychlorinated Aliphatic Hydrocarbons (PAHs), BTEX and Chlorinated Aliphatic Hydrocarbons (CAHs).

Chimeuse is particularly contaminated with heavy metals (Cu, Ni and Zn) whereas Morlanwelz and Mechelen-Vilvoorde are contaminated with chlorinated solvents. PAHs results are not available yet.

- *Ecotoxicological tests*

  - *Chronic toxicity test with B. calyciflorus*

  Chronic toxicity tests using rotifera were executed in 2 days with EC_{50} estimation which is the concentration of test substance which results in a 50% inhibition of the reproduction

  - *Acute toxicity test with Niphargidae and Gammaridae species*

  Acute toxicity tests using Amphipoda were executed in 4 days with LC_{50} estimation which is the concentration of test substance which results in a 50% of mortality.

  Acute toxicity tests were performed on a sample from Morlanwelz site (P6) using, on the one hand, *Niphargidae* species and, on the other hand, *Gammarus pulex*, a typical freshwater crustacean. The LC_{50} value could not be calculated as there was no mortality during the test.

- *Ecotoxicological Risk Assessment, methodology*

  Hazard of a substance to the environnement can be estimated as PEC/PNEC ratios. The Predicted Environmental Concentration (PEC) is the estimated or measured concentration of a chemical in an environmental compartment. The Predicted No Observed Effect Concentration (PNEC) is the concentration below which exposure to a substance is not expected to cause adverse effects.

  If PEC/PNEC < 1 → No hazard for the environment

  If PEC/PNEC > 1 → Hazard for the environment

  Usually, established OECD (Organisation de Coopération et de Développement Economiques) tests are performed to determine the ecotoxicity of substances. Toxicity values can be available in the litterature, otherwise they can be estimated using Quantitative Structure-Activity Relationships (QSARs).

  PNEC is then estimated by applying safety factors or using statistical extrapolation method.

Pollutant concentrations are available for the different polluted sites and are used as PEC value (because we have no data on its produced/imported quantities, its uses and release patterns…).

So, the PEC/PNEC ratio can be calculated for each pollutant separately.

- *Case study: Morlanwelz site*

Ground- and surface water were sampled at Morlanwelz site. Boreholes P6, P3 and P16 and Haine river downstream and upstream were sampled.
Contaminant concentration according to temporal variation at Morlanwelz site:

- BTEXs: Concentrations were higher in January 2006 than the other years. Except ethylbenzene and *m, p*-xylenes of January 2006, the concentration of these pollutants was lower than the background level defined in the AGW 12 September 2002 (2ppb – 2µg/L).
- VOCLs: Concentrations of VOCLs were similar during the different months except cis-1,2-dichloroethene. Except cis-1,2-dichloroethene and 1,2-dichloroethene, the concentrations of VOCLs was lower than the background level defined in the AGW 12 September 2002 (10ppb – 10µg/L).

Chronic toxicity tests were performed in laboratory using the rotifer *Brachionus calyciflorus.* Results are nearly similar according to the period of time. P6 borehole is more toxic than P3, P16 and Haine River. Moreover, there is no difference in the results of Haine upstream and downstream. Ecotoxicological risk was calculated for each piezometer at Morlanwelz site. Risk differs between piezometers and can be really high, especially for VOCLs P3 piezometer.
Pollutant concentrations are not yet available for P16 and Haine upstream. So, the risk could not be estimated.

- *Future prospects*

New sampling and test campaign will be performed on the three selected sites.

Remarks
HH: asks if there are already results for the upstream part of the Haine river.

- SC: not yet.

Comparison and validation of risk assessment tools+ Field works (D. Caterina, ULg-HG)

The presentation was focused on two main topics:

- *Comparison and validation of risk assessment tools*

In the last follow-up committee meeting in December 2007, a selection of risk assessment tools was presented. The choice of them was based on several criteria, such as: type of risk concerned, type of contaminant managed, the possibility to take into account the transport of contaminants… 5 softwares were initially selected: RBCA Toolkit, Risc Workbench, SADA, FIELDS and DESYRE. However, for the comparison and validation of risk assessment tools, it was decided to focus on the results they provide for the transport of dissolved contaminants. Only RBCA Toolkit and Risc Workbench allow that. Later, two others risk assessment tools that also allow to model transport were added: Misp and Remedial Targets Worksheet.

There are some differences between these four tools from a conceptual point of view. For example, Risc Workbench and Misp consider the processes of advection, dispersion-diffusion, sorption-desorption and degradation for the vertical migration in the unsaturated zone while RBCA considers only advection and degradation, and Remedial Targets Worksheet only advection. For the transport in the saturated zone, they all consider the processes of advection, dispersion-diffusion, sorption-desorption and degradation, but with different solutions of the equation of transport.

These tools were tested on two case studies: Sclaigneaux and Flémalle.

The first one is a site located near the city of Andenne which lies in the alluvial plain of the Meuse River and which is contaminated mainly with mercury. The contamination is located in the unsaturated zone composed of backfill deposit. The saturated zone is composed of gravels. Evolution of concentrations in function of time is observed at a well located 50 meters downstream of the source of contaminant. Parameters chosen for the simulations are mainly coming from literature because there are few data available for the site. Results provided by simulations on different softwares showed no arrival of contaminant at the well after 100 years. From 100 years, Misp shows first major arrival of contaminant while other softwares show only low arrival of contaminant. This difference can not be explained for the moment other than in differences in conceptual model implemented in software.

The second case study is a site located near the city of Liège which lies in the alluvial plain of the Meuse River and which is contaminated with a wide panel of pollutants (though it was decided to focus only on benzene). The site has already been fully investigated in the scope of the European Aquaterra project. There are thus a lot of available data on it. A numerical model using Modflow and RT3D is also available. Simulations provided by analytical models have been compared to results provided by the numerical model considering a source of pollution located in the saturated zone. Evolution of concentrations in function of time has been observed in three different wells located respectively at 20, 40 and 80 meters downstream of the source of contaminant. Results of simulations in the two nearest wells are quite similar to the ones provided by Modflow/RT3D: nearly the same time of first arrival and the same order of concentration reached in the wells. At 80 meters, results provided by analytical models showed an overestimation compared to the Modflow/RT3D results of concentration reached in the well. This behaviour can be explained by the fact that in the numerical model, at 80 meters of the source of contaminant, the Meuse River plays an important role in the attenuation in the attenuation of the concentrations, what cannot simulate analytical models.

First conclusions concerning the use of such models can be drawn. They can be useful at an early stage of the project when information regarding the complexity of the natural environment may be lacking. In addition, they are generally easy to use. In a near future, they will be validated using numerical models (HydroGeoSphere, SUFT3D, Modflow/RT3D) with synthetic examples.

- *Field works:*

The second part of the presentation was dedicated to field works. First, a proposal for the application of the Finite Volume Point Dilution Method (FVPDM) in Vilvoorde and Chimeuse. FVPDM is an efficient tracer technique developed by ULg-HG to quantify and monitor the variations with time of Darcy fluxes in relation with changes in hydrogeological conditions. In Vilvoorde, the selected well to perform the technique is SB2, located near the Zenne River. In Chimeuse, two wells have been selected for the test: P15 and P20 located both near the edge of the site and in the middle of main contaminant plumes. Pre-calculation needed for the design and dimensioning of the test are presented. Unfortunately, for SB2, due to the simultaneity of a low hydraulic conductivity, a low hydraulic gradient, a small screen length and a small diameter of the well, the estimated time of tracer injection is calculated as quite long and the injection flow rate would be very small. In Chimeuse, due mainly to higher hydraulic conductivity, it appears that the test would be easier to be performed than in Vilvoorde.

The second topic of the field work was dedicated to first results of the monitoring in Morlanwelz. Three probes and one pluviometer have been installed on the site during the last months. Correlations between sets of data coming from them are sometimes clearly visible (for example relations between the water table in the upper aquifer made of alluvia and the precipitations or relations between the level of water in the river and precipitations). Anyway, these sets of data will be analyzed more in details using statistical tools in a near future.

Remarks:

Mapping land cover, modelling recharge and runoff (O.Batelaan, VUB)

The presentation was composed of 4 main topics:

- *Land cover mapping*

Land cover is an important factor determining the spatial and temporal variation in infiltration and ground water recharge. Available land-use data sets are too strongly generalised for hydrological modelling within urbanised/industrialised watersheds, both spatially and thematically. Complex areas are represented by abstract land-use classes with heterogeneous composition (e.g. industrial area, low-density urban area) which, from a hydrological point of view, are difficult to parameterize. The use of high-resolution sensors (1 meter resolution) allow detailed mapping of land cover, but spectral resolution of these sensors (4 bands) is too limited to extract hydrologically relevant classes. This is why an object-oriented image interpretation approach was used to get land cover.

During the last meeting (December 11th 2007), the VUB showed the obtained land-cover map for the Zenne study area, but some confusions remained between buildings and roads, between bare soil and roads and between water and shadow. To improve the accuracy of the classification, the 6 used classes (water, bare soil, meadow, mixed forest, buildings and roads) were changed in 8 classes. The buildings and roads classes were changed in 3 new classes: grey surfaces, red roofs and bright roofs, and a new shadow class was added.

This new classification improved the accuracy of the land-cover map. The last step of the classification process is the postclassification of the shadow objects. The shadow objects are reassigned to one of the 7 land-cover classes, because shadow hides the actual land cover type

Applying these modifications, the final land cover map of the Vilvoorde area could have been obtained. It was then used as input for the WetSpass software. This software allows estimating spatially distributed run-off, evapotranspiration and recharge in function of land cover, topography and soil type.

- *Run-off simulation*

Spatially distributed run-off was obtained with WetSpass. Results for the winter and the summer periods were presented and compared to results coming from the land-use map AGIV2001 (20 meters resolution). It appears that run-off shows higher spatial variability with high resolution satellite imagery.

- *Recharge simulation*

Spatially distributed recharge was obtained with WetSpass. Results for the winter and the summer periods were presented and compared to results coming from the land-use map AGIV2001 (20 meters resolution). It appears that recharge shows higher spatial variability with high resolution satellite imagery.

- *Groundwater modelling Vilvoorde*

A groundwater model of the Vilvoorde area has been developed based on a previous one developed by VITO. Results coming from WetSpass have been implemented in the new model. Field data (including drillings and geomecanical tests) have also been incorporated into the model. The calibration of it is sufficiently accurate and first simulations for the transport of contaminants considering only advection have been performed.

Remarks:

Economic analysis of groundwater degradation due to brownfields: methodological framework and key issues (C.Hérivaux, Brgm)

- *Activities carried out as part of the part of the WP5:*

- Contribution for setting up a transdisciplinary framework: D1.2 « Methodology for integration of process studies and development of a decision support tool »
- Development of a methodological framework to assess environmental damage due to groundwater degradation by brownfields: D5.1 « Economic analysis applied to groundwater degradation due to contaminated sites: typology of environmental damage »
- Proposition and diffusion of a discussion draft among FRAC-WECO partners and end-users: « Objectives and scope of the economic analysis applied to groundwater degradation due to former industrial contaminated sites »
- Organisation of meetings to discuss how the economic analysis can be adapted to the assessment of groundwater degradation by brownfields and suit the best the end-users' needs

- *Presentation of main results:*
  - Typology of services provided by groundwater

  A change in groundwater quality will result in a change in the level of services provided by the groundwater to the society (i.e. damage in case of degradation/ benefits in case of improvement). The typology can be adapted to each specific groundwater unit under study.

  Three main types of services and related values:
    - Groundwater 'as a resource': direct use values → can generally be quantified with market based techniques
    - Groundwater 'itself': indirect use values and non use values → more difficult to quantify, require the implementation of valuation methods
    - Groundwater 'as a discharge into surface water': indirect use values → can be quantified by methods directly applied to surface water
  - Overview of economic valuation methods that can be used

  Economic valuation methods to be used will depend on the type of services provided by the groundwater to the society

  Two main types of methods:
    - **-** Market based techniques : Economic values are derived from existing market prices for inputs (production values) or outputs (consumption values) → use values only
    - - Valuation methods: aim to assess public willingness to pay/ to accept (WTP/WTA) for a change in the water quality method:
      - ***Revealed preference methods***: WTP is measured indirectly by assuming that this value is reflected in the costs incurred to travel to specific sites or prices paid to live in specific neighbourhoods → not relevant to valuate groundwater degradation
      - ***Stated preference methods***: individual are asked directly in a social survey format, for their WTP for a pre-specified

environmental change → unique methods able to assess non-use values

Contaminated land policy comprises both soil and water contamination

Numerous differences between contaminated sites/soil and water management (e.g. policy context, competent authorities, management scale, risk assessment, financial versus economic analysis, water standards) + differences between administrative regions

Contaminated site management generally focusses on a local scale whereas groundwater management requires an analysis at the groundwater scale

→ It is necessary to combine as part of FRAC-WECO two different management scales ('individual site level'= Pressures level and 'strategic level'= State level)

In densely former industrial areas, combined effects of several contaminated sites on a groundwater body may lead to an important degradation of the resource even if the individual effects of these contaminated sites are low

→It is necessary to work at the groundwater boby scale to take into account the combined effects of contaminated sites on groundwater resources

EU Water Framework Directive and Groundwater Daughter Directive require to conduct economic analysis at the water body scale

In case of risk of not achieving good chemical status by 2015 → a programme of measures is required based on a <u>cost-effectiveness</u> analysis → in case of disproportionate costs, a <u>cost-benefit analysis</u> is required

- **Selection of a pilot case study to test and apply economic analysis of groundwater degradation by brownfields**
  The groundwater body RWM 073 'Alluvions et graviers de Meuse' is selected as a pilot case study
  Groundwater body at risk of not reaching good chemical status by 2015 only <u>due to contaminated sites;</u> High density of former contaminated sites (99.8/100km²)
  →WP5 proposes to assess costs and benefits that would result from the improvement of the groundwater quality
  Design of a programme of measures and assessment of its <u>costs</u>
  Assessment of <u>benefits</u> by a 2 steps approach: (i) assessment of direct benefits that would occur for water users (market based method); (ii) assessment of the willingness to pay of people to improve groundwater quality (contingent valuation)

Planning for the end of 2008:

- Characterisation of the ***<u>state</u>*** of the groundwater body and expected evolution
- Characterisation of former/ current/ potential water users that would benefit from the improvement of the quality of the groundwater body (***<u>impacts</u>***)
- Assessment of **benefits** for water users that could be brought by an improvement of the groundwater body quality (december 2008)

Quantification and stimulation of the degradation of Chlorinated Aliphatic Hydrocarbons in the aquifer at three locations at the Zenne site in Vilvoorde-Machelen (W.Dejonghe, VITO)

The presentation was focused in two main points:

- *Results batch degradation test:*

- *Results column degradation test:*

2.2. Perspectives for the second part of the project (S. Brouyère)

With the current research efforts, it is possible to evaluate and model as accurately as possible groundwater and contaminant fluxes at the « entry point » in the water resource system. However, it is not sufficient to assess risk on water resources as a whole due the fact that there are often multiple sources of contaminants acting on the degradation of water resources. This is why it is important for the continuation of the project to consider an upscaling of the study area to the (ground)water body.

At this scale, it will be necessary to use a cartographic approach for risk assessment. The suggested basis for the development of such approach is the HG-ULg physically-based groundwater vulnerability assessment and mapping technique: APSÙ method (protection of aquifers by evaluating their sensitivity – vulnerability). The technique uses the Source-Pathway-Receptor approach and is driven by two concepts: land surface dangerousness (= possibility for contaminants to migrate from the source to receptor) and underground attenuation capacity (=Pollution retention/ reduction factors reducing the danger to which the receptor is exposed (travel time, mass reduction…).

The APSU technique is based on three interrogations and three associated criteria:

- If pollution occurs, how long will it take for it to reach the groundwater table?
  - Time of transfer
- If the pollution reaches the water table, how will be the level of potential contamination?
  - Concentration level
- How long the contamination will be likely to last?
  - Duration

Up to now, the technique considers intrinsic vulnerability which takes into account inherent geological, hydrological, hydrogeological properties of land surface and underground with the assumption of conservative contaminants.

Further developments of the technique are required to fit with the research of FRAC-WECO:

- taking into account specific vulnerability (specific behaviour of contaminants such as: sorption, degradation…);
- integrating risk of contaminant lateral dispersion;

- combining groundwater vulnerability and risk assessment.

Results of ongoing research will be integrated to the technique as follows:

- land use mapping and hydrological budgeting (*task of VUB*) will be used to determine the land surface dangerousness;
- risk assessment tools and models (*task of HG-ULg*) will be used to quantify simplified to advanced water and contaminant flux and routing in the catchment;
- specific behaviour of contaminants (*task of VITO*) will be integrated into database for specific vulnerability assessment;
- toxicity and ecotoxicity of contaminants (*task of ULg-LEAE*) will be used as criteria for groundwater vulnerability assessment.

The proposed case study is the groundwater body scale RWM073 located between the cities of *Engis* and *Herstal,* composed of gravels and alluvial deposits of the Meuse River. The work plan for the study of RWM073 is the following:

- inventory of contamination sources;
- land-use mapping and hydrological budgeting;
- groundwater flow and contaminant transport modelling.
    - Groundwater vulnerability and risk assessment cartography.
        - Socio-economic analysis at groundwater body scale.

Remarks:

Project FRAC-WECO

Minutes of the meeting

Authors : D. Caterina – S.Brouyère	
Project : FRAC-WECO	
Flux-based Risk Assessment of impact of Contaminants on Water resources and ECOsystems	
Date : 20 January 2009	Location : **Liège (Belgium)**

TIMETABLE

9.30 - 9.50:	General work progress	(A. Dassargue, ULg-HG)
9.50 - 10.10:	Ecotoxicological risk assessment, methodology and results	(S. Crèvecoeur, ULg-LEAE)
10.10 - 10.30:	Validation of risk assessment tools, field works and modelling of RWM073	(D.Caterina, ULg)
10.30-10.50:	Coffee break	
10.50 - 11.20:	Socio-economic analysis on RWM073	(C.Hérivaux, Brgm)
11.20 - 11.50:	Landuse recharge mapping and groundwater modelling for Vilvoorde and outlook to phase 2	(J. Dujardin, VUB)
11.50 - 12.20:	Study in batch and column set-ups of the stimulated degradation of Chlorinated Aliphatic Hydrocarbons in the aquifer at the Zenne site	(W. Dejonghe, VITO)
12.20 - 13.30:	**Lunch break**	
13.30 - 16.30:	Discussion with the follow-up committee • Debriefing of the mid-term evaluation of the project • Regional scale approach on RWM073: o Discussion on the methodology o Agreement on each project partner expected contribution o Time table for the next 2 years	

Participants:

Project partners:
ULg-HG: S. Brouyère (SB), A. Dassargues (AD), D. Caterina (DC), P. Jamin (PJ)
ULg-LEAE: S. Crevecoeur (SC), J-P. Thomé (JPT)
VITO: W. Dejonghe (WD)
VUB: O. Batelaan (OB), J. Dujardin (JD)
Brgm: C. Hérivaux (CH)
Follow-up Committee:
R. Therrien (RT), M. Chevreuil (MC), J. Barth (JB), C. Popescu (CP), F. Van Wittenberge (FW)
Belspo:
S.Verheyden (SV)
Absents: L. Diels (VITO), E. Haubruge (Faculté Universitaire des Sciences Agronomiques de Gembloux), L. Hoffmann (Centre de Recherche Lippmann), K. Van de Wiele (OVAM), D. Springael (KUL).

1. Objectives of the meeting

- Presentation to the follow-up committee and to Belspo of research progress during last six months of year 2.
- Discussion with the follow-up committee about the debriefing of the mid-term evaluation of the project and about the regional scale approach on RWM073.
- Preparation of the first phase report.

2. Subjects discussed

Morning session

2.1. Research progress

General work progress (A. Dassargues, ULg-HG)

The presentation was an introduction to the FUC meeting. It was focused on 3 points:

- Comments about the mid-term evaluation of the project and reporting for Belspo
  - o recommendations of the evaluation panel not in line with recommendations of the follow-up committee;
  - o far too much time dedicated to various reporting.
- Overview of meetings held during year 2
- Brief description of works performed by workpackages

Ecotoxicological Risk Assessment, methodology and results (S. Crèvecoeur, ULg-LEAE)

The presentation was focused on the following points:

- **Sampling:**

New sampling of groundwater and surface water were collected at the different sites during 2008 and analyzed to evaluate the parameter EC_{50} (chronic toxicity test using *B. calyciflorus*). The samples were taken in boreholes as well as in the surface water. The physico-chemical parameters results remained similar along the first phase of the project.

- **Analysis of contaminants:**

All these samples were analysed for different contaminants: VITO for CAHs and BTEX, Laboratory of Oceanography (SC-3) for heavy metals and Laboratory of Food Analysis (SC-3) for PAHs.

Chimeuse is contaminated with heavy metals (As, Cd, Cu, Ni and Zn). The pollution at this site is characterized by a great spatial heterogeneity, with hotspots of arsenic, copper, nickel and zinc.

Machelen-Vilvoorde site is characterised by a spatial heterogeneity of CAHs (vinyl chloride, cis-1,2-dichloroethene and 1,1-dichloroethane concentrations are generally higher than the normative values). Zenne River is contaminated with PCBs, but results show a decrease in the concentration of these compounds between year 2007 and 2008.

At Morlanwelz site, the concentrations of heavy metals are generally below the normative values. Chlorinated Aliphatic Hydrocarbons (CAHs) pollution levels at this site showed quite large differences. In fact, Haine River is not contaminated with these pollutants. Groundwater is essentially contaminated with trichloroethene except P3 piezometer where concentrations of cis-1,2-dichloroethene, tetrachloroethene and vinyl chloride were also higher than the normative value.

- **Ecotoxicological tests and risk assessment:**

In the laboratory, all samples, containing a **mixture** of pollutants, were tested for their chronic toxicity, using *Brachionus calyciflorus* (Rotifera). Results vary according to the studied site, the sampling period, the concentration of pollutant, but remain similar during the first phase of the project.

At Morlanwelz site, all the three groundwater sampling points were toxic to *B. calyciflorus* after 48 hours exposure and their EC_{50} ranged from 66.47% (P16 – less toxic) to 12.24% (P6 – more toxic). EC_{50} could not be calculated for Haine River as there is less than 50% of inhibition of the reproduction rate (less than 48%) in the pure sample.

Note: During the sampling campaigns of year 2008, the Haine River was fed by the base-flow from groundwater.

So, on the one hand, toxicity values are available **for a mixture of pollutants** from laboratory tests (task 3.2.4) and, on the other hand, a risk can be assessed **for each pollutant** separately using measured concentrations and data from literature.

Ecotoxicological risk was calculated for each piezometer at the different studied sites. A clustering analysis performed at Morlanwelz site shows that the risk assessment is linked to pollutant concentrations.

Several pollutants show hazard to the environment, differing from one polluted site to another. The risk at Vilvoorde site is especially related to CAHs contamination. On the contrary, heavy metals (As, Cu, Ni, Pb, Zn) are problematic at Chimeuse. At Morlanwelz, high concentrations of CAHs and of several heavy metals have been detected and may pose a risk to the environment. These analytical results can be compared with the ecotoxicological data obtained in the laboratory.

Whole mixture effects can be assessed by testing the mixture in its entirety (done during the 1st phase of the project). However, this approach will not identify the chemicals responsible for interactions. Actually, the overall toxicity of the mixture could be equal to the sum of each pollutant toxicity (additivity), less than the sum (antagonism), or greater than the sum (synergism). So, during the 2nd phase of the FRAC-WECO project, if possible, we will include in the risk assessment the relations between the different pollutants of the mixture.

After bibliographic research, we have to choose the best approach before integrating the toxicity of mixtures to assess the risk in the project.

- **Future activities:**

During 2009, sampling campaigns will take place on the RWM073 groundwater body (alluvial deposits of the Meuse River between Engis and the North of Liège). Same steps will be performed on these samples (*i.e.* analysis of pollutants, chronic toxicity tests achieving, ecotoxicological risk assessment…). First of all, pollutant concentrations and other available ecological or ecotoxicological data will be collected.

During the 2nd phase of the FRAC-WECO project, if possible in the risk assessment (task 4.2) the relations between the different pollutants of the mixture (synergism, antagonism, additivity) will be included.

Comparison and validation of risk assessment tools+ Field works (D. Caterina, ULg-HG)

The presentation was focused on four main topics:

- **Validation of risk assessment tools**

In the last follow-up committee meeting in June 2008, a selection of risk assessment tools was presented and described in details. These are: RISC Workbench, RBCA Toolkit, MISP and Remedial Targets Worksheet. During last months of year 2, a comparison of analytical models included in each of these tools with a numerical model built with HydroGeoSphere was performed based on their capacity to simulate the transport of dissolved contaminants for a source of pollution located respectively above and below the water table.

For the first case study, the source of pollution was set in the satured zone using typical hydrogeological parameters met in the alluvial gravels of RWM073. Results obtained with analytical models turned out to be very close to results provided by the

numerical model. A sensitivity analysis on main parameters was also performed showing only minor differences between models.
The second case study was dedicated to a source located in the unsaturated zone. Unfortunately, tools such as Remedial Targets Worksheet, RBCA Toolkit and MISP proved not to be able to manage such sources or at least use analytical models in the unsaturated zone that are far too much simplified to be compared with HydroGeoSphere. The comparison with the numerical model is only conceivable with RISC Workbench even though it uses very simplified approach and different parameters. First simulations have shown major differences between results provided by these two models. These differences are normal in a certain way because of the different approach and parameters used to describe the unsaturated zone in both models.

- **Field works:**

The second topic of the presentation was dedicated to field works and more particularly to the application of the Finite Volume Point Dilution Method (FVPDM) in Vilvoorde. FVPDM is a tracer technique developed by ULg-HG to quantify and monitor the variations with time of Darcy fluxes in relation with changes in hydrogeological conditions. Several wells (SB1, SB2 and PB9) were selected to perform the technique. Prior to test FVPDM, slug tests were performed in each of these wells to estimate the hydraulic conductivity in order to dimension correctly the technique. With these data, we were able to perform the test on SB2 and PB9. Results have allowed us to estimate Darcy fluxes in the vicinity of tested wells. In comparison with Darcy fluxes calculated by the numerical model developed by VUB, results of FVPDM are in the same order of magnitude.

- **Modelling of RWM073:**

In order to develop a model of the groundwater body RWM073, it was necessary to have the locations of potentially contaminated sites and punctual receptors. This was made by extracting the information from the database WALSOLS (for contaminated sites) and from the hydro-database of the Walloon Region (for punctual receptors). First discretization of the area was made using GMS.

- **Future activities:**

Research efforts have to be made during first months of year 3 to clarify the way how process studies (complementary field investigations, modelling) and economic analysis are going to interact from a practical point of view.
By the same time, there will be a continuation of data acquisition and mining for ongoing investigations in the test sites, in particular in RWM073.
Simulations on the numerical model built with MODFLOW/MT3D for RWM073 will be carried out during phase 2 of the project, using first standard value for recharge and then, when data from the VUB will be available, calculated recharge from WETSPASS.
It is also foreseen to create a database with properties of main contaminants found in RWM073.

Remarks:

RT: How do you plan to use analytical models included in selected risk assessment tools in the scope of the project?

- <u>DC:</u> In area where we have a poor characterisation, these analytical models that do not need lot of time and data to be run could be used to compute contaminant fluxes reaching a defined receptor.

Economic analysis of groundwater degradation due to brownfields: Potential benefits expected from an improvement of the RWM073 quality – First results (C.Hérivaux, Brgm)

- **Context of the analysis:**

In the scope of the Water Framework Directive (WFD), programme of measures and economic analysis required to reach good chemical status in the case of groundwater bodies at risk due to contaminated sites are a challenging task. Indeed, remediation measures are expected to be very expensive, time required for remediation may be very long, and uncertainties concerning the pollution level, costs and effectiveness of measures may be great.

Groundwater is generally not used anymore as a resource in these groundwater bodies, so it is difficult to anticipate if market benefits can be expected from an improvement of water quality and if people are willing to pay to contribute for the improvement of the water quality. Research efforts performed in the scope WP5 have raised specific questions such as: How much will it cost? How long will it take to be effective? WP5 will address these questions by

- setting the framework to:
  - assess expected benefits in case of groundwater quality improvement in a context of groundwater body at risk of not reaching good status due to brownfields;
  - compare it to the costs required for the implementation of programme;
- applying this framework to the groundwater body RWM073.

- **Framework:**

In order to set a framework, several questions need to be answered: who may benefit from an improvement of alluvial gravels quality? Where? When?

Who ? Activities or people that are sensitive to water quality and that currently use or may use in the future the alluvial gravels as a resource i.e. population and economic activities sensitive to water quality

Where? The aquifer of gravel alluvial deposits between Namur and Visé (RWM072+RWM073)

When? Contrasted scenarios are designed based on assumptions concerning the evolution of the alluvial gravels chemical status, the evolution of water demand and the evolution of water supply strategies of water users located in the studied area:

- **one baseline scenario** that considers the evolution of water demand but no change in terms of alluvial gravels quality nor in terms of water supply strategies;
- **several breaking scenarios** that consider the evolution of water demand but also an improvement of alluvial gravels quality and potential adaptations of water supply strategies in the case study area.

2060 is chosen as a relevant time horizon to assess the effects of these scenarios as it is considered sufficient to take into account (i) time required to implement measures, (ii) time required to observe the effectiveness of the measures and (iii) time required to change the water supply strategies and to observe economic impacts.

In order to see what kind of benefits can be made in case of an improvement of the groundwater quality, it is necessary to have a good understanding of the current water supply strategies. Water supply strategy can be split into two parts: the user's water choice and the water supplier's choice. The choice of a water supply strategy may be influenced by the groundwater quality. Potential adaptations in water supply strategies may appear in case of an improvement of groundwater quality. There are three main types of adaptations: 1) treatment of the water abstracted from the alluvial gravels can be reduced or abandoned, 2) water users currently supplied by drinking water network may be interested to drill their own well, 3) drinking water utilities may be interested to increase their use of alluvial gravels as a resource. Combination of **effects** needs to be taken into account.

Effect 1: decrease in water treatment costs:

Description of the effect: in a situation where groundwater quality reaches good status, water treatment (corresponding to industrial pollution abatement) is expected to be abandoned thus resulting in an avoided cost (i.e. in a potential benefit).

Who may benefit from this effect? Drinking water utilities and economic activities that currently abstract water from the alluvial gravels aquifer through private wells and that have to treat the water to comply with their quality requirements. After having extracted data from the DGRNE database and having performed interviews of several companies, it appears that the agro-food industry is the major sector sensitive to water quality regarding industrial pollution.

Expected direct and indirect impacts :

- positive impacts on drinking water utilities or economic activities through a diminution in production costs;
- positive impact on the environment through a diminution in waste water treatment discharges;
- possible improvement of the image of products produced within the case study area.

2 types of costs induced by industrial micropollution can be distinguished:

- a direct cost related to the treatment of water which directly relies on the quality of water;
- an indirect cost corresponding to the protection and surveillance of water to reduce the risk/fear of contamination even if there is no current and local contamination.

Results:

Scenario of alluvial gravels groundwater quality improvement (from 2030) has shown that 1.3 million m3/year could be concerned by a decrease in treatment cost which results in an annual benefit of 0.65 million €/year.

Effect 2: Turning from drinking water supply to private supply:

Description of the effect: if the groundwater quality is supposed to be significantly improved to reach WFD objectives, water users that were reluctant to use groundwater for quality reasons may change their water supply strategy to a private well supply if it is worth from an economical point of view.

Who may benefit from this effect? Water users currently connected to the public water network for water quality reasons and located on the alluvial gravels aquifer. We focus here on potential impacts on economic activities. A research in the CILE water company database gave information on non-domestic consumers connected to the public network for 8 municipalities.

Expected direct and indirect impacts:

- positive impacts on drinking water utilities or economic activities through a diminution in water supply for those who changed their strategy on the basis of financial arguments;
- negative impact on drinking water utilities management (diminution in the charged drinking volume: increase in drinking water price, difficult to predict future water demand, risk to overestimate investments;
- negative impact on the environment: an increase in the number of boreholes induces a significant risk of pollution of aquifer, loss of control of the water volumes abstracted.

Results:

About 800,000 m3/year water may be concerned by this effect (~ 16 % of the non domestic drinking water consumption). Annual expected benefits are estimated at 2.10 million €/year, to be shared among 147 companies, which makes a mean private benefit of about 12,000 € per year per company.

Effect 3: increase in the use of alluvial gravels for drinking water production:

Description of the effect: for the drinking water sector, a change in the type of water resource used for drinking water production may result in benefits for the drinking water utilities and consumers, in case of cheapest water production cost.

Who may benefit from this effect? Only the drinking water sector is considered in this analysis.

Expected direct and indirect impacts:

- positive impacts on drinking water utilities and consumers through a decrease in drinking water production costs;
- negative impact on drinking water utilities and consumers through a diminution in the charged drinking water volume from other water resources: increase in drinking water production price.

Results:

Different scenarios were tested:

- **Scenario A:** it consists in a partial change in drinking water strategies of riparian municipalities, i.e. a change in the type of resources used to produce drinking water: the use of alluvial gravels in drinking production for the studied area increases from 23% to 61-62%. With that scenario, net benefit is estimated between 0.6 and 0.9 million €/year.
- **Scenario B:** it consists in a change in drinking water supply strategies of riparian municipalities to 100% from alluvial gravels. With that scenario, net benefit is estimated between 2.1 and 2.3 million €/year.

- **Future prospects:**

A complementary assessment will be carried out in the second phase of the project in order to assess the population willingness to pay to improve the RWM 073 quality.

Remarks:

SV: asks if it is possible that the quality of groundwater from alluvial gravels continues to deteriorate in the future.

- SB: No because, nowadays, environmental measures are more severe than in the past.

SV: asks if from a geological point of view, there are differences between RWM072 and RWM073.

- AD: explains that there are no real differences from a geological point of view between RWM072 and RWM073. They are both composed of alluvial gravel deposits of the Meuse River. The only difference between RWM072 and RWM073 is the density of contaminated sites which are more numerous in RWM073 making it at risk of not achieving good chemical status by 2015 as required by the WFD.

Landuse-recharge mapping and groundwater modelling for Vilvoorde and Outlooks to Phase 2 *(J.Dujardin, VUB)*

The presentation was composed of 4 main topics:

- **Land cover mapping**

Land cover is an important factor determining the spatial and temporal variation in infiltration and groundwater recharge. Available land-use data sets are too strongly generalised for hydrological modelling within urbanised/industrialised watersheds, both spatially and thematically. Complex areas are represented by abstract land-use classes with heterogeneous composition (e.g. industrial area, low-density urban area) which, from a hydrological point of view, are difficult to parameterize. The use of high-resolution sensors (1 meter resolution) allow detailed mapping of land cover, but spectral resolution of these sensors (4 bands) is too limited to extract hydrologically relevant classes. This is why an object-oriented image interpretation approach was used to get land cover.

During the first follow-up committee meeting (December 11th 2007), VUB showed the obtained land-cover map for the Zenne study area, but some confusions remained between buildings and roads, between bare soil and roads and between water and shadow. To improve the accuracy of the classification, the 6 used classes (water, bare soil, meadow, mixed forest, buildings and roads) were changed in 8 classes. The buildings and roads classes were changed in 3 new classes: grey surfaces, red roofs and bright roofs, and a new shadow class was added.

This new classification improved the accuracy of the land-cover map. The last step of the classification process is the postclassification of the shadow objects. The shadow objects are reassigned to one of the 7 land-cover classes, because shadow hides the actual land cover type

Applying these modifications, the final land cover map of the Vilvoorde area could have been obtained. It was then used as input for the WetSpass software. This software allows estimating spatially distributed run-off, evapotranspiration and recharge in function of land cover, topography and soil type.

- **Run-off simulation**

Spatially distributed run-off was obtained with WetSpass. Results for the winter and the summer periods were presented and compared to results coming from the land-use map AGIV2001 (20 meters resolution). It appears that run-off shows higher spatial variability with high resolution satellite imagery.

- **Recharge simulation**

Spatially distributed recharge was obtained with WetSpass. Results for the winter and the summer periods were presented and compared to results coming from the land-use map AGIV2001 (20 meters resolution). It appears that recharge shows higher spatial variability with high resolution satellite imagery.

- **Groundwater modelling at Vilvoorde**

A groundwater model of the Vilvoorde area has been developed based on a previous one developed by VITO. Results coming from WetSpass have been implemented in the new model. Field data (including drillings and geomecanical tests) have also been incorporated into the model. The calibration of it is sufficiently accurate and first simulations for the transport of contaminants considering only advection have been performed.

- **Future activities:**

The approach developed during phase 1 need to be upscaled to the groundwater body. Because of the large area covered by RWM073, lower resolution data will be used (SPOT 5 with a multispectral resolution of 10 m and a panchromatic resolution of 5 m). Lower resolution data induce the use of a new methodology called the “stratified approach”.

Remarks:

AD: Why does the approach developed during phase 1 can not be used anymore at the scale of the groundwater body?

- JD: Because of the large area of the groundwater body.

Study in batch and column set-ups of the stimulated degradation of Chlorinated Aliphatic Hydrocarbons in the aquifer at the Zenne site in Vilvoorde – Machelen (W.Dejonghe, VITO)

The presentation was focused on the following points:

- **<u>Results batch degradation test:</u>**

Batch tests with aquifer and groundwater obtained from the locations SB2, PB26 and SB3 (Vilvoorde site) were run and all stimulated conditions (by adding molasses, lactate, sediment or sediment extract) are degrading the 2 ppm of vinyl chloride (VC) very quickly. Non-stimulated conditions show no degradation.

For SB2, the degradation rate of VC in function of stimulate is the following: sediment > lactate > sediment extract > molasses.

For PB26, lactate > sediment extract > sediment > molasses.

When the VC is totally degraded, DCE is spiked to the flasks and its degradation is followed. The degradation of DCE for SB3 is similar with all the different stimulates.

- **<u>Results column degradation test:</u>**

The column degradation tests have advantages over the batch degradation tests, such as:

- Dynamic instead of static
- *In situ* concentrations of CAHs
- Groundwater at *in situ* groundwater velocity over columns: 50 mL/day = 47 m/year

To better simulate the *in situ* conditions, aquifer columns were set up. These columns were filled with aquifer obtained from the location SB1 at 28 m from the Zenne. Groundwater polluted with the *in situ* concentrations of CAHs (100 µg/l DCE and 800 µg/L VC) are pumped with a speed of 50 ml/day or 47 m/year over this aquifer. Samples for CAH-analyses are taken at the inlet, outlet but also after different contact distances between the groundwater and the aquifer. First results indicated that no degradation of DCE and VC occurred in the natural attenuation columns. Therefore the CAH-degradation in the columns was stimulated with lactate (0.054 mg C/day), sediment extract (0.054 mg C/day) or by placing a sediment column in front of the aquifer column. This sediment column acts as a bio-barrier since the CAHs are already degraded until a certain extent in this column so that lower concentrations of CAHs are flowing together with dissolved organic carbon and CAH-degrading bacteria from this sediment column into the aquifer column. However, due to the low concentrations of carbon sources, no stimulation of CAH degradation could be observed in the aquifer columns (data not shown). In a further step, the concentration of added carbon sources were increased till a final concentration of 0.5 mgC/day of lactate or sediment extract was reached in the columns. Due to gasformation, we have currently problems with the sampling of these columns. The effect of the increased DOC on the degradation of DCE and VC will be further studied in 2009.

- **<u>Planning, study further the CAH degradation in:</u>**

Batch experiments:

- How to stimulate the CAH degradation in aquifer taken at different positions of the site?
- Continue degradation test at 12 ℃
- Study VC, DCE, TCE, PCE degradation

- Determine kinetic parameters and biomass factors from the batch tests so that they can be used in the models

Column experiments:

- How to stimulate the CAH degradation in aquifer taken at position SB1 at the Zenne site?
- Study VC, DCE, TCE, PCE degradation
- Determine kinetic parameters and biomass factors from the column test so that they can be used in the models

Afternoon session

2.2. <u>Debriefing of the mid-term evaluation of the project</u>

<u>SB:</u> - reminds problems encountered during the mid-term evaluation of the project, i.e. the fact that the project was evaluated by experts that did not follow it from the beginning and that in some of their questions, it was obvious that they were not specialists in the studied domain.

- proposes to suggest to Belspo to include the follow-up committee members in the panel experts that have to evaluate the project. It would be more relevant.
- proposes that the consortium writes a document describing all comments and suggestions and then to send it to the follow-up committee members that could approve it or not.

2.3. <u>Regional scale application: RWM073</u>

The objective of this topic is to clarify the methodology that will be applied on RWM073 and to agree on each project partner expected contribution.

<u>SB:</u> - reminds why the groundwater body RWM073 was chosen.

- what is now needed is a criteria to evaluate risk and vulnerability at the groundwater body scale (= how to evaluate the state of the resource, i.e. define a status indicator)

<u>CH:</u> - emphasizes that in the scope of future WP5 activities, a status indicator of the quality of groundwater in alluvial gravels of RWM073 is absolutely necessary in order to evaluate costs of a program of measures.

<u>JPT:</u> - ULg-LEAE can provide a status indicator by assessing the ecotoxicological risk.

<u>RT:</u> - in order to test different scenarios of remediation, analytical models studied in WP4 can be used. Due to low computation time, lots of simulations can be run with

those models what will allow to perform an uncertainty analysis. That kind of study was already performed by A. Fries.

- proposes to send information about that study to consortium.

SB: - the groundwater model which is developed will not be able to deal with remediation scenarios. It will just be possible to calculate a global status of groundwater and eventually assess the relative impact of a source of contaminant in the global degradation of the resource. An uncertainty analysis is not foreseen because it will take too much time.

AD: - proposes to use the SEQ-ESO approach to compute a status indicator of the groundwater resource.

- will send information about SEQ-ESO to all partners.

SB: - the problem with the SEQ-ESO approach lies in the fact that the ecotoxicological risk is not taken into account.

- thinks that it is up to the Walloon Region to decide how to calculate a status indicator.

CH: - will need the status indicator for the end of 2009. ULg-HG should at least study two scenarios with its numerical model. The first one is a scenario where no action on pollutant sources is taken. The second one is a scenario where all sources of contaminants are removed.

SB: - to achieve these scenarios, it is important to receive data of recharge coming from VUB before the end of 2009.

OB: - needs soil data on RWM073 to calculate recharge.

SB: - soil data are available at the Walloon Region. A formal request must be made.

SB: - requests a meeting with RW end-user in order to discuss of the status indicator.

2.4. First phase report

The contributions of each partner to the first phase report are expected to be sent for **Tuesday 27th 2009 at noon the latest**. It is advised to structure the document WP by WP.

Project FRAC-WECO

Minutes of the meeting

Authors : P.Jamin – S.Crevecoeur – J.Dujardin – W.Dejonghe – S.Brouyère
Project : FRAC-WECO
Flux-based Risk Assessment of impact of Contaminants on Water resources and ECOsystems
Date : October 8th 2009 — Location : **Liège (Belgium)**

TIMETABLE

11.00 - 11.30:	General work progress	(A. Dassargue, ULg-HG)
11.30 – 12.00:	Land use mapping and hydrological modeling on RWM073	(J.Dejardin, VUB)
12.00 – 12.30:	Regional-scale risk assessment for water resources and ecosystems: general methodology and first results	(P.Jamin, S.Brouyère, ULg-HG)
12.30 – 13.30:	Lunch break	
13.30 – 14.00:	Batch and column set-ups of the stimulated degradation of Chlorinated Aliphatic Hydrocarbons in the aquifer at the Zenne site	(W. Dejonghe, VITO)
14.00-14.30:	Ecotoxicological risk assessment using a TRIAD-like approach	(S.Crèvecoeur, LEAE-Ulg)
14.30 – 15.00:	BRGM activities: Socio-economic analysis on RWM073	(C.Hérivaux, BRGM ; S.Brouyère, ULg-HG)
15.00-16:00	Discussion with the follow-up committee, conclusions of the meeting	

Participants:

Project partners:
ULg-HG: S. Brouyère (SB), A. Dassargues (AD), P. Jamin (PJ), P. Orban (PO), Fabien Dollé (FD)
ULg-LEAE: S. Crevecoeur (SC), J-P. Thomé (JPT)
VITO: W. Dejonghe (WD)
VUB: O. Batelaan (OB), J. Dujardin (JD), Franck Canters (FC)
BRGM: absent
Follow-up Committee:
M. Chevreuil (MC), J. Barth (JB), L. Lagadic (LL), C. Popescu (CP), F. Van Wittenberge (FW)
Guests:
CILE: J-M. Compère (JMC)
Belspo:
S.Verheyden (SV)
Absents:
L. Diels (VITO), E. Haubruge (Faculté Universitaire des Sciences Agronomiques de Gembloux), L. Hoffmann (Centre de Recherche Lippmann), K. Van de Wiele (OVAM), D. Springael (KUL), J Leclercq (SPAQuE).

1. Objectives of the meeting

- Presentation to the follow-up committee and to Belspo of research progress since beginning of the 2nd phase of the project.
- Presentation to the follow-up committee and to Belspo of the methodology to reach the objectives of the 2nd phase of the project.
- Discussion with the follow-up committee about the progress of the project.
- Planning of administrative and scientific reports.

2. Research progress

2.1 General work progress (A. Dassargues, ULg-HG)

The presentation was an introduction to the meeting. It was focused on 2 points:

- Overview of meetings held during year 3
- Brief description of works performed by workpackages

2.2 Landuse mapping and hydrological modeling on RWM073 (J. Dujardin, VUB)

We decided to upscale the approach to the level of the groundwater body so a new classification methodology will be used. Because of the large area covered by the RWM073 catchment we will have to make use of lower resolution data. We decided to work on SPOT5 data with a multispectral resolution of 10 m and a panchromatic resolution of 5 m and this type of data allows us to cover the entire study site with one image. A stratified classification approach will be applied, distinguishing between built-up areas (urban and industrial land use) and natural/agricultural land use. For the natural areas a multi-temporal pixel classification will be used, for the urban and industrial areas a sub-pixel classification approach will be used to be able to characterize the proportion of imperviousness at the sub-pixel scale.

For the multi-temporal approach 3 SPOT5 images were ordered (spring, summer and autumn), but till now no good images were acquired because of the clouds, so we decided to start working on an archive satellite image, a Landsat ETM+ image of 2001 (MS 30 m and PAN 15m resolution).

Before starting the classification of the Landsat image we had to change the georeference system to Lambert72 using a Quickbird reference image of the same area. 15 ground control points and 15 check points were selected in both images. These points were used to calculate a transformation matrix that is needed to resample the Landsat image to the new georeference system. A RSME of 14 m was obtained.

The first step in the stratified classification approach is the land-cover classification of all the pixels of the Landsat image. 15 clusters of pixels were obtained after an unsupervised classification of the satellite image. After a visual interpretation some clusters could be merged while some clusters had to be separated in new clusters to obtain the 6 wanted land-cover classes: water, grass, trees, grey urban, bright urban and bare soils. After the application of some post-classification rules an overall accuracy of 90% and a Kappa index-of-agreement of 86% were obtained.

In a second step all the urban pixels (grey urban and bright urban) were put together in one class, resulting in an urban mask. All the urban pixels will be classified with a sub-pixel classification approach to determine the proportion of imperviousness in each urban Landsat pixel. Several remote sensing unmixing techniques exist, but in this case we decided to apply a non-linear spectral unmixing using a neural network; A Multiple Layer Perceptron will make use of a back-propagation learning rule to predict the fraction of imperviousness from observed spectral radiances. The same Quickbird image as used before is used to train the classification model: the amount of impervious Quickbird pixels of 1 by 1 m in an urban Landsat pixel of 30 by 30 meter is calculated. Before training the classification model a temporal filtering of both images was necessary to detect all the landcover changes between both images. After this temporal filtering 1250 Landsat pixels were randomly selected as training pixels and 1250 other independent Landsat pixels were used as validation. The training data is used to determine the mathematical relationship between the input and the output data of the classification model. The input data for this sub-pixel classification model is the spectral information of individual Landsat pixels (red, blue, green, nir, mir, ndvi and ratios between the different spectral bands), and the output of the model is the fraction of imperviousness within the individual Landsat pixel. After training and validating the model an absolute error of 13% was obtained, and the sub-pixel classification model was applied to all the urban pixels of the Landsat image. Finally, when we combine the stratified classification approach we obtain a land-cover map of the RWM073 area with the natural areas classified on the pixel level (grass, forest, bare soil and water) and the urban areas classified on the subpixel level giving the fraction of imperviousness inside every urban pixel.

This land-cover information will be used in the coming weeks as an input for the high-resolution groundwater recharge simulation using WetSpass. A multi-temporal analysis of the lancover is also planned for the next months.

Remarks:

JB: remarks that surface water is considered as impervious what is confirmed by JD.

2.3 Regional-scale risk assessment for water resources and ecosystems: general methodology and first results (S. Brouyère & P. Jamin, ULg-HG)

The presentation was focused on three main topics: the general context of the RWM073 groundwater body, the methodological approach for risk assessment in this GW body and the description of the on going activities.

At the end of the first phase of the FRAC→WECO project it was decided to upscale the area of study from site scale to groundwater body scale. Indeed, the groundwater bodies located on around the industrial area are at risk of non reaching a good status in terms of the European legislation. Risk assessment is therefore necessary in such groundwater bodies. The classical schema for risk assessment is the “Sources-Pathways-Receptors” schema. But at this regional scale, the number of sources, receptors, their diversity (point or diffuse) and the complexity of the pathways between them require to use a new approach based on the fluxes in order to take into account the addition of the sources.

Based on S-P-R schema, the conceptualization of the risk assessment can be set. First, the identification of the problem start with a list of sources of contaminated sites (including location, type and behaviour of pollutant, concentrations, …), a list of receptors (location, point or global receptors,…) and a description of the pathways (geology, hydrogeology, contaminants properties,…). All the data will be gathered in one geodatabase that are linked all the part of the S-P-R schema. Since all the polluted sites are not characterized, most of them remain "potentially polluted". So that will lead to make assumptions in order to assess the contaminations. This way to proceed required a flexible treatment because of the variable knowledge on the three part of the S-P-R. Different tools will be used depending on the level of knowledge (analytical with poor level, numerical with high level).

Finally, one of the most important part of a regional risk assessment process is to define quality criteria for the whole groundwater body. The idea is to consider all pollutant fluxes reaching the groundwater and sum their on a certain volume of groundwater. But the main problem consist in choosing this groundwater volume (total volume of GW, renewable volume,…). So we end-up with a criteria based on the delineation of the contaminant plumes within witch an indicator of the quality status is given and summed on the whole groundwater body. This indicator will probably be an adapted version of the SEQ-ESO currently used within the Walloon Region.

Three main activities are carried out at the moment by ULg-HG. The first one is the data mining about pollutant sources and receptors. It consists in consulting database and data collecting in SPAQuE. Precise data were collected for only a few numbers of sites what means that a lot of sites remains "potentially polluted". Secondly, a database is being developed. It links a polluted site with activities than have been taking place, associated pollutants, environmental data and list of receptors. It is able to give a list of pollutants probably encountered from a given activity and *vice versa*. Behind this data base also lays a table regrouping the physical and chemical properties such as solubility, Kow, K_H,… of about 80 pollutants. The third activity running is the groundwater flow and transport modelling. Groundwater flow is modelled in the whole watershed feeding the RWM073 and transport will be running only on RWM073. Moreover, simplified test cases are developed to test the application of the SEQ-ESO and its aggregation on the whole groundwater body.

The planning for the next months is to work on the development of the quality criteria and to work on the RWM073 (SPR database, GW modelling). The goal is to have a first running application with a more or less calibrated model, a selection of contaminant sources by the end of 2009.

Remarks:

MC: worried about how to deal with non-characterized sources.

SB: Three ways of dealing: (1) deterministic approach with sources that we know, (2) probabilistic approach with activities that are probably polluting and (3) back-tracking approach when we have data on plume but not about the source.

2.4 Batch and column set-ups of the stimulated degradation of Chlorinated Aliphatic Hydrocarbons in the aquifer at the Zenne site (W. Dejonghe, VITO)

The presentation was focused on the following points:

* Batch degradation of DCE
* Batch degradation of TCE
* Verifying the degradation potential by searching for Dehalococcoides.
* Transfer approach to RWM073

VITO studied further at batch level the degradation of DCE and TCE in aquifer and groundwater obtained from three locations at the Zenne site. For DCE degradation constants were determined for the three locations. The degradation constants increased when more DCE was added to the batch flask. There are however still some questions that have to be resolved concerning these degradation constants. For the TCE test, the amount of biomass was determined for the different locations. By using Q-PCR the number of *Dehalococcoides* but also the catabolic genes *tce*A (conversing TCE to ethene), *vcr*AB (DCE to ethene) and *bvc*A (VC to ethene) were determined

Remarks:

JB: There is also aerobic degradation.

AD: It would be nice to have a degradation constant that we can integrate in the transport GW model.

2.5 Ecotoxicological risk assessment using a TRIAD-like approach (S. Crévecoeur, ULg-LEAE)

* New methodological approach based on TRIAD approach concept:

During the second phase of the FRACWECO project, a TRIAD-like approach will be used to assess the water quality of the groundwater body “Gravels and alluvial deposits of the Meuse River between Engis and Herstal – RWM073”, located in an industrial area of the Walloon Region in Belgium. This methodology is adapted from classical TRIAD approaches (originally and usually applied for sediment quality assessment). In the aquatic compartment, less experience are available on the practical use of the triad.

The methodological approach integrates factors such as chemistry (chemical identification and quantification) and ecotoxicology (laboratory bioassays). The ecological component (in situ alteration) used in the classical Triad approach will not be integrated in the groundwater risk assessment due to lack of information with respect to groundwater organisms.

The different lines-of-evidence, (LoE: chemistry and ecotoxicology) are combined in the approach using qualitative and quantitative integration approaches. Results from all tests can be made comparable across the various LoE by uniform scaling method. So, zero to one subindexes (1 means “strong effect/high risk” and 0 means “no effect”) combining results from each discipline can be assessed (Chemical and Ecotoxicological Risk Indexes) and all variables can be projected into one integrated risk number (Environmental Risk Index).

* Validation of the methodology:

Chimeuse and Morlanwelz sites were used to validate the DIAD approach using pollutants and ecotoxicological results from phase 1.

- *Chemical Risk Index:*

The Chemical risk index (ChemRI) was assessed by using a sequence of successive steps: concentrations of pollutants (historical and field data) were compared to normative value (trigger value from Walloon Region) and a risk number (between 1 and 0) was assessed for each class of pollutants and globally for each sampling piezometers and for the whole studied sites.
On the one hand, the results confirm the widespread metal contamination (As, Cd, Cu, Ni, Pb and Zn) at Chimeuse site. In fact, global ChemRI is similar to ChemRi estimated for heavy metals. On the other hand, Global ChemRI at Morlanwelz site is represented by heavy metals, mineral oils and chlorinated compounds contamination (except Haine River). There is also a spatial heterogeneity between the different piezometers.

- *Ecotoxicological Risk Index:*

Chemical and physical analyses are not able to detect all dangerous substances present in water including the products of reactions between them. Additionally, these kinds of analyses can inform only about the amount of single contaminants but not the total contamination of water. Application of biotests with different organisms can indicate general stress as a result of complex mixtures, and provide information about potential hazard to aquatic life.

An ecotoxicological risk index (EtoxRI) can be assessed using results (expressed in percentage) from several laboratory bioassays using different species (Crustacea, Amphipods of the family Gammaridae and planktonic species, Rotifera) and endpoints (survival rate and reproductive performance).
The EtoxRI was characterised by spatial heterogeneity (some piezometers and Haine River are less toxic). In general, chronic toxicity (EtoxRI chronic) is more sensitive than acute toxicity (EtoxRI acute).

- *Environmental Risk Index:*

The results from all tests are made comparable across the various components of the Diad (chemistry and ecotoxicology) by uniform scaling method. Scaling of results is not part of the description in standard guidelines and is a new concept. Different methods have been used to interpret and represent “Diad” components.
Qualitative methods have often been applied to determine the degree of degradation of each station and of each site. So, chemistry and toxicity data are combined in the “Diad” using tabular matrix or pie charts. In tabular matrix, the different responses are shown as positive or negative signs to indicate a possible risk and can be linked to risk indicators (no risk, moderate risk, high risk…). The similarities between the samples can also be represented using pie-charts. It represents integration of all lines-of-evidence (contamination and toxicity using the different class of pollutants and bioassays, respectively) using colours coming from the SEQ-ESO system. Different conclusions can be made using the integration of the results: according to the piezometer, there is a strong evidence for pollution-induced degradation, some chemicals are not bioavailable, the toxicity is caused by only one or two compounds or unmeasured toxic chemical(s) are causing toxicity. The qualitative methods have the advantage of the simplicity of interpretation, although no quantification is provided.
There is also **quantitative approach** which integrates all information in a single numerical value. Risk indices obtained from the two disciplines (ChemRI and EtoxRI) are combined in order to estimate an environmental risk index (EnvRI), from zero to one, corresponding to no effect up to maximum effect. The difference

between the final score and the theoretical score 1 (the score for a site with strong effects/high risk for all parameters) gives an indication of the risks (and its magnitude) for ecosystem health at each of the sites.

* Conclusions:

None of the two DIAD components (chemistry and ecotoxicology) could reliably predict the other one; *i.e*, the weight-of-evidence approach using the two components has been considered a more complete evaluation of toxic effects from groundwater than any one component alone.

This study provides evidence of the poor health status of Chimeuse (EnvRI = 0.9144) and Morlanwelz (EnvRI = 0.7244) sites as a result of heavy metals (Chimeuse site) and mineral oils, CAHs, PAHs pollution.

* Future activities:

After collection of all available data on RWM073 (pollutants concentrations, past and recent activities…), the diad approach will be applied to other sites rich in data. So, ecotoxicological tests (using different species and endpoints) and pollutants analysis (SC3) were and will be performed on groundwater samples from the field. Scenarios have to be made concerning sites with only data on past and recent activities.

In conclusion, this approach will allow classifying the case study into categories according to the degree of contaminant-induced degradation. Furthermore, it will provide a helpful decision support in order to determine the micro-pollutant concentrations which can not be exceeded in the environment to prevent ecological damages to the ecosystem.

Remarks:

SC: explains that physico-chemical parameters will be integrated in the Diad approach.
LL: agrees the proposition.
JB: recommends completing lab tests with data coming from literature.

2.6 BRGM activities: Socio-economic analysis on RWM073 (C.Hérivaux, Brgm)

Following the requirements of the Water Framework Directive, a programme of measures should be proposed for each water body at risk of not reaching good status by 2015. In case of disproportionate costs derogation may be justified on the basis of a cost-benefit analysis. This economic analysis is a challenging task in case of groundwater bodies at risk due to brownfields: remediation measures are expected to be very expensive, time required for remediation may be very long, great uncertainties concerning costs and effectiveness of the measures. Moreover as groundwater resources are generally not used anymore as a resource, it is difficult to anticipate (i) if market benefits could be expected from an improvement of the groundwater quality and (ii) if people would be willing to contribute to this quality improvement).

BRGM comes in 3 types of activities: general methodological approach, ensuring that it reaches the expectations of end-users, cost of the program of measures and assessment of potential benefits of improving the quality of the MESO.

General methodological approach.

The indicator developed by HG-ULg base on SEQ-ESO will be used as an indicator of effectiveness for the cost-effectiveness analysis performed by WP5. The use of this basis seems to be in indicator line with end-users' expectations since it is the indicator currently used by water managers. Those water managers need an assessment of the cost required to improve the RWM 073 groundwater quality because they need to justify if they want to introduce a WFD derogation, for instance by proving disproportionate costs. By now, simplified assessment is only based on the implementation of excavation. The management plan should be completed by December 2010 → BRGM plan to assess the cost of program of measures by June 2010. Several studies were already been performed in the Walloon Region to valuate the benefits related to an improvement of water status but only about the market benefits. Concerning benefits not related to the use of water as a resource, studies were performed in the Walloon Region only for surface water. For groundwater, values were obtained by benefit transfer from other studies not performed in the Walloon Region.

What is technically feasible in terms of groundwater body quality improvement? How much will it cost to reach these objectives? If several measures are possible, which one is the most cost-effective?

The task of BRGM about these questions starts now and is composed of three steps.

- Step 1 (Dec 2009): Collect data on hydrogeology, pollution sources and types of pollutants, current groundwater quality and improvement objectives expressed with the use of the SEQ-ESO indicator
- Step 2 (March 2010): Propose a typology of potential measures that could help to improve groundwater quality and associated unit costs expressed in €/m3 pumped or in situ as a function of the type of pollutants
- Step 3 (June 2010): Identify and assess costs of combinations of measures that should be implemented to reach objectives of groundwater quality improvement expressed by the use of the SEQ-ESO indicator

What are the expected benefits of such groundwater quality improvement? Can they balance the costs required to implement the measures?

The assessment of the expected market benefits has been carried out during 2008. Three kind of potential benefits expected on current or (potential) use of the resource from an improvement of the RWM073 groundwater body were assessed:

- Effect 1: Decrease in treatment costs
- Effect 2: Change in the type of water supply resource/ development of private wells

- Effect 3: Increase in the use of the groundwater body as a resource for drinking water production

The results show a relatively low expected market benefits estimated between 3.3 and 4.4 million € from 2030 (i.e. between 1.3 and 1.8 million € when discounted). The total discounted sum of benefits on the 2008-2060 period is estimated between 23.8 and 32.4 million €.

The assessment of the non market benefits is a more complex task, carried out by contingent valuation, *i.e.* quantitative survey on the perception by the population of the Meuse alluvial plain. The objectives of such a survey are to characterise the knowledge and perception by the population of the groundwater body, its quality level and the relevance to improve its quality. An economical value can be given by assessing the value people would be willing to contribute to the improvement of the groundwater body quality and the mean value of the willingness to pay (WTP) in €/household/year can be estimated. Finally a non-market value can be given for the groundwater body by aggregation of the value WTP.

This survey consists in 4 main steps: design of the survey, selection of targeted population and sample, test of the survey (face to face interviews) and mailing, before to be able to perform the econometric analysis of answers.

3. Debriefing of the mid-term evaluation of the project

JB: Clearly defining the links between each team and workpackage will help us for the second phase of the project. The more spots the stronger is the case. Suggestion to feed in advance the final report to improve the integration of all the parts.
A bit worried about the contingent valuation. How people can estimate a value for groundwater, a part of the water that they know nothing about. OK for surface water but hard with groundwater.

MC: Each team has developed or changed their approach or methodology to the groundwater body scale.

LL: There is a great improvement with the groundwater body scale concept.
The modelling approach is in the right way. It is interesting and realistic to work with plume of pollutants. LL is not convincing by the link with microbiology (VITO. Concerning ecotoxicology the approach is now more appropriate.
WD: The groundwater body will be divided into clusters. The problem is that degradation is slowly, so it is difficult to apply the approach to the groundwater body. A literature review will be performed. Vito can help WP5 by saying that Natural attenuation is occurring or not and thus decrease or not the remediation costs.
JB: Will you perform some tests on site?
WD: No, just on the Zenne site because it is too expensive.
JB: Laboratory experiments can be transposed to the field but lots of uncertainties!

LL: Economic analyse is useful to the manager. How to communicate on this? At which level (people? scientists?)? The different data can be easily comprehensive to end-users.
SV: Proposed to write a flyer/folder to present the methodology of the project and spreading it as publicity. Other projects have already done this king of thing but always too late, at the end of the project. It is better sooner. If we want to organize a workshop by the end of the project we have to inform Belspo as soon as possible! The workshop is not requested but much appreciated.

SB: ask WD to have a look to the remediation costs that will be calculate by BRGM on French market data to seem if they are in the same range that the cost in Belgium.

CP: Walloon Region is happy with the work and the using of SEQ-ESO as status indicator. Still a bit curious by the way to integrate ULg-EAE and VITO part at the groundwater body scale.

4. Report/administration

SB: reminds us that we have to write an annual report for year 3 and that the contributions of each partner are expected to be sent for mid-November.
There is a new evaluation in July: we have to send a first draft of the final report around this moment in order to receive comments.

SB: would like to see the follow-up committee more involved in the report.

Project FRAC-WECO

<u>Minutes of the meeting</u>

Authors : Ph. Orban, P. Jamin, S. Brouyère	
Project : FRAC-WECO	
Flux-based Risk Assessment of impact of Contaminants on Water resources and ECOsystems	
Date : December 6th 2010	Location : **Liège (Belgium)**

TIMETABLE

10.50 – 11.00:	General work progress	(A. Dassargue, ULg-HG)
11.00 – 11.25:	Regional Risk Assessment	(P. Jamin, S. Brouyère, ULg-HG)
11.25 – 11.50:	Remote sensing and Land-cover mapping for the quantification of groundwater recharge in complex urbanised environments	(J. Dejardin, VUB)
11.50 – 12.15:	Ecotoxicological risk assessment using a TRIAD-like approach and Toxic Units	(S. Crèvecoeur, LEAE-Ulg)
12.15 – 12.40	Sorption and degradation of organic compounds: from site specific experience to regional generic data	(W. Dejonghe, VITO)
12.40 – 13.30:	Lunch break	
13.30 – 14.00:	Valuing the costs and benefits of remediating groundwater contaminated by brownfields: An application to the Meuse alluvial aquifer	(C. Hérivaux, BRGM)
14.00 – 15.00:	Integration of the works performed in each group	(S. Brouyère, ULg-HG)
15.00 – 15.30:	Administrative Issues	(S. Brouyère, ULg-HG)
15.30 – 16:00	Discussion with the follow-up committee, conclusions of the meeting	

Participants:

Project partners:
ULg-HG: S. Brouyère (SB), A. Dassargues (AD), P. Jamin (PJ), Ph. Orban (PO), Fabien Dollé (FD);
ULg-LEAE: S. Crevecoeur (SC), J-P. Thomé (JPT);
VITO: W. Dejonghe (WD);
VUB: O. Batelaan (OB), J. Dujardin (JD);
BRGM: C. Hérivaux (CH).
Follow-up Committee:
SPW-DESO: C. Popescu (CP), *ULaval:* R. Therrien (RT)
Guests:
VMM: Stefaan Hermans (SH)
Belspo:
/
Absents:
J. Barth (GeoZentrum Nordbayern), M. Chevreuil(UPMC-P6), J-M. Compère (CILE), L. Diels (VITO), E. Haubruge (Faculté Universitaire des Sciences Agronomiques de Gembloux), L. Hoffmann (Centre de Recherche Lippmann), L. Lagadic (INRA), J Leclercq (SPAQuE), D. Springael (KUL), K. Van de Wiele (OVAM), F. Van Wittenberge (SPGE), S. Verheyden (Belspo)

1. Objectives of the meeting

- Presentation to the follow-up committee and to Belspo of research progress since beginning of the 2nd phase of the project.
- Presentation to the follow-up committee and to Belspo of the methodology to reach the objectives of integration of the works of the 2nd phase of the project.
- Discussion with the follow-up committee about the progress of the project.
- Planning of administrative and scientific reports.

2. Research progress

2.2 General work progress (A. Dassargues, ULg-HG)

The presentation was an introduction to the meeting. It was focused on 3 points:

- overview of administrative and reporting made last year;
- overview of meetings held during year 4;
- brief description of works performed by workpackages.

2.3 Regional Risk Assessment (P. Jamin, ULg-HG)

The presentation was focused on two main topics: the presentation of the complete methodology of regional risk assessment and its application the groundwater body RWM073.

The regional risk assessment methodology is composed of seven steps.

(1) The creation and the feeding of a geodatabase with all data required for risk assessment (Sources, Receptors, hydrology, topography, hydrogeology …).

(2) Since the information of pollutant sources are very poor and the only available data are a list of potentially polluting industrial activities, development and use of a activity-pollutant matrix were essential to define actual sources of contamination.

(3 and 4) The behaviour of the contaminants through the unsaturated and the saturated zone is calculated. The leaching in the unsaturated zone can be calculated using analytical solution for each point source based on contaminant and soil properties. The transport of contaminant through the saturated zone is calculated using modelling technique at the scale of the groundwater body. Groundwater flow is calculated using MODFLOW and transport of contaminant using MT3D, both under GMS interface. The aim of this step is to generate maps of contaminant plumes for different contamination scenarios and for specified time steps.

(5 and 6) Based on the discretisation required by the modelling and the result of the transport simulation, each cell of the grid can be classified using the SEQ-ESO groundwater quality system. This system gives a quality indicator ranging form 100 (good status) to 0 (bad status) based on different contaminant concentration. At the end of step 6, a map of the groundwater body is obtained with colour code for each cell representing the chemical status.

(7) This last step aims to provide a global quality status for all the groundwater body by the aggregation of quality index using weight-average procedure.

This SEQ-ESO-based methodology has the advantage to be compliant with the ongoing legislation in the Walloon Region, fits very well with the EU WFD which promotes the use of aggregated indicators (spatially and for several pollutants) able to reflect trends in groundwater quality.

The methodology was firstly tested on simplified cases to be sure of its complete feasibility. Several contaminants with contrasted properties and modelling choices such as cell size, hydraulic dispersivity and transport calculation methods were tested to assess their effect on the final global quality indicator.

The application on the groundwater body RWM073 had started last year with creation of the geodatabase, of the activity-pollutant matrix and the first development of groundwater flow model. During 2010, the geodatabase was fed with all relevant data and the final global quality index calculated for some pollution scenarios. One of them was to consider all industrial sites potentially releasing benzene, characterized industrial brownfields and tank station. Modelling was performed for the aquifer of the alluvial plain of the Meuse River. Groundwater flowing from the hills is taken into account by prescribed flux boundary conditions. Simulation over 20 years shows a decreasing of the global quality index of 45 points on 100 with stabilization after 5 or 6 years.

Using abilities developed for other research program, a GIS-based application is currently developed to be able generate all grid files for MODFLOW/MT3D directly under ArcGIS environment and thus be significantly faster for running different pollution scenarios.

The planning for the last months of the project is to finalize the work on the groundwater flow and transport model. To deal with the problem of uncertainties in the type and amount of contaminant that should be found in the groundwater for different industries, a statistical approach will be developed. To perform such an analysis, the French database ADES that contains all the chemical analysis of groundwater samples taken around industrial sites in France is used.

Remarks:

SH: What do you mean by regional scale?

PJ: The model is 40 km long and 2 km wide

SB: Regional scale is related to groundwater body in the sense of the EU directive

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SH: Use of the NACE code, do you take into account all the pollutants?

PJ: Yes, an activity-pollutant matix has been created, so we are able to define, for each type of industry, the list of pollutants that are potentially present in the soils and/or in the groundwater. The activity-pollutant matrix includes a list of 75 pollutants among the most representative in groundwater (BTEX, PAH, VOCl, Heavy metals …)

SB: Focus on some of the pollutants in function among others of their mobility. Use of the ADES database to develop a statistical approach and to define what are the contaminants really found near each type of industry.

SH: Is the model calibrated for transport?

PJ: No, difficult with the size of the model to perform calibration with concentration measured at the field scale.

SB: The matrix of contaminant properties can be fed with field data. A probabilistic approach could be developed to take into account the uncertainty.

RT: How do you go from the map with an index of quality per cell to the global quality index?

PJ: Weighting by the volume of water within each cell

SB: If different contaminants are present, the SEQ-ESO provides a link between the concentration and a quality index for each contaminant. The worst index is representative of the cell.

RT: Which kind of data is used to calibrate the groundwater flow model?

PJ: Only with piezometric heads. It's not possible to identify in the flux data of measured in the Meuse River an increase of the Meuse flux due to a small part of the alluvial aquifer and data on Meuse River flow are to imprecise.

SB: It is not the goal of the project to reproduce the groundwater dynamic in the alluvial plain. The main driver for the contaminant fluxes is the recharge.

2.4 <u>Remote sensing and Land-cover mapping for the quantification of groundwater recharge in complex urbanised environments (J. Dujardin, VUB)</u>

We decided to upscale the approach to the level of the groundwater body (PHASE II), so a new classification methodology was used. Because of the large area covered by the RWM073 catchment we had to make use of lower resolution data. We decided to work on SPOT5 data with a multispectral resolution of 10 meters and a panchromatic resolution of 5 meters. This type of data allows us to cover the entire study site with one image. A stratified classification approach was adopted, distinguishing between built-up areas (urban and industial land use) and natural/agricultural land use. For the natural areas we decided to use a multi-temporal classification to characterize the different types of crops, trees, etc. For the urban and industrial areas a sub-pixel classification was used to be able to characterize the proportion of imperviousness at sub-pixel scale. We started to work on an archive Landsat ETM+ image of july 2001 while waiting for the SPOT5 data. In the first step of the stratified approach the Landsat image was classified on pixel level, resulting in 6 land-cover classes: water, grass, forest, grey urban, bare soil and bright roofs. In the second step of the stratified approach all the urban pixels (grey urban and bright roofs) were characterized at sub-pixel scale to determine the fraction of imperviousness inside every urban pixel.

For the multi-temporal approach 3 SPOT5 images were ordered (spring, summer and autumn), but, because of the clouds, no good images were acquired, so once again the methodology had to be adapted. To be able to characterize in more detail the natural areas of the RWM073 site a combination of the obtained land-cover map of the RWM073 site at pixel level and a land-cover map of the Walloon Region (COSW) was preformed. The COSW of the WR could provide us information about the different types of crops present in the RWM073 are, so by crossing both images, we were able to characterize the different types of vegetation inside the natural areas of the RWM073 site (e.g. the land-cover class Forest could be subdivided in 3 types of forest classes). After the combination of those 2 maps 12 hydrological more relevant classes were obtained: urban, bare soil, agriculture, meadow, orchards, shrubs, grass, spruce, water, deciduous forest, coniferous forest and mixed forest.

The obtained land-cover information is used as an input for the high-resolution groundwater recharge simulation using WetSpass. Before starting the simulations some data preparation was done, like creating temperature maps, potential evapotranspiration maps, precipitation maps, etc. for summer and winter season.

In WetSpass, every landuse class is characterized by a given fraction of imperviousness, and all these values are grouped in the landuse parameter tables. But with the supixel classification approach, every urban pixel has his own fraction of imperviousness. So the WetSpass model will have to be adapted (the code has to be changed). Instead of using these landuse parameter tables as an input in WetSpass to obtain information about the fractions inside the pixels of a certain landuse class, WetSpass will have to get this information from input grids, containing the different types of fraction for every pixel. Therefore 8 grids will be created, containing the fractions of imperviousness, vegetation, open water and bare soil in every pixel, and this for summer and winter season. Once these grids are made, they will be used as input into WetSpass.

For the moment the changes in the WetSpass code are still ongoing, so in the meanwhile a ‘rough’ estimation of the groundwater recharge has be done using WetSpass but with land-cover information only on pixel level, so the only landuse input for WetSpass that was used is the obtained land-cover map on pixel level. A mean yearly recharge of 249±104 mm/y was obtained for the RWM073 site, with a mean summer recharge of 9±26 mm/6 months and a mean winter recharge of 240±97 mm/6 months.

In the next months we will further implement the sub-pixel classification of the Landuse in WetSpass to be able to simulate the groundwater recharge and runoff with a high resolution. And we will also adapt the WetSpass model to obtain monthly simulations instead of seasonal simulations.

Remarks:

RT: The studied area is larger than the groundwater model?

JD: Yes, the size of the studied area is based on the size of the Landsat image.

RT: Near the Meuse River, some of the values of recharge become negative. Do you model exfiltration?

JD: Yes in summer, negative values are due to high ETR and exfiltration.

RT: Is the WetSpass model calibrated with flux data in the Meuse River?

OB: Difficult, same remarks than for the groundwater model.

RT: Do you have computed global value (runoff = X % of precipitation, for example) and compared these values with values obtained with classical techniques?
JD: No but could be interesting

2.5 Ecotoxicological risk assessment using a TRIAD-like approach and Toxic Units (S. Crévecoeur, ULg-LEAE)

A complete methodology was used to assess the ecotoxicological risk of Chimeuse Est site integrating Groundwater Quality TRIAD-like approach, Toxic Unit approach and multivariate analysis.

Groundwater Quality TRIAD-like (GwQT) approach:

GwQT is based on measurements of chemical concentrations (chemistry), laboratory toxicity tests (ecotoxicity) and physico-chemical analyses (pH, conductivity…). These components are combined in the approach using qualitative (pie-charts using colours coming from the SEQ-ESO system, triangular representation and tabular matrix) and quantitative (using 0 to 1 risk indices) integration approaches.

GwQT approach application confirms the widespread measured metal contamination (As, Cd, Cu, Ni, Pb, Zn) at Chimeuse Est site. ChemRI and PhysRI were generally the higher and the lower risk indices, respectively. Concerning ecotoxicological component, rotifer (*Brachionus calyciflorus*) chronic test and algae (*Pseudokirchneriella subcapitata*) were the most sensitive among the test species. Cluster analysis using risk indices detect spatial similarity and dissimilarity among sampling piezometers:

- P28 and P24 are less contaminated and less toxic;
- P29 is the more heavily contaminated piezometer and show high level of toxicity;
- P23, P25 and P26 are characterized by moderate to relatively high EtoxRI and PhysRI and are heavily contaminated.

Toxic Unit approach:

Toxic Unit approach was used to determine the pollutants causing the toxicity. The overall toxicity of the mixture could be equal to the sum of each pollutant toxicity (additivity, ΣTU =1), less than the sum (antagonism, ΣTU >1) or greater than the sum (synergism, ΣTU <1). Toxic Unit concept can be mathematically expressed as the following equation: $TU_i = C_i / L(E)C_{50,i}$, where C_i gives the concentration of the component *i* in a mixture which elicits 50% of effect, and $EC_{50,i}$ denotes the concentration of that substance which provokes 50% of effect if applied singly (collected from literature and ecotox databases). A more than additive effect (synergism) was indicated for all bioassays, except with *Daphnia magna* (antagonism, “less than additive”). Therefore, mixture toxicity is higher (lower for *Daphnia magna* bioassay) to the toxicity that would be expected if we sum each pollutant toxicity. Among the metals, copper (followed by zinc and cyanides) posed highest risk to aquatic species. Results demonstrate that no single test is certain to give conclusive results, wherefore it is preferable to use a battery of bioassays.

Multivariate statistical analysis, Principal Component Analysis (PCA):

PCA was used to establish correlations between the studied parameters and to point out those responsible for the variability. Factor 1 (accounting for 47% of the variance) links almost all heavy metals (except As) with the toxicity responses of rotifera. This factor is only representative at P29 indicating high pollution level due to these pollutants and high toxicity. Factor 2 (20% of the variance) combines chlorinated compounds associated with biological responses and is prevalent at P26.

Conclusions:

- None of the three TRIAD-like components (ecotoxicity and physical-chemical measurements) could reliably predict the other one.
- Toxic Unit approach: a small amount of a very toxic chemical (*e.g.* Cu) in the mixture can have a much larger effect on the biological response than a large amount of a slightly toxic chemical (*e.g.* Zn).
- The multivariate analysis can be used as an exploratory tool to complement the TRIAD-like approach.

→ Combination of complementary results seems to be the best approach to determine sites at risk

→ This study provides evidence of the poor health status of Chimeuse Est site.

Future prospects and planning:

- A paper named “Groundwater quality assessment using a TRIAD-like approach”, explaining GwQT methodology with an application on Morlanwlez (and Chimeuse) sites, is submitted.
- 3 deliverables have to be written for December 2010

Remarks:

No remarks concerning applied methodology of the LEAE-ULg specific work.

2.6 -.<u>Sorption and degradation of organic compounds: from site specific experience to regional generic data (W. Dejonghe, VITO)</u>

Works done have consisted of:

- continuation of aquifer batch degradation tests with VC, DCE, TCE and different carbon sources;
- determination of VC, DCE, and TCE degradation constants from aquifer batch tests Zenne;
- comparison with values, from University Sheffield and literature;
- synthesis of degradation constants for benzene and benzo(a)pyrene from literature to feed the groundwater model in function of site condition (Eh, pH…);
- determination of biomass involved in degradation by Q-PCR approach;
- review of literature on cost remediation techniques.

<u>Remarks:</u>

<u>RT</u>: Does k degradation constant varies with space/as a function of the carbon source.

<u>JD</u>: At Zenne site, degradation does not occur without stimulation (addition of carbon source). Best degradation rates are obtained by addition of Zenne sediments (carbon source does not deplete).

2.7 <u>Valuing the costs and benefits of remediating groundwater contaminated by brownfields: An application to the Meuse alluvial aquifer (C. Hérivaux, Brgm)</u>

Following the requirements of the Water Framework Directive, a programme of measures should be proposed for each water body at risk of not reaching good status by 2015. In case of disproportionate costs derogation may be justified on the basis of a cost-benefit analysis. This economic analysis is a challenging task in case of groundwater bodies at risk due to brownfields: remediation measures are expected to be very expensive, time required for remediation may be very long, great uncertainties concerning costs and effectiveness of the measures. Moreover as groundwater resources are generally not used anymore as a resource, it is difficult to anticipate (i) if market benefits could be expected from an improvement of the groundwater quality and (ii) if people would be willing to contribute to this quality improvement).

BRGM comes in 3 types of activities: general methodological approach, ensuring that it reaches the expectations of end-users, cost of the program of measures and assessment of potential benefits of improving the quality of the MESO.

General methodological approach.

The indicator developed by HG-ULg base on SEQ-ESO will be used as an indicator of effectiveness for the cost-effectiveness analysis performed by WP5. The use of this basis seems to be in indicator line with end-users' expectations since it is the indicator currently used by water managers. Those water managers need an assessment of the cost required to improve the RWM 073 groundwater quality because they need to justify if they want to introduce a WFD derogation, for instance by proving disproportionate costs.

What is technically feasible in terms of groundwater body quality improvement? How much will it cost to reach these objectives? If several measures are possible, which one is the most cost-effective?

The task of BRGM about these questions is composed of three steps.

- Step 1: Collect data on hydrogeology, pollution sources and types of pollutants, current groundwater quality and improvement objectives expressed with the use of the SEQ-ESO indicator.
- Step 2: Propose a typology of potential measures that could help to improve groundwater quality and associated unit costs expressed in €/m3 pumped or in situ as a function of the type of pollutants
- Step 3: Identify and assess costs of combinations of measures that should be implemented to reach objectives of groundwater quality improvement expressed by the use of the SEQ-ESO indicator

What are the expected benefits of such groundwater quality improvement? Can they balance the costs required to implement the measures?

The assessment of the expected market benefits has been carried out during 2008. The results show a relatively low expected market benefits estimated between 3.3 and 4.4 million € from 2030 (i.e. between 1.3 and 1.8 million € when discounted). The total discounted sum of benefits on the 2008-2060 period is estimated between 23.8 and 32.4 million €.

The assessment of the non market benefits is a more complex task, carried out by contingent valuation, *i.e.* quantitative survey on the perception by the population of the Meuse alluvial plain. The objectives of such a survey are to characterise the knowledge and perception by the population of the groundwater body, its quality level and the relevance to improve its quality. An economical value can be given by assessing the value people would be willing to contribute to the improvement of the groundwater body quality and the mean value of the willingness to pay (WTP) in €/household/year can be estimated. Finally a non-market value can be given for the groundwater body by aggregation of the value WTP.

This survey consists in 4 main steps: design of the survey, pre-testing, recruitment of interviewers, training session, selection of targeted population and survey, before to be able to perform the econometric analysis of answers. The survey has been performed between 13th – 17th September 2010. 531 face-to-face interviews have been completed. A first analysis of the results have been realised showing that the non-marked value attributed by people to the groundwater resource of the alluvial plain of the Meuse River is higher than expected.

Remarks:

Question were focused on contingent evaluation of non market value of the groundwater

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AD: Is it clearly explained to the participants that they can not drink the groundwater of the alluvial plain?

CH: Yes, clearly explained in the questionnaire and with maps explaining from where comes the water that the people drink.

WD: What was the proposed program of measure?

CH: No technical program was detailed to the people but a simple general explanation to say that remediation consists mainly of soil excavation and groundwater treatment.

SB: Non-market value is higher than the market value!

CH: That's the role of the contingent valuation. For some people if the water is not used, the water has no value. This study shows the contrary, people have motivation to increase the groundwater quality for future generation.

OB: What are the potential benefices of mitigation explained to the people?

CH: The benefices are not direct but potential uses of groundwater (for example for gardening) could be done for example in 15 years.

OB: These positive results are linked to a general positive feeling for environment.

CH: People were really interested by the questionnaire

SB: Could be interesting to present the result for example in local newspaper.

3. Integration of the works performed in each group

SB: The objectives of the discussion are to identify priorities for the next months and to develop, with the follow-up committee, new ideas for integration of the works.
The final report should reflect this integration. It should not be only the sum of the works performed by each team but an integrated document usable for different end-users.

3.1 Integration between VUB - ULg-HG

Spatially distributed recharge computed by VUB will be integrated in the groundwater model. Recharge is a key parameter driving the mobility of contaminant.

OB: Recharge is computed by VUB on a monthly basis, the groundwater flow model is in steady state.
RT-AD: ULg-HG could develop a transient groundwater model.
SB: What is the interest? Is it very relevant with long time scale.
RT-AD: Take into account transient sources.
SB: First tests could be performed with transient data on the synthetic case.

SB: Another challenge will be the mapping between the meshes used by each team.

SB: At the moment, the recharge applied to the groundwater model is 90 mm. Is-it consistent with data computed by VUB?
JD: Difficult to answer, the study-area of VUB is larger than the groundwater model.
SB: Could you focus your result on the alluvial plain?

3.2 Integration between ULg-LEA - ULg-HG

SC: Difficult to integrate the TRIAD-Like approach in the RRA approach and the SEQ-ESO. We propose to use PNEC, NOEC, L(E)C50 values found in literature to propose for each contaminant and each species an index of ecotoxicological quality of groundwater based on the SEQ-ESO principles. These value can be stored into pollutant database. With this system, cumulative effects of contaminant are not taken into account.

JPT: We could also use Toxic units?

SC: Toxic units are sample related. It is thus difficult to extrapolate.

SB: It is important to propose in the final report perspectives for future developments.

3.3 Integration between VITO - ULg-HG

WD: Database developed by ULg-HG has been fed with experimental data and literature data from VITO. It is still difficult to have data on pollutant degradation to incorporate in the groundwater model. The data are site specific and depend on conditions (pH, eh…) prevailing on the site.

SB: What are the assumptions we should make? What is done for modelling site not yet characterized? Could you provide us some guidelines, key parameters to identify?

OB: It could be a stepwise procedure.

3.4 Integration between BRGM - VITO - ULg-HG

CH: Evaluation of the cost of programme of measure is difficult to realize as data about contaminated sites (how many sites, where, type of contaminant…) are missing.

PJ: BRGM could give us information about possibilities and efficiency of remediation programmes. With The RRA, we could compute the improvement in terms of global quality of the groundwater body.

SB: It could be interesting to test the methodology on a virtual aquifer.

CP: The derogation asked to EU is related to sulphate and ammonium linked to old mine activities.

SB: Not the scope of the project, we deal with impact of brownfields.

3.5 Presentation by Stefaan Hermans of the WEISS project

LIFE project with the objective to quantify pollutant emission to water.

Brownfield is a potential source of contaminant for surface water via groundwater.

Project at the scale of the Flemish Region but only data for 300 brownfields.

SB: We are facing the same problem within FRAC-WECO, the estimation of the source.

4. Administrative Issues

4.1. Project prolongation

Teams have asked for a project prolongation (VUB, BRGM, HG-ULg).
A 6 month report has been decided and will be asked to Belspo. Each team has to provide AD with an estimation of the budget that will be transferred for the prolongation. The procedure is a single report for the consortium.

4.2. Final report

The final report has to integrate the work of the different partners and can not be only the sum of reports done individually by each partner.
The report should be organized into 2 parts. The first part will be about 20 pages and describing the FRAC-WECO project according to the proposed table of content (see below). The second part will be more like appendixes with details of each team works and precision on methodologies, assumptions, results …

AD : Don’t forget to fill in the administrative report.

1. **Introduction**

    a. *General context and objectives*

Contaminated sites = treat for GW resources and ecosystems

Relevant working scale is groundwater body

EU Water Framework Directive, Groundwater Directive …

    b. *Challenges – Research needs*

Concepts and Indicators for GWQ – GWRA – ERA

Concepts and Methods for quantification of Water and Contaminant fluxes from sources to receptors

Economic consideration of the value of water – remediation costs – programmes of measures

    c. *Supporting cases studies*

Presenting real application cases from local to regional scale

    d. *Report structure*

Brief explanation of report structure

2. **Conceptual schema**

    a. *Scale of application (regional)*

Why the relevant working scale is groundwater body

    b. *Data requirements and management*

Data needed for normal risk assessment are somehow different and more complex at regional scale.

Data management and handling

    c. *Description of indicators and risk assessment concepts*

Description of RRA methodology

    d. *Water and Contaminant fluxes through the catchment*

GW Recharge

GW modelling

Contaminant properties (sorption – degradation)

Tanking contaminant sources uncertainties into account

… ?

3. **Socio-economic analysis**

a. *Groundwater valuation*

Market and non market expected benefits from a clean groundwater body

b. *Estimates for remediation costs at regional scale*

Concepts for estimating remediation cost from general regional data

c. *Programs of measures (DCE)*

4. **Applications**

a. *Local scale*

Application on the Zenne site

b. *Regional scale*

Application on RWM073 groundwater body

5. **Conclusions and perpectives**

a. *Main outcomes of the project*

General conclusions about developed methodology and application

b. *Valorization*

Future or ongoing valorization

c. *Perspectives*

6. **References**

* I think not 200 references but around 5 or 10 really focus reference per team

7. **Annexes**

a. *Methods*

More detailed methodology (that can be organized WP by WP or more focused to one aspect of a team particular objective)

b. *Publications*

Publications that come from this project

FINAL SCIENTIFIC REPORT

Flux-based Risk Assessment of the impact of Contaminants on Water resources and ECOsystems

-

FRAC-WECO

SCIENCE FOR A SUSTAINABLE DEVELOPMENT

Annexe 3

Determination of degradation constants and biomass numbers for a site contaminated with chlorinated aliphatic compounds – Zenne site as a case study

Contents

1. Introduction

At the Zenne site in Machelen-Vilvoorde, Belgium, a groundwater plume of approximately 1.2 km, contaminated with chlorinated aliphatic hydrocarbons, (CAHs), is flowing from the nearby aquifer into the River Zenne. The area is contaminated as a result of industrial activities. For chlorinated aliphatic hydrocarbons reductive dechlorination, performed by certain anaerobic bacteria in the aquifer compartment, is one of the most important removal mechanisms. Since CAH degradation can only occur in the presence of an electron donor creation of an *in situ* biological reactive zone, through the injection of a carbon source into the aquifer near the river, was chosen as a remediation approach for aquifer compartment remediation. To this end, during the FRAC-WECO project, different batch conditions were run to determine at lab-scale the most appropriate carbon source to stimulate the CAH degradation in aquifer material obtained from three locations at the Zenne site.

This report includes experiments for selection of electron donors to stimulate CAH degradation in aquifer in batch set-ups. The specific purposes are to:

1- Determine kinetic parameters of the intrinsic and stimulated vinyl chloride (VC), cis-*cis*-1,2-dichloroethene (*c*-DCE), and thrichloroethene (TCE) reductive dechlorination activity in aquifer material by means of microcosm batch tests.

2- Determine the number of CAH-degrading bacteria and relevant catabolic genes that are present in the aquifer before and after the stimulation of CAH degradation.

The here obtained parameters can then be used in the reactive transport model developed by ULiege in the FRAC-WECO project. This model can then predict how much CAHs will come into the river under different site conditions.

2. Material and methods

2.1. SAMPLE COLLECTION

Groundwater was collected from three different monitoring wells SB-2, PB-26 and SB-3, which are located in the test area at approximately 3.5, 200 and 500 m distance from the right riverbank of the River Zenne (Figure 1). Groundwater was sampled using a peristaltic pump and polyethylene sample tubes. Before collecting samples, the depth of the groundwater was measured and the boreholes were properly purged until electrical conductivity, dissolved oxygen (DO), pH, temperature and oxidation-reduction potential (ORP) parameters were stabilized. These parameters were measured by means of a flow-through cell and a multimeter equipped with electrodes for temperature and electrical conductivity, pH, DO and ORP. All groundwater samples were collected in 2 L glass bottles by filling them from bottom to top and allowing overflow until the volume of the bottle was changed two times.

Aliquots of groundwater samples were taken for chemical analyses as follows: samples for analyses of CAHs and the dissolved hydrocarbons methane, ethene and ethane were either collected in duplicate into 10 mL headspace vials containing 100 µL concentrated H_3PO_4. Five mL sample was transferred into the vials and immediately closed by using Teflon-lined caps. Samples for the inorganic parameters sulphate, nitrate and nitrite were collected in 10 mL plastic bottles. Moreover, 10 mL of water for cation analyses was filtered through a 0.45 µm sterile filter and brought to plastic vials containing 0.2 mL concentrated HNO_3. Finally, 10 mL sample was also filtered through a 0.45 µm sterile filter and transferred to a 10 mL plastic vial for DOC analyses.

Aquifer samples were drilled at location Pb26 (Figure 1) near monitoring and collected from 7-8 mbs in a liner of 1 m length with an inner diameter of 3.5 cm. At location SB-2 and SB-3, three aquifer liners of 1.2 m length and an inner diameter of 5 cm were collected from 7.2 to 10.5 mbs during borehole drilling. All liners were transported to the lab and stored at 4°C under a 100% nitrogen atmosphere before use.

Sediments of the Zenne were collected at post 26 (Figure 1), using a 4 cm diameter piston sediment sampler. Undisturbed samples were transferred into PVC bottles on the field.

Once in the laboratory, all the samples collected were stored at 4°C until its use in experiments. All the aliquots for chemical characterization were also stored at 4°C, except DOC samples that were stored at -20°C, until analyses.

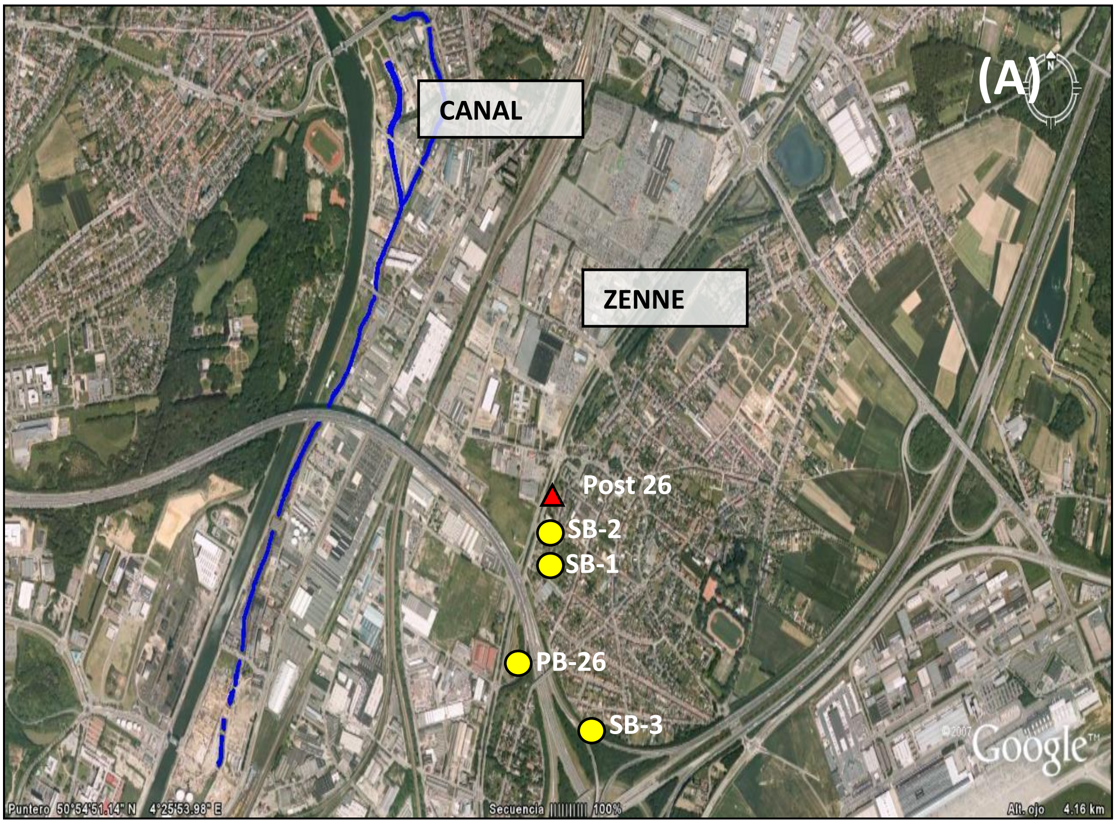


Figure 1- Site map of Vilvoorde (Belgium) showing the River Zenne, the nearby canal, the location of the sampled monitoring wells (yellow dots) and the location of surface water and sediment collection (red triangle).

2.2. BATCH DEGRADATION TESTS

Batch microcosms were performed in order to investigate the VC, *c*-DCE and TCE biodegradation capacity of aquifer material and groundwater collected from three different locations in the test area (PB-26, SB-3 and SB-2) (Figure 1). Under anaerobic atmosphere, an amount of 37 g of wet, well mixed aquifer material was suspended in 90 mL of groundwater (from the same location of the aquifer material) in sterilized 160 mL serum bottles under anaerobic conditions. Four different experimental conditions were set up in duplicate for each of the three locations: natural attenuation, abiotic control, sediment and lactate amendment. No external carbon source was added to natural attenuation conditions. In the abiotic controls, microbial population was inhibited by adding formaldehyde (1%). Sediment microcosm tests were set up for each selected location with 37 g of homogenized river sediment instead of aquifer material and the corresponding groundwater was added as the liquid phase (90 ml). In lactate microcosms, lactate was added from anaerobic and sterile stock solutions of sodium lactate prepared in mineral water to reach a final TOC of 300 mg/L in the microcosms (same level as TOC concentration in the additional tests amended with sediment extract).

Four additional conditions were also tested for the PB-26 location: groundwater control and stimulation with molasses, sedimented extract of river sediment and centrifuged sediment extract. The sediment extracts were prepared as follows: an amount of 125 g of homogenized wet sediment was suspended in 300 mL of PB-26 groundwater. The resulting suspension was either sedimented overnight to obtain sedimented extract or centrifuged to obtain the centrifuged sediment extract. Main idea was that in the centrifuges sediment extract, only the DOC that is present in the sediments will be added to the aquifer. In the sedimented extract on the other hand, not only DOC but also bacteria present in the sediment will be added to the aquifer. Molasses was added in a similar way as lactate and also to a final TOC of 300 mg/L.

Once all the microcosm tests were set up, bottles were sealed with aluminum crimp caps containing Teflon-lined butyl-rubber septa and spiked with 2 ppm VC. The microcosm tests were incubated in the dark at 12°C and headspace samples were analyzed at regular intervals to measure the concentration of CAHs and methane, ethene and ethane. Each time the analysis was done, the flasks were previously spiked with 1 mL of nitrogen gas to prevent the entrance of oxygen in the bottles during headspace analyses. VC was spiked 3times. When the VC degradation test was completed, the aquifer material was collected from previous VC degradation batch tests performed in the same conditions (and used in new set of tests for c-DCE degradation). The recovery of aquifer material from VC tests was performed by means of centrifugation and, when needed, new aquifer material was added. Again an amount of 37 g of wet, well mixed recovered aquifer was suspended in 90 mL of groundwater (from the same location of the aquifer material) in sterilized 160 mL serum bottles under anaerobic conditions. The bottles were spiked with 2 ppm of c-DCE and incubated under the same condition as VC test. When *c*-DCE degradation test was completed, the same procedure was repeated for TCE test.

Microcosm condition	Aquifer (g)[a]	Ground-water (mL)	Lactate (mM C)[c]	Molasses (mM C)[c]	Formal-dehyde (mL)	Aquifer extract (mL)	Sediment (g)	Sediment extract (mL)	Sediment extract centrifuged (mL)	Aquifer extract (mL)
Natural attenuation	37	90	-	-	-	-	-	-	-	-
Abiotic control	37	90	-	-	1	-	-	-	-	-
Groundwater control [b]	-	120	-	-	-	-	-	-	-	-
Lactate	37	90	32	-	-	-	-	-	-	-
Molasses [b]	37	90	-	32	-	-	-	-	-	-
Sediment	-	-	-	-	-	-	37	-	-	90
Sediment extract (sedimented) [b]	37	-	-	-	-	-	-	90	-	-
Sediment extract (centrifuged) [b]	37	-	-	-	-	-	-	-	90	-

[a] Weight in wet basis

[b] Conditions tested only for the PB-26 location

[c] Units in mM of carbon

Table 1-- Details of batch microcosm test performed for the PB-26, SB-2 and SB-3 locations at the Zenne site

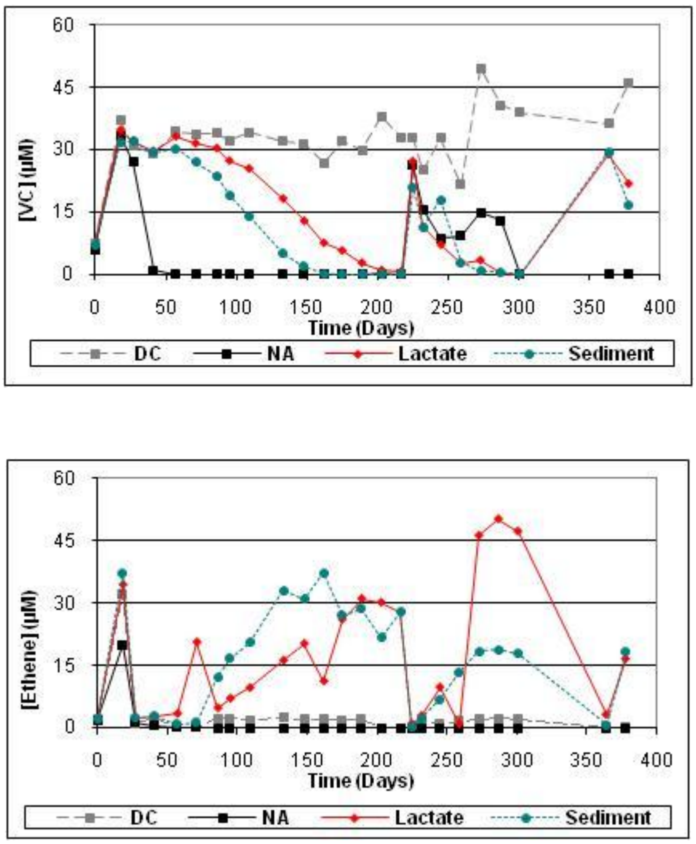
2.3. REAL-TIME PCR QUANTIFICATION OF CAH DEGRADING BACTERIA AND CATABOLIC GENES

DNA extraction was done from ~500 mg of each aquifer sample. The FastDNA Spin Kit for Soil (MP Biomedicals, Solon, OH, USA) and using bead beating was done according to the manufacturer's instructions. Real-time PCR quantification was performed using the iQ5 iCycler (BioRad) and PCR amplifications were performed with the iQ SYBR Green Supermix kit (BioRad). All assays were performed in triplicate in 25 μl reactions and no-template controls were included. Primers for real-time PCR quantification of 16S rRNA genes of total bacteria and *Dehalococcoides* and its reductive dehalogenase genes (*tceA*, *bvcA*, *vcrA*) were selected from literature (Adrian et al., 2007; Futamata et al., 2007; Smits et al., 2004). Primers were used at a final concentration of 200 nM. Real-time PCR amplification parameters for the *Dehalococcoides* 16S rRNA gene assay were: 10 min at 95°C, followed by 40 amplification cycles of 15 sec at 95°C, 30 sec at 50°C, 30 sec at 72°C. Melt curve analysis was performed from 50°C-95°C in steps of 0.5°C and 10 sec at each step. For *Desulfitobacterium*, *Dehalobacter*, and total Bacteria, conditions were the same as described above, but at an annealing temperature of 60°C and melt curve analysis from 60°C - 95°C. Real-time PCR amplification parameters for the RDase gene assays were: 10 min at 95°C, followed by 40 amplification cycles of 15 sec at 95°C, and 1 min at 58°C (*bvcA, vcrA*) or 60°C (*tceA*). As real-time PCR standards T7-SP6 PCR-products were used that were amplified from pGEMT-Easy clones carrying the 16S rRNA gene of *Dehalococcoides*, or the *orfAB* genes of the targeted RDase gene. Respective gene copy numbers were calculated as copies / g of aquifer sample. Total *Archaea* were quantified using primers and methods described by Da Silva et al., with genomic DNA extracted from *Methanospirillum hungatei* as a standard. The *dsrA* gene was quantified according to Wilms et al., with the exception that only 2.5 *μ*L of template DNA was utilized instead of 10 *μ*L. The standard for *dsrA* calibration was genomic DNA from *Desulfovibrio vulgaris* (ATCC 29579; GenBank accession number NC_002937), whose genome contains one copy of the *dsrA* gene.

3. Results

3.1. RESULTS OF STIMULATION OF TCE DEGRADATION IN AQUIFER COMPARTMENT AT BATCH LEVEL

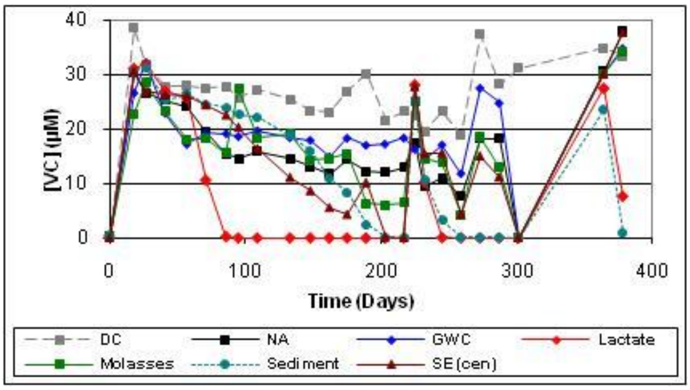
Batch cultures of stimulated degradation of CAHs in aquifer compartment by addition of carbon sources were conducted. The results of VC degradation and its non-toxic daughter product (ethene) at three locations at the Zenne site (SB2, Pb26, and SB3) are shown in Figure 2-4.



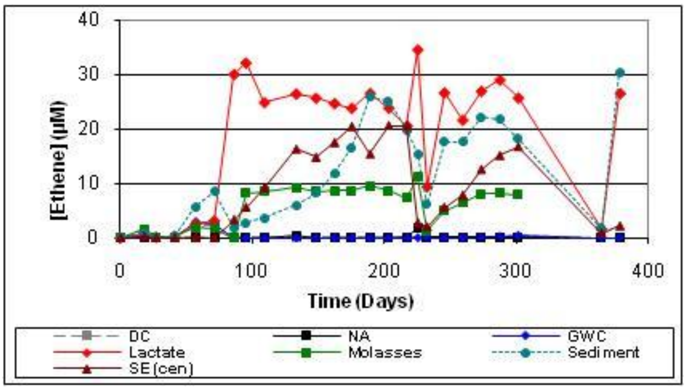
a

b

Figure 2- (Stimulated) VC degradation in microcosms with aquifer and groundwater from location SB2 (a) to non-toxic end product ethene (b) in batch cultures. NA: natural attenuation, DC: dead control.



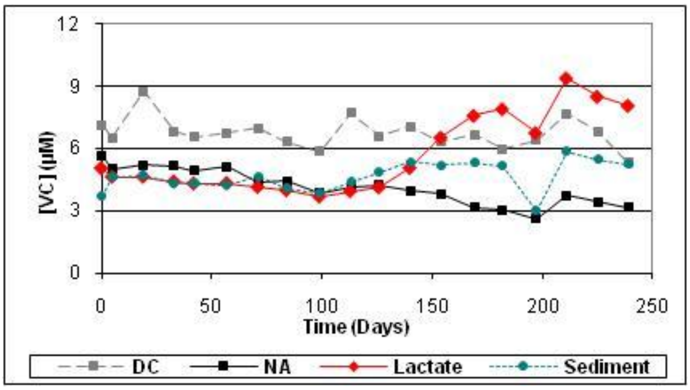
a



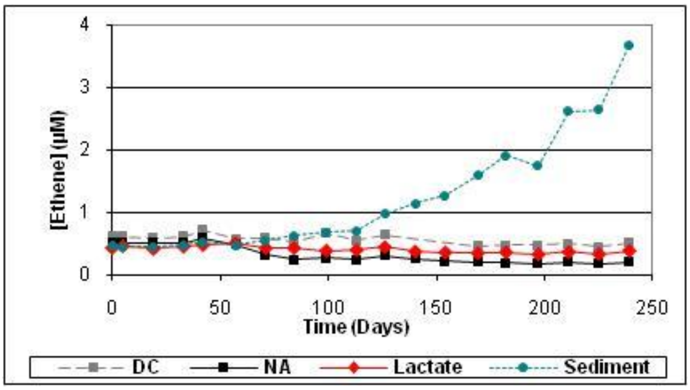
b

Figure 3- (Stimulated) VC degradation in microcosms with aquifer and groundwater from location PB26 (a) to non-toxic end product ethene (b) in batch cultures. NA: natural attenuation, DC: dead control, GW: ground water control, SE (cen): sediment extract obtained after centrifugation.

As it can be seen in Figures 2-4, VC degradation starts after a lag phase of around 100 days. It is only the lactate condition at PB26 which has the shortest lag phase. No degradation was abserved in DC and NA conditions at all three locations. At location SB2, it seems that there is degradation in NA condition (Figure 2a). However there is no ethene formation as end product (Figure 2b). At SB2 location, sediment and lactate have the highest stimulation effect on VC degradation. At location PB26, lactate has better performance from sediment during first spike, however, during the second and third spike, no big difference can be seen in these conditions. In this location, sediment extract (centrifugated) has better performance than lactate, but still not as good as sediment and lactate. Surprisingly, no degradation can be seen at SB3 location after 8 months of experiment. This location is close to the source of the pollution and has high CAH concentration which might have hindered VC degradation at this location.



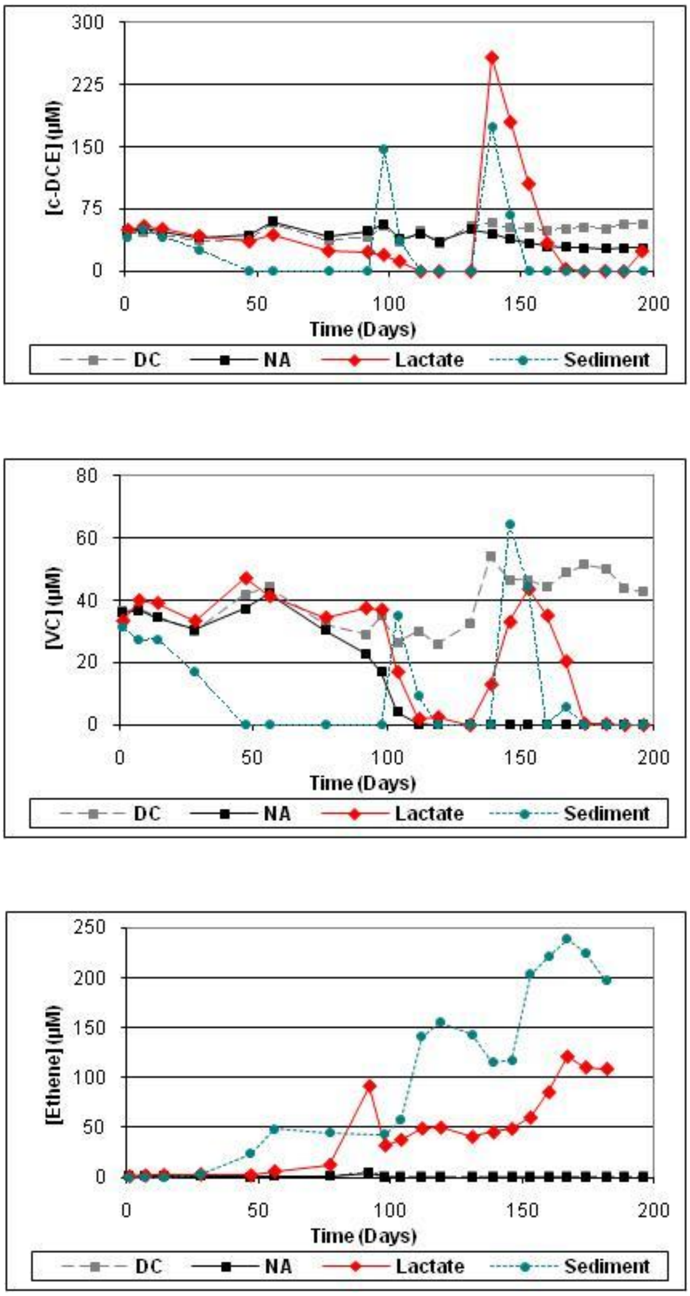
a



b

Figure 4- (Stimulated) VC degradation in microcosms with aquifer and groundwater from location SB3 (a) to non-toxic end product ethene (b) in batch cultures. NA: natural attenuation, DC: dead control.

The results of *c*-DCE degradation and its daughter product at three locations at the Zenne site (SB2, Pb26, and SB3) are shown in Figure 5-7.

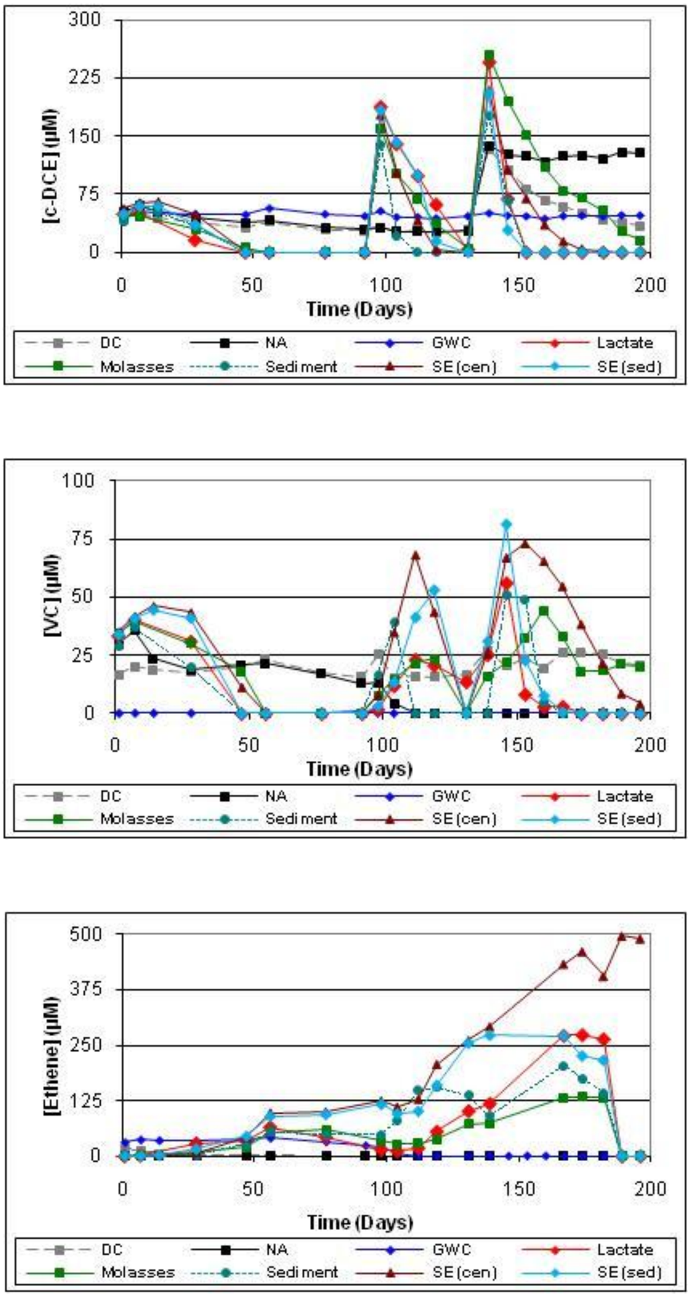


a

b

c

Figure 5- (Stimulated) *c*-DCE degradation in microcosms with aquifer and groundwater from location SB2 (a) to VC (b) and non-toxic end product ethene (c) in batch cultures. NA: natural attenuation, DC: dead control.

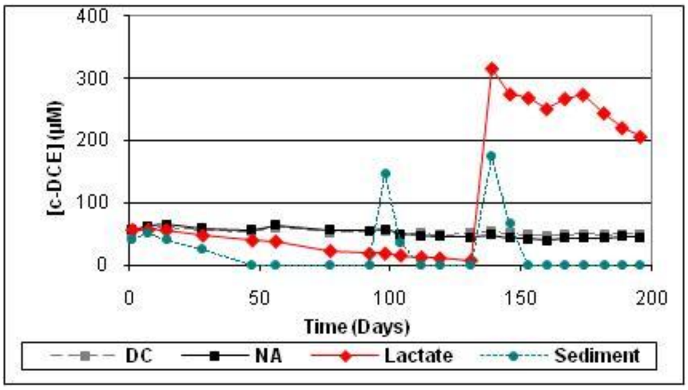


a

b

c

Figure 6- (Stimulated) *c*-DCE degradation in microcosms with aquifer and groundwater from location PB26 (a) to VC (b) and non-toxic end product ethene (c) in batch cultures. NA: natural attenuation, DC: dead control, GW: ground water control, SE (cen): sediment extract obtained after centrifugation, SE (sed): sediment extract obtained after sedimentation.



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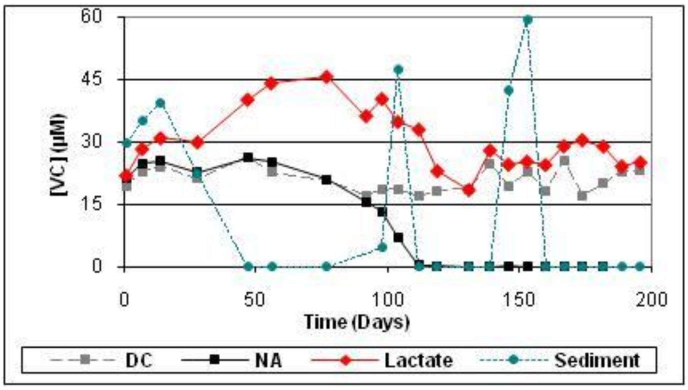

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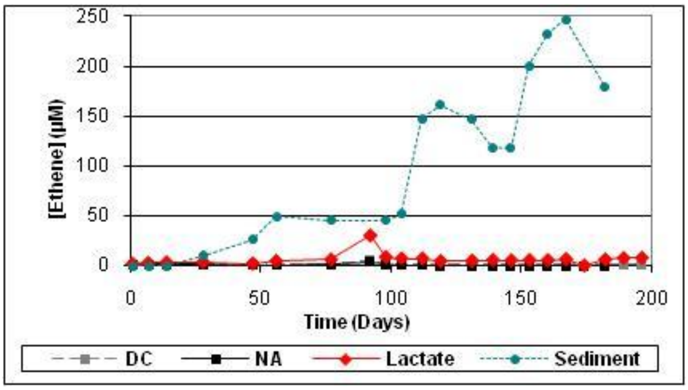
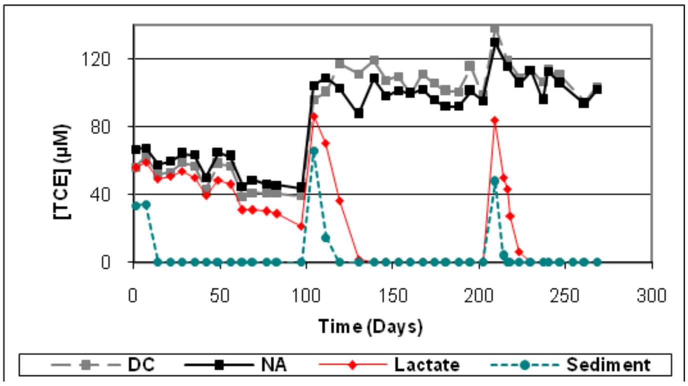


c

Figure 7- (Stimulated) *c*-DCE degradation in microcosms with aquifer and groundwater from location SB3 (a) to VC (b) and non-toxic end product ethene (c) in batch cultures. NA: natural attenuation, DC: dead control.

As it can be seen from Figure 5-7, no degradation of c-DCE was observed in un-amended conditions (NA, DC, GWC) at all three locations with no formation of daughter product. These results are in accordance with the results of VC degradation and further verify that CAH degradation in aquifer compartment of Zenne river is possible only in presence of external carbon sources that provide necessary electron donors for reductive dechlorination. C-DCE degradation started after a lag phase of 30 days. Sediment and lactate had the best performance, followed by sediment extracts and molasses. At SB3 location, only sediment condition started c-DCE degradation and its stepwise degradation to daughter products. Addition of lactate did not stimulate c-DCE degradation at this location which is in accordance with the results of VC test (Figure 4).

The results of TCE degradation and its daughter product at three locations at the Zenne site (SB2, Pb26, and SB3) are shown in Figures 8-10.



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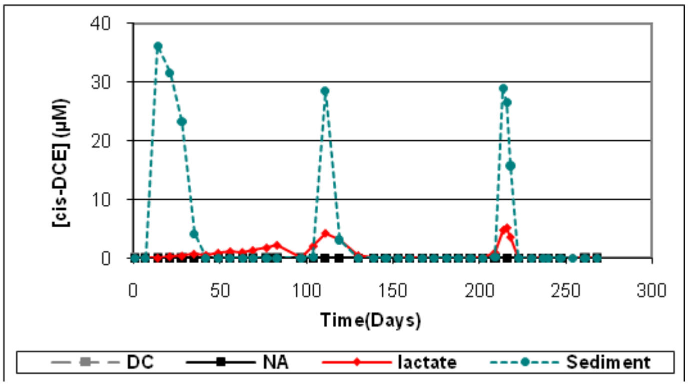

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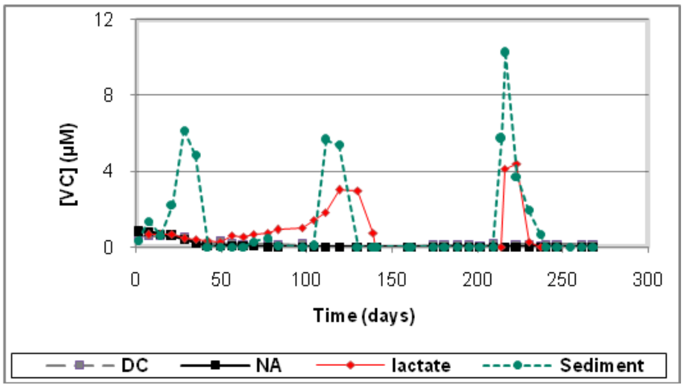

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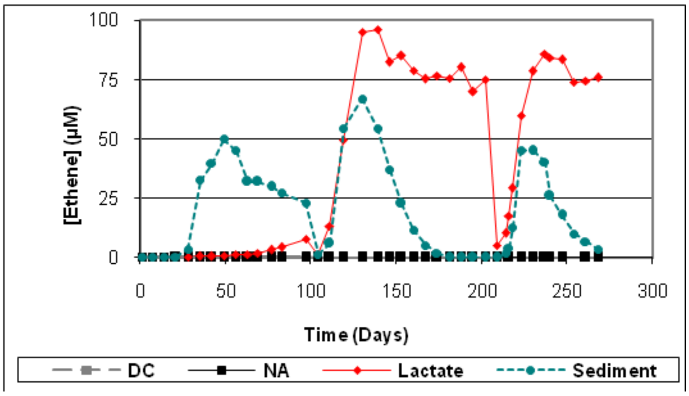
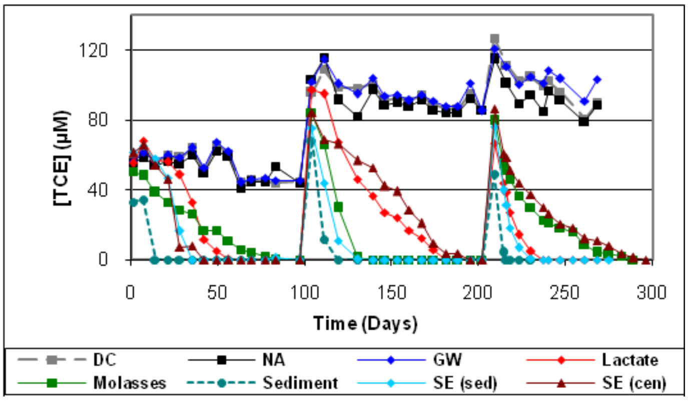


d

Figure 8- (Stimulated) TCE degradation in microcosms with aquifer and groundwater from location SB2 (a) to *cis*-DCE (b), VC (c) and non-toxic end product ethene (d) in batch cultures. NA: natural attenuation, DC: dead control.



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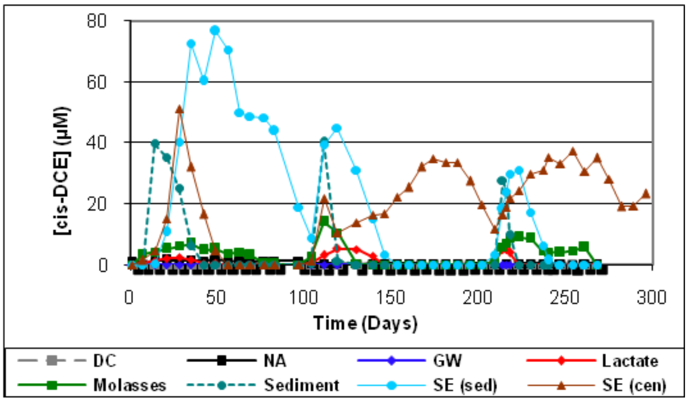

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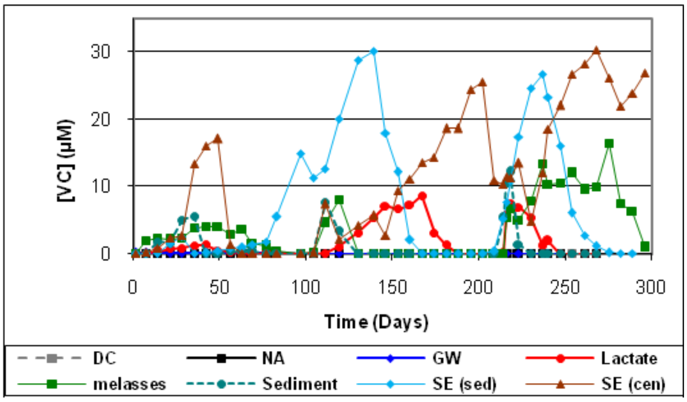

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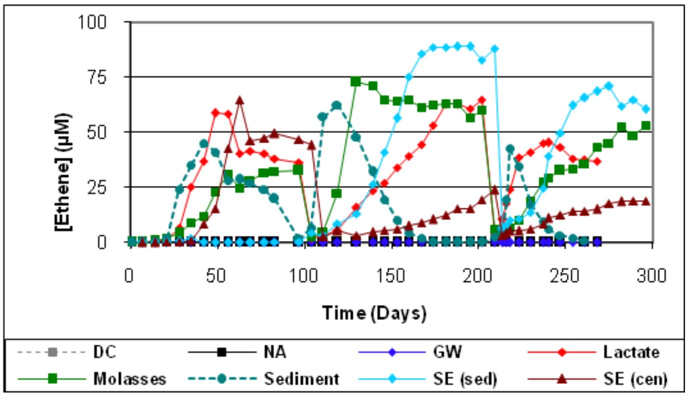

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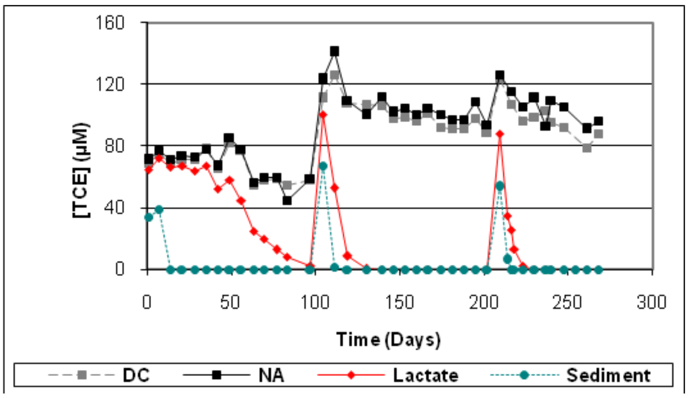
Figure 9- (Stimulated) TCE degradation in microcosms with aquifer and groundwater from location PB26 (a) to *cis*-DCE (b), VC (c) and non-toxic end product ethene (d) in batch cultures. NA: natural attenuation, DC: dead control, GW: ground water control, SE (sed): sediment extract obtained after sedimentation, SE (cen): sediment extract obtained after centrifugation.



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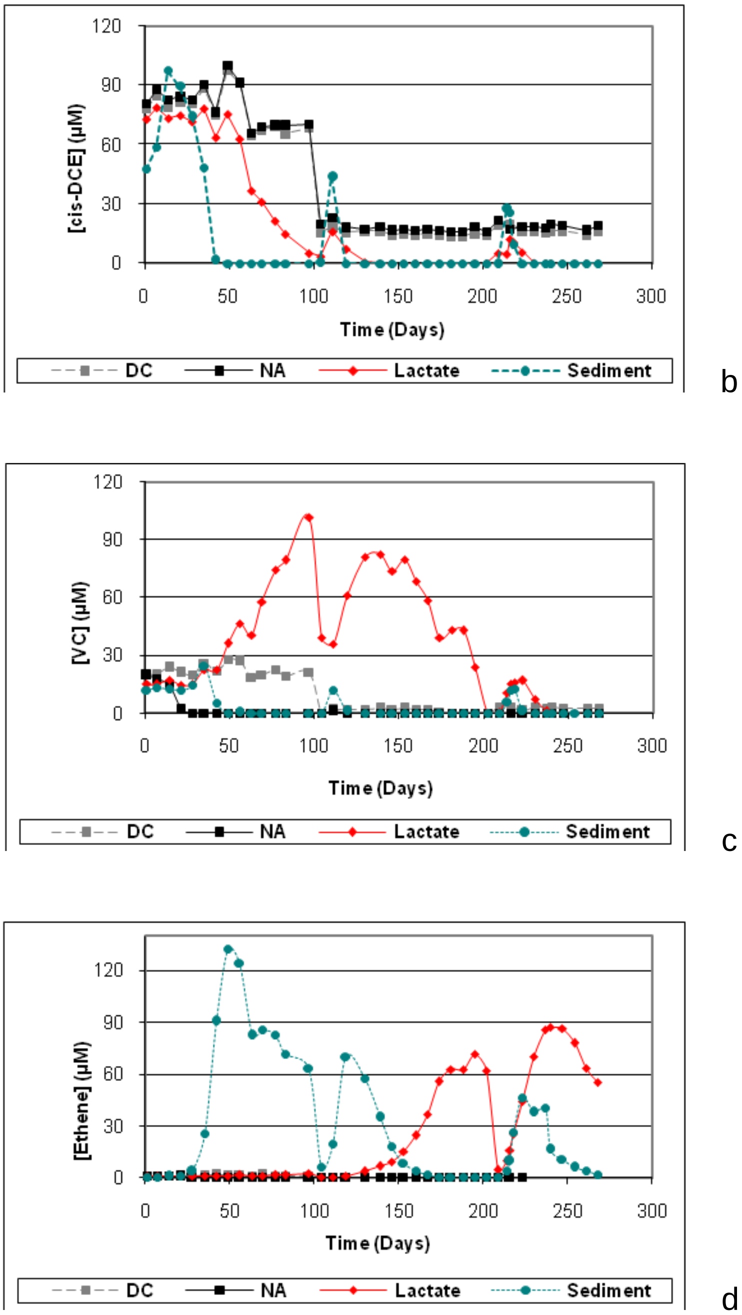

Figure 10- (Stimulated) TCE degradation in microcosms with aquifer and groundwater from location SB3 (a) to *cis*-DCE (b), VC (c) and non-toxic end product ethene (d) in batch cultures. NA: natural attenuation, DC: dead control.

As it can be seen from Figures 8-10, no degradation was observed in un-amended cultures and degradation happened only when external electron donors (lactate or molasses, Zenne River sediment, or an extract of the river sediment) were added to the microcosms. This shows that in order to tackle the CAH plume in the aquifer compartment, addition of external carbon sources is inevitable. Addition of river sediment showed the highest stimulation and resulted in a complete reductive dechlorination of initial 11 $mg \cdot L^{-1}$ TCE to non-toxic ethene in all three spikes and the three studied locations. In these sediment amended microcosms, TCE degradation started without a lag phase. This can be due to the presence of a high number of dechlorinating bacteria in river sediments which degraded TCE in shortest time (see 3-3-1, 3-3-2 and 3-3-3). Methane production was also more pronounced in sediment microcosms which shows presence of active methanogenic community in river sediment which can create strong reducing conditions and also compete with dehalogenating bacteria for electron donor (data not shown). Also ethane formation was observed only in microcosms amended with river sediment (data not shown). This shows that the river sediment is rich in a microbial community capable of complete degradation of TCE to ethane which is missing in the aquifer compartment (see 3-3-1, 3-3-2 and 3-3-3). After river sediment, the results of lactate amended microcosms was noticeable. However, in these microcosms, TCE degradation was accrued after an initial lag phase (SB2 and SB3 35 days and PB26 21 days). In microcosms supplemented with lactate, molasses or a sediment extract, compared to the initial TCE spike, TCE was degraded much faster after the second and third TCE spike. This is due to growth of halorespiring bacteria after the first TCE spike and/or establishment of efficient syntrophic and competitive reactions between those bacteria and electron donor providing organisms or organisms competing for available resources, respectively (see point 3-3-1, 3-3-2 and 3-3-3). In these microcosms, TCE degradation was stalled at ethene level and no ethane was produced (data not shown). Overall, the microcosm studies clearly demonstrated the presence of a larger TCE dechlorination potential in the eutrophic Zenne sediment compared to the aquifer adjacent to the river. None of the amended microcosms were as efficient in TCE degradation as those to which sediment was added. This shows that aquifer compartment not only lacks electron donor, but also efficient electron donor providing organisms and/or dehalogenating community.

3.2. DETERMINATION OF DEGRADATION CONSTANTS

Using measured concentrations of contaminants and their reduction in time, the biodegradation rate constants were calculated for all three locations using first order kinetics.

As it can be seen from Table 2, compared to first spike, degradation constants are dramatically increased in third spike at SB2 and Pb26 locations. Also in accordance to this shift, half life times of VC degradation show huge decrease. However, at SB3, as a result of low degradation constants, VC degradation half lives were dramatically increased. The same trend can be seen for c-DCE degradation at SB2 and Pb26 (Table 3). The only different condition is molasses which has lower degradation constant in third spike than the first spike. This shows that at this condition, the microcosms lost their initial activity in *c*-DCE degradation. However, at SB3, the *c*-DCE degradation potentials has increased compared to VC batch cultures. High degradation potentials at SB3 location is observed in TCE degradation test which lead to dramatic decrease in TCE degradation half life compared to VC and c-DCE degradation tests (Table 4).

Batch cultures	**SB2**		**Pb26**		**SB3**	
	K (day^{-1})[a]	**$T_{1/2}$ (days)[b]**	**K (day^{-1})**	**$T_{1/2}$ (days)**	**K (day^{-1})**	**$T_{1/2}$ (days)**
NA[c]	ND[d]	ND	ND	ND	ND	ND
DC[e]	ND	ND	ND	ND	ND	ND
Lactate	0.019-0.114	37.07-6.11	0.145-0.455	4.790-1.52	0.0029	239.02
Molasses			0.089-0.225	7.820-3.08		
Sediment	0.039-0.817	17.59-8.48	0.020-0.163	34.83-4.26	0.0015	462.1
SE (cen)[f]			0.079-0.163	8.730-4.26		
SE (sed)[g]						

[a] K degradation constant

[b] $T_{½}$ half life time of contaminant

[c] NA natural attenuation

[d] ND no degradation

[e] DC dead control

[f] SE(cen) sediment extract obtained after centrifugation

[g] SE(sed) sediment extract obtained after sedimentation

Table 2- Degradation constant and half life time of VC from VC batch cultures (the values of first and third spikes.are shown).

Batch cultures	SB2		Pb26		SB3	
	K (day^{-1})[a]	$T_{1/2}$ (days)[b]	K (day^{-1})	$T_{1/2}$ (days)	K (day^{-1})	$T_{1/2}$ (days)
NA[c]	ND[d]	ND	ND	ND	ND	ND
DC[e]	ND	ND	ND	ND	ND	ND
Lactate	0.101-0.230	68.63-3.01	0.209-0.592	3.31-1.17	0.015-0.006	47-8-119.51
Molasses			0.149-0.038	4.56-18.29		
Sediment	0.153-0.747	4.53-0.93	0.248-0.671	2.8-1.03	0.154-0.797	4.49-0.87
SE (cen)[f]			0.252-0.655	2.75-1.06		
SE (sed)[g]			0.256-0.169	2.71-4.10		

Table 3- Degradation contant and half life time of *c*-DCE from *c*-DCE batch cultures (the values of first and third spikes.are shown). Legend: see Table 2.

Batch cultures	SB2		Pb26		SB3	
	K (day^{-1})[a]	$T_{1/2}$ (days)[b]	K (day^{-1})	$T_{1/2}$ (days)	K (day^{-1})	$T_{1/2}$ (days)
NA[c]	ND[d]	ND	ND	ND	ND	ND
DC[e]	ND	ND	ND	ND	ND	ND
Lactate	0.010-0.669	68.63-1.04	0.171-0.220	4.05-3.15	0.062-0.358	11.23-1.93
Molasses			0.156-0.358	4.45-1.93		
Sediment	0.771-1.143	0.90-0.61	0.904-0.812	0.77-0.85	0.791-0.782	0.88-0.89
SE (cen)[f]			0.413-0.373	1.68-1.86		
SE (sed)[g]			0.344-0.091	2.02-7.63		

Table 4- Degradation constant and half life time of TCE from TCE batch cultures (the values of first and third spikes.are shown). Legend: see Table 2.

3.3. DETERMINATION OF THE NUMBER OF CAH-DEGRADING BACTERIA AND RELEVANT CATABOLIC GENES THAT ARE PRESENT IN THE AQUIFERBEFORE AND AFTER THE STIMULATION OF CAH DEGRADATION BY DIFFERENT CARBON SOURCES.

To determine the numbers of bacteria involved in the degradation of CAHs, Quantitative PCR was used to quantify different species and catabolic genes involved in the degradation of CAHs. More specifically, *Dehalococcoides*, *Desulfitobacterium* and *Dehalobacter* species were quantified since they are often detected in sites polluted with CAHs. *Dehalococcoides* is involved in the conversion of TCE to VC and subsequently to ethene while *Desulfitobacterium* converts PCE to TCE and finally c-DCE. *Dehalobacter* is known to degrade chloroethanes. The catabolic genes *tce*A, *vcr*A and *bvc*A convert respectively TCE to VC, DCE to ethene and VC to ethene. Especially the detection of *vcr*A and *bvc*A is very important at the site since they convert the toxic VC to the harmless ethene. Eubacterial and Archae bacterial detection result in a view on the total microbial population while sulphate reducing bacteria (detected through the *dsr*A gene) are often competing with CAH degraders. All these genes were quantified in the samples obtained from the stimulated batches that were inoculated with TCE but not c-DCE and VC. The obtained biomass numbers can be used in the reactive transport model developed by ULiege in the FRAC-WECO project.

3.3.1. Microbial population involved in the (stimulated) TCE degradation in the PB26 batch aquifer samples

The total bacterial numbers are, compared to all other batch conditions applied, highest (up to 10^9 copies / gram sample) in the sediment and molasses batches (Figure 11) Also in these conditions, the *dsr*A genes are detected in high number (also above 10^8 copies / gram sample) signifying the presence of sulphate reducing bacteria (SRB). However, SRB appear in all Pb26 samples. *Dehalobacter* and *Desulfitobacterium* were not detected in all Pb26 samples at the end of the second spike. *Dehalococcoides* was detected (10^2-10^5 copies / gram sample) in all treatment conditions except the natural attenuation batch. At the end of the third spike archaea is detected in lactate and the SE centrifuged and SE sedimented batches. Probably conditions stimulated the growth of the archaea. The bacterial numbers do not change when compared to those of the second TCE spike. *Desulfitobacterium* is also detected in these batches.

Presence of reductive dehalogenase genes

The reductive dehalogenase genes were not detected in groundwater and natural attenuation batches after both second and third TCE spikes (Figure 11). The *tceA* gene was detected in the sediment batches and the molasses batches. This is important for the degradation of TCE from these batches. The *bvcA* and *vcrA* are the dominant genes, being present in all the different batch conditions. These genes remain prominent also at the end of the second TCE spike. The higher numbers of *bvcA* and *vcrA* over *Dehalococcoides* are discussed below. In the batches amended with lactate the *tceA* gene is not detected, it is likely that *Dehalococcoides* that habour this gene are outcompeted in the presence of lactate but do well in the batches with other electron donors.

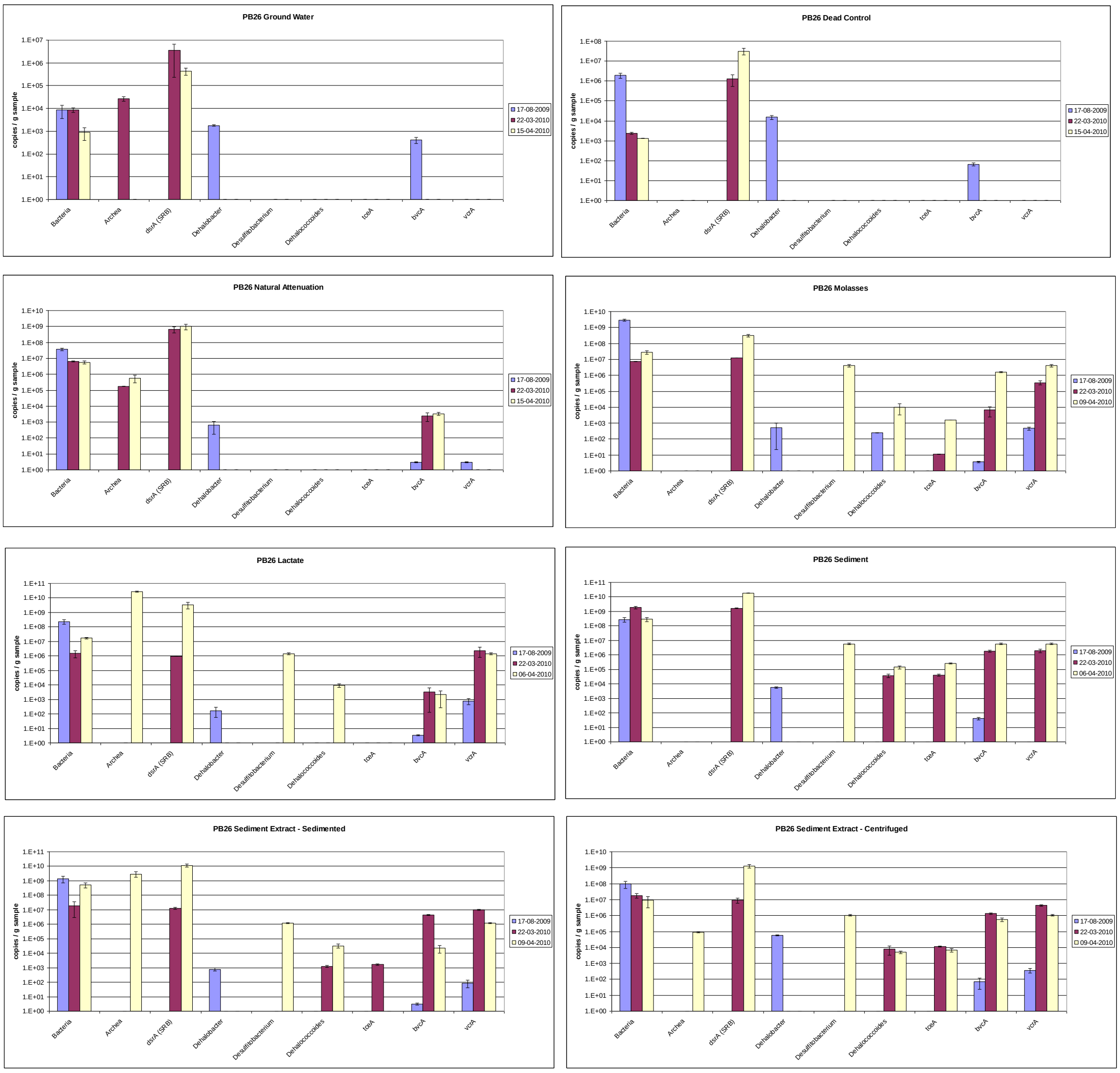

Figure 11- Quantitative PCR for archaea, bacteria, dechlorinating populations *Dehalobacter, Desulfitobacterium, Dehalococcoides,* sulphate reducing populations (dsrA (SRB)) and reductive dehalogenases (*tceA, vcrA* and *bvcA*) in batches of PB26 stimulated with different electron donors. Only one batch for each tested condition is shown.

3.3.2. Microbial population involved in the (stimulated) TCE degradation in the SB2 batch aquifer samples

For the aquifer material obtained from location SB2, at the end of the second TCE spike none of the dechlorinating populations are detected in all the samples (Figure 12) but at the end of the third TCE spike *Desulfitobacterium* and *Dehalococcoides* are detected in the sediment and lactate batches. High numbers of Archaea are observed in the lactate amended batches being 2-3 fold higher than bacteria at the end of both second and third TCE spikes. In the sediment batches the Archaea and SRB are observed only at the end of the third TCE spike.

Presence of reductive dehalogenase genes

For location SB2, *Dehalococcoides* and the reductive dehalogenases were detected in the sediment and lactate batches but not in the natural attenuation batches (Figure 12). In the sediment samples the *bvc*A gene appears to be the dominant gene while the *vcr*A gene dominates in the lactate batches.

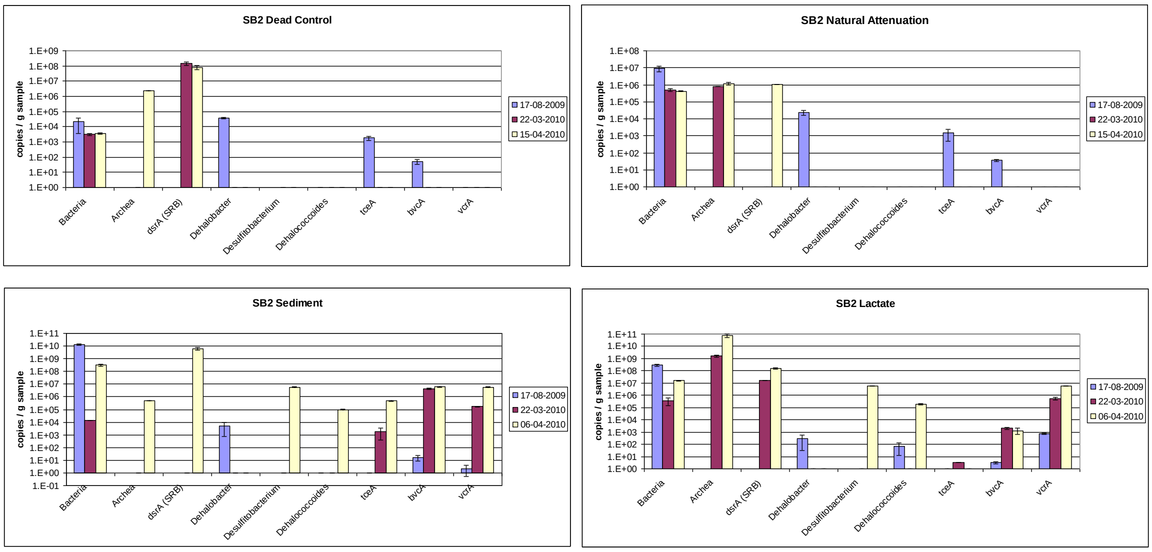

Figure 12- Quantitative PCR for Archaea, bacteria, dechlorinating populations *Dehalobacter, Desulfitobacterium, Dehalococcoides,* sulphate reducing populations (*dsr*A (SRB)) and reductive dehalogenases (*tceA, vcrA* and *bvcA*) in batches of SB2 stimulated with different electron donors. Only one batch for each tested condition is shown.

3.3.3. Microbial population involved in the (stimulated) TCE degradation in the SB3 batch aquifer samples

In the aquifer obtained from location SB3, Archaea are observed in the lactate and natural attenuation batches at the end of second TCE spike and are not detected in the sediment batches. Only *Dehalococcoides* is observed as a dechlorinating population in the lactate batches at the second TCE spike. *Desulfitobacterium* is detected at the third TCE spike in both the lactate and sediment batches. SRB populations are also present in these batches.

Presence of reductive dehalogenase genes

Dehalococcoides and the reductive dehalogenases were detected in the lactate batches at the end of both the TCE spikes (Figure 13). In the sediment samples the *Dehalococcoides* is only detected at the second spike at 10^6 copies / gram sample. There is also an increase in the *tce*A genes in the sediment samples at this time point. The *bvc*A and *vcr*A genes remain above 10^6 copies / gram sample in the lactate and sediment batches. In the natural attenuation batches *bvc*A and *vcr*A are detected at the end of the third TCE spike.

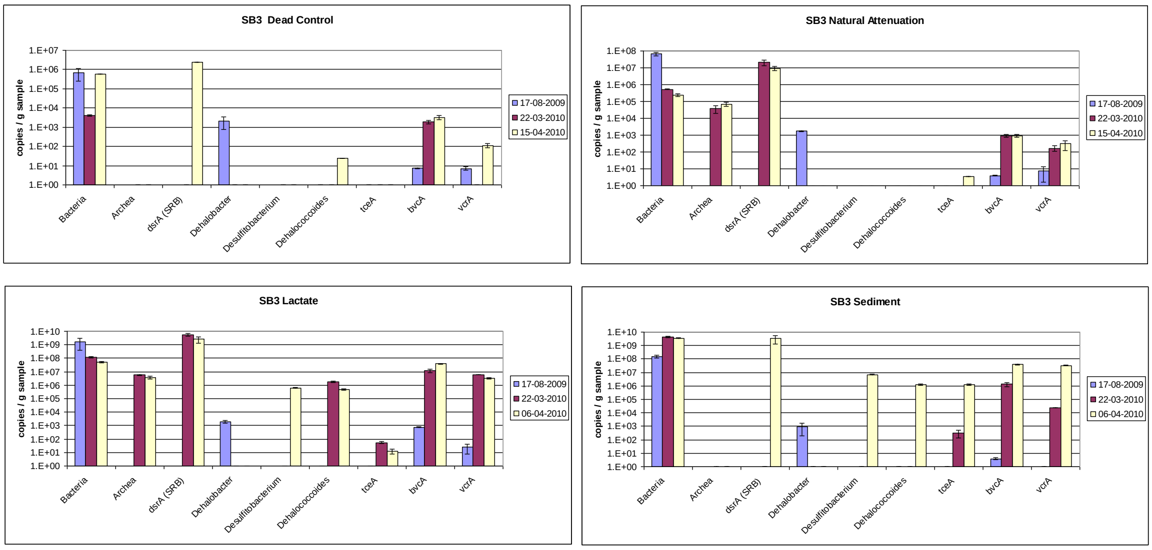

Figure 13 - Quantitative PCR for Archaea, bacteria, dechlorinating populations *Dehalobacter, Desulfitobacterium, Dehalococcoides,* sulphate reducing populations (dsrA (SRB)) and reductive dehalogenases (*tceA, vcrA* and *bvcA*) in batches of SB3 stimulated with different electron donors. Only one batch for each tested condition is shown.

3.3.4. General Remarks microbial community investigation

A general trend of more reductive dehalogenases than *Dehalococcoides* can be observed in all the samples. Several reasons can be attributed to this 1) the presence of cDCE/VC dechlorinating bacteria that are closely related to *Dehalococcoides*, but possibly not picked up by the current *Dehalococcoides* qPCR primer set used in these analyses. Indeed, novel groups of organohalide respiring bacteria, in consortia with *Dehalococcoides* populations that reductively dechlorinate PCE to cDCE have recently been identified in river- and marine sediments by stable isotope probing experiments (Kittelmann & Friedrich, 2008a; Kittelmann & Friedrich, 2008b). Hence, it is not unlikely that yet undiscovered groups harbour cDCE and VC dechlorinating ability shown by the presence of the *bvc*A and occasionally the *vcr*A genes.

4. Conclusions

The analyses of carbon sources suggested that the river sediment was the best carbon source for all three tested locations and has the highest effect in increasing the number of CAH degrading bacteria and the degradation rate of VC, c-DCE and TCE. Lactate had less effect on biostimulation at the first spike of the CAH compounds, but its effect on CAH degradation is similar to the river sediment at the third spike. The results also showed that sediment extracts have less efficiency in stimulation of CAH degradation and in increasing microbial numbers leaving out the possibility of using sediment extracts for field application. Besides, the difficulties in their preparation and handling make them less interesting choice compared to easily accessible and more efficient soluble carbon source such as lactate and molasses. We did not find effect of sample locations on CAH degradation rates from these batch experiments.

The here obtained VC, c-DCE and TCE degradation constants and biomass numbers can be used in the reactive transport model developed by ULiege in the FRAC-WECO project. They can be used to determine the decrease in the concentration of CAHs when these pollutants are transported through the groundwater from the source of pollution to the receptor. We have however to admit that these constants are very site dependent. However, by taking a certain range (e.g of 5%) around these constants, they can be used to predict which amount of pollutant will reach the river under the tested conditions.

5. References

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Smits TH, Devenoges C, Szynalski K, Maillard J, Holliger C (2004). Development of a real-time PCR method for quantification of the three genera *Dehalobacter, Dehalococcoides*, and *Desulfitobacterium* in microbial communities. *J Microbiol Methods* **57:** 369-78.

FINAL SCIENTIFIC REPORT

Flux-based Risk Assessment of the impact of Contaminants on Water resources and ECOsystems

-

FRAC-WECO

SCIENCE FOR A SUSTAINABLE DEVELOPMENT

Annexe 4

Ecotoxicology

Contents

1. Introduction and General context

Several methodologies have been developed to estimate groundwater vulnerability and to determine areas with high pollution potential and delineating aquifer protection zones. However, a universal approach has not been developed yet (Dimitriou et al., 2008). To date, the assessment of the qualitative and quantitative status of groundwater is based almost exclusively on chemical and hydrogeological parameters (Steube et al., 2009).

A conceptual groundwater risk assessment approach adapted from Long and Chapman's (1985) original TRIAD approach, applied for sediment quality assessment was developed. This approach, referred to as "Groundwater Quality TRIAD-like (GwQT)", combines chemical data with laboratory bioassays and key physico-chemical variables to evaluate the impacts of pollutants on selected organisms. The overall study of these three components provides an assessment of the environmental risk. To our knowledge, this study presents the first application of the TRIAD approach on the groundwater system. This new concept is a starting point for groundwater characterization and is open for improvement and adjustment.

It was validated on local scale (Chimeuse and Morlanwelz sites) as more data are required at a regional scale.

However, this approach ignores which particular contaminants may be causing the observed biological effects. Furthermore, the contribution of the individual compounds to the observed mixture toxicity and their specific interactions cannot be inferred from a whole-mixture study alone.

The Toxic Unit approach (TU) was used in combination with the TRIAD-like approach to identify micro-pollutants which contributed to effects observed in the bioassays.

2. Methodology and development of Ecotoxicological indicators

The ecotoxicological risk and quality of groundwaters were determined by applying a complete methodology integrating TRIAD-like approach and Toxic Unit approach.

2.1. GROUNDWATER QUALITY TRIAD-LIKE APPROACH

The “Groundwater Quality TRIAD-like” (GwQT) approach is based on measurements of chemical concentrations (chemistry), laboratory toxicity tests (ecotoxicity) and physico-chemical analyses (pH, conductivity…). Chemistry analysis provides information on the presence and levels of pollutants, but does not provide information on biological hazard they might cause. Laboratory bioassays are thus used to determine whether the sampled groundwater is toxic to aquatic organisms. In our approach we include evaluation of “key” physico-chemical variables such as pH, conductivity as alternative tools to groundwater community structure (used in classical TRIAD approach). Considering the lack of information to the ecological component (taxonomy, autecology and physiology of groundwater organisms) and the limited accessibility of underground ecosystems, such alternative tools are important.

These components are combined in the GwQT using qualitative (triangular representations, pie-charts and tabular matrices) and quantitative integration approaches. The advantage of the qualitative methods is the simplicity of interpretation, although no quantification is provided. Results from all components are made comparable using zero to one subindices corresponding to no effect up to maximum effect. The TRIAD-like approach is explained in detail in Deliverable D.1.5 (Crévecoeur & Thomé, 2010).

It will allow the classification of sites into categories according to the degree of contaminant-induced degradation.

2.2. DESCRIPTION OF DESIRED LAND-USE

The first step of the TRIAD-like approach is to describe what is known about the site, *e.g.* groundwater characteristics, identification of potential contaminants, pathways and receptors. The situation of the site and the current and future land-use have to be defined (Weeks et al., 2004).

2.3. SITE SPECIFIC MEASUREMENT INSTRUMENTS: CHEMISTRY

The first component of the TRIAD is environmental chemistry. Specifically, identification and quantification of contaminants present in the groundwater samples must be undertaken.

Total concentration of pollutants is integrated into risk index (Chemical risk index, ChemRI) by using a sequence of successive steps (Jensen and Mesman, 2006). Concentrations of pollutants are compared to normative value and a risk number (between 1 and 0, the lower the score, the better the quality) is assessed for each class of pollutants and globally for each sampling point using Independent Action (IA) model.

Independent Action is represented by “Response Addition Model”, which sum the effects of each component. The chemicals are assumed to behave independently of one another (Backhaus et al., 2008).

2.4. SITE SPECIFIC MEASUREMENT INSTRUMENTS: PHYSICO-CHEMISTRY

All parameters (conductivity, pH, nutrients, …) used for water characterization are generally not integrated in the classical TRIAD approach. However, the physico-chemical component is part of GwQT as these parameters are critical to the survival and growth of aquatic life.

Physico-chemical Risk Index (PhysRI) is assessed by applying the same sequence of successive steps as for ChemRI, except for pH parameter. Indeed, this parameter is comprised in a range of values from 6.5 to 9.2, characterized by “no risk”. Outside of this range, the risk increase. Risk values can be assigned for several pH data using SEQ-ESO (“Système d’Evaluation de la Qualité des Eaux Souterraines”), groundwater quality indicator developed and currently applied in the Walloon Region (Belgium), thresholds and minimum values (DGARNE, 2010). A curve was drawn using these values (Figure 1). Risk (R_3) for pH is assessed using the equation of the curve (determined using Statistica 8.0 software) according to pH data (Fig. 1). Afterwards, results are scaled to obtain “0” for “no risk” and “1” for “high risk” ($1 - R_3 = R_4$).

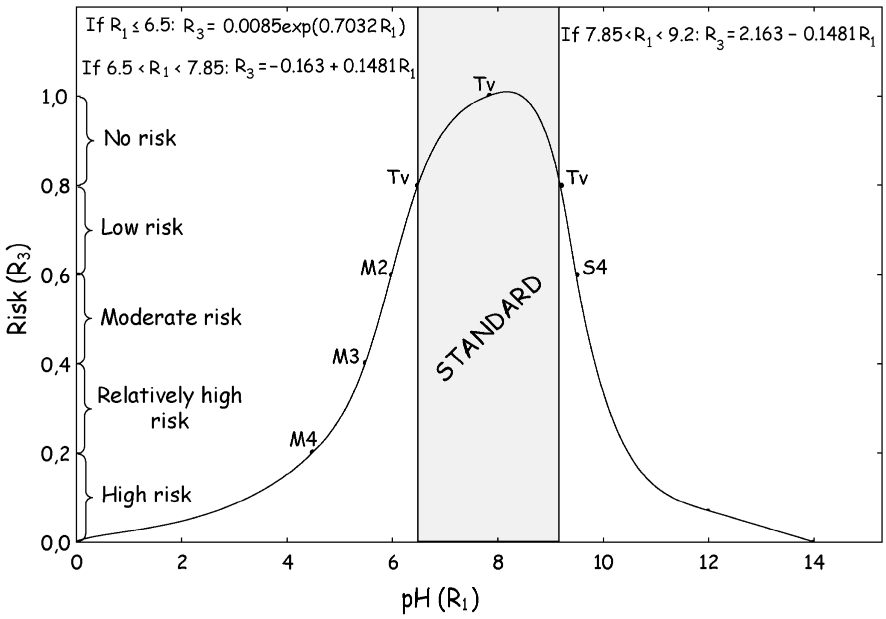

Figure 1. Risk assessed for pH value (Tv, Trigger value and M2, M3, M4 and S4, thresholds values from SEQ-ESO system).

2.5. 2.3.1.4. SITE SPECIFIC MEASUREMENT INSTRUMENTS: ECOTOXICITY

Application of biotests with different organisms can indicate general stress as a result of complex mixtures, and provide information about potential hazard to aquatic life.

An Ecotoxicological Risk Index (EtoxRI) is assessed by dividing the results from bioassays (*e.g.* mortality in the pure sample), expressed as a percentage, by 100 (Jensen and Mesman, 2006). A global EtoxRI is estimated as the mean of the different RIs (Dagnino et al., 2008).

2.6. 2.3.1.5. INTEGRATION OF THE RESULTS

The quantitative integration method integrates all information in a single numerical value, the Environmental Risk Index (EnvRI). The difference between the final score and the theoretical score 1 gives an indication of the risks (and its magnitude) for ecosystem health at the studied site (Den Besten et al., 1995). In the integration procedures, arbitrarily assigned weighting factors (wf) are applied to the diverse indices on the basis of their ecosystem relevance (Dagnino et al., 2008). Chemistry is the more direct measure, but toxicity is given equal weight because of the possibility that unmeasured chemicals are present (Bay and Weisberg, 2008). The physico-chemical component is also an important parameter. In this study, unequal weighting among components was used (wf =1). The Environmental Risk Index is calculated using the following equation (adapted from Dagnino et al., 2008):

$$EnvRI = \frac{(wf_{CHEM} * ChemRI) + (wf_{PHYS} * PhysRI) + (wf_{ETOX} * EtoxRI)}{(wf_{CHEM} + wf_{PHYS} + wf_{ETOX})}$$

Qualitative methods have often been applied to determine the degree of degradation of each studied site. Therefore, contamination, physico-chemistry and toxicity data are combined in the TRIAD-like approach using tabular matrix, pie charts and triangular representation.

In tabular matrix, the different responses are shown with positive or negative signs to indicate a possible risk (Chapman, 1990).

Different levels of probability in the similarities between stations can be represented using pie charts. It represents the integration of all the components using colours coming from the SEQ-ESO system (DGARNE, 2010) and risk indicators (Table I).

ChemRI & PhysRI	EtoxRI	Risk Indicator
$0.00 < RI \leq 0.20$	$PE \leq 10\%$	No risk (- -)
$0.20 < RI \leq 0.40$	$10\% < PE < 50\%$	Low risk (-)
$0.40 < RI \leq 0.60$	$50\% \leq PE < 100\%$	Moderate risk (±)
$0.60 < RI \leq 0.80$	PE = 100% (at least 1 test)	Relatively high risk (+)
$0.80 < RI \leq 1.0$	PE = 100% (all tests)	High risk (+ +)

Table I. Representation of TRIAD-like components in classical pie-charts and risk classification according to SEQ-ESO colours (PE, Percentage of Effect; RI, Risk Indice), adapted from DGARNE (2010) and Persoone et al. (2003).

The three indices can be displayed in graphical form as three segments (for Contamination, Toxicity and Physico-chemistry) with a common origin (“0”, no risk), where the lengths of each segment equals the values of the risk index for the three groups of determined parameters (Chapman, 1990).

The different methodologies used in the representation and interpretation of the TRIAD-like results have been shown to be complementary.

2.7. TOXIC UNIT APPROACH

The Toxic Unit approach (TU) was used to identify micro-pollutants which contributed to effects observed in the bioassays.

This concept can be mathematically expressed as the following equation: $TU_i = C_i / L(E)C_{50,i}$, where C_i gives the concentration of the component *i* in a mixture which elicits 50% of effect, and $EC_{50,i}$ denotes the concentration of that substance which induces 50% of effect if applied singly (collected from literature and ecotox databases). Assuming that the effects of pollutants with a similar mode of action are mainly additives, individual Toxic Unit values were added to estimate the toxicity of groups of compounds such as ΣTU values for metals, PAHs or organochlorine compounds (*Lahr & al, 2003*).

In one approach to characterize joint effects, the sum of all TU_i can be used. $\sum TU_i$ values < 1, = 1, or > 1 were taken as proof of synergism (‘‘greater than additive”), simple additivity or antagonism (‘‘less than additive”), respectively (*De Laender & al, 2009*).

3. Application on the Chimeuse test site

Groundwater Quality TRIAD-like approach was applied on Chimeuse Est site located in the gravels and alluvia of the Meuse River, close to the city of Liège (validation of the methodology on Morlanwelz site, paper in submission).

It is an area of intensive heavy industry: coking plant and chemical industry with ammoniac production, coal distillation, artificial fertilizers and sulphuric acid production. All industrial activities stopped in 1961. Chimeuse Est site became a grassy and woody fallow land. Contamination at this site is especially characterized by hydrocarbons, cyanides and heavy metals.

Sampling of groundwater. Boreholes were selected on Chimeuse Est Site (P23, P24, P25, P26, P28 and P29) and sampled between August 2009 and June 2010 (5 campaigns).

TRIAD-like components. The "Groundwater Quality TRIAD-like" applied at Chimeuse Est site is represented by the following measurements (Figure 2):

(a) Chemical concentrations: chemical analyses of homogenized groundwater samples for heavy metals (As, Cd, Cr, Cu, Ni, Pb & Zn) and cyanides (analysed by Laboratory of Water Resources, ULg), some PAHs (analysed by Laboratory of Food Analysis, CART-ULg), BTEX and chlorinated compounds (CAHs, analysed by VITO);

(b) Toxicity tests using the planktonic species *Brachionus calyciflorus* (chronic and acute tests) and other bioassays (using bacteria, algae, other planktonic species and amphipoda) for P23 and P26 samples;

(c) Physico-chemical measurements such as pH and conductivity.

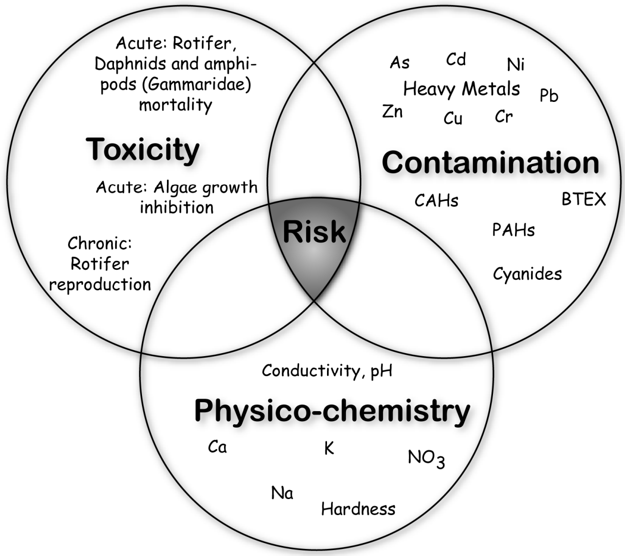

Figure 2. Schematic representation of the components of the TRIAD-like approach.

Groundwater toxicity and physical-chemical data. Results for the ground- and surface water chemistry and toxicity and for the physico-chemical parameters data are summarized in Table II.

Variable	Guidelines	Groundwater samples					
		P23	P24	P25	P26	P28	P29
Metals : (µg/L)							
Arsenic	10	19.0 ± 10.38	30.3 ± 8.50	333.3 ± 205.0	4.1 ±1.93	3.4 ± 1.51	1.72 ± 0.19
Cadmium	5	2.6 ± 1.53	0.5 ± 0.00	0.5 ± 0.0	4.9 ± 5.34	0.5 ± 0.0	101.88 ± 35.34
Chromium	50	5.0 ± 3.43	6.2 ± 3.10	7.4 ± 5.3	3.9 ± 1.57	2.9 ± 1.57	16.22 ± 13.19
Copper	100	17.3 ± 10.20	3.0 ± 0.89	3.0 ± 1.0	201.3 ± 302.05	8.8 ± 11.62	4838.20 ± 2178.93
Nickel	20	28.6 ± 7.64	3.7 ± 1.61	11.3 ± 12.3	68.0 ± 89.33	6.7 ± 6.71	1113.96 ± 485.54
Lead	10	14.1 ± 12.62	1.0 ± 0.00	1.2 ± 0.4	51.4 ± 54.92	1.0 ± 0.0	77.56 ± 28.96
Zinc	200	749.7 ± 418.14	15.0 ± 0.00	15.0 ± 0.0	479.5 ± 757.73	17.9 ± 3.66	15482 ± 6423.80
BTEX : (µg/L)							
Benzene	10	18.7 ± 23.71	<1.0	<1.0	<1.0	<1.0	60.4 ± 37.97
Toluene	700	0.8 ± 0.49	<0.5	<0.5	<0.5	<0.5	0.9 ± 0.53
Ethylbenzene	300	1.1 ± 0.25	<1.0	<1.0	<1.0	<1.0	1.1 ± 0.18
Xylenes	500	2.4 ± 1.39	<1.5	<1.5	<1.5	<1.5	4.3 ± 2.1
PAH's	-	0.050 ± 0.017	<0.005	<0.005	0.056 ± 0.022	<0.005	<0.005
Cyanides	70	65.3 ± 12.68	15.6 ± 23.70	23.0 ± 29.5	37.6 ± 72.90	71.0 ± 37.64	18.5 ± 2.69
CAHs : (µg/L)							
Vinyl chloride	5	<2.0	<2.0	<2.0	14.8 ± 11.11	<2.0	<2.0
1,2-Dichloroethene	50	<2.0	<2.0	<2.0	11.8 ± 2.69	<2.0	<2.0
Trichloroethene	70	<0.5	<0.5	<0.5	124.8 ± 110.85	<0.5	<0.5
Physico-chemical parameters :							
pH	6.5 - 9.2	6.6 ± 0.57	6.8 ± 0.12	7.4 ± 0.8	6.5 ± 0.57	7.0 ± 0.2	3.88 ± 0.11
Conductivity (µS/cm)	2100	3624 ± 90	2738 ± 81	2584 ± 48	3950 ± 450	2628 ± 86	3464 ± 457
Na (mg/L)	150	223.70	126.10 ± 45.96	297.5 ± 243.95	156.00	129.90	32.07 ± 2.21
K (mg/L)	12	46.15 ± 3.89	12.11 ± 0.28	13.45 ± 2.48	25.6 ± 14.00	12.25 ± 1.91	2.03 ± 2.08
NO3 (mg/L)	50	0	22	13	0	27	58
NH4 (mg/L)	0.5	10.8	0.04	10.8	0.88	0.10	3.2
Hardness (°d)	37.8	55	27	100	88	0.5	40
Toxicity (%):							
Brachionus calyciflorus mortality	-	77.2 ± 17.25	50.6 ± 14.78	61.0 ± 23.3	84.5 ± 16.91	29.1 ± 11.44	91.67 ± 16.67
B. calyciflorus inhibition of the reproduction	-	85.3 ± 14.67	61.5 ± 9.24	60.1 ± 4.6	87.0 ± 9.64	46.6 ± 12.19	98.21 ± 2.45
Daphnia magna mortality	-	90.0 ± 17.32	nd	nd	61.8 ± 10.28	nd	nd
Gammarus pulex mortality	-	89.8 ± 11.95	nd	nd	14.7 ± 9.73	nd	nd
Vibrio fischeri inhibition of the bioluminescence	-	0.0	nd	nd	0.0	nd	nd
Pseudokirchneriella subcapitata growth inhibition	-	94.7 ± 9.24	nd	nd	100.0 ± 0.0	nd	nd

Table II. Contaminant concentrations (expressed as µg/L, mean ± standard deviation), physico-chemical parameters, acute and chronic toxicity tests for water sampled at different locations at Chimeuse Est site.

3.1. TRIAD-LIKE APPROACH APPLICATION - RISK INDICES

The groundwater quality of the studied site is assessed using a TRIAD-like approach based on 0 to 1 indices, the lower the score the better the quality. The results of the methodological approach are shown in Table III.

TRIAD components	Groundwater samples						
	P23	P24	P25	P26	P28	P29	Chimeuse Est site
Chemistry							
ChemRI	0.9943	0.7782	0.9854	0.9984	0.7367	1.0000	0.9155
ChemRI Heavy metals	0.9820	0.7758	0.9792	0.9779	0.5170	1.0000	0.8720
ChemRI BTEX	0.4352	0.0000	0.0000	0.0959	0.0000	0.7211	0.2087
ChemRI Cyanides	0.4790	0.0000	0.1978	0.1945	0.4721	0.2084	0.2586
ChemRI CAHs	0.0103	0.0083	0.0064	0.8936	0.0074	0.0028	0.1548
Physico-chemistry							
PhysRI	0.6596	0.4557	0.5554	0.5483	0.4462	0.7872	0.5754
Ecotoxicology							
EtoxRI	0.8308	0.5603	0.6053	0.7485	0.3785	0.9494	0.6788
EtoxRI Acute	0.8087	0.5060	0.6100	0.6267	0.2906	0.9167	0.6264
EtoxRI chronic	0.8529	0.6146	0.6007	0.8702	0.4664	0.9821	0.7312
EnvRI	0.8282	0.5981	0.7124	0.7651	0.5205	0.9122	0.7232

Table III. Risk indices values of the TRIAD-like components for groundwater at Chimeuse Est site (each borehole and globally; “0” for “no risk” and “1” for “high risk”).

The global ChemRI is similar to the ChemRI estimated for heavy metals, except P28. Benzene is also problematic at P23 and P29. Cyanides are present everywhere, except at P24. On the contrary, a risk caused by chlorinated compounds is only assessed at P26. The TRIAD-like approach application confirms the widespread measured metal contamination (As, Cd, Cu, Ni, Pb, Zn) at this site.

PhysRI is lower compared to ChemRI. Groundwater sampled at P29 is acid and is responsible for high PhysRI.

The ecotoxicological parameter is characterised by spatial heterogeneity, from moderate to relatively high risk.

Results show statistically significant differences (ANOVA followed by Tukey test, $p < 0.05$) among the three risk indices for P23, P24 and P26 and between ChemRI and the two other risk indices for P25 and P28. On the contrary, groundwater sampled at P29 show statistically significant differences only between ChemRI and PhysRI (Figure 3).

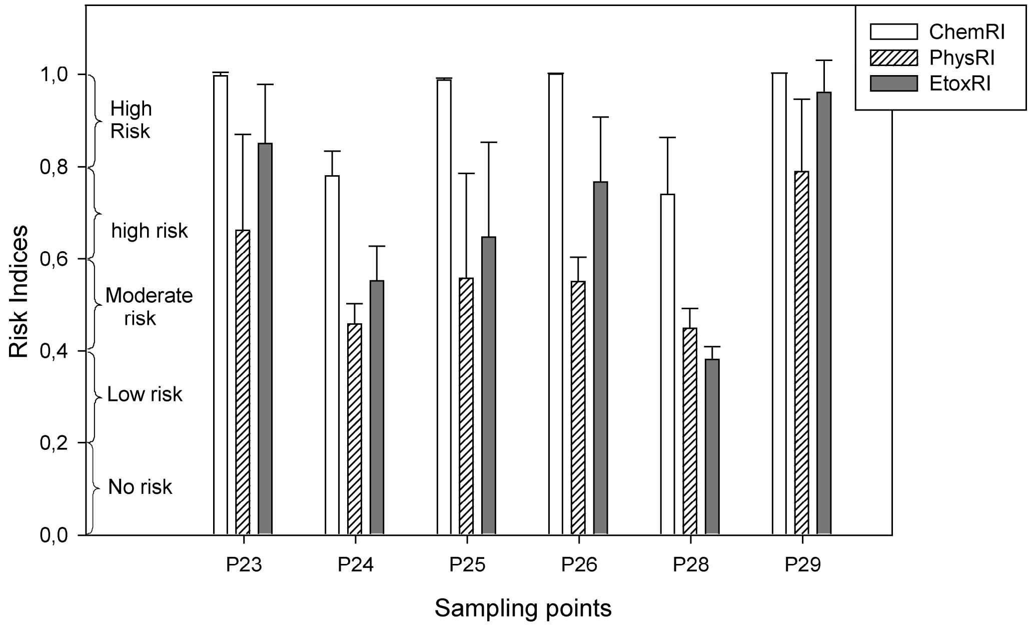

Figure 3. Risk indices (ChemRI, PhysRI and EtoxRI) representation for the different sampling points at Chimeuse Est site.

In addition of quantitative results, risk indices can be compared using graphical presentation.

3.2. 2. TRIAD-LIKE APPROACH APPLICATION, QUALITATIVE REPRESENTATION

TRIANGULAR REPRESENTATION. Symmetrical triaxial graph (Figures 4) illustrates the three groundwater TRIAD-like components for the whole studied site. The area of the triangles is an indicator of pollution-induced toxicity.

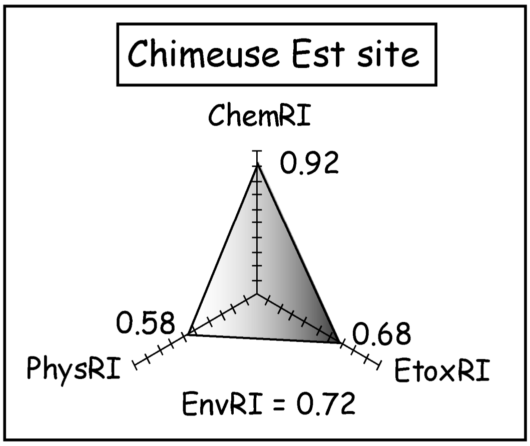

Figure 4. Results obtained from the integration of both physical-chemical and ecotoxicological components in the characterization of groundwater sampled at Chimeuse Est site, triangular representation.

The response intensity of the chemical component for groundwater sampled at Chimeuse Est site was higher.

Summary indices in triangular format provide a simple and highly visual data presentation which can be explained to and understood by non-scientists. However, there is a substantial loss of information and the significance of any spatial impact cannot be determined statistically (Hollert & al, 2002).

TABULAR DECISION MATRIX AND PIE-CHARTS. Samples from Chimeuse Est site were classified as having elevated chemistry, physico-chemistry and toxicity (*e.g.* evidence of metal-induced degradation) or not (Table IV).

Chemistry	Physico-chemistry	Toxicity	Samples	Possible conclusion
+	±	-	P28	Chemicals are not bioavailable.
+	±	±	P24	Pollution-induced degradation.
+ +	±	±	P25	Some chemicals are not bioavailable or the observed toxicity is caused by only one or two physical-chemical component.
+ +	±	+	P26	Strong evidence for pollution-induced degradation.
+ +	+	+	P29, P23	Strong evidence for pollution-induced degradation.
+ +	±	+	Whole Chimeuse Est site	Strong evidence for pollution-induced degradation.

Table IV. Information provided by differential TRIAD responses are shown as either positive (+) or negative (-) signs, Chimeuse Est site, adapted from *Chapman & al* (1996).

The variance in the individual component can also be represented graphically using pie chart diagrams and colours from the SEQ-ESO system (Table I and Figure 6).

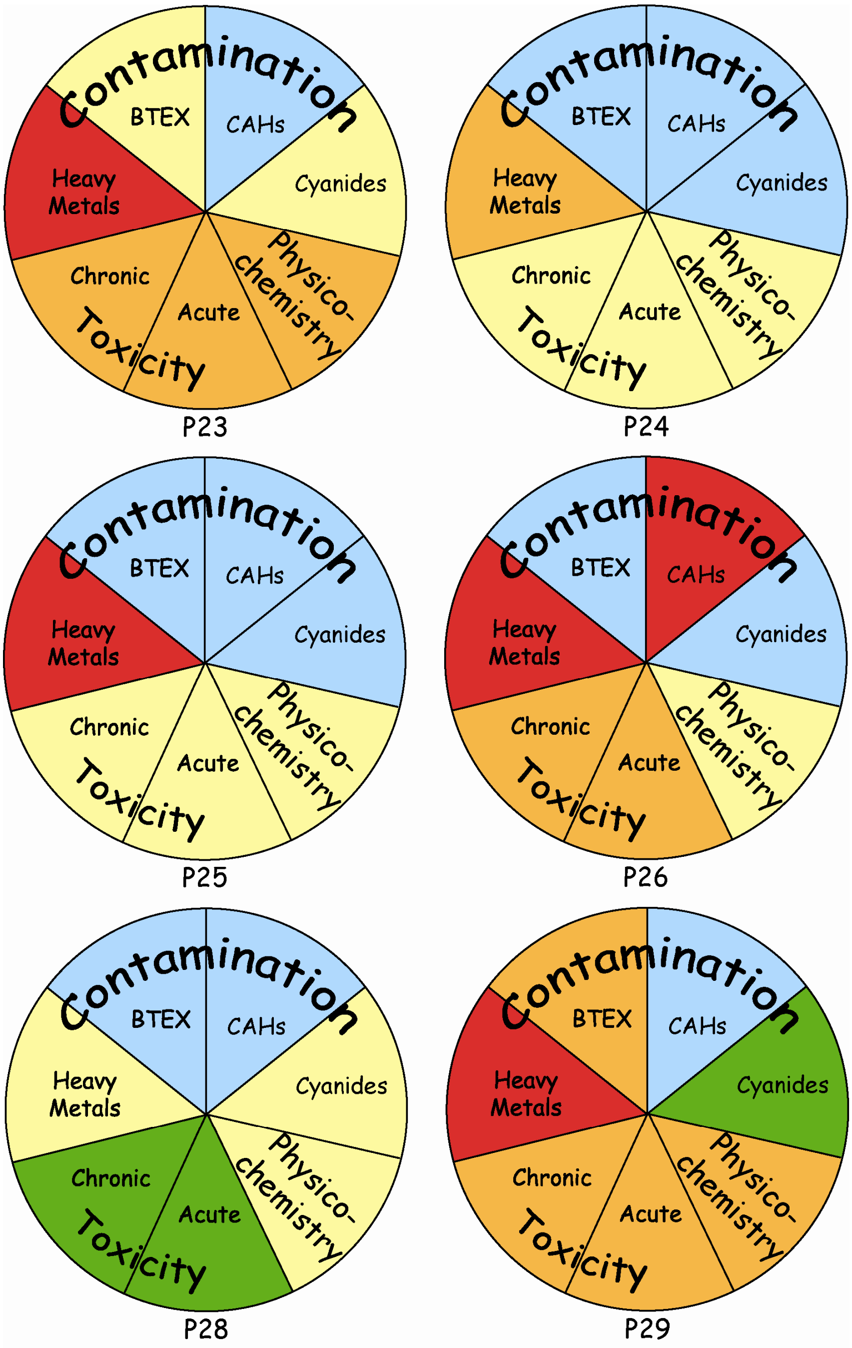

Figure 6. Pie charts representation for each sampling points at Chimeuse Est site.

Results obtained using qualitative representation determine that groundwater samples from Chimeuse Est site are especially contaminated by heavy metals, except P26 that is also contaminated by CAHs. P24 and P28 are less contaminated.

These results confirm those obtained from risk indices data. However, without the results from the quantitative approach, information about the magnitude of the risk and about the variance between samples and between the different measurements inside each component (chemistry, toxicity, physico-chemisty) would have been lost.

In conclusion, the GwQT provides evidence of the poor health status of groundwater at Chimeuse Est site (EnvRI = 0.7232) as a result of heavy metals pollution (CAHs at P26) with spatial heterogeneity among sampling points.

None of the three TRIAD components (chemistry, physico-chemistry and ecotoxicity) could reliably predict the other one; *i.e*, the approach using the three components has been considered a more complete evaluation of toxic effects from groundwater than any one component alone. When they are used in an integrative way, more reliable information about the environmental condition is provided (Cesar & al, 2007).

Integration of new variables such as biomarkers, other bioassays, other physico-chemical measurements and studies of bioavailability should contribute in the future to the improvement of this integrated approach for the characterization of groundwater quality. Moreover, higher numbers of sampling points per site and samples are crucial to reduce uncertainties.

3.3. TOXIC UNIT APPROACH

A more than additive effect (synergism) was indicated for all bioassays (*e.g. Brachionus calyciflorus* chronic bioassay, Figure 7), except with *Daphnia magna* (antagonism, “less than additive”). Therefore, mixture toxicity is higher (lower for *Daphnia magna* bioassay) to the toxicity that would be expected if we sum each pollutant toxicity.

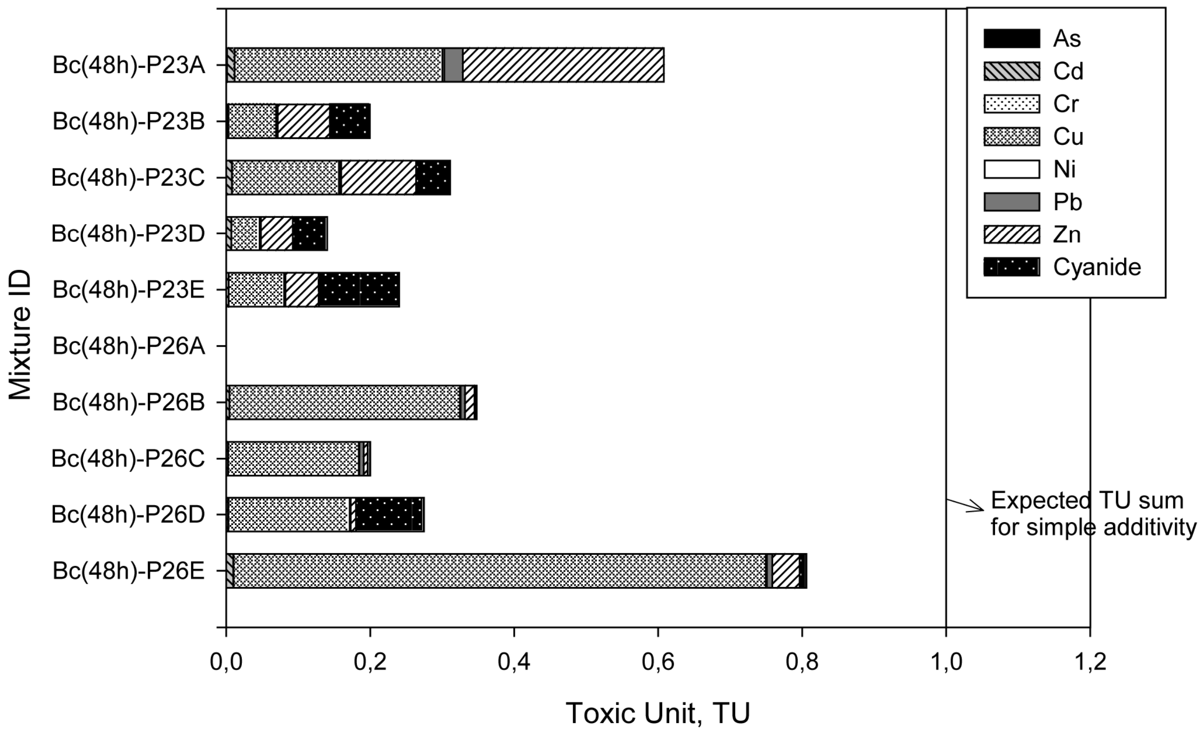

Figure 7. Toxic Units sum in 9 mixtures of groundwater sampled at Chimeuse Est site (P23 and P26), *Brachionus calyciflorus* (Bc) chronic bioassay.

Among the metals, copper (followed by zinc and cyanides) posed highest risk to aquatic species. Furthermore, results demonstrate that no single test is certain to give conclusive results, wherefore it is preferable to use a battery of bioassays.

A small amount of a very toxic chemical in a mixture can have a much larger effect on the biological response than a large amount of a slightly toxic chemical. Therefore, the Toxic Unit approach is a useful tool to determine the pollutant causing the toxicity.

Chemicals at concentrations as low as 10% of their respective Water Quality Standards have been found to be toxic when acting together as a mixture such as Cu, Cd. These results indicate that groundwater quality guidelines for individual chemicals could underestimate the overall exposure effect, and therefore would not be protective. The implication here is that regulatory limits for individual metals may not be sufficiently protective, particularly when the element is occurring in a mixture (Cooper & al, 2009).

On the contrary, concentrations of vinyl chloride, trichloroethene and nickel are higher than trigger values in some groundwater samples but are not responsible for the observed toxicity.

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FINAL SCIENTIFIC REPORT

Flux-based Risk Assessment of the impact of Contaminants on Water resources and ECOsystems

-

FRAC-WECO

SCIENCE FOR A SUSTAINABLE DEVELOPMENT

Annexe 5

Socio-economic Cost-Benefits analysis

Contents

1. Introduction/ Context and objectives

1.1. APPLYING THE WFD IN THE CASE OF GROUNDWATER BODIES CONTAMINATED BY BROWNFIELDS

Following the requirements of the Water Framework Directive, a programme of measures selected on the basis of a cost-effectiveness analysis (CEA) should be proposed for each water body at risk of not reaching good status. In case of disproportionate costs derogation may be justified on the basis of a cost-benefit analysis (CBA).

This economic analysis is a challenging task in case of groundwater bodies located in heavily industrialised and urbanized area and historically contaminated by brownfields. Remediation measures are expected to be very expensive and time required for remediation may be very long. As groundwater resources are generally not used anymore as a resource it is difficult to anticipate (i) if market benefits could be expected from an improvement of the groundwater quality and (ii) if people would be willing to contribute to this quality improvement.

Specific questions raised in the FRAC-WECO project are: How much will it cost to improve the quality of a groundwater body currently degraded by brownfields? How long will it take? What is the (May we expect a) potential economic value of a groundwater resource currently degraded by brownfields?

1.2. VALUING THE BENEFITS: TYPES OF ECONOMIC VALUES TO BE CONSIDERED

Changes in the state of the aquatic system may lead to positive impacts (benefits) or negative impacts (damage). Impacts are characterised as the change of goods and services provided by aquatic systems that lead to change in human welfare. The concept of total economic value (TEV) can be used to provide a measure of the economic value of an environmental asset (Pearce *et al.*, 2006). Any improvement in water status (for instance after the implementation of remediation measures) leads to *environmental benefits* (positive impacts) that may be defined as the TEV of the physical environmental improvement of the water system. The TEV of groundwater is calculated as the sum of use values (including direct and indirect use values) and non-use values (Brouwer, 2006).

Use values are associated with the direct or indirect, current or potential future use of the water resource:

- *Direct use values* involve human interaction with the resource itself. It may be consumptive or extractive use (e.g. domestic, public, commercial, agricultural and industrial supply, fisheries). Direct use value leads to activities that would not take place if that quantity and quality of water did not exist.
- *Indirect use values* derive from the ecological services provided by the groundwater resource as a support of living organisms or as water discharge to connected surface waters and associated ecosystems (*ecosystem benefits*).
- *Option values* represent the amount which certain users may be willing to pay to secure access to and use of groundwater at some time in the future and include the value stemming from future use of groundwater.

Non-use values are not related to any actual or potential future use but refer to values attached to the water resource conservation based on considerations that, for instance, the resource should be preserved for future generations.

Classical CBA often take into account only direct use values to assess the low range of benefits of groundwater quality improvement. These values may be obtained with the implementation of market-based methods (e.g. averting behaviour, replacement costs). However, in the case of groundwater currently contaminated and not much used, direct use values are expected to represent a small part of the TEV. Contingent valuation is the unique method enabling to integrate both use and non-use values in the TEV. However, its application to groundwater resource improvement remains scarce, especially in the case of groundwater resources with low expected direct use values.

1.3. PROPOSED METHODOLOGY

The general methodology proposed by the FRAC-WECO project combines a valuation of remediation costs at the groundwater body scale, a valuation of market benefits through the averting behaviour approach and a valuation of the TEV expected from a groundwater quality improvement through a the implementation of the contingent valuation method.

2. Valuing the benefits expected from an improvement of groundwater quality: Methodology and results

2.1. 2.2 VALUING THE BENEFITS

2.1.1. Direct use/ option use values

a. Methodology

Market benefits may occur to current and future potential water users i.e. those that could be impacted (positively or negatively) by a change in the groundwater quality. Types of water users concerned are those that are sensitive to water quality and more precisely that are sensitive to industrial micropollution, at least for one of their uses of water. Using the averting behaviour approach (Abdalla, 1994; Rinaudo et al., 2005), adaptation strategies that water users may undertake in case of groundwater quality improvement have been simulated.

The water supply strategy can be split into two parts (**Erreur ! Source du renvoi introuvable.**): (i) the water user's choice to be supplied by the public network, by its own or by both (the water user may purchase water from the public network only for some water uses that are sensitive to water quality) and (ii) the water supplier's choice (i.e. the water user itself or the public water company) to use the groundwater under study, other resources or both for water supply.

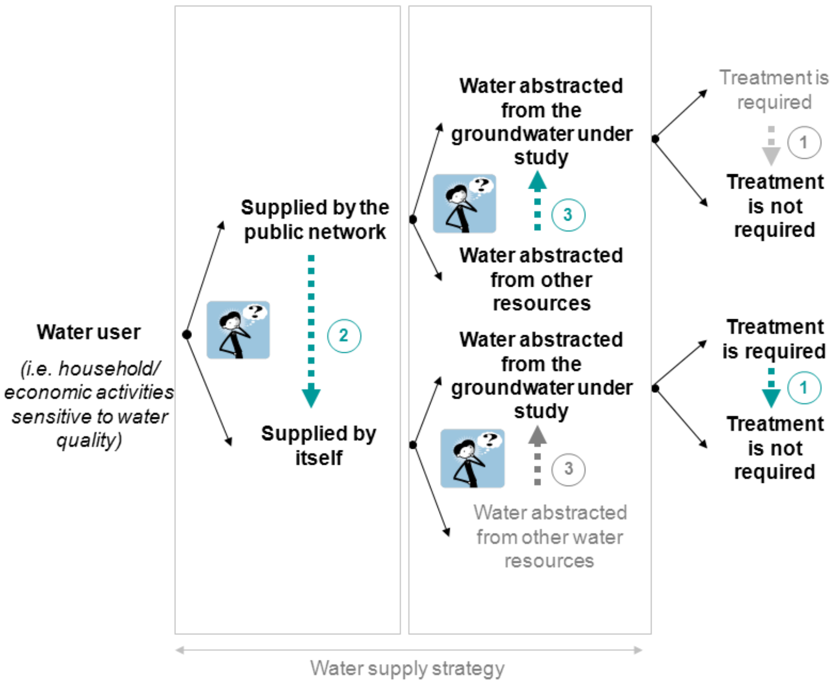

Figure 1. Water supply strategies and adaptation in case of groundwater quality improvement

Three main types of adaptations of the water supply strategies in case of groundwater quality improvement have been simulated and assessed (**Erreur ! Source du renvoi introuvable.**):

- **Water treatment may be reduced or abandoned (adaptation n°1).**
  In a situation where groundwater quality reaches good status, water treatment is expected to be abandoned thus resulting in an avoided cost i.e. in a potential benefit. The decrease in water treatment costs may positively impact water users that currently abstract water from the groundwater under study through private wells and that have to treat the water to comply with their quality requirements (due to industrial micropollution). Positive impacts are expected for these water users through a decrease in their water production costs. Positive impacts on the environment are expected through a decrease in water treatment discharges into the environment. Another possible indirect impact is the improvement of the image of products produced within the case study area and positive outcome on companies' results.
- **Water users currently supplied by the public network may be interested to turn to private groundwater supply (adaptation n°2).**
  If the groundwater quality is supposed to be significantly improved to reach WFD objectives, water users that were reluctant to use groundwater for quality or security reasons may change their water supply strategy to a private well supply if it is worth from an economical point of view. Positive impacts can be expected on economic activities through a decrease in cost of water supply for those who changed their strategy on the basis of financial arguments. This potential benefit may also be associated with negative impacts both on public water utilities management and on the groundwater resource. In fact, a decrease in the charged water volumes will result in an increase in the water price for public water consumers due to an increase in the unit public water production cost (fixed costs may be important) and to an increase in the sanitation charges (same waste water volumes to be treated but decrease in the charged water volumes). Moreover, an increase in private supply strategy may make it more difficult for district authorities to predict future water demand and to plan investments accordingly, with a risk to overestimate them (Montginoul *et al.*, 2005). High number of individual boreholes also represents a significant risk of pollution of aquifers as private tube wells are not always constructed according to standards and as boreholes may join up previously distinct layers (Montginoul *et al.*, 2005).
- **Water users with private wells may be interested to increase their use of the groundwater under study (adaptation n°3).**
  A change in the type of water resource used for water production may result in a benefit for water users if the cost to produce water from the groundwater under study is lower than from the water resources currently used. This effect is analysed only for public water producers. Positive impacts on water users

are expected through a decrease in water production costs. Direct impacts of a change of water supply strategy consist in the difference in the unit production costs between the water resources. Negative impact on water users are also expected through a decrease in the charged water volume from other water resources i.e. an increase in water production price.

b. Results and discussion

The understanding of the water supply strategies in place in the case study areas was made possible by the use of databases provided by the DGRNE and the CILE and by experts' consultation (representatives of drinking water sector and economic activities). Concerning the public water sector, data were gathered at the public water supply area (PWSA) scale.

Potential market benefits to be expected from an improvement of the RWM 073 groundwater quality to a 'good water status' may reach 3.3 to 4.4 million € per year from 2030 (Table 1).

When considering a low increase in RWM073 groundwater abstraction by the public water sector, the main benefit is expected to arise from the fact that non-domestic water users will probably turn from the public network supply to private supply (Effect 2: 60% of the total benefit), the remaining being related to the decrease in treatment costs for those who currently abstract water from the RWM073 groundwater (Effect 1: 20%) and to the increase in the use of this groundwater as a resource for public water production (Effect 3: 20%). When considering a higher increase in RWM073 groundwater abstraction by the public water sector, the main benefit is expected to arise from Effect 2 (44% of the total benefit) and from Effect 3 (41%).

As these benefits are expected to appear from 2030, discounting can be used to express these future benefits and compare them to the cost that would be required today to implement a programme of measures. The discounted benefit expected for year 2030 is estimated between 1.3 and 1.8 million € (Table 1 and Figure 2). The sum of discounted benefits on the 2008-2060 period is estimated between 23.8 and 32.4 million € (Table 1).

Benefits related to the effects 1 and 2 (19 million € on the 2008-2060 period) are expected to occur for the companies that currently use or may use the RWM073 as a resource i.e. located on the RWM073 aquifer. Benefits related to the effect 3 are expected to be redistributed to public water consumers at the sub-basin level through the water bill: from 19.4 to 26.4 million € for the domestic sector i.e. households (81%) and from 4.5 to 6.2 million € for the non-domestic sector (19%) on the 2008-2060 period.

	Annual benefits (M€/year, from 2030)			**Discounted**(2) annual benefit in 2030 (M€/year)	Sum of **discounted**(2) benefits (M€,
	Expected "direct	Expected "indirect	Expected annual benefit		

			impact” (1)	impact” (1)			2008-2060)
①	Decrease or abandonment of water treatment		0.7	n.a.	0.7	0.3	4.8
②	Turning from public network supply to private supply		2.1	-0.2	1.9	0.8	14.2
③	Increase in the use of RWM073 as a resource	Low increase	2.1	-1.4	0.7	0.2	4.7
		High increase	6.9	-5.2	1.8	0.7	13.4
① + ② + ③		Low	**4.9**	**-1.6**	**3.3**	**1.3**	**23.8**
		High	**9.7**	**-5.4**	**4.4**	**1.8**	**32.4**

(1) in reference to Figure 7

(2) discount rate r=4%

Table 1. Synthesis of expected benefits per effect

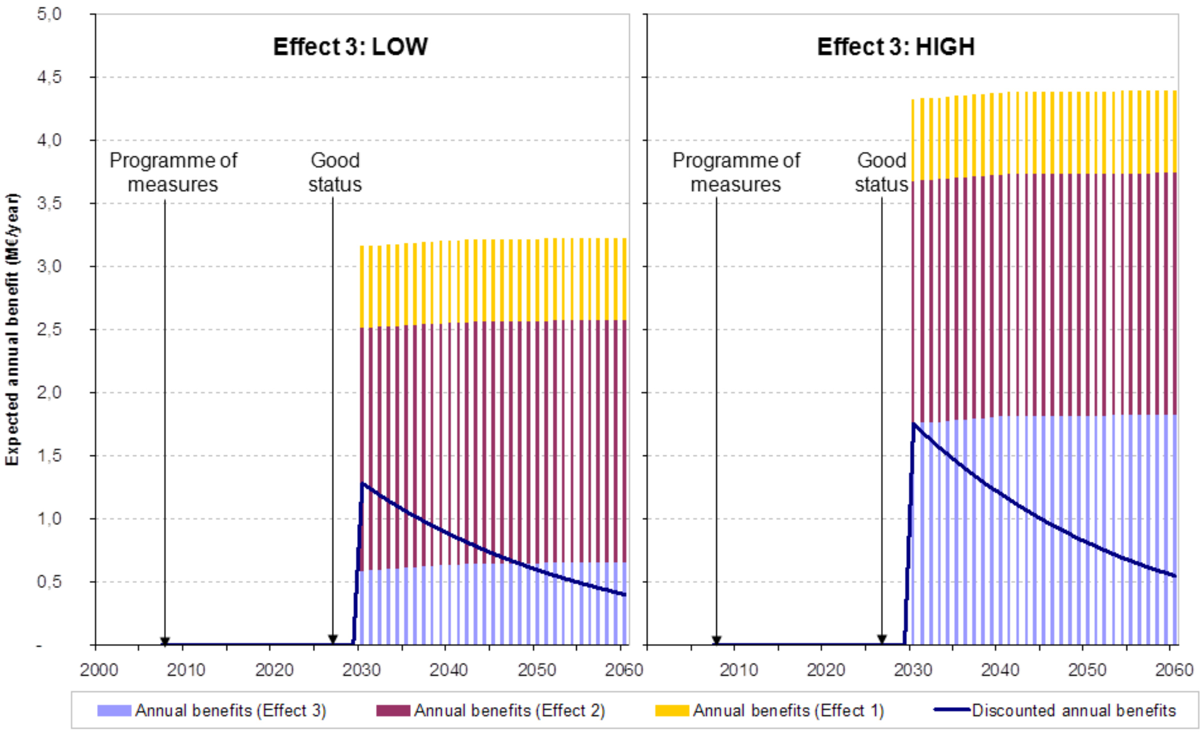

Figure 2. Expected annual benefits in case of RWM073 quality improvement

Potential economic impacts have not all be quantified, especially environmental impacts (e.g. decrease in water treatment discharges into the environment due to effect 1, increase in the risk of groundwater pollution due to effects 2 and 3). Further it is worth to mention that result and methodology adopted are dependent from important assumptions. For instance, it is very difficult to approach the individual reasons of companies for skipping from one supply to the other (namely from public water supply to private groundwater supply). Here the assumption was made that companies have a rational economical behaviour which is in fact not always the case, before all for a decision linked with security.

The framework developed in this report to assess potential market benefits related to direct use and option use values is applicable to other groundwater bodies that face similar quality degradation problems. The results of a similar assessment applied to an other groundwater body would however probably be totally different: results are strongly dependent from case study specifics. Indeed both the characteristics of the water resource (e.g. depth, capacity), the economic context (e.g. density of economic activities sensitive to water quality, population growth), and the structure of the drinking water supply (e.g. existence of alternative resources, type of infrastructure set to produce DW) have a strong influence of the market benefits expected from the improvement of the quality of a groundwater body.

2.1.2. Total economic value

a. Methodology

A contingent valuation was developed on the Meuse alluvial aquifer (between Engis and Herstal, namely the RWM073 groundwater body). This method consists in implementing a quantitative survey on the perception by the population of the Meuse alluvial plain. The aim is: (i) to characterise the knowledge and perception by the population of the groundwater body, its quality level, the relevance to improve its quality and (ii) to assess the value people would be willing to contribute to the improvement of the groundwater body quality.

The questionnaire is structured into four main sections, with a total of 33 questions:

- Section 1 presents the groundwater body under study. The information part consists in a short text describing the functioning of an alluvial aquifer and the location of the part under study of the Meuse alluvial aquifer. The text is completed by a scheme describing the functioning of an alluvial aquifer and two maps showing the geographic extent of the case study area. It is followed by a series of knowledge and perception questions. Respondents are asked if they live above the aquifer under study. A series of 25 maps (A4 paper) combining Google Earth views and aquifer boundaries are used for this purpose. A short text completed by a map also explains the origin of tap water city by city.
- Section 2 summarizes the groundwater quality problem today and in the future if no action is undertaken. A text explains that the groundwater quality is currently degraded by urban and industrial pollution. The issue of brownfields and polluting pressures they exert on groundwater is described. Impacts of groundwater pollution on the current uses of the resources are also discussed.

Respondents are asked about their knowledge about this situation and the likelihood level they attach to the description of the situation.

- Section 3 presents a scenario of groundwater quality improvement. Proposed measures and expected impacts on groundwater quality and groundwater uses are listed. Respondents are asked if they attach importance to the groundwater quality improvement and if they find the scenario realistic. They are then asked if (and how much) they would be willing to contribute financially for such a scenario through an increase of the water bill. Reasons of the choice provided by the respondent are then analysed.
- Section 4 deals with socio-economic characteristics of the respondents, with classical questions related to gender, age, employment, education, size of the household, income, but also questions related to the attachment to Liege, encountered environmental problems, quality of the information provided in the questionnaire and difficulty to answer to the WTP question.

The following scenario of groundwater quality improvement was proposed: “Given the urban and industrial activities currently located on the case study area, it is not realistic to believe that groundwater could retrieve its natural quality level. However it is possible to improve its quality. If acting today, groundwater quality improvement could be obtained by 15 years. The following measures are proposed: (a) eliminate all historic pollution sources that did not reach by now the groundwater body (e.g. by excavating polluted soils) and (b) clean up groundwater already contaminated by industrial pollutants (e.g. by pump and treat process)”.

Benefits expected by 15 years would be the following (Table 2):

Type of groundwater use	Current situation	Expected benefits
Current and future direct use	Groundwater use is to be avoided, especially in the vicinity of brownfields (including for gardening) with the exception of some industrial uses. No use for tap water production	Possibility to use groundwater for gardening also in the vicinity of brownfields
		Possibility to use groundwater in some specific areas to produce tap water for Liege if there were needs in the future
Non use	Groundwater quality will remain degraded for several decades	Possibility to transmit a groundwater body of better quality to future generations
Indirect use	Contribution to the degradation of the Meuse water quality	Improvement of the quality of water feeding the Meuse, improvement of flora and fauna living conditions

Table 2. Benefits expected from the improvement scenario by type of groundwater use

The questionnaire was tested from the 9^{th} to the 11^{th} June 2010 by three BRGM researchers. 56 face-to-face interviews were completed in the cities of Liège, Flémalle, Amay and Seraing.

The sampling area is composed of 11 communes located at least partly on the RWM073 groundwater body and those partly located on the RWM072 groundwater body at a maximum distance of 5 km upstream and downstream the groundwater body under study (Figure 3).

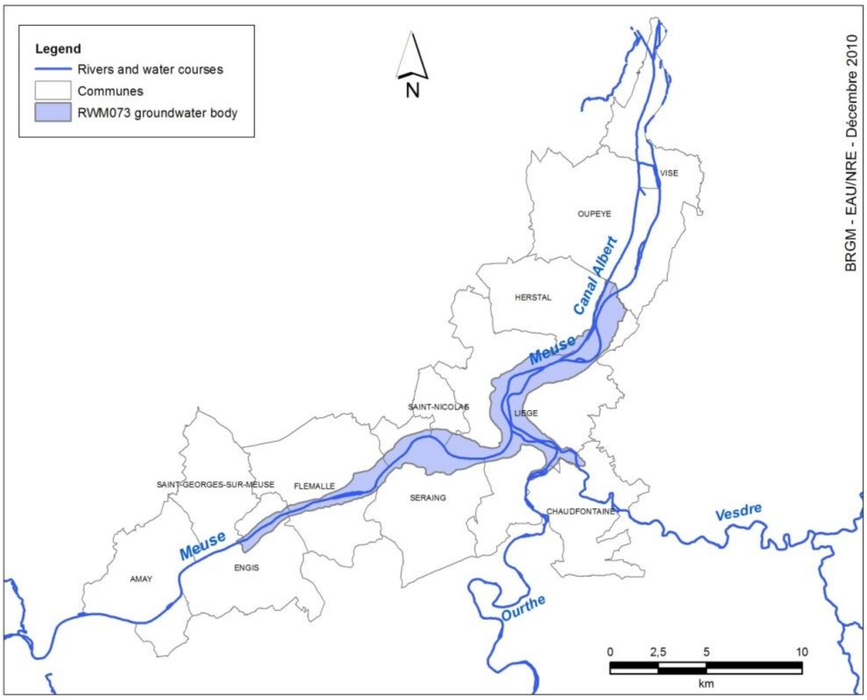

Figure 3. Sampling area and selected communes

A team of 6 students and 4 engineers/ researchers was constituted at the beginning of September. A half day training session was organised at the University of Liege the 9th September 2010. Quotas were defined by age and sex.

b. Results and discussion

The questionnaire was administered from the 13th to the 17th September 2010 in the communes of Liège, Engis, Amay, Visé, Oupeye, Herstal and Seraing. 531 face to face interviews were completed. Table 3 provides some general characteristics of this sample.

Characteristics	
Sample size	531
Age (mean)	47
Sex (% of men)	47
Employment (% employed)	34
Mean net income (€/household/month)	1900
Mean household size	2.3
% living above the RWM073 groundwater body	42
% depending from the RWM073 for tap water	0

% using water from a well in the RWM073	1.5

Table 3. General characteristics of respondents

As expected, the proportion of RWM 073 water users is very low (1.5%). Direct use values are thus expected to represent a small part of the value people attach to the improvement of the groundwater quality. However, 98% of the respondents consider it is important to improve the RWM073 groundwater quality and 66% would be willing to contribute financially to this improvement by an increase in their water bill (Figure 4).

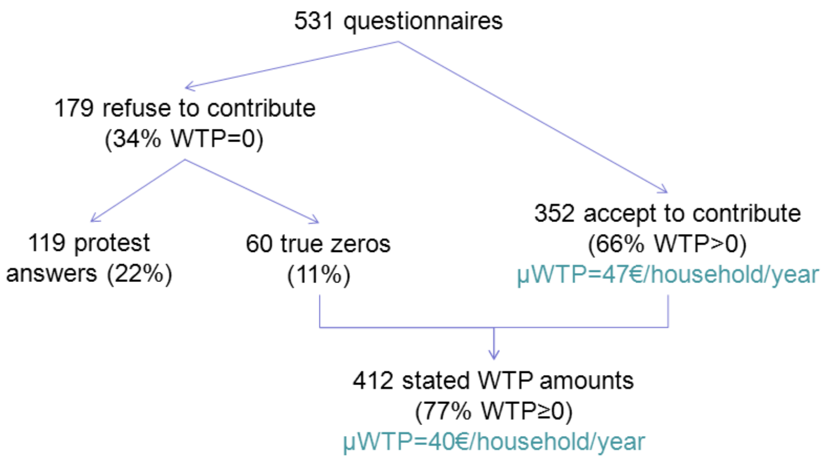

Figure 4. Proportion of different types of answers

The main motivation for paying is related to future generations and to the Meuse quality improvement (Table 4). 34% of the respondents refusing to pay are classified as “true zeros”: they attribute a zero value to the scenario because their income level is too low or they don’t feel concerned by the groundwater quality improvement (Table 5). The other respondents refusing to pay are classified as protest answers: they refused/ failed to reveal the value they attribute to the scenario. The most commonly cited reason for protest answer was that respondents felt they already paid enough tax, followed by the polluters should pay (Table 5).

Respondents motivation for paying	Motivation quoted (N=352)	Main motivation (N=349)
Possibility to transmit a groundwater body of better quality to future generations	284 (81%)	170 (49%)
Improvement of the quality of water feeding the Meuse, improvement of flora and fauna living conditions	270 (77%)	77 (22%)
Possibility to use groundwater in some specific areas to produce tap water for Liege if there were needs in the future	215 (61%)	78 (22%)
Possibility to use groundwater if you have or if you plan to have a well	73 (21%)	12 (3%)

Table 4. Motivations for paying

Respondents motivation for refusing to pay	Motivation quoted (N=179)
We already pay too many taxes	58 (32%)
My income level does not allow me to pay	51 (28%)
The polluter pays principle should apply	46 (26%)
Money should be better spent	20 (11%)
Other reasons (protest answers)	20 (11%)
I would accept to pay but not through an increase in the water bill	19 (11%)
I don't feel personally concerned, I don't expect any benefit from this scenario	12 (7%)
Lack of confidence	9 (5%)

Table 5. Motivations for refusing to pay

The average willingness to pay (WTP) is 46.9 €/household/year when only positive WTP are considered. The average WTP is 40.1 €/household/year when true zeros are included. The Figure 5. Mean positive WTP observed by former commune (old boundaries)Figure 5 depicted the geographical distribution of the mean positive WTP by former commune (old boundaries[1]).

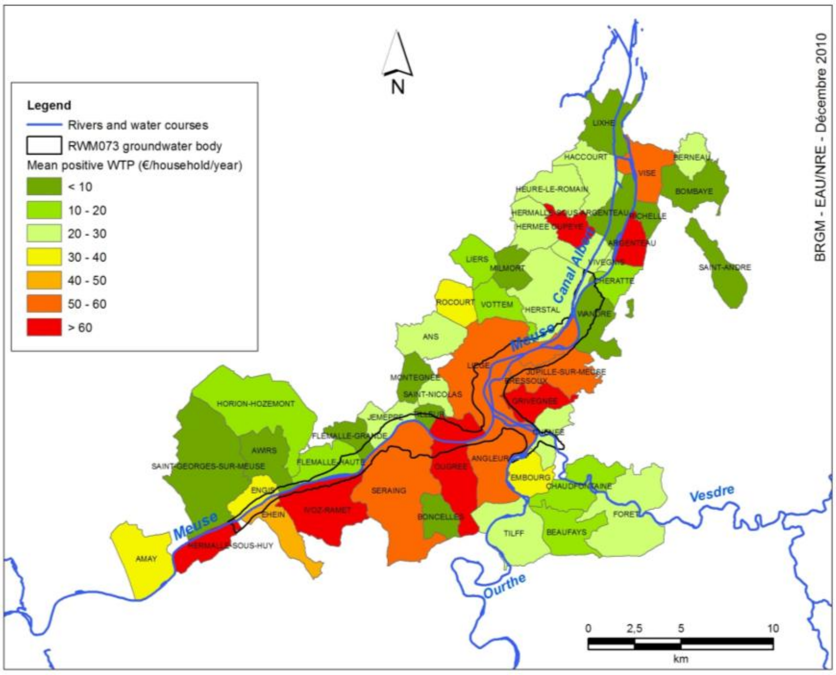

Figure 5. Mean positive WTP observed by former commune (old boundaries)

A multivariate analysis is currently carried out to identify the factors explaining the variations in the stated willingness to pay. The statistical analysis is split into two steps. We first model the decision to participate financially to the scenario with logistic regression. We then conduct a series of OLS regressions to identify the factors explaining the variations of the stated WTP amount.

[1] From 1961 to 1983 the number of Belgian communes has been reduced from 2663 to 589. In this report we use the term "former commune" to refer to a commune of 1961 and the term "commune" to refer to a commune of 1983.

First results of the logistic regression model show that location of the respondent, realism and importance levels attached to the scenario, perception of the risks related to groundwater quality degradation, types of groundwater use, exposition to environmental problems and socio-economic characteristics (gender, children, education, income) are significant factors explaining the decision to contribute to the scenario.

First results of the OLS regression models show that location of the respondent, perception of the risks related to groundwater quality degradation, number of benefits attached to the scenario, main types of benefits attached to the scenario, exposition to environmental problems, socio-economic characteristics (gender, children, education, income) and difficulty to answer to the WTP question are significant factors explaining the variations in the stated WTP amount.

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