Surface and ground water interaction processes inside the Eau Blanche river basin (Dinant synclinorium – Belgium)

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ABSTRACT. Gauging river flows, measurement of in-situ parameters (such as electrical conductivity, pH and temperature) and major ions analysis were used to examine, at 8 selected sections, the groundwater inflow to the Eau Blanche River during a base flow recession period. Comparison of specific inflows between each section has permitted to identify positive and negative deviations, which were used to identify underground water inflows or outflows. Major ion analyses showed a clear evolution of river water chemical composition that could be related to the increasing amount of limestone aquifers composing the drainage area of the river. A simple two component mixing model confirmed the major influence of the limestone aquifer on the river chemistry; additional (probably anthropogenic) inputs of nitrates and chlorides were located.

KEYWORDS: Eau Blanche, river discharge, specific inflow, solute inflow, water mixing model.

1. Introduction

In 2005, the Walloon government initiated the "Synclin'Eau" research project. This project falls within the scope of the European Water Framework Directive 2000/60/CE. Its main purpose consists in characterizing groundwater bodies in the Walloon Region of Belgium. Within this context, interactions between rivers and groundwater resources were studied (Brouyere & al., 2009). Studying these interactions is important for determining sustainable limits of groundwater extraction and to guarantee the minimum base flow that allows preservation of river biodiversity. Different approaches have been used. One of them consisted in measuring flow and hydrochemical parameters at different sections of the river during a recession period. Application of this method on a mid-sized Walloon river (the Eau Blanche) and the results are presented in this paper.

2. Study area

The Eau Blanche River, located in the south-western area of Belgium, drains an area of 257 km². The Eau Noire and the Eau Blanche Rivers are the principal tributaries of the Viroin River (Fig. 1). The studied section of the Eau Blanche River is 35.8 km in length, and extends from its spring in Seloignes until the junction of the Eau Noire River at Nismes. Within the studied section, several karstic springs occur as discrete seepage points from the limestone aquifers to the river (Thys & Michel, 2009).

Geologically speaking, the Viroin basin is located on the southern flank of the Dinant Synclinorium. Its catchment area, entirely composed of Palaeozoic fractured sedimentary rocks, shows a general west-east bedding direction with a dip of 30° oriented to the north. Locally, Z folded geological structures are observed. Early and Late-Devonian terrigenous



Figure 1. Hydrogeological map of the Eau Blanche catchment and tributaries

Station	EB1 Seloignes	EB2 Villers-la-Tour	EB3 Saint-Remy	EB4 Chimay amont	EB5 Chimay aval	EB6 Virelles	EB7 Aublain
Sampling date	8/05/2008	8/05/2008	8/05/2008	8/05/2008	9/05/2008	9/05/2008	9/05/2008
Distance from spring (km)	4,1	7,1	8,8	10,8	11,2	13,8	21,5
Q (m³/s)	0,047	0,099	0,114	0,28	0,443	0,568	1,1
pH in-situ (13/05/2008)	7,12	7,16	7,72	7,59	7,62	8,12	7,93
T° in-situ (13/05/2008)	16,2	14,1	14,2	13,2	13,1	13,5	13,6
Conduct. in-situ (13/05/2008)	133	175	255	483	480	535	552
рН	6,9	7,4	7,7	7,8	7,8	8,0	7,9
Conduct. 25°(µS/cm).	108	143	211	407	423	471	474
Total hardness (°fr)	3,9	5,8	9,5	20,4	21,4	22,5	25,1
TDS (mg/l)	70,9	101,49	158,44	341,46	362,05	390,89	415,98
Ca++ (mg/l)	11,41	18,18	32,71	73,24	72,56	90,17	87,47
Mg++ (mg/l)	2,43	2,95	3,38	5,28	7,92	9,30	8,05
Na+ (mg/l)	5,25	4,72	5,10	5,99	6,23	7,44	8,46
K+ (mg/l)	1,65	1,89	1,74	1,78	1,92	2,01	1,98
Fe+++ sol.(mg/l)	0,10	0,06	0,05	0,03	0,03	0,03	0,03
Fer total (mg/l)	0,29	0,23	0,17	0,10	0,12	0,09	0,08
Mn++ sol. (mg/l)	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005
Mn++total (mg/l)	0,06	0,06	0,05	0,03	0,03	0,02	0,02
NH4+ (mg/l)	< 0.100	< 0.100	< 0.100	< 0.100	< 0.100	< 0.100	< 0.100
Cl ⁻ (mg/l)	7,11	7,54	7,77	11,45	11,02	13,52	15,35
SO4 (mg/l)	9,57	10,86	13,30	19,25	18,91	21,31	22,53
NO2 ⁻ (mg/l)	< 0.200	< 0.200	< 0.200	< 0.200	< 0.200	< 0.200	< 0.200
NO3 ⁻ (mg/l)	5,54	6,60	7,00	15,26	15,20	16,52	14,50
F ⁻ (mg/l)	< 0.200	< 0.200	< 0.200	< 0.200	< 0.200	< 0.200	< 0.200
H2PO4 ⁻ (mg/l)	1,01	1,20	1,11	1,40	1,18	1,41	1,41
CO3 (mg/l)	0,01	0,07	0,26	0,67	0,84	1,17	1,00
HCO3 ⁻ (mg/l)	26,83	47,43	86,02	207,10	226,25	228,01	255,20
CO2 (mg/l)	2,20	1,30	1,10	2,50	2,30	1,70	2,50
SiO2 (mg/l)	4,00	2,88	2,24	3,21	3,66	2,96	1,65

Table 1. Variation of the water chemical composition along the Eau Blanche River talweg.

deposits (essentially shales, sandstones and quartzites) compose, respectively, the southern and northern part of the catchment (Barchy & Marion, 1999; 2001). These are transversely separated by important Mid-Devonian limestone formations (also interrupted by smaller Eifelian detritic episodes). Generally, soils are less than 1.25 m thick, clayey in the north, loamy in the center and loamy with pebble loading in the south (Remy, 1990).

From a hydrogeological point of view, the principal geological formations are defined into aquifer, aquitard or aquiclude units in function of their hydraulic conductivity (Dossin et al., 2006). These units are represented in Fig. 1. Givetian and Eifelian limestones represent the major aquifers and cover 15% of the studied area. Because of their low permeability, all the detritic formations (Early and Late Devonian formations) are grouped within aquiclude or aquitard units.

The investigated area is occupied by rural settlements and the majority of land is used for pasture, forest and, to a lesser extent, crop fields. Water chemical analysis, operated on numerous wells in the area, shown concentration values that were lower than the WHO norms for the groundwater (Dossin et al., 2006). However, anthropogenic influences on groundwater chemistry are locally detected as shown by anthropogenic nitrate concentrations (concentration values higher than 40 mg/l).

3. Methods of investigation

3.1. Hydrology

To investigate groundwater-surface water interactions, flow measurements have been carried out on six different river gauging stations with a portable electro-magnetic flowmeter (FLOW-mate MODEL 2000). Two limnigraphs, owned by the Public Service of Wallonia, are located at Aublain (site 7) and Nismes (site 8) providing continuous measurement of the river discharge.

3.2. Sample collection

Sampling and gauging were performed during the 8th and the 9th of May 2008 during a long groundwater recession period (Fig. 2). For this particular period, the baseflow is assumed to be exclusively due to groundwater discharge. Conductivity, pH and temperature were recorded in situ during the sampling. Unlike discharge, physic-chemical parameters are strongly subject to daily fluctuations. Consequently a second campaign is performed on the 13th of May during which these parameters, at all stations, are surveyed in a short time lapse (2 hours).



Figure 2. Daily rainfall and hydrograph for the Eau Blanche River (Aublain and Nismes gauging stations).



Figure 3. Hydrogeological profile and longitudinal changes in the baseflow discharges of the Eau Blanche

3.3. Hydrochemistry analysis

Samples for chemical analysis were collected at each gauging station (except in Nismes), on which major ionic species were analysed by the ArGEnCo Department of the University of Liege (Belgium). Major cations (Na⁺, K⁺, Ca²⁺ and Mg²⁺) and dissolved silica were analysed by flame atomic absorption spectrometry, while nitrogen species (NO₃⁻, NH₄⁺) and chloride were determined by potentiometric titration. Alkalinity was determined using the gram titrimetric method, from which individual carbonate species (CO₃⁻²⁻, HCO₃⁻ and dissolved CO₂) were calculated using the equilibrium formulas proposed by Rodier (1996). Analysis of Mn and Fe were performed by colorimetry using o-phenantroline. Orthophosphate was determined by the colorimetric heteropoly blue method.

The charge balance error (CBE), i.e. the fractional difference between total cations and total anions based on the major dissolved ions, was calculated for each sample. All CBE values were in the range of less than 5% and therefore, considered as satisfactory. Only sample $n^{\circ} 1$ (see Table 1) had a small, but significant excess of cations (10%), which might be related to additional negative species that were not quantified or to analytical error.

The chemical characteristics of Station 8, which is

located downstream the confluence between the "Eau Blanche", the "Eau Noire" and the Brouffe Rivers will not be considered in this paper.



Figure 4. Specific inflow (Is) measured for each river segments.



Figure 5. Hypothetical groundwater transfers between catchment 3 and 4.



Figure 6. Longitudinal changes in pH, T and electrical conductivity of the Eau Blanche River (pH, T and EC measured the 13th May 2008).





4. Results & discussion

4.1 Flow rate and in-situ parameters measurements

River discharges and general parameters measured at different gauging station are presented in Fig. 3. Measured discharges vary from 0.05 m³/s to 1.1 m³/s. In general, flow increases significantly downstream from site to site, confirming the gaining character of the river. At the junction of the Eau Blanche with the Bardompré

river (between stations 4 and 5), discharge increases dramatically from 0.28 $m^3\!/s$ to 0.44 $m^3\!/s.$

Specific inflow (I_s) has been calculated at each considered segment. It is calculated by subtracting the upstream from the downstream discharges, normalized by the drainage area of the considered segment (the segment number identifies the segment located upstream the gauging station number). The average water input is 0.01 m³/s/km². The figure 4 clearly shows that segments 3 and 4 are the two main outliers : they show,



Figure 8. Piper triangular diagram of water analysis of the Eau Blanche River.

This leads us to think that a certain amount of groundwater bypasses segment n° 3 to flow to and to recharge the next river segment. For the northern part of catchment 3, these transfers would most probably occur in the Givetian limestone formations as indicated on Fig. 5. If we assume that the bordering Eifelian shales, located at the south, act as an impermeable hydrogeologic limit, the groundwater fluxes, that flow though the Givetian aquifer parallel to the stratification, intersect the riverbed just upstream of station 4. At the south of catchment 3, complementary groundwater losses could also occur through the Eifelian limestone in the direction of a regional main karstic spring located in the eastern neighbouring catchment.

From upstream to downstream, all physico-chemical parameters show significant variations (Fig. 6). Electrical conductivities (EC) and pH both increase downwards, indicating the progressive changes of the surface water chemistry. The largest increase in EC is observed between stations 3 and 4, passing from 255 to 483 μ S/cm in just 2 km distance. The pH-profile varies between 7.1 and 8.1 and shows two remarkable jumps at stations 3 and 6. These two parameters are highly influenced by the nature of the rocks composing the drainage area of each river segment (also confirmed in 4.2). The EC increasing at stations 3 and 4 suggests a strongly mineralised input, coming respectively from the Eifelian and Givetian limestones.

River temperature decreases significantly, and reaches a minimum $(13.1C^{\circ})$ at the stations 4 and 5. As station 5 is located downstream of the Bardompré stream confluence, the low temperature of the surface water indicates that the river is mainly fed by groundwater. Decreasing temperatures are clearly related to the amount of groundwater discharging to the river from the Givetian limestone.

So, a simple analysis of specific inflows at different sections of a river allows to identify surface and groundwater interactions. This kind of investigations should be more systematic as they seem to provide a great deal of information considering the little time invested to acquire the data (in our case, only two days). In-situ physico-chemical parameters such as EC, pH, T° are good information sources that could be used to provide a better interpretation and argumentation to locate and assess groundwater inflows to the surface water. By choosing more gauging stations, other groundwater-surface interaction should be identifiable.

Water chemical composition of the river at different sampling sites is presented in Table 1.

As indicated by the in-situ EC-profile (Fig. 6), total dissolved solids (TDS) increases significantly downstream, ranging from 71 mg/l at sampling site 1 to 415 mg/l at sampling site 7. The largest variations are observed for bicarbonate, calcium, iron and magnesium (Fig. 7). Iron occurs as the only element decreasing significantly downstream.

The representation of cation and anion distribution in a Piper triangular diagram (Fig. 8) shows the water is classified as a Ca-HCO3 type. For all samples, Ca and HCO3 represent respectively 50% and 85% of the total cationic and anionic charge.

From stations 1 to 4, an increased mineralization and a constant enrichment in calcium are observed, which can clearly be attributed to the increasing relative presence of Eifelian and, further downstream, Givetian limestone in the concerned subcatchments. Ca/Mg ratio increases also, raising from 4.7 to 13.9. At station 5, the Ca/Mg ratio falls to 9.2. This significant decrease can only be attributed to the mixing of the Eau Blanche with the Bardompré tributary. The surface water of this tributary is less mineralized due to a limited outcrop of limestone in the basin. At station 6 and 7, ionic proportions stabilise, but mineralization continues to grow with TDS increasing from 362 mg/l to 416 mg/l.

4.2 Mass balance calculations

As indicated above, water of the Eau Blanche River is of the calcium-bicarbonate type. But concentrations of the major ions $(Ca^{2-} and HCO_3^{-})$ vary considerably along the river flowpath, reflecting the different chemical types of groundwater inputs. To highlight the influence of lithology on river chemistry, we determined the solute inflow to the river by using a simple "chemical mixing model". This approach has already been widely used by a number of authors (Genereux and Pringle, 1997; Cook et al., 2003) to quantify rates of groundwater inflow, but rarely for correlating bedrock lithology and variability of baseflow chemistry.

The "chemical mixing model" can be expressed as follows (Ellins et al., 1990) :

$$C_{i} = \frac{C_{2} - C_{1}}{I(x_{2} - x_{1})}Q_{2} + C_{1}$$

where *I* is the groundwater inflow rate per unit of stream length $(m^3/s/m)$, $Q_2(m^3/s)$ is the flow rate of the river downstream of the groundwater inflow (at x_2 in m), $C_1(mg/l)$ is the concentration of





the solute in streamflow at an upstream point x_1 (m), C₂ (mg/l) is the concentration of the solute downstream (at x_2), C₁ is the concentration of the solute inflow at the considered segment (between x_1 and x_2).

In figure 9, the calculated C_i are plotted and compared to the relative proportion of limestone aquifer composing each catchment corresponding to the specific segment of the river. Results are presented for calcium, sulphate, nitrate and chloride. These ions all present significant variations (Table 1) and they are supposed to behave conservatively in the considered mixing process.

The best correlation is found for calcium ($R^2=0.931$), showing clearly the close interactions existing between river and aquifer during baseflow conditions. Calculated solute inflow varies from less than 10 mg/l in the segments where the bedrock consists in shales and sandstones (stations 1 and 2) to more than 110 mg/l (stations 3 and 6), where limestone bedrock is dominant. Those values correspond roughly to normal Ca²⁺ concentrations measured in most wells located in Givetian or Eifelian formations (Dossin et al, 2006).

Concentrations of nitrates and chloride increase downwards the river (Fig. 9). The two component mixing equation allows us to localise the maximal inputs. Both species show very similar patterns, with minimum C_i at station 1 and maximal C_i reached at station 4 and 6 (respectively, 20.9 mg/l and 21.2 mg/l for nitrates and 14 mg/l and 22.4 mg/l for chlorides). Even if drinking water norms are not exceeded, calculated concentrations in chloride and nitrate are significantly above the average natural composition of European rivers (Meybeck, 1979; 1982), showing alteration of the river water chemistry due to human activities. The peaks observed for both species at station 6 can clearly be attributed to the mixing of river water with urban wastewater from Chimay (see Fig. 1). At station 4, the origin of the observed peak concentrations is less evident, but the pollution is most probably coming from contaminated groundwater flowing from the Givetian limestone aquifer, as we assume that the biggest inflow on this segment is provided by this aquifer (cf. 4.1). There is no groundwater hydrochemical analysis performed in this particular zone that could confirm this.

Solute inflow calculated for sulphate presents variations between 10 mg/l and 30 mg/l, with maximal values reached at stations 3 and 6, where limestone aquifers are most present. This range of values corresponds roughly to normal sulphate concentrations measured in most wells located in the Givetian or Eifelian formations (Dossin et al, 2006). Like calcium, a clear relationship (R²=0.839) is found between concentrations of solute inflow and the amount of limestone formations that crop out in the segments catchments. But unlike nitrate and chloride, deciding whether the principal source is natural or anthropogenic is less evident. Peak concentrations observed at station 3 are not coincident to the peaks of nitrate and chloride observed at station 4. For this reason, we can suppose a different source for sulphate than nitrate and chloride at this particular station. In the studied zone, the most probable natural source of sulphates in limestone is pyrite, whose presence in Eifelian and Givetian carbonates is reported by Preat & Mamet (1989; 2006).

5. Conclusions

The results presented in this paper demonstrate the value of simple hydrophysical and hydrochemical properties of a river at different sections during a baseflow recession period.

Initially, flow measurements coupled to simple water quality indicators (pH and electrical conductivity) provided interesting information about the hydrogeological functioning of the catchment. Theoretical groundwater fluxes have been suggested, but long term monitoring should be carried out to confirm this.

Subsequently, basic major ion analysis confirmed the dominating influence of limestone aquifers on the surface water chemistry. A close correlation was found between certain major species (Ca and SO_4) and the proportion of aquifer limestone formations composing the catchments. The simple mass balance approach permitted the localization of the highest inputs of nitrate and chloride to the river. Going deeper into this kind of study

would involve more specific geochemistry, including isotope analysis, and synchronized sampling of surrounding wells and springs.

6. Acknowledgements

The authors want to thank the Public Service of Wallonia who funded the "Synclin'EAU" project during which the presented investigations were conducted.

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Manuscript received 26.04.2011 ; accepted in revised form 22.11.2011 ; available on line 15.02.2012