Selenium mobility in a major Chalk aquifer (Lille metropolis, northern France): contaminants cycles driven by geology, redox processes and pumping

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Abstract

Chalk groundwater in northern France presents selenium (Se) concentrations from <10 to 70 µg L⁻¹, partly exceeding the latest European Framework Directive's drinking-water limit value of 20 µg L⁻¹. Better to understand the heterogeneous dynamics of Se, we used a combination of geochemical, isotopic and geophysical tools on a study site belonging to the Metropolis of Lille, France. This approach provided a fine understanding of the Se fate in a dynamic redox system constrained by geology, related redox processes and pumping, illustrating how local *versus* global controls affect the Se cycling. A remarkable redox sequence controls element transfers in groundwater with a progressive creation of reductive conditions. Highlighted by geophysical tools, a wide fracture corridor in the Chalk formation disrupts the geological setting of this redox sequence. Under pumping, this corridor allows the mixing of oxygenated groundwater with groundwater under reducing conditions. The evolution of isotopic compositions of sulphate molecules confirms the global reduction trend of sulphates, while pyrite oxidation occurs very locally, together with high Se concentrations. Pyrite is expected to play a predominant role in Se mobility in the Chalk aquifer. Se and other redox sensitive elements (Fe, Mn, N and S) undergo multiple redox cycles, resulting in a Se-rich redox front that migrates downward over time within the water-level fluctuation zone of the porous Chalk. With the decreasing trend of water levels caused by global changes, a Se stock could be immobilized in the unsaturated zone, but nitrate content and redox conditions in the saturated zone will be major drivers for Se mobility.

1. Introduction

Selenium (Se)—a non-metallic element of nutritional and toxicological importance—has been intensively studied in terms of biological effects and environmental concern, notably because

of its Janus-faced properties (toxicity vs. antioxidant, mutagenic vs. anti-mutagenic) that are highly dependent on its concentration and speciation (Brozmanová et al., 2010; Rayman, 2000; Vinceti et al., 2013). Se mobility, toxicity, bioavailability and bioaccumulation are linked to its speciation, and are controlled by sorption and redox reactions (Sharma et al., 2014). Se occurs in various oxidation states (VI, IV, 0, -II), as inorganic species and as organo-Se complexes. The most common Se species within surface water, groundwater and soil are selenate (Se(VI), SeO_4^{2-}) and selenite (Se(IV), SeO_3^{2-}) oxyanions that are highly soluble, though Se(IV) adsorbs to solids more strongly at neutral pH (Neal and Sposito, 1989). SeO_4^{2-} with the highest oxidation state can be chemically reduced to SeO_3 , which can be further reduced to elemental Se(0) or selenomethionine (SeMet) that may then be volatilized as dimethyl selenium (DMSe). Selenium intake through drinking water occurs mainly in its inorganic form that is generally more toxic than organic compounds, Se(VI) being the most toxic species (Tugarova et al., 2013).

Excess Se levels in agricultural soil or within subsurface agricultural drainage- and ground-waters have caused severe health problems in animals and humans, e.g. in the United States (Ohlendorf and Santolo, 1994), China (Yang et al., 1983) or India (Bajaj et al., 2011; Dhillon and Dhillon, 1991)... Se occurs naturally as a trace element in geologic formations, mainly shale, e.g., (Kulp and Pratt, 2004; Mast et al., 2014; Parnell et al., 2016; Stillings and Amacher, 2010; Tuttle et al., 2014), conglomerates (Dhillon and Dhillon, 2014), coal (Liu et al., 2013) and sediments (Beisner et al., 2009; Cary et al., 2014; Masscheleyn et al., 1991).

The general increase in water demand, and the change in amounts and periods of natural recharge in the current times of global climate change, modify groundwater levels and saturation conditions of Earth's critical zone and thereby the biogeochemical cycle of chemicals like Se (Mitchell et al., 2012). The result is the risk of delivering water that does not comply with drinking water standards. For the purpose of health control, the recent version of the European Water Framework Directive WFD (2020/2184) has increased the Se threshold value for human consumption to $20 \mu\text{g L}^{-1}$, compared to $10 \mu\text{g L}^{-1}$ in the initial WFD

(2000/60/EC). An increase up to $30 \mu\text{g L}^{-1}$ can be accepted if a natural origin of Se is shown, although a reassessment of a safe upper limit of Se of $1 \mu\text{g L}^{-1}$ in drinking water is recommended as toxic effects of Se species occur at low concentrations (Barron et al., 2009; Vinceti et al., 2013).

Redox processes in groundwater are complex because they are linked to kinetics and to a microbially activated network of reactions ; contaminant fate in redox-dynamic systems thus needs specific studies (Borch et al., 2010). Selenium oxyanions can be microbially reduced via dissimilatory reduction processes mainly to insoluble elemental Se(0) (Oremland et al., 1989), which can be further reduced to selenide, Se(-II) (Fernández-Martínez and Charlet, 2009; Herbel et al., 2003; Séby et al., 1997). Under reducing conditions, Se(0) and Se(-II) become the dominant species (Zhang and Moore, 1996). Microorganisms can also produce volatile Se-methyl forms and Se-II organic compounds (Chasteen and Bentley, 2003).

Bacterial respiration will transfer electrons from an energy source (organic matter or minerals such as FeS_2), termed electron donor, to oxygenated species or electron acceptors like dissolved dioxygen (O_2), nitrate (NO_3^-), or selenate Se(VI), Mn(IV), Fe(III), and sulphate (SO_4^{2-}) (Bailey, 2016). In groundwater, the chemical reduction of SeO_4^{2-} to SeO_3^{2-} occurs after reduction of O_2 and NO_3^- . Abiotic redox reactions also play an important role in Se cycling (Breynaert et al., 2008). A variety of Fe(II)-bearing minerals can enhance abiotical Se(IV) or Se(VI) reduction to Se(0), such as green rust, pyrite or mackinawite (Breynaert et al., 2008; Kang et al., 2011; Schellenger and Larese-Casanova, 2013). However, little is known about the Se oxidation. Under aerobic conditions, microbial oxidation promote both Se volatilization, retention (Darcheville et al., 2008) and production of Se(VI) from Se(0) (Dowdle and Oremland, 1998). The oxidation of Se-bearing pyrite by O_2 or NO_3 releases Se(VI) into groundwater (Stillings and Amacher, 2010). Finally, Se(IV) sorbe more than Se(VI) onto organic matter, clay, iron oxides and iron sulphides (Coppin et al., 2009; Goldberg et al., 2007).

Earlier, we studied the spatial disparities in Sr isotopic signatures, and Sr and Se contents in the Chalk aquifer along the northern edge of the Paris Basin (France) to successfully identify Se origins in the aquifer (Cary et al., 2014). The present study focuses on the redox processes affecting Se dynamics in the same Chalk aquifer. Because the large-scale evolution of surficial systems can be controlled by very localized biogeochemical processes, we propose a multi-scale and interdisciplinary characterization, from bedrock to aquifer. Geophysical imaging and solid analysis documented the spatial geological heterogeneities. The processes affecting groundwater chemistry were assessed along with monitoring of the wells, and the analysis of $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ of sulphate. This approach led to a fine understanding of the Se cycle, constrained by the geology of the Chalk aquifer of Northern France and by related redox processes as well as by pumping, illustrating how it is controlled either by both local and global constraints.

2. Geological and hydrogeological context

The north of France is part of the northern margin of the Paris Basin, one of the main geological units of Western Europe. Local outcrops range from Late Cretaceous to the Quaternary (*Figure Fig. 1*). The "Dièves" clayey marls of Early and Middle Turonian age are up to 70 m thick. The overlying Senonian-Turonian white Chalk is up to 70 m thick. Above, local Tertiary deposits are composed of Louvil clays (Early Thanetian; 9-12 m thick), the Ostricourt sands (Late Thanetian; >30 m thick locally) and the Orchies or Flandres clays (Early Ypresian; 10-15 m thick). The Quaternary silt covers all Meso-Cenozoic formations. In the Deûle valley, the modern alluvial deposits are sand, clay and clayey sand, and locally peat layers and gravel beds. The alluvium is 2 to 5 m thick in the study region. With the "Dièves" as the impermeable base, the upper part of the white Chalk corresponds to the aquifer exploited in the wellfields in the south of Lille Metropolis. Groundwater flows in the Chalk aquifer through a network of faults and open fissures that is well developed at 10-20 m depth, and where the main water inflow occurs (Walaszek et al., 2021). From 1981 to 2010,

the average annual rainfall was 742 mm with an effective rainfall of 186 mm (25%), the main recharge area being close to Emmerin.

About 30% of the drinking and tap waters for Lille Metropolis is pumped from four main well fields tapping the Chalk aquifer southwest of Lille: Emmerin, Houplin-Ancoisne, Les Ansereuilles and Seclin (Fig. 1). The Emmerin and Houplin-Ancoisne well fields will be referenced hereafter as E-HA, but here we mainly focus on the Les Ansereuilles well field with 26 pumping wells, which is parallel to the Deûle canal. The groundwater, which is unconfined southwest of the Deûle, flows northwest to become confined under the alluvial cover. The A10-A15 well area (Fig. 1) evolves towards local confinement due to the presence of more than 10 m of Tertiary Louvil clays over the Chalk (Cary et al., 2014).

The water levels in the study area vary according to pumping and recharge (Fig. 2). The main water direction flows from NE to SW (well A15 to A10). However, there may be, very locally, another flow direction from well A13 towards well A15 as already observed in a hydrodynamic model based on extraction volumes (Bessière et al., 2015) due to high exploitation rates in well A15. The flow in the fractured corridor between A12 and A13 is unknown.

Figure 1: Study site and cross section (RP11) in the well fields of southern Lille. The colour of the pumping wells indicates the maximum concentration of selenium in groundwaters from 2013 to 2017. The piezometric map presents simulated levels with the hydrogeological model.

3. Material and methods

3.1 Solids analysis

Solids were sampled in the Templeuve quarry near the study site and also in a borehole close to well A13. The samples were ground and dissolved chemically (aqua regia + HF), and the concentrations were analysed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) at BRGM. An extraction sequence with chemicals was used for determining the Se content in pyrite and the degree of pyritization of Se, based on the work of (Huerta-Diaz and Morse, 1990): 2.5 g of sediment was placed in contact with a 1M HCl solution to extract the so-called reactive fraction for 24 hours at room temperature. Though this reactive fraction is

generally accepted by the scientific community for divalent metals, it is, however, only indirectly admitted for Se (Peters et al., 1997; Sharma et al., 2014).

After centrifugation, the supernatant was recovered for iron and selenium analyses and the solid was again washed with a 10M HF solution at room temperature for 24 hours. This washing step was proposed by Huerta-Diaz and Morse (1990) in order to remove elements that are associated to silicates and alumino-silicates before pyrite extraction. Indeed, concentrated nitric acid used to dissolve pyrite may also result in partial extraction of some elements from silicate phases. It is worth noted that this step is not considered here as a specific extraction and the recovery solution was therefore not analysed. The solid recovered was rinsed with Milli-Q water and finally put in contact with concentrated HNO₃ for 2 hours at room temperature. During this step, the pyrite was solubilized and the selenium extracted. Fe and S were then determined by ICP-AES (Agilent, model 5110 VDV) to quantify the pyrite content and to check that the Fe/S molar ratio was 0.5. Se was determined by ICP-MS (Agilent, model 7900) using a collision-reaction chamber under hydrogen flow and by targeting the ⁷⁸Se isotope. From these extractions, it was possible to calculate the degree of pyritization (DOP, Equation 1) and the degree of trace selenium pyritization (DTSeP, Equation 2) as follows (Huerta-Diaz and Morse, 1990):

$$DOP = [Fe]_{pyrite} / ([Fe]_{pyrite} + [Fe]_{HCl}) \text{ (Eq. 1)}$$

$$DTSeP = [Se]_{pyrite} / ([Se]_{pyrite} + [Se]_{HCl}) \text{ (Eq. 2)}$$

3.2 Water analyses

The initial sampling and analysis work (June 2011 to March 2013) concerned 20 wells as described in Cary et al. (2014). Although a complete chemistry analysis was conducted, only selected data are presented here. Measurements of the physical and chemical parameters (temperature, conductivity, pH, Eh (Pt/Ag AgCl), and dissolved oxygen) were made *in situ*. The groundwater samples were then filtered in the field at 0.45 µm. In the sample sets, the S and Se speciation were determined, with concentrations of total S, S₂O₃, S²⁻, SO₃, total Se,

Se(VI) and Se(IV) being measured by HPLC-ICP-MS after separation. Dissolved Fe(II) was analysed in the field by colorimetry. Dosage of total organic carbon (TOC) and dissolved organic carbon (DOC) was carried out on the raw solution after oxidation with sodium persulphate in a hot acid medium. The $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ of the sulphate were analysed on raw water. The $\delta^{34}\text{S}$ of sulphates was measured from SO_2 obtained from CdS precipitate after SO_4 reduction with addition of cadmium acetate. S and O isotopic compositions were determined on SO_4 using a Delta S mass spectrometer (Thermo Finnigan) with a precision of 0.3‰. Isotopic compositions use the usual δ -scale in ‰ according to $\delta_{\text{sample}} (\text{‰}) = (R_{\text{sample}} / R_{\text{standard}} - 1) \times 1000$, where R is the $^{34}\text{S}/^{32}\text{S}$ atom ratio, from V-CDT (Vienna - Canyon Diablo Troilite) isotope ratio standards.

The second campaign took place in November 2017, with sampling and water analysis for chemistry, $\delta^{13}\text{C}_{\text{DIC}}$, and gas sampling and analysis. Total DOC was extracted as CO_2 by water sample acidification with H_3PO_4 . The CO_2 extracted under vacuum was purified before analysis by mass spectrometry. Results are given in $\delta^{13}\text{C}_{\text{TDIC}}$ vs. PDB (in ‰). Gases were analysed by the BRGM laboratory using a Trace GC Ultra Thermo Fisher Scientific gas chromatograph (Thermo Scientific, with FID detector). The gases investigated were CO_2 , H_2 , O_2 , N_2 , H_2S , CH_4 with injection valves of 25 μL and 250 μL . Detection limits were 0.001% (v/v) for CO_2 , O_2 and N_2 , 0.005% (v/v) for H_2 and H_2S , and 0.0002% (v/v) for CH_4 .

Finally, available chemical data of the Lille Metropolis were taken from the trimestrial water-quality surveys (2013 to 2017), which only present total Se concentrations.

3.3 Geophysical imaging

Knowledge of the complex organization of geological formations, such as the presence of clays that can induce groundwater confinement and thus the modification of the redox conditions controlling the mobility of selenium, or the fracturing of the chalk that can induce preferential water circulations, is an essential lock. To image the subsurface, we used geophysics, and in particular electrical resistivity tomography. The applied Direct-Current

resistivity method, imaging the resistivity distribution in the subsurface, is widely used for hydrogeological purposes (Revil et al., 2012) and references therein).

A 2-D resistivity profile (RP) was measured in August 2019 about 200 m to the northwest of the Ansereuilles well field, from well A10 to well A15 (RP11, Fig. 1). For data acquisition, a multi-electrode Syscal Pro Switch system (IRIS Instruments) was connected to 96 stainless electrodes 5 m apart. Both dipole-dipole and reciprocal Wenner-Schlumberger arrays were considered; the former for its good resolution of surface levels and lateral resistivity variations, the latter for its sensitivity to vertical resistivity variations that clearly identify horizontal geological levels (Loke, 2015). After data filtering ($V_{\min} \geq 0.1$ mV, $I_{\min} \geq 20$ mA, $Q \leq 5\%$), the electrode topography was incorporated. The Chalk roof and Dièves roof interfaces from the 3-D geological model of the study area (Picot and Bourguine, 2010) were also included to improve the results. Then, a robust-type inversion with RES2DINV software (ver. 4.10) was run (Loke, 2020). The RMS error of the resulting resistivity section was 5.8% after five iterations. Interpretation of the 2-D resistivity model was supported by the drilling logs of wells A10 to A15 (BSS, BRGM) and the geological map (Desoignies and Sangnier, 1968).

4. Results

4.1 Geological setting

For the Quaternary formations, the surface R1 layer (1 to 5 m thick) is moderately resistive at 30-35 Ω m (Fig. 2). Mostly consisting of Quaternary silt (Desoignies and Sangnier, 1968), resistivity values in R1 near the Deûle River (300-350 m) suggest a rather sandy facies.

The underlying conductive C1 horizon has a resistivity below 20-25 Ω m and mostly consists of Quaternary alluvium. It is on average 10 m thick (Desoignies and Sangnier, 1968), but locally varies from 5 to 15 m, according to undulations in the roof of the underlying horizon. Quaternary alluvium mainly is found in the southwest part of the RP11 profile; it is exposed to the northeast and its thickness is difficult to evaluate. Here, C1 lies on the highly conductive C1' horizon with an average resistivity below 5 Ω m. According to the

numerous drill logs available along the profile, C1' corresponds to the Louvil Clay (Thanetian, Eocene).

For the Senonian-Turonian Chalk and the Dièves, the C2 layer is moderately resistive, between 25 and 50 Ωm (Fig. 2). Below, the R2 unit shows resistivity values over 50-60 Ωm . From a lithological viewpoint, both C2 and R2 units correspond to the Senonian-Turonian Chalk. Although the roof of the C2 layer is very irregular along the profile, we observed a progressive deepening from SW to NE whose maximum amplitude is about 15 m. Within the R2 resistive unit, we noted a 60-m-wide area where the resistivity slightly decreases ($\sim 30 \Omega\text{m}$, C2') close to well A13 (abscissae 600 to 660 m on Fig. 2). Finally, the C3 conductive horizon has a resistivity of less than 25 Ωm , being the electrical substratum of the resistivity section. Analysis of the drill logs indicates that this layer corresponds to Lower Turonian (Dièves) marl.

Figure 2: a) 2-D resistivity inversion model along the RP11 profile in Les Anseureilles well field measured in August 2019, and static water levels measured on 31/08/2019 (see Fig. 1 for the location of the RP profile) ; b) Description of the lithology from a drill log near well A13

4.2 Selenium in the geological formations

The Chalk formation of the Templeuve quarry had Se contents below the quantification limit ($QL=1 \text{ mg kg}^{-1}$) whereas the Tertiary and Quaternary formations contained relatively high Se concentrations (Table 1). The highest Se values, 3.57 and 4.87 mg kg^{-1} , were measured in the upper part of the Thanetian Ostricourt Sand and in the Ypresian Orchies Clay,

respectively. Quaternary silt had rather high Se contents (4.1 mg kg^{-1}). Total organic carbon content was 0.27% in Quaternary silt and 0.5% in the Ypresian clay. X-ray diffraction (XRD) patterns of the Chalk show over 99% calcite, traces of quartz ($\sim 1\%$) and, in the reddish parts of the Chalk, traces of siderite and possibly hematite. Ypresian clay and the top of the Thanetian sand show XRD patterns indicating a large presence of quartz and illite, together with pyrite.

More locally, the samples at 11.8, 13.3 and 14.2 m depth of the borehole at well A13 (Table 1) contain an assemblage of zeolite (7-19%), smectite (69-84%) and opal-CT already described in the British Thanetian (Huggett and Knox, 2006) that may be a typical assemblage of this age, confirming the hypothesis that the clay overlying Chalk in Les Ansereuilles is Thanetian Louvil Clay ((Cary et al., 2014) . The other minerals in the $<2 \mu\text{m}$ fraction below 11.8 m, are illite (8-11%), chlorite (1-2%) and quartz. The samples contained up to 4.6 mg kg^{-1} Se at the bottom of the profile, above the Chalk at 13 m depth (Table 1). High Se levels (4.8 mg kg^{-1}) were also found in the banks around well A13, consisting of ash waste from the old thermal plant. At 8.5 m depth, solids are enriched in Fe (7.5%), Se (3.9 mg kg^{-1}) and organic matter (0.54%).

Pyrite grains, up to 5 mm large, were found between 7 and 14 m depth in well A13. Both fine-grained and coarser sediments at this depth range contain up to 0.85 wt% pyrite according to the semi-quantitative XRD patterns. The largest pyrite grains were sampled manually at 7, 8.5 and 8.8 m depth; after washing the grains with acid solutions (see previous section), the selenium concentration was estimated for nine replicates of different pyrite-grain samples. We found a Se concentration of 1.2 mg kg^{-1} with an RSD of 22%. In raw sediment, several chemical extractions were needed for understanding the Se distribution, especially as related to pyritic compounds (Table 1, Fig. 2). Se concentrations in pyrite are generally below 0.01%, except in the A13 sample at 5.5 m depth where the maximum content is observed (1.1%). Overall, these concentrations are higher than the values measured in well-crystallized pyrite grains. Table 1 shows that a significant fraction of total Se is included in pyrite with values between 6 and 29% (see Fig. 2 of SI). The DTSeP is

still higher (35-74%), meaning that the “mobile Se” (defined by the fraction extracted with a 1 M HCl solution) is well trapped in the pyrite fraction (see Fig. 2 of SI).

Table 1: Chemical composition (bulk) and mineralogy (bulk and <2 µm fraction) of the regional and local geological formations (sampled at the vicinity of well A13).

4.3 Spatial and temporal variability of groundwater chemistry

The results are presented in Table 2 and on Figs 3 and 4, the sampling points being shown on Fig. 1. Groundwater displayed pH varying from 6.8 (well A4) to 7.3 (well A24). The redox potential varied from 177 mV (well A26) to 460 mV (well E5, Emmerin). The physical and chemical parameters of the groundwater showed a significant spatial variability. The E-HA groundwater had low SO_4^{2-} and high NO_3^- concentrations, but the groundwater of the confined end-member (wells A25 to A28) stood out in having high Cl and SO_4^{2-} concentrations. Comparatively, the groundwater in wells A12 and A13 had high SO_4^{2-} and low NO_3^- concentrations. For each point, time variations are represented by the range of values in Figs 3 and 4; they are best expressed for Se values in the wells of the redox sequence, where Se contents can double during a year.

For S speciation, S^{2-} and $\text{S}_2\text{O}_3^{2-}$ were measured <QL, whereas low amounts of SO_3^{2-} were found in most groundwater samples (not shown in Table 2). For Se speciation, all groundwater samples had Se(VI) concentrations at levels over the QL. Only the groundwater in wells A12 and A13 had low amounts of Se(IV) ($0.27\text{-}1.39 \mu\text{g L}^{-1}$), Se(VI) being the major aqueous phase. Table 3 shows dissolved gas values in 7 wells of the redox sequence and three wells of the catchment. Methane is present in increasing concentrations from wells A12 to A15, but absent elsewhere. Well A13 contains clear peaks of CO_2 and O_2 , but less N_2 than in the other wells.

Table 2: Physical and chemical composition of groundwater samples from 2011 to 2019. DO is dissolved oxygen. TOC is for Total Organic Carbon. The precision is $\pm 0.3\%$ on $\delta^{18}\text{O}_{\text{SO}_4}$ and $\delta^{34}\text{S}_{\text{SO}_4}$ and $0.1 \mu\text{g L}^{-1}$ on Se(VI) and Se(IV).

Table 3: Gas concentrations in groundwater sampled in November 2017.

4.4 The $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ isotopic composition of groundwater

The Emmerin groundwaters have positive isotopic compositions for $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ of sulphate, whereas all other groundwaters show negative $\delta^{34}\text{S}$ (Table 2). Houplin-Ancoisne groundwaters show a high variability of $\delta^{34}\text{S}$ (-30 to -5‰ including error bars) and $\delta^{18}\text{O}$ (0 to 6‰) during the whole monitoring year, similar to those observed in the Les Ansereuilles well field that shows $\delta^{34}\text{S}$ varying from -27.4‰ (A12) to -5.7‰ (A23). Monthly monitoring of well A13 showed a stable $\delta^{34}\text{S}$ ($\delta^{34}\text{S}$ close to -20‰) and $\delta^{18}\text{O}$ variations (around 6‰). A decrease of $\delta^{18}\text{O}$ values occurred in groundwater from February to May, followed by an increase until next winter with the highest $\delta^{18}\text{O}$ in February-March, back to the initial values.

5. Discussion

5.1 Geophysics and hydrogeology

The geophysical results highlight two essential elements from a hydrogeological point of view. First, they confirm the presence of Louvil Clays (C1') and define their geometry (Fig 2). To the southwest, these clays are lenticular within recent alluvial deposits (C1) and evolve into a continuous level to the northeast, thanks to a deepening of the underlying horizon. The transition between Quaternary alluvium and Louvil Clays is progressive, and we cannot define a precise limit between those two units. This thickening of the Louvil Clays leads to a progressive confinement of the Chalk aquifer from southwest to northeast.

Beyond the 600 m abscissa, the Louvil Clays are 7 to 15 m thick according to the well logs (A13, A14 and A15, Fig. 2), but the thickness of the corresponding C1' electrical horizon varies from 10 m (A13) to about 20 m (A14, A15). The upper conductive part of the Chalk (C2) corresponds to its weathering-related fractured and productive part (Portal et al., submitted). Starting at well A13, we suggest that the very low resistivities in the upper part of the Chalk are due to the presence of Louvil clay that may have infiltrated the underlying Chalk and settled along the walls of the macro- and microporosity. This clay coating could

explain the low resistivities observed for weathered Chalk in this area. It also has strong hydrogeological consequences, as it contributes to increasing water-residence time and thus enhances water-rock interactions.

Secondly, geophysics show a local resistivity decrease (C2') into the resistive Chalk (R2, Fig. 2). We interpret this 60-m-wide area as a large fracture corridor. Such structures are well known in basement contexts (Acworth, 1987) and their more conductive signature, compared to that of fresh basement rock, had already been observed (Belle et al., 2019; Comte et al., 2012; Descloitres et al., 2008). To our knowledge, few other geophysical studies have focused on the Chalk aquifer, probably because it is an easily exploitable water resource. However, recent work on the hydrogeological setting of the Chalk aquifer in Normandy (France) has highlighted similar multi-decametric zones of resistivity decrease within the resistive Chalk, related to regional or local faults (Meire et al., 2019; Portal et al., 2020). The geophysical anomaly identified close to well A13 may result from alteration due to the presence of faults. It probably extends on either side of the RP11 profile, following a N110-N130 orientation inherited from the regional trend of Carboniferous basement tectonic structures, thus constituting a preferential groundwater circulation pathway that may favour the mixing of groundwaters of different origins under the impulse of pumping.

5.2 Se contents in rock

The geological units of the northern region show heterogeneous Se contents, comparable to those of the formations of the whole Paris Basin (Table 1). Whereas Ypresian clay commonly has the highest Se concentrations of Paris Basin sediments (695 mg kg⁻¹ in Lower Ypresian lignitic Black Sands, 11.8 mg kg⁻¹ in Lower Ypresian Clay (Gourcy et al., 2011), the Se contents of the Tertiary and Quaternary formations in the Lille region are much lower (4.6-4.9 mg kg⁻¹). Moreover, the highest Se values of the study area are found in basal Thanetian Louvil Clays overlying the Chalk (4-4.6 mg kg⁻¹). The Se content of Quaternary silt in the Lille region is clearly higher than that observed in agricultural soil developed on Quaternary deposits in Belgium, ranging from 0.1 to 0.7 mg kg⁻¹ (De Temmerman et al., 2014). Overall,

the soils of northern France and Belgium are known to be Se-depleted, the Se being supplied by Se-rich mineral fertilizers, containing up to 200 mg kg⁻¹ Se, as well as animal manure (ADEME, 2007) to ensure correct Se contents in wheat.

The “primary” presence of Se is indeed linked to Quaternary deposits when present (e.g., aerial loess vs. erosion of Tertiary Se-enriched sediments), and local ‘hot spots’ of Se-enriched soil reaching 1 mg kg⁻¹ are known in the north-eastern part of the Paris Basin including the Lille region (Baize et al., 2010). Generally speaking, the Se content of bedrock and soil in the Lille region is comparable to that of other Se-rich geological regions in the world and can present Se values over 1 mg kg⁻¹, which is considered as the toxic level (Bailey, 2016). The processes leading to high Se concentrations in groundwater thus remain to be understood.

5.3 The local Chalk groundwater chemistry

The chemical facies of the groundwater samples are bicarbonate-calcium type (Ca-Mg-HCO₃, see Piper diagram in Fig. 1 in Supporting Information) and evolve between two facies (Fig 3): (1) the upstream oxic E-HA groundwater type where dissolved O₂ varies from 4.8 to 8.9 mg L⁻¹, with high NO₃ and low sulphate concentrations; and (2) the confined type with semi-oxic groundwater of well A26 under continuous Tertiary cover, with a very low O₂ content (0.3 mg L⁻¹), a nitrate content <QL and high sulphate concentrations indicating denitrification and a long residence time with long water-rock interaction (Cary et al., 2014). The pH range is similar to that in other parts of the unconfined Chalk aquifer in France and England (Edmunds et al., 1987; Négrel and Petelet-Giraud, 2005).

HCO₃ contents vary between 256 and 506 mg L⁻¹, the lowest values occurring in the Emmerin well field and the highest in well A13 (Table 2). These values are above the usual ones in the English Chalk aquifer (Edmunds et al., 2003), in the Somme region (Négrel and Petelet-Giraud, 2005), or in the south of the Paris Basin (Brenot et al., 2008). Similarly, sulphate concentrations in the study site are all above the ones measured in the Chalk aquifer in the Somme (Négrel and Petelet-Giraud, 2005; Fig. 3). The sulphate content in

wells A12 and A13 is higher than the threshold value in English Chalk (Edmunds et al., 2003).

Compared to the general trend in the Chalk aquifer in France and the UK, the higher mineralization in the Lille region probably originates from exchange with the underlying Carboniferous aquifer and/or the overlying Tertiary sediments. Here, at around 100 m depth below the Chalk in the studied well fields, the Carboniferous contains Viséan evaporites and its groundwater is highly mineralized (Bernard et al., 1981). Upwelling of mineralized fluids may occur through deep-seated faults in the basement and Chalk, particularly near the study site, but this hypothesis has not yet been proven. However, the role of Tertiary sands and clays as sources of mineralization of the Chalk aquifer (Bernard, 1979) is coherent with the high K ($>15 \text{ mg L}^{-1}$) and SO_4 ($> 100 \text{ mg L}^{-1}$) values observed in wells tapping the confined Chalk (wells A25 to A28, Fig. 3 and Table 2). Interestingly, in spite of the reductive conditions in this confined part of the aquifer and sufficient available organic carbon (1.35 mg L^{-1}), SO_4^{2-} remains present in groundwater.

Figure 3: Binary diagrams showing element concentrations in the groundwater of the Chalk aquifer at the study site. All circles are from the quality monitoring of the EML from 2013 to 2017; all other points were acquired in 2011-2013 and 2017-2019.

5.4 Geochemical processes of the redox sequence

The continuum of wells A16-A11-A12-A13-A14-A15 along the Deûle channel constitutes a remarkable redox sequence (Fig. 4) over a very short distance (1600 m). Plotting data chronicles from Lille Metropolis for 2013-2017 and recent monitoring studies, shows that the range of concentrations of each parameter is large as it varies with time under the

constraints of natural recharge and pumping. The general transition from oxic to anoxic conditions, driven by clay overlying the Chalk, is rapid but progressive, and the increase in reductive conditions strictly respects the sequence of microbially mediated oxidation-reduction reactions. Thus increase represents the thermodynamic order of the reactions $O^0/O^{II} > N^V/N^0 > Se^{VI}/Se^{IV} > Mn^{IV}/Mn^{II} > Fe^{III}/Fe^{II} > S^{VI}/S^{IV}$ (Stumm and Morgan, 1996), as already described from England (Edmunds et al., 1987). The measured O_2 -content range is typically included in the respiration threshold ($0.03\text{--}2.0\text{ mg L}^{-1}$), indicating a transition state between the oxidation of organic matter by oxygen and by nitrate (Ashok and Subrata, 2015). Confined conditions cause very low O_2 content ($0.26\text{ to }0.50\text{ mg L}^{-1}$, Fig. 4) and nitrate tends to be reduced (from $25\text{--}30\text{ mg L}^{-1}$ in A16 to $<QL$ in A14 and A15) with the production of NH_4 (mean of 0.55 mg L^{-1} in well A14) and traces of NO_2^- (Fig. 4). Reduction of nitrate can be associated with oxidation of organic matter, but also with oxidation of reduced minerals (Parmentier et al., 2014), as pyrite was identified in Thanetian clay. Organic carbon is present in the clayey sediment ($0.35 - 1.80\%$ dw) overlying the Chalk, and also occurs in aqueous phase in well A13 ($1.5\text{ to }3.2\text{ mg L}^{-1}$). Assuming that this organic matter is bioavailable for bacterial metabolism, its oxidation produces inorganic carbon according to the reaction given in Equation 3:

The organic matter was modelled as CH_2O , although natural organic matter can exhibit different formulae; the resulting production of protons should be different. The production of N_2 is proven with high values in wells A12 and A13 (1.3 and 1.4 mmol L^{-1} , respectively, Table 3), which are higher than those of E-HA, except for well H11. A denitrification process as in Equation 3 typically goes through a temporary production stage of NO_2^- and leading to the final production of NH_4^+ , both of which have been identified in groundwater samples. Oxidation of organic matter acidifies the system, but no notable acidification was found in well A13, where the pH range is $6.8\text{--}7.3$, or in the other studied wells (Table 2). The pH is probably buffered by calcite dissolution from Chalk, which explains the high Ca contents of

wells A12, A13, A14 and A15 compared to the other Les Ansereuilles wells (Cary et al., 2014; Table 2). The production of HCO_3^- according to Equation 2 can contribute to the relatively high content observed in the studied groundwater. Better to assess the HCO_3^- origin, the $\delta^{13}\text{C}$ of dissolved inorganic carbon was measured on some samples, ranging from -14.20‰ to -11.6‰ with a pH ranging from 6.73 to 7.1. These values are typical of the Chalk aquifer in unconfined or semi-confined conditions, and are interpreted as resulting from dissolution of the carbonate matrix (Kloppmann et al., 1998). The concentrations of dissolved manganese increase in groundwater along the transect A16 to A15, with a maximum in well A12. Dissolved iron concentrations follow the same trend with a general increase reaching the highest values in well A14. Mn- and Fe-oxihydroxides reduction is most probably the main process here. The presence of dissolved methane in wells A12-A13-A15 (Table 3) confirms that organic matter is probably first biologically or chemically degraded in CO_2 , and then reduced by CH_4 , although the measured redox potential does not represent a CH_4/CO_2 couple or a very reductive system.

The continuum of wells shows high SO_4^{2-} values associated with high Se values and low NO_3^- values (Fig. 3). However, such high Se concentrations are not coherent with the local reductive conditions, so we suspect another process than reduction to be active here as well. An oxidation reaction may be the main process here; a very interesting element of this redox sequence is that an oxidative flow crosses a progressively settled anoxic state. Indeed, the monthly monitoring of well A13 showed dissolved O_2 content varying with time from 2.5 to 4.8 mg L^{-1} , these values being higher than those in wells A12 or A14 (Table 3; Fig. 4). We can thus assume that dissolved O_2 is probably introduced in the system by water flowing through the fractured corridor near A13 (Fig. 2). The introduction of dissolved O_2 superimposes a secondary “oxidation sequence” on the predominant reduction reactions. Such oxidation reactions laterally are effective over short distances, governed by flow direction and groundwater mixing, and by the reaction rates, as illustrated by the low dissolved O_2 content in wells A12 and A14 (Table 2; Fig. 4). The slight decrease of dissolved

iron in well A13, mainly as Fe(II), can be linked to the presence of dissolved oxygen causing Fe(III)-oxide precipitation (Fig. 4), even if chemical Fe(II) oxidation can also occur under anaerobic conditions in the presence of Mn(IV), NO_3^- , and NO_2^- (Kappler and Straub, 2005). Illustrated by the slight decrease in dissolved Fe- and Mn concentrations, the best expression of oxidation are the high values of SO_4^{2-} and Se concentrations, mainly as Se(VI), in well A12 (Fig. 4). The presence of a certain amount of dissolved O_2 in A13 makes pyrite oxidation possible (Eq. 4), present in reducing environments and commonly identified in Chalk porosity (Edmunds et al., 1987). It also leads to the presence of Fe^{2+} (Eqs 4 and 5) further oxidized into Fe(III), and NO_3^- reduction (Eq. 6) resulting in the high SO_4^{2-} concentrations of wells A13 and A12, and in denitrification (Zhang et al., 2012).

SO_3^{2-} , a product of pyrite oxidation found in well A14 at low levels, is not stable and rapidly oxidizes to sulphate in the presence of oxygen or any other oxidizing agent. Acidity produced in Eq. 4 and 5 would be buffered by calcite dissolution.

Figure 4: Redox sequence in the Les Anseres field well presenting the geophysical profile and the chemical composition of groundwater in each well. Distance is calculated relative to well A10. PZ56 is not in the continuum, but slightly southeast under the same geological conditions.

It is worth noting that the processes within the water-level fluctuation zone are dynamic and that the redox front position varies with time, laterally but also vertically, in the water-level fluctuation zone. The oxidation processes linked to mixing with oxic waters are distributed laterally around well A13 according to the main flow driven by pumping. Towards

well A15 under complete reduced conditions, O_2 and NO_3^- will be rapidly reduced, whereas towards A12, which is not denitrified, the mixing slows down the creation of reductive conditions. This example provides an interesting illustration of the complex “permanent” transient states of groundwater.

5.5 Constraints related to the isotopic composition of sulphate molecules in groundwater

In the Chalk aquifer near Lille, several potential sources of dissolved sulphates can be identified. The $\delta^{34}S_{SO_4}$ in E-HA well fields (+0.4 to +1.6‰) most likely originates from atmospheric deposition and fertilizers (-6 to +21‰), (Vitòria et al., 2008) (Table 2). For the other groundwater samples, a large variability of negative $\delta^{34}S$ values is noticed between wells (Figs. 6 and 7), matching the general composition of pyrite (Thode, 1991), of local pyrite and local solid Chalk (respectively $\delta^{34}S_{SO_4}$ of -20‰, and -10 to 15‰; Simon, 1986)).

The first hypothesis lies in a mixing between the E-HA pole and the T-Q end-member as defined in Cary et al. (2014), with $\delta^{34}S$ of Louvil Clays: -37 to -40‰ (Bernard et al., 1981). The negative values of sedimentary sulphides in the T-Q end-member are coherent with their marine origin. In the redox sequence (Fig. 5) where only Louvil clay is present, the mixing line correctly fits values of wells A15, A26 and E-HA, but it does not explain all the points. A SO_4^{2-} excess is found in well A14, and a deficit for PZ56 and A12. The annual variability of $\delta^{34}S$ in well A13 is not completely explained; some points belong to the general area of sulphates deriving from pyrite dissolution, and other points correspond to the sulphate reduction line (Figs 6a and b). As pumping induces groundwater mixing, the decreasing and variable rates of oxidized water reaching wells A12, A13 and A14 through the fractures of the corridor should constrain the processes controlling $\delta^{34}S_{SO_4}$ and SO_4 concentrations.

The second hypothesis then must consider fractionation processes. All the wells of the redox sequence are well explained by the reduction line (slope -2, Figs 6a and b). The observed increase in $\delta^{34}S_{SO_4}$ (+16.8‰) and $\delta^{18}O$ (+ 4.5‰) from wells A12 to A15 is interpreted as resulting from kinetic S-isotope fractionation enhanced by bacterial sulphate

reduction, causing a preferential enrichment in ^{34}S and ^{18}O in the residual SO_4^{2-} . The Rayleigh equation (Mariotti et al., 1988) can be used to describe isotope fractionation :

$$\delta_r = \delta_0 + \varepsilon \ln \frac{C}{C_0} \text{ (Eq. 7)}$$

where δ_r and δ_0 are residual and initial sulphate reservoirs, ε is the isotopic enrichment factor and C/C_0 is the remaining sulphate fraction. The Rayleigh equation was calculated for ε - 30‰ and -10‰ with the T-Q end-member as the initial source. This range of ε may represent a natural variability of conditions, with various rates of fractioning due to evolving redox conditions and processes (Detmers et al., 2001). All points are correctly explained by the range included in the two curves modelling bacterial sulphate reduction. The enrichment factor of -10‰ explains the composition of PZ56 and well A12, whereas that of -30‰ better corresponds to the other wells of the sequence. This difference may be due to the fact that PZ56 and well A12 are not pumped, contrary to the other wells. It is possible that alternating oxidation-reduction cycles caused by pumping enhance the reduction process beyond normal denitrification and Fe-oxide dissolution. We expect that this effect is less visible in the non-exploited wells.

However, SO_4^{2-} concentrations in wells A12-A13-A14 are expected to decrease with increasing reducing conditions, as is the case for A15, but they do not vary significantly (Fig 5). This means that, although SO_4^{2-} is reduced by microorganisms, this may be compensated by an increase in the contribution of pyrite oxidation in wells A12 and A13. The low variability of the $\delta^{34}\text{S}_{\text{SO}_4}$ of sulphates is observed in wells A13 (n=13) and A12 (n=2) data, because sulphur isotopes essentially undergo no fractionation during pyrite oxidation to sulphate (Van Stempvoort et al., 1994).

Figure 5: Variations of $\delta^{34}\text{S}$ (normalized to Vienna Canyon Diablo Troilite) of sulphate molecules in groundwaters versus $1/\text{SO}_4^{2-}$ from the well fields of southern Lille. Data from Carboniferous groundwater are from Gourcy et al. (2013). The error bar is within the point.

Figure 6: a) $\delta^{34}\text{S}_{\text{SO}_4}$ vs $\delta^{18}\text{O}_{\text{SO}_4}$ in groundwater from the well fields (2011-2017) and monitoring data of well A13; b) Zoom on the redox sequence area. Bibliographic data are from (Bernard, 1979; Gourcy et al., 2013; Simon, 1986). The error bar is within the point.

5.6 Processes driving selenium speciation and mobility

In the redox sequence of Les Ansereuilles, the general scheme of Se concentrations in groundwater shows Se values around 20 µg L⁻¹ under oxic conditions that evolve to very low values under progressively reducing conditions (MEL data of Fig. 4; Table 2). As expected, Se(VI) is the main inorganic Se form in these groundwaters, except for wells A12 and A13 where low Se(IV) concentration values were detected (Fig. 4 and Table 2). This is coherent, as reducing conditions promote the reduction of Se(VI) and Se(IV) ions to insoluble elemental Se(0). In spite of this general scheme, a large increase in Se concentrations in well A12 and, to a lesser extent, in A11 and A13, was noted (Figs. 3 and 4).

As already mentioned for the sulphur cycle, the mixing with oxidized water flowing from the fracture corridor probably superimposes oxidation of reduced Se species, pyrite playing a major role in controlling Se mobility and speciation. As part of the general redox sequence, the creation of reducing conditions imposes simultaneous reduction of NO₃, Se(VI) and SO₄²⁻ that significantly removes Se from water (Nkansah-Boadu, 2019; Oremland et al., 1999; Tan et al., 2018). Precipitation of pyrite induces reduction of soluble Se(IV) and Se(VI) (Mitchell et al., 2013), and Se adsorption or incorporation in the crystal lattice (Diehl et al., 2012; Naveau et al., 2007). The reduction of aqueous Se(IV) by pyrite is dominated by the following reaction in Equation 8 (Kang et al., 2011):

In addition, Se(-II) can be immobilized on the surface of pyrite as a result of a reduction reaction, leading to the formation of Se(0) (Liu et al., 2008). Se(0) can also be transformed to FeSe₂ (ferroselite) with the depletion of Se(IV) (Kang et al., 2016). Not detected in the Louvil Clays, perhaps because of its presence in very small amounts, FeSe₂ that precipitates under reducing conditions in anoxic environments (Ryser et al., 2005), may be present in the water-level fluctuation area in the Chalk. Under the local oxidizing conditions induced by groundwater mixing and in view of the values in the nearby Houplin-Ancoisne well field (Fig 3), we can assume that the oxidizing groundwater may contribute a certain amount of Se

(probably around $10 \mu\text{g L}^{-1}$) and nitrate ($60\text{-}70 \text{ mg L}^{-1}$) from the local geochemical background. Furthermore, organic matter can be degraded by aerobic heterotrophic bacteria, releasing Se that was complexed with insoluble organic molecules, as illustrated by the presence of organic carbon (DOC 1.7 to 2.9 mg L^{-1}) in groundwater of well A13. Se(IV) adsorption with Fe-Mn-oxide precipitation potentially is another major process (Xu et al., 2020).

The highest Se values are found with low amounts of dissolved O_2 ($0.5\text{-}4 \text{ mg L}^{-1}$) and nitrate ($15\text{-}30 \text{ mg L}^{-1}$), but high SO_4^{2-} values ($>170 \text{ mg L}^{-1}$; Fig. 3). This range of values reflects the nitrate reduction area, which is accompanied by oxidation of Se-bearing pyrite and of Se reduced phases produced by microorganisms during an earlier anoxic phase. Indeed, Se included in sulphides—pyrite, marcasite or mackinawite—can be released during their oxidation by sulpho-oxidizing bacteria. Moreover, theoretical calculations of Se^{2-} or $\text{Se}(0)$ oxidation by NO_3^- and O_2 show favourable Gibbs free energies for their oxidation by NO_3^- , indicating that NO_3^- can act as an electron acceptor for Se oxidation (Wright, 1999). As the distance to the corridor increases according to the pumping-induced flow directions, the general dynamic is a decrease of oxic conditions with less intense oxidation, resulting in very low Se and NO_3^- concentrations.

Except for the redox sequence, NO_3^- concentrations above 10 mg L^{-1} in groundwater (grey circles on Fig. 3) are associated with Se concentrations limited to $20 \mu\text{g L}^{-1}$, which is defined as the maximum natural threshold value (Fig. 3). This reflects oxic conditions, where pyrite is not usually present. The decrease of Se values from 20 to $<0.5 \mu\text{g L}^{-1}$ corresponds to NO_3^- values from 10 mg L^{-1} to <0.5 , which means that NO_3^- and SeO_4^{2-} reduction can occur simultaneously. This is coherent with bibliographic data from microbiological laboratory experiments, with threshold values of $5\text{-}10 \text{ mg L}^{-1}$ of NO_3^- above which Se(VI) reduction is inhibited (Tan et al., 2018; Thouin et al., 2019).

In view of the above, pyrite plays an important role. In the Louvil Clays, it contains 7 to 29% of the total Se stock, $48\text{-}61\%$ of the available stock already being associated with pyritic compounds, meaning that most of the “bioavailable” Se is already trapped in these

reduced sulphur compounds. We do not know the Se content of pyrite contained in Chalk, but we can assume that its potential as a Se-release source or for Se-trapping is important and will grow with time. Indeed, the superimposition of multi-year alternations of oxidation and reduction processes has generated a large and variously crystallized pool of pyrite in the Chalk porosity controlled by water-level fluctuations in the Chalk aquifer.

5.7 Short- and long-term contaminants cycles

Considering relatively short cycles at a multi-annual scale, groundwater goes through transient states according to recharge, mixing with waters from the fracture corridor, and pumping. This suggests that Fe, Mn and associated trace metals S and Se, undergo multiple cycles of oxidation, mobilization, and re-reduction, resulting in a metal-rich redox front.

For longer cycles, we can suppose that the redox front has been migrating downward since emersion of the region, and that this migration is dependent on overall changes in recharge and exploitation. In the main wells of the study area, the present-day dynamic level reaches its lowest depth in the Chalk aquifer and moves ever closer down to the estimated non-productive zone of the aquifer, after 50 years of large (± 20 m) variations in the water-level depth. The base of the Louvil Clays therefore remains mainly unsaturated, today.

With -8% of precipitation and +4% of evapotranspiration since 2016 (MeteoFrance data), relative to the 1981-2010 period (Picot and Bourguine, 2010), the local climate-change effect is dominated by a sharp decrease in groundwater recharge (-7%), and over three to four months instead of six, before. Although demand is growing, the official extraction rates were decreased from 37 to 31 Mm³/year between 2016 and 2020, to preserve the well field that has reached its maximum capacity. Under these conditions, the transfer of elements from the primary Louvil Clays source probably has been notably reduced, especially for metals, Se and organic matter, which may become a limiting factor for future redox reactions.

Only complete cessation of pumping would lead to a heightening of water levels, creating the conditions for increasing water stocks in the Chalk. If we consider the imprints of overall changes, evolution scenarios should be drawn for predicting Se speciation. Durable

exploitation of the well field should stabilize water-level fluctuations and the unsaturated zone. The Se-in-Chalk stock would not increase, Se mobility would be driven by pyrite formation and dissolution, and bacterial reduction processes would depend on geology constraints. It would thus be interesting to assess the role of Se in pyrite-formation rate, as trace elements such as Ni or As respectively accelerate or inhibit pyrite formation (Baya et al., 2021). However, a large reduction in pumping or abandonment of the well field would recreate the reductive conditions for lowering Se mobility, e.g., by stocking Se in the pyrite pool of the Chalk, but would also increase Se(IV) concentrations until the conditions are favourable for Se(0) formation. To better understand the effects of global climate change on the biogeochemical cycling of redox-sensitive elements, a reactive transport model (Shultz et al., 2018) could be used and coupled with the existing hydrogeological model for testing various scenarios of groundwater use.

6. Conclusions

The selenium cycle is affected by processes of a redox sequence, potentially leading to high Se concentrations in groundwater. The spatial and temporal disparities of Se concentrations in a dynamic system, are controlled by geological and hydrogeological constraints—here the presence of Se-enriched Louvil Clays that progressively confine the Chalk aquifer—and by variations in the water-level depth induced by recharge and pumping. Our conceptual scheme presents the main reductive processes in the Les Ansereuilles succession near Lille (France), and the superimposition of localized oxidation processes, mainly pyrite oxidation, on the investigated Critical Zone, resulting in a Se hot spot (Fig. 7). Here, the Se-rich redox front has been steadily migrating downward in the water-level fluctuation zone of the Chalk aquifer.

Over the past years, low recharge has not compensated groundwater exploitation and the recent pandemic has further increased a growing water demand. However, the pool of Se in the Chalk aquifer may not increase very much in the coming years, as the base of the

Louvil Clays, a Se source, will remain under unsaturated conditions. The key challenge remains the mobility of the Se pool in the Chalk aquifer, linked with the presence of pyrite. Concerning the other parts of the well fields, outside the redox sequence, Se mainly occurs in Quaternary sediments, where the natural background concentration range is 10-20 $\mu\text{g L}^{-1}$. Increased precipitation or flooding is expected to lead to a potential change in soil redox conditions, coupled with rapid input of oxygen, and possibly nitrates, into the system, as well as a major impact on biogeochemical processes and Se mobility.

Key parameters for evaluating Se mobility under global change, are changes in nitrate concentrations in groundwater and in bacterial activity in the water-level fluctuation zone. Most of the well fields being in agricultural land, the challenge is to develop strategies for limiting nitrate entries to improve groundwater quality. However, Se distribution and speciation, which are controlled by redox reactions and biogeochemical processes, must first be better assessed through considering the complete Se biogeochemical cycle, including solid and organic Se forms. To fully unravel the reactivity and transfer of Se, Se isotopes should be useful indicators.

Figure 7: Lateral evolution of reductive reactions along the A10-A15 transect and local superimposition of oxidation reactions. The taps symbolize groundwater pumping rates and well closure due to high Se contents (A12 and A11). The geophysical profile shows resistivity variations, from low (blue) to high (red), and illustrates the progressive confinement of the Chalk aquifer by the Louvil Clays (in deep blue). The Chalk is divided in green (productive) and orange (less productive) parts where the pumps are now located. The main flow direction is indicated (wells A13 to A10), and also a possible secondary one (A13-A15) that may vary with pumping intensity. The large arrows symbolize reductive reactions that are laterally staggered with oxidation processes. The fracture corridor near well A13 supplies oxygenated groundwater to the reductive system by mixing, that superimposes local oxidation reactions symbolized by the blue double arrows. The reaction domains are drawn at well scale (about 200 m spacing). Organic carbon provides electrons to the reduction reactions.

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