

HYDROGEOCHEMICAL MODELLING OF THE ALSACE GROUNDWATER POLLUTION BY THE POTASH MINE SPOIL HEAPS

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ABSTRACT: The Alsace alluvial water table has undergone a huge saline pollution related to the exploitation of the Alsace potash mines during almost one century. In addition to the spread of water with high salinity, observations reported a loss of concentration of sodium compared to chloride along the water flow, and in the mean time an increase in calcium concentration. These observations advocate for a cation exchange mechanism, made possible by the existence in the Rhine aquifer of montmorillonite, a clay which enables such an exchange. The hydrogeochemical model is built with the numerical code KIRMAT, and as simulation results are in agreement with measures, it tends to validate the exchange hypothesis, and also gives a tool to study and forecast this pollution evolution in the future.

KEYWORDS: hydrogeochemical model, potash mine, saline pollution

RESUME: La nappe alluviale d'Alsace a subi une importante pollution saline liée à l'exploitation des mines de potasse durant près d'un siècle. Outre la propagation d'eaux à forte salinité, des observations ont fait état d'une perte de concentration en sodium par rapport aux chlorures au long de l'écoulement de la nappe, et parallèlement une augmentation des concentrations en calcium. Ces observations plaident pour l'existence d'un mécanisme d'échange cationique, rendu possible par la présence de montmorillonite au sein de l'aquifère rhénan, argile capable de tels échanges. Le modèle hydrogéochimique construit à l'aide du code de calcul KIRMAT permet de rendre compte d'un certain nombre de mesures, tendant ainsi à valider l'hypothèse de l'échange, et fournit ainsi un outil pour l'étude et la prévision de l'évolution future de cette pollution.

MOTS-CLEFS: modèle hydrogéochimique, mine de potasse, pollution saline

1. Introduction

The alluvial water table of the Upper Rhine valley constitutes one of the most important underground water tanks of western Europe, abundantly exploited for agriculture, industry and drinking water supply. The issue of the groundwater quality is therefore of a major importance. Nowadays, this water has become unsuitable with consumption in its upstream part, because of a chloride pollution. High chloride concentrations were observed since the 1960s (Figure 1), and the main cause of this phenomenon lies in the mining brines infiltration from the potash mines exploitation (Bauer *et al.*, 2005).

Indeed, a layer of potassium salt between 600 and 1000m of depth in the south of the Upper Rhine valley, of lower Oligocene age, was exploited by the Alsace potash mines since 1910 till 2002. The ore in question is sylvinitite, it approximately contains 24% of potassium chloride, 60% of sodium chloride and 16% of insoluble. The salted residues were deposited in the form of spoil heaps near the mine shafts. Under rain action on these spoil heaps, water, by runoff and percolation, was

loaded in salt (Figure 2), infiltrated groundwater and progressed then in the flow direction, forming high salinity bands.

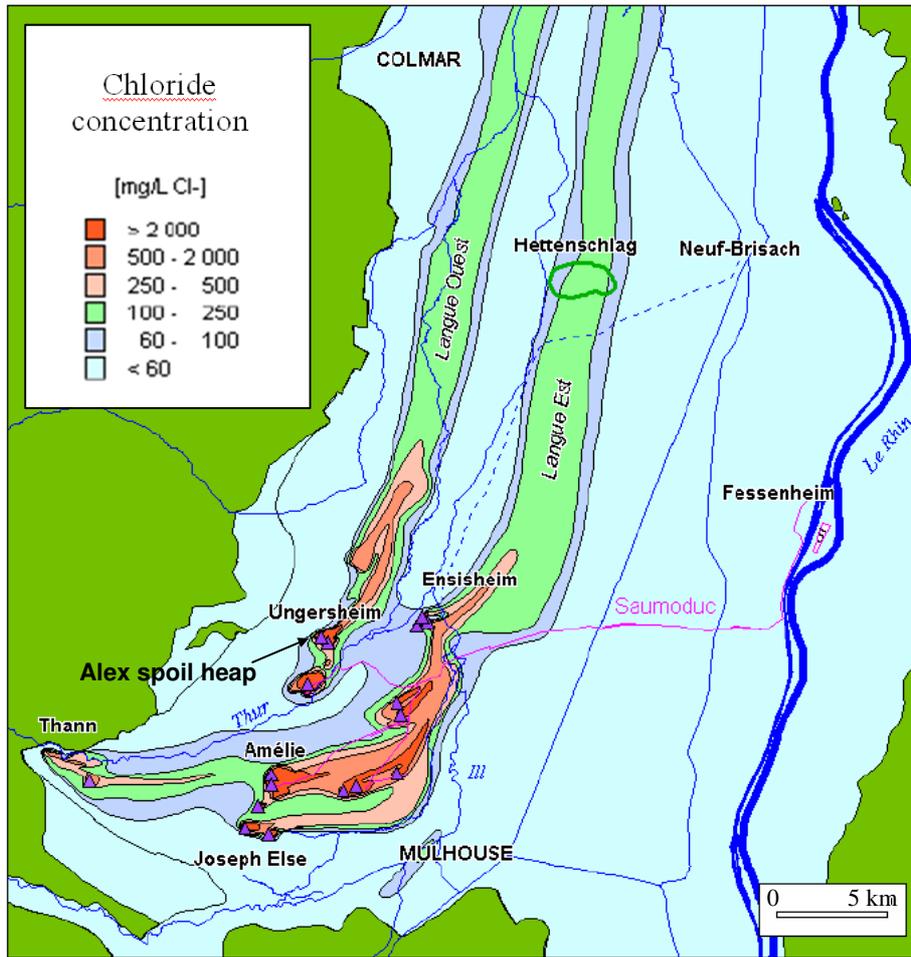


Figure 1. Pollution map in 2005, from Elsass (2007).

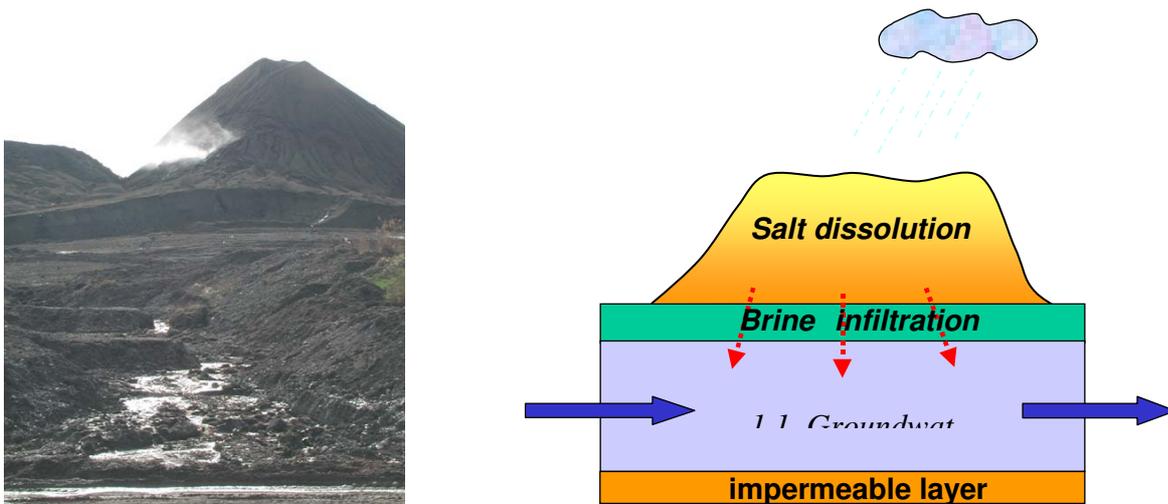


Figure 2. Picture of a potash mine spoil heap, and scheme of brine infiltration into groundwater.

2. Pollution history

At the beginning of the 1970s, the global volume of the spoil heaps was about 20 millions m³, on an area of 170 ha, which contained 15,000 millions kilograms of salt (Duprat *et al.*, 1979). Starting from 1976, the Alsace Potash Mines (MDPA) have taken action to reduce brine infiltrations in groundwater. Among these actions, there are: the collection of runoff waters from spoil heaps and their evacuation to the Rhine river. These actions had rapidly a positive impact. Towards 1989, in order to go faster, spoil heaps have been treated by active dissolution, i.e. they have been sprayed. Collectors have been installed to recover brines, channelling them into a pipeline that carries them to the Rhine river. But it appears that this phase of active dissolution has led to heavy infiltrations in groundwater (BRGM, 2006).

3. Hydrogeological setting and geochemical context

3.1. Geology

The Upper Rhine Valley belongs to a large scale geological graben structure, formed in the Cenozoic, the Rhine graben, which is over 300 km long and 40 km wide. It is bordered by two horst zones which are the French Vosges Mountains to the West and the German Black Forest Mountains to the East. The Alsatian part of the Upper Rhine valley in France represents about two thirds of the graben-width and is bordered to the East by the Rhine river. The plain itself consists of Tertiary marls and Pliocene and Quaternary alluvial deposits and loess, which represent the groundwater reservoir. More details about geology setting can be found in Simler *et al.* (1979).

3.2. The alluvial aquifer and groundwater

The alluvia thickness increases from the Vosges edge to the center (100 to 200 m in the south of Strasbourg and 200 to 250 m in the North-East of Colmar). This thick sedimentary mass consists of a more or less coarse sand alternation and gravels, with some intercalations of clays and silts. The whole forms an important hydrous reserve, on a marleous substratum, with a gutter shape.

The supply is ensured by the infiltration of the Ill and Rhine rivers, the two main rivers which dominate the superficial hydrography of the Rhine valley. Groundwater has a quite fast displacement in the main direction SSW-NNE, and a minor displacement from the Vosges edge to the Rhine.

3.3. Mineralogical composition

Many drillings carried out through the alluvial plain enabled to note a prevalence of sand (15-30%) or gravel (20-50%) compared to rollers, and more or less important clay layers, but of which the thickness does not exceed a few meters. In sand, it has been found quartz, calcareous particles (15-20%) and muscovite. Mineralogical analyses of Rhine and Ill sediments show a high proportion of quartz, about 15% of clays, a little more feldspar for Rhine, and microcline, plagioclase and calcite for Ill. Clay materials are divided into: kaolinite (10%), chlorite (15%), illite(15-50%) and illite/smectite(10-50%), among which montmorillonite (Tricca, 1997).

4. Study area

We focused on three kilometers downstream from the spoil heap Alex (Figures 1 and 3). In this part of the Rhine aquifer, hydrodynamical properties are sharply different from the main part of the alluvial aquifer, due to the different geological material that make it up: particularly, hydraulic conductivity is far lower, (BRGM, 2006). The aquifer can be divided into three layers, the first and the second layers have a thickness between 5 and 20 meters, and the third one is smaller. Wells have enabled to perform water analyses, at a determined depth. For our study we have analysed a set of samples collected within a single layer of this system - the second one - in order to have a first approximation of the geochemical evolution of groundwater along a flow line.

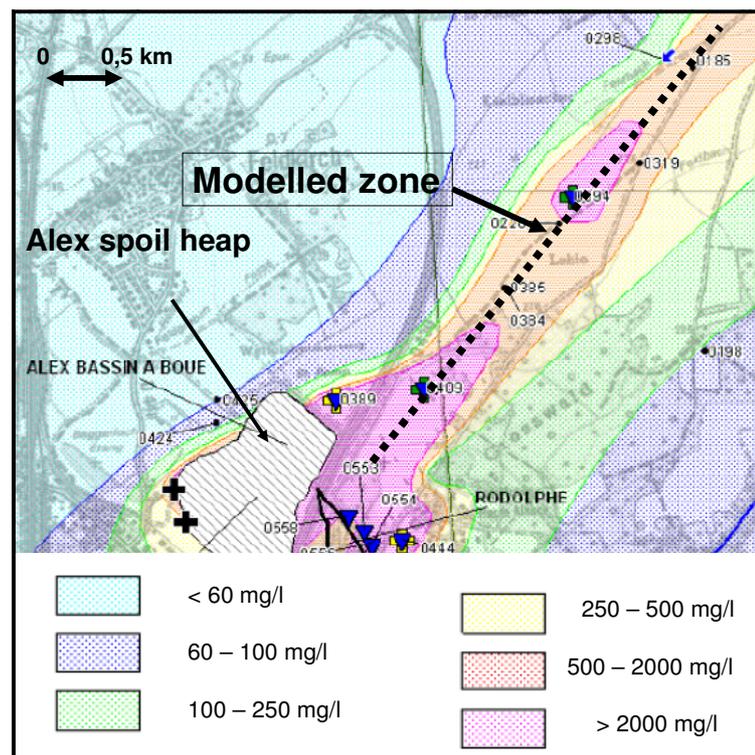


Figure 3. A chloride pollution map of the modelled zone, downstream from the spoil heap Alex.

5. Numerical model

To study the saline pollution evolution and its geochemical consequences, we have built a coupled hydrogeochemical model from the previous zone, due to the numerical code KIRMAT.

5.1. KIRMAT code

The hydrochemical code KIRMAT (Gérard *et al.*, 1998) is a one dimensional code, whose discretization method is the classical finite difference, and which uses thermodynamic and kinetic formulations for dissolution and precipitation. The chemical and the conservative transport mass balance equations are solved simultaneously due to an explicit scheme and a one-step algorithm.

5.2. Hydrodynamical model

According to the specific form of the Upper Rhine aquifer, its gutter shape and the fact that the main flow direction is in one direction NNE-SSW, it can be considered that the one dimensional model is a first good approximation.

Meshes are 50 meters long, Darcy's velocity is 2.8 m/year, the porosity of 15%. The coefficient of dispersion is 1000 m (Gelhar *et al.*, 1992), except on the first kilometer downstream from spoil heap, where it is 10 meters to take into account the mixing zone.

5.3. Geochemical model

Several studies dealing with the saline pollution of Rhine groundwater have shown that, in addition to calcite dissolution and precipitation, there are exchange reactions between the alkalis brought by saline groundwater and the calco-alkalis from clays (essentially Ca from montmorillonites) (e.g.: Durand, 2003). The model that we have developed takes these two reactions into account and only these reactions; the porous matrix consists of 1% of montmorillonite, and 99% of inert material:

- Calcite dissolution/precipitation:

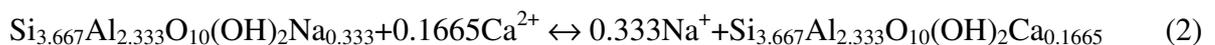


Dissolution and precipitation are modelled thermodynamically.

- Cation exchanges in montmorillonite

For this clay, Na^+ and Ca^{2+} cations and water fill interfoliaceous space, and several observations give a report on ionic exchanges between Na and Ca within these chlorinated water clays (Kloppmann *et al.*, 2001), with a preferential tendency to integrate Na^+ ions rather than Ca^{2+} (Cerling *et al.*, 1989).

Its initial composition is the following: Ca end-member, 81.25%; Na end-member: 18.75%. KIRMAT enables to model exchanges in clays considered as solid solutions. The mechanism of exchange that we studied, between the ions sodium and calcium on clays, can be illustrated by the following reaction:



The cation couple is described by only one thermodynamic equilibrium constant (Fritz, 1981). With the assumption of ideal solid solution, for which the end-member activities are equal to their molar fraction the relations characterizing the exchanges are the following:

$$\frac{[\text{Na}^+]}{[\text{Ca}^{2+}]^{0.5}} = K_{\text{Na/Ca}} \frac{[\text{Na}_{\text{fixed}}]}{[\text{Ca}_{\text{fixed}}]} \quad (3)$$

5.4. Time dependant pollution

We have modelled the pollution history into four stages: (1) 1910-1976 is the period of pollution by infiltration; (2) 1977-1989 is the period of the first anti-pollution actions, leaving only a residual pollution; (3) 1990-2001 is the period of active dissolution and high pollution; (4) 2002-2005 is a period for which pollution is stopped.

6. Results and conclusion

Measures of 2005 are compared with the results of our simulation from 1910 to 2005. Each period of pollution history brings its contribution to the spatial distribution of chloride concentration (Figure 4).

During pollution periods (1) and (3), Ca^{2+} concentration, due to cation exchange, is higher than during a simple transport process (\uparrow). For periods (2) and (4), when pollution is stopped or is less important, Ca^{2+} concentration tends to decrease in time by dilution and even a little by a reverse cation exchange (\downarrow) (Figure 5). The spread of chlorides has been accompanied by a significant change in the chemical composition of ground water, which can be understood by a major role of Na-Ca cation exchange.

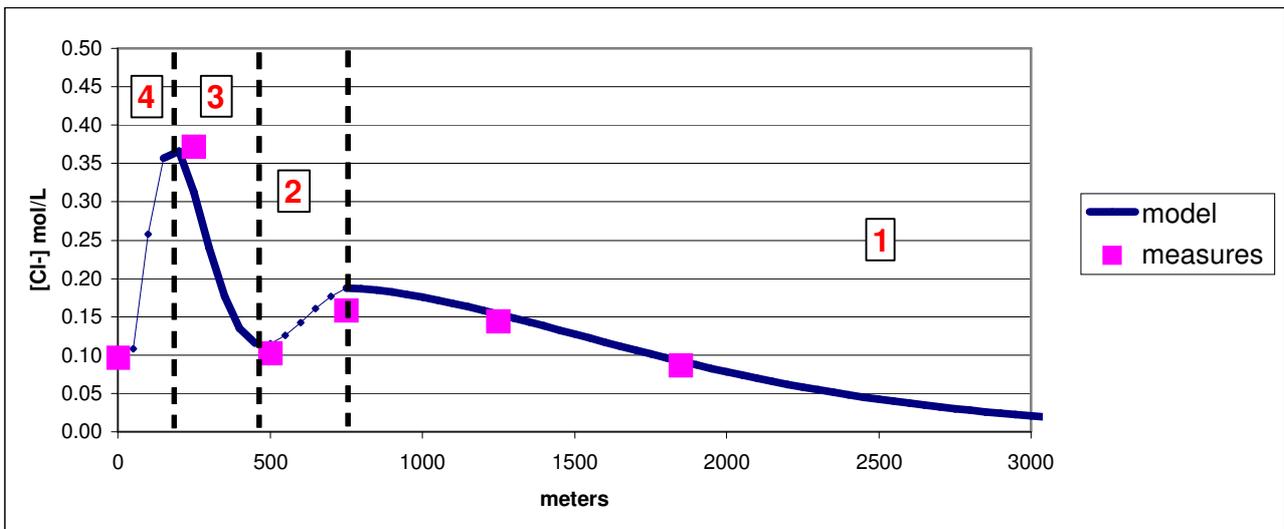


Figure 4. Spatial distribution of chloride concentration downstream from spoil heap Alex corresponding to the different stages of pollution: (1) 1910-1976 ; (2) 1977-1989 ; (3) 1990-2001 ; (4) 2002-2005.

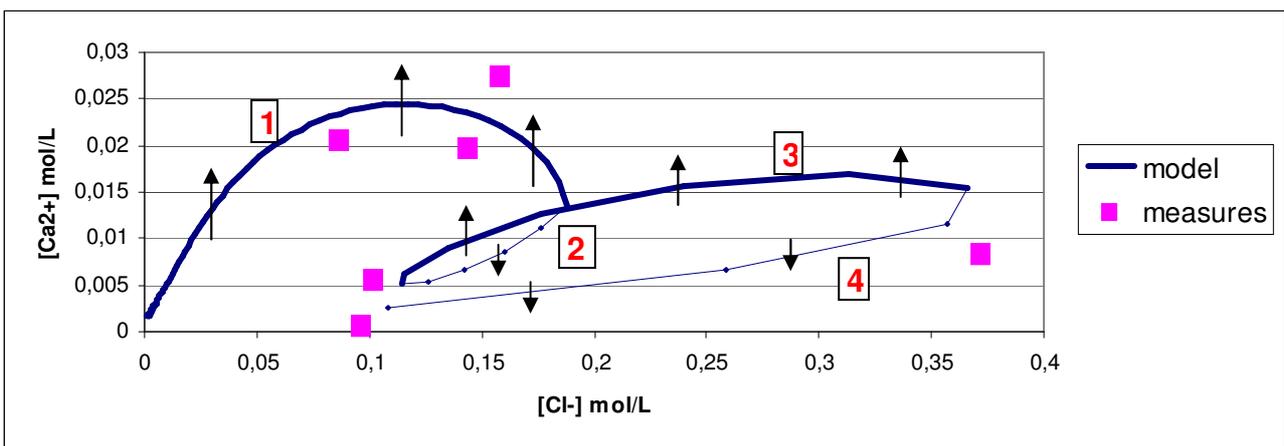


Figure 5. Calcium concentration versus chloride concentration downstream from spoil heap Alex.

A simulation of natural remediation enables to forecast that for the three kilometers downstream from the spoil heap, chloride content will be reduced under the limit of non-drinking water (250 mg/l or 7.05 mmol / l) after about 320 years in the best case.

Thus, the coupled hydrogeochemical model tends to validate the cation exchange mechanism; it enhances our understanding of the aquifer system submitted to a saline pollution, qualitatively and quantitatively, and gives a tool to forecast the pollution evolution.

7. Références

- Bauer M., Eichinger L., Elsass P., Kloppmann W. and Wirsing G. (2005). *Isotopic and hydrochemical studies of groundwater flow and salinity in the Southern Upper Rhine Graben*. International Journal of Earth Sciences, Vol 94, 565-579.
- BRGM (2006). *Modélisation de la salure profonde au droit et en aval du bassin potassique*, rapport final, BRGM-54389-FR.
- Cerling T.E., Pederson B.L. and Von Damm K.L. (1989). *Sodium-calcium ion exchange in the weathering of shales; implications for global weathering budgets*. Geology; Vol 17; 552-554
- Duprat A., Simler L., Valentin J. (1979). *La nappe phréatique de la plaine du Rhin en Alsace*. Université Louis Pasteur-Strasbourg 1, Sciences Géologiques, Mémoires, Vol. 60, 266 p.
- Durand S. (2003). *Traçage géochimique des transferts de matière dans l'hydrosystème de la vallée du Rhin supérieur: apport des déséquilibres isotopiques ^{238}U - ^{234}U - ^{226}Ra* . PhD Thesis, Louis Pasteur University, Strasbourg I, France.
- Elsass P. (2007). Historique de la pollution saline des MPDA, Journées d'information MPDA/BRGM, la salure de la nappe d'Alsace, le cas du bassin potassique, 8-9 octobre 2007, Ecomusée d'Alsace, Ungersheim.
- Fritz B. (1981). *Etude thermodynamique et modélisation des réactions hydrothermales et diagénétiques*. Sciences Géologiques, Mémoires, Vol. 65, 197p.
- Gelhar L., Welty C. and Rehfeldt K. (1992). *A Critical Review of Data on Field-Scale Dispersion in Aquifers*. Water Resour. Res., Vol 28(7), 1955–1974.
- Gérard, F., Clement, A., Fritz, B. (1998). *Numerical validation of a Eulerian hydrochemical code using a 1D multisolute mass transport system involving heterogeneous kinetically controlled reactions*. Journal of Contaminant Hydrology, Vol 30, 201–216.
- Kloppmann W., Négrel P., Casanova J., Klinge H., Schelkes K. and Guerrot C. (2001). *Halite dissolution derived brines in the vicinity of a Permian salt dome (N German Basin). Evidence from boron, strontium, oxygen, and hydrogen isotopes*. Geochimica et Cosmochimica Acta, Vol 65, Issue 22, 4087-4101.
- Simler L., Valentin J., Duprat A. (1979). *La nappe phréatique de la plaine du Rhin en Alsace*. Sciences Géologiques, Mémoires, Vol. 60, 266 p.
- Tricca A. (1997). *Transport mechanisms of trace elements in surface and ground water: Sr, Nd, U and REE evidence*. Ph.D. Thesis, University Louis Pasteur, Strasbourg, France, 234 p.