# Biogeochemical Processes during the Infiltration of River Water into an Alluvial Aquifer

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Biogeochemical processes occurring during infiltration of surface water from the Lot River into an alluvial aquifer are described using chloride as a natural tracer of water mixing in a well field where a Cl--rich aquifer water is recharged with a Cl-poor river water. Near the river bank a slightly reduced zone (depleted in O<sub>2</sub>, DOC, NO<sub>3</sub>, Na, and K and enriched in Mn, Ca, Mg, bicarbonate, and silica) is observed. Sulfate behaves conservatively. Nearest to the infiltration zone some of the pH-regulating processes are not at equilibrium. These phenomena can all be explained by bacterial degradation of organic matter in the river bank sediments and weathering of minerals along the infiltration path. In some cases (degradation of DOC and dissolution of calcium and magnesium carbonates) a semiquantitative confirmation of the stoichiometry of the reactions is given. Zinc is efficiently filtered after the first 10-15 m of the bank sediment-alluvion system. Some chemical changes occurring in the reduced zones are reversible (depletion of dissolved oxygen, dissolution of Mn). Others are not.

### Introduction

Because of easy access and high productivity, alluvial aquifers supply a very significant amount of drinking water in many countries (1-3). A large fraction (up to 90%) of the water pumped from such aquifers can come directly from a neighboring river by infiltration through its bottom and bank sediments. By pumping in the aquifer rather than directly in the river, it is hoped that the porous geological medium (river bank sediments followed by aquifer solids) acts as a natural physical, biological, and chemical filter by retention of suspended solids and microorganisms and adsorption, precipitation, or degradation of river-borne chemical pollutants (3-5). It is therefore crucial to have good knowledge of the filtering capacity of the river-alluvial aquifer system, and the expected benefits must be evaluated in terms of the overall biogeochemical processes occurring in the system. Biological activity in the sediments can have detrimental effects on the water quality (5-11). It is not uncommon, for example, to find Fe and Mn in the water pumped, due to dissolution of manganese and iron oxides (1). While these two metals are not highly toxic, they do lead to very serious quality problems (taste, odor, color, staining, corrosion).

The most investigated field site with respect to the processes described above is located on the Glatt River, Switzerland, where river water infiltrates through the bank sediments to become the upper layer of the local aquifer (8). The most significant chemical changes were found to occur within the first few meters of infiltration and were related to microbial degradation of organic matter (7–9). Further changes along the flow path were attributed to solubility adjustments controlled by calco-carbonic equilibria and to mixing with a deeper aquifer of different chemical composition (10).

Here we describe the results of another field investigation of hydrogeochemical processes occurring during the infiltration of river water into an alluvial aquifer through river bank sediments. While previously published investigations (6-11) describe geochemical changes occurring along the river-groundwater infiltration path, no calculations have been provided to correct these variations for the simple physical mixing of river and groundwater, though this was recognized as important in the Glattfelden study (11). Using chloride as a natural tracer of water mixing in a well field where a Cl--rich aquifer water is recharged with a CI-poor river water, we describe a methodological approach which allows a semiquantitative evaluation of these processes when surface water from the Lot River penetrates an alluvial aquifer under the influence of an operating well field.

# Field Site

The site is located ~200 km east of Bordeaux, France (Figure 1), in the Garonne River drainage basin. The alluvial system (Figure 2) is made up of two 5-m layers—loamy alluvions at the surface above the aquifer formation of gravel with clay. It overlies relatively impermeable Lower Hettangian formations. Before significant pumping began, this alluvial aquifer recharged the Lot River. Nine wells now pump an average of 140 m<sup>3</sup> h<sup>-1</sup>, and piezometric levels indicate that a large fraction of the water comes from the nearby Lot River infiltrating through bank sediments. Preliminary estimates for the recharge and average flow velocity are 0.05 m<sup>3</sup> d<sup>-1</sup> m<sup>-2</sup> and 3-5 m d<sup>-1</sup>, respectively.

The sediments from the Lot River are contaminated with Cd and Zn (12) coming from tailings of abandoned smeltering activities ~20 km upstream. Typical values in the river sediments around the well field zone are 15  $\mu$ mol g<sup>-1</sup> for Zn and 0.1  $\mu$ mol g<sup>-1</sup> for Cd) (13). The potential migration of these toxic elements from the river sediments toward the aquifer and its wells is thus of great interest for the well field under study.

## Methods

Water was sampled in September 1990 from the operating wells in the well field as well as from the surface (0.5-m depth) of the Lot River near the closest wells. Nonconservative parameters (pH, alcalinity, temperature, dissolved oxygen) were measured on site following sampling, and sample contamination by oxygen during sampling was minimal. Sampling was done through a bypass port in each well pumping system. Dissolved oxygen was measured within minutes after sampling. Anions, cations, and dissolved organic carbon (DOC) were analyzed offsite following proper conditioning (filtration with 0.45- $\mu$ m pore-size cellulose Millipore filters, followed by acidification with Suprapur HNO<sub>3</sub> for cations and H<sub>2</sub>SO<sub>4</sub> for DOC). Dissolved cations were measured by ICP or flameless atomic absorption and dissolved anions by ion



Figure 1. Location of the study area.



Figure 2. Schematic representation of the study area.

chromatography; DOC was measured by colorimetry (following oxidation by sodium persulfate).

The analytical precision for the range of concentrations of our samples was  $\sim 5\%$  for major anions and cations, 10% for trace metals and DOC, 1-2% for dissolved oxygen, and  $\pm 0.02$  unit for pH. The maximum uncertainty in the alkalinity was  $\pm 0.05\%$ .

#### **Results and Discussion**

Measurement of the Mixing of River and Aquifer Water in the Well Field. Long-term chemical monitoring, carried out for the local water authority (Agence de l'Eau Adour-Garonne), shows that the dissolved chloride contents of the Lot River and of its alluvial aquifer are quite stable and different. The average values over a 3-year period are  $(1.3 \pm 0.2) \times 10^{-4}$  mol L<sup>-1</sup> in the river and (3.3) $\pm 0.3$ )  $\times 10^{-4}$  mol L<sup>-1</sup> in the aquifer. In June and July, the chloride content in the Lot is usually higher (by up to a factor of 2). These values were omitted from our calculations of the average concentration. We can therefore use chloride concentrations as an index of mixing between two end members (aquifer water and river water). The chloride values used for the end members in our calculations were the concentrations measured during our September 1990 field survey (i.e.,  $1.1 \times 10^{-4} \text{ mol } L^{-1}$  for the river and  $3.0 \times 10^{-4}$  mol L<sup>-1</sup> for the aquifer).

By comparing the  $Cl^-$  concentrations in each well with measured values in the Lot River and in the alluvial aquifer prior to operation of the well field, it is possible to estimate the degree of mixing of these two end members according to the following formula, where C is the concentration of chloride and x the fraction of water originating directly from the Lot River:

$$C_{\text{well}} = xC_{\text{Lot}} + (1-x)C_{\text{aquifer}}$$
(1)

With the exception of one well (located 350 m from the river) whose physicochemical parameters are not affected by pumping operations (this well is used as the aquifer



Figure 3. Fraction of water coming from the river in the wells of the well field.

water end member for chloride concentration because its chemical signature is identical to that of private wells prior to the beginning of well field operation), application of eq 1 indicates that 80 to nearly 100% of the water extracted from the other boreholes originates from the Lot River (Figure 3). This is true even if three of the wells are located between 60 and 140 m from the river. A large fraction of the water pumped in the well field thus comes from recharge of the aquifer by the river. These results are in agreement with hydraulic model calculations based on piezometric levels.

A Chemical Steady-State Assumption. If we assume that the river-aquifer system is at steady state (i.e., invariant chemistry both at the time of sampling and over the period of time needed for the river water to reach the wells), the biogeochemical processes occurring in the river bank and in the alluvial aquifer during the sampling campaign (i.e., September 1990) can be unambiguously identified and quantified by comparing the observed values for a given parameter with the theoretical concentrations which should be obtained if there was only physical mixing of water samples of two different origins (using eq 1 with C now as the concentration of the given parameter). Parameters involving only physical mixing of river and aquifer water should lie close to the theoretical mixing line (Figure 4). Observed values significantly lower than this theoretical line indicate a biogeochemical process resulting in the consumption or disappearance of the chemical parameter studied (e.g., biological consumption, precipitation, adsorption, or evaporation) while values higher than those predicted by physical mixing must result from in situ production (e.g., porous matrix dissolution, desorption, or biological production) or from an external source.

The assumption of steady state can be contradicted by two observations: Photosynthetic activity in the river is capable of inducing significant diurnal variations in some of the chemical characteristics of the river water (10, 11,14). Longer term temporal variations (such as seasonal cycles) can also occur (11).

The effect of photosynthesis and respiration in the Lot River was studied near our well field a few weeks before the investigation reported here (15). Daily changes were observed for temperature (19–25 °C), pH (8.0–8.7), dissolved oxygen (190–350  $\mu$ mol L<sup>-1</sup>), alcalinity (1.3–1.6 mmol L<sup>-1</sup>), sulfate, Ca, Mg, Na, and Zn. Though they do lower its precision, none of these ranges of values significantly affect our methodological demonstration.

Seasonal variations in the Lot River near our well field are presently under investigation. Their effect on a single sampling campaign should however be quite limited since it has been clearly suggested by other authors working on



Figure 4. Variation of dissolved component concentrations and pH as a function of an index of conservative mixing (calculated from the chloride content of the well water samples and of the two end members, unperturbed aquifer water, and Lot river water). (In each diagram the straight line is the theoretical physical mixing line. No such theoretical mixing line is plotted for pH because this parameter is not conservative with physical mixing even in the absence of biogeochemical reactions. For the dissolved oxygen, in Figure 4a, the dotted straight line is the theoretical mixing line between oxygen-depleted water from wells close to the river and the aquifer end member.)

the Glattfelden site (Switzerland) that most of the biogeochemical processes occurring during the infiltration of river water through river banks take place within the first few meters after infiltration (7-10). In other words, water sampled in the biogeochemically active zone of our aquifer certainly has a residence time in the aquifer of no more than 10-20 days.

**Biogeochemical Processes.** The concentrations of dissolved oxygen and DOC decrease abruptly as the river water passes through the first 15-20 m of sediments and aquifer solids (Figure 4a and b). This can be explained by the mineralization of dissolved organic compounds by the microorganisms of the river sediments, according to the Redfield equation:

$$DOM + 138O_2 \rightarrow 106CO_2 + 16NO_3^- + HPO_4^{2-} + 122H_2O + 18H^+$$
 (2)

where DOM is  $(CH_2O)_{106}(NH_3)_{16}(H_3PO_4)$ .

When oxygen consumption exceeds supply, the medium becomes reducing. Beyond this "reduced zone" the water is mixed with aquifer water but the observed  $O_2$  values which lie above this new physical mixing line (dotted line in Figure 4a) reveal the existence of an external source of dissolved oxygen. This input is most certainly caused by recharge through the unsaturated zone above the aquifer (rain and irrigation). One hundred meters downstream from the reduced zone (mixing index of 80%), the percolating water has almost reached the background aquifer value (ca. 140  $\mu$ mol L<sup>-1</sup>). After its partial disappearance (due to bacterial activity), the DOC concentration remains constant even though oxygen is still present. This remaining DOC must be due either to its nonbiodegradable nature or to a decrease in bacteria population along the flow path.

Dissolved oxygen is not the only electron acceptor for the bacterial degradation of organic matter. Nitrate accepts additional electrons and this is evident in the  $NO_3^$ concentration observed in situ, which is significantly lower than the mixing line (Figure 4c). Such a denitrification, even when some oxygen is still present, has also been observed by other authors (9-11). Nitrate increases again later along the infiltration path with the fraction of aquifer water because of mixing with nitrate-rich alluvial aquifer water (Figure 4c).

As water infiltrates through the river sediments and the porous matrix aquifer, it becomes enriched in calcium, magnesium, carbonate alkalinity and silica (Figure 4f-i). These chemical components come from the weathering of calcium and magnesium carbonates and from quartz dissolution, according to the reactions

$$Ca_{(1-x)}Mg_{x}CO_{3} + H^{+} \rightarrow HCO_{3}^{-} + (1-x)Ca^{2+} + xMg^{2+}$$
(3)
$$SiO_{2} + 2H_{2}O \rightleftharpoons H_{4}SiO_{4}$$
(4)



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Figure 5. Stoichiometry of dolomite and mixing index.



Figure 6. Observed and calculated pH values as a function of conservative mixing.

through their participation in cation-exchange reactions with Na or K as described by eq 5. Both alkali ions are removed in the infiltration zone (Figure 4j for Na), but the quantities involved are more than 1 order of magnitude smaller that the amounts of Ca and Mg solubilized

$$2B^{+} + AX_{2} \rightleftharpoons A^{2+} + 2BX \tag{5}$$

(with A = Ca or Mg and B = Na or K). For the same reason (i.e., no K is solubilized), no weathering of aluminosilicate minerals, such as described in eq 6, appears to be occurring.

$$KAlSi_{3}O_{8}(s) + H^{+} + 4.5H_{2}O \rightarrow K^{+} + 2H_{4}SiO_{4} + 0.5Al_{2}Si_{2}O_{5}(OH)_{4}(s)$$
(6)

Sulfate seems to behave conservatively (Figure 4k). This is not surprising since the river bank is not sufficiently reducing for sulfate reduction to S(II), which would induce dissolved S removal (through precipitation of sulfide minerals).

Upon infiltration of the river water, the pH generally decreases to  $\sim 6.8$  (Figure 4d). A high value of 7.7 is observed in one of the wells. This is surprising because, as observed in other alluvial aquifers (Deûle, France, and Glatt, Switzerland) (6, 11), reaction 1 should result in a decrease in pH. The EQ3/6 code (16) was used to calculate the theoretical pH if the system were at equilibrium. For the wells closest to the river bank, the calculated pH values demonstrate the absence of equilibrium (Figure 6). This is most likely explained by a different response time of the system to eqs 2 and 3. The respiration reaction induces a pH decrease, which in turn provokes a pH increase resulting from the dissolution of calcareous material (dolomite). At the beginning of the flow path of the infiltrating water, the carbonate dissolution must be slow with respect to the microbial respiration. A locally high  $pCO_2$  (10<sup>-1.9</sup>, as calculated with EQ3/6) induces a dip in the evolution with transport of the calculated pH (Figure 6)

Manganese is strongly remobilized in the zone of maximal oxygen depletion (Figure 4e). It is removed from

solution when the medium is reoxygenated. As also observed by other authors (9-11), Mn is solubilized even though there is still some oxygen present in solution (ca.  $30\,\mu\text{mol}\,\text{L}^{-1}$ ). When the water again becomes more oxidized  $(>60 \,\mu mol \, L^{-1})$ , not only is Mn removed from solution but its concentration becomes lower than that in the river. This larger solubility of manganese in the Lot River may be due to a larger extent of complexation with organic matter (more DOC in the river) and/or to a lower adsorption (less available adsorbing surfaces compared to the aquifer sediments). Seasonal trends affected the local remobilization of Mn in the Glatt River site (11). A large dissolution of manganese was observed during summer months. More oxidizing conditions in winter lead to precipitation of Mn and temporary storage in the riverbed sediments and in the aquifer.

The high dissolved manganese concentrations observed in some of the wells clearly do not come from the river water (Figure 4e). They most probably originate from remobilization of Mn in river sediments (11) and/or aquifer solids (17). The solubility of manganese in natural aquatic systems can be controlled by several mechanisms.

The reduction of manganese oxides (whether they are of sedimentary or biogenic origin) is rapid in the presence of electron donors (sulfide, Fe(II), but also organic compounds) (18). Manganese oxide reduction can be microbially mediated, even under aerobic conditions (19).

The strong decrease in dissolved Mn in the water flow path following the fast increase upon infiltration might be explained by various processes: redox, adsorption, and precipitation reactions.

Precipitation of MnCO<sub>3</sub> can be ruled out in our site (in September 1990) because the dissolved manganese in all of the wells and in the Lot River is at least 1 order of magnitude lower than the concentration necessary for equilibrium with rhodochrosite [calculations carried out with EQ3NR111 (16), considering a solubility product of  $10^{-10.41}$  (20)]. All of the samples collected during our campaign are, however, in equilibrium with MnO<sub>2</sub> (pyrolusite) [solubility product of  $10^{0.028}$  for the reaction written as  $2Mn^{2+} + 2H_2O + O_2(g) = 2pyrolusite + 4H^+$ (16)].

The chemical oxidation of Mn(II) by oxygen is slow in homogeneous solutions at pH <8. The oxidation rate is enhanced considerably in heterogeneous systems where manganese is first adsorbed to a mineral surface and thereafter oxidized (21). If we apply the equation of Davies and Morgan (21) for the abiotic oxidation of Mn(II) to our system

$$-d[Mn^{2+}]/dt = [Mn^{2+}][OH]^{2}[O_{2}](k_{1} + k_{2}[solid])$$
(7)

where  $k_1$  and  $k_2$  are the homogeneous and heteregeneous rate constants with respective values, at 25 °C, of ca. 4 ×  $10^{12}$  mol<sup>-3</sup> d<sup>-1</sup> and (1–5) ×  $10^{18}$  mol<sup>-4</sup> d<sup>-1</sup>. For an initial dissolved Mn of 2 µmol L<sup>-1</sup>, a pH of 7, and a dissolved oxygen content of 60 µmol L<sup>-1</sup>, estimating very roughly the minimum removal rate of Mn as 0.075 µmol L<sup>-1</sup> d<sup>-1</sup> (for 20 d of travel through the aquifer between the well of maximum Mn concentration to the next one where Mn has been removed), the contribution of homogeneous reactions is very small with respect to heterogeneous processes (ratio 1:10<sup>4</sup>) and the surface catalyzing solids required for them are ca. 10 µmol L<sup>-1</sup>. For a 5% porosity in the aquifer (estimated from two pumping tests), the concentration of active surface sites should be ~0.6 µmol  $g^{-1}$ . This concentration is quite small compared to realistic solid MnO<sub>2</sub> concentrations in aquifer solids (e.g., 5–15  $\mu$ mol  $g^{-1}$  in core samples from our alluvial aquifer).

The peak in dissolved manganese is thus certainly due to in situ solubilization [most likely of  $MnO_2(s)$ ]. Sorption of Mn(II) followed by surface oxidation to  $MnO_2(s)$ removes the dissolved Mn later in the flow path.

Dissolved cadmium is always below our detection limit (of  $5 \text{ nmol } L^{-1}$ ). Zinc in river-borne water is very efficiently removed from solution in the first 10 m of sediments and alluvions (Figure 4l), even though the bottom river sediments are significantly contaminated by this metal (15  $\mu$ mol g<sup>-1</sup>). As none of the common minerals tested with EQ3/6 came close to controlling the solubility of zinc, its removal must be due to adsorption reactions. It could also be favored by the degradation of dissolved organic compounds (dissolved complexing agents) in the river bank. These observations are consistent with those of the Glatt River site (9-11), where dissolved zinc and cadmium increased after the first 3-5 m of infiltration (reaching values of 470 and 5.5 nmol  $L^{-1}$  for Zn and Cd, respectively), followed by a decrease to aquifer values similar to those of the river water. These authors attributed the increase in heavy metal concentration to decreasing pH as river water infiltrates through river sediments and the later decrease in concentration to adsorption processes. In our study, the spatial resolution near the river bank is limited and we may have missed such a peak in dissolved heavy metals. It is interesting to note that even though in our investigation the Lot River water contains more dissolved Zn than the Glatt River and the Lot River sediments can be safely estimated to present a higher metal content than those of the Glatt, the water infiltrated in our well field does contain less dissolved zinc ( $<15 \text{ nmol } L^{-1}$ ) than the groundwater in the Swiss site (up to 470 nmol  $L^{-1}$  and a aquifer value in the range of 20-70 nmol L<sup>-1</sup>).

These observations demonstrate or confirm the occurrence of various processes as water infiltrates from the river through its bottom and bank sediments into the aquifer and mixes with groundwater. Respiration by microorganisms and oxidative degradation of organic molecules lead to the creation of a reduced zone. In the reduced zone, we observe a minimum in dissolved oxygen and maxima in dissolved manganese and nitrate degradation. Calcium and magnesium carbonates and quartz are weathered, releasing Ca, Mg, and Si into the infiltrating water.

The use of Cl<sup>-</sup> as a tracer allows us to attempt to quantify some of these processes. In the reduced zone, some species are consumed (2 mg L<sup>-1</sup> or 1.7 × 10<sup>-4</sup> mol L<sup>-1</sup> DOC, 2.2 × 10<sup>-4</sup> mol L<sup>-1</sup> dissolved oxygen, 2.5 × 10<sup>-5</sup> mol L<sup>-1</sup> nitrate, 1.5 × 10<sup>-5</sup> mol L<sup>-1</sup> sodium, 8 × 10<sup>-7</sup> mol L<sup>-1</sup> zinc, 1.5 × 10<sup>-7</sup> mol L<sup>-1</sup> protons) while others are produced (1.6 × 10<sup>-6</sup> mol L<sup>-1</sup> manganese, 6 × 10<sup>-4</sup> mol L<sup>-1</sup> calcium, 1 × 10<sup>-4</sup> mol L<sup>-1</sup> magnesium, 1 × 10<sup>-3</sup> mol L<sup>-1</sup> bicarbonate, 1 × 10<sup>-3</sup> mol L<sup>-1</sup> silica). The (DOM degraded)/(O<sub>2</sub> consumed) ratio is 1.3, which corresponds exactly to the stoichiometry of eq 2.

Some of the few simple stoichiometric equations suggested by Jacobs et al. (10) to describe the chemical changes taking place in the water during its infiltration are semiquantitatively verified here (our eqs 2 and 3). Others were either not observed (our eq 6) or at most of little significance (our eq 5).



Figure 7. Schematic description of the biogeochemical processes in the infiltration path flow.

## Summary and Conclusions

The chemical changes in the infiltration flow path from the Lot River to an adjacent aquifer were followed using chloride as an indicator of physical mixing of the river water with groundwater. The chemical reactivity close to the river is very significant with respect to the aquifer water composition (Figure 7). Two types of processes occur. A first series leads to irreversible reactions: weathering produces enriched Ca, Mg, bicarbonate, and Si concentrations, reductive reactions lead to denitrification, and adsorption reactions remove zinc from solution (11, 22). A second series comprises processes which lead to the formation of the so-called *reduced zone*, and most of them are reversible. As long as microbial activity, which is very intense in the river sediments, consumes more oxygen than what is brought by the water coming from the river, the environment becomes reduced. This leads to dissolution of manganese oxides. Further along, when the microbial activity decreases, and when additional oxygen can be supplied by the permeable unsaturated zone. the water environment becomes oxidized again. Manganese is removed from solution by a combination of adsorption and surface oxidation reactions.

Our observations are coherent with other investigations (9-11). They do unambiguously show the extent of chemical changes with respect to physical dilution. While the irreversible reactions (production of Ca, Mg, HCO<sub>3</sub>, and Si and denitrification) are not detrimental to the water quality, some of the reversible processes can produce water of locally poor quality (presence of Mn). These processes, however, can disappear if enough oxygen becomes available via the unsaturated overlying soil zone (i.e., if it is not too impermeable). The quantities involved are quite large (e.g., degradation of 200 g of DOC h<sup>-1</sup> and a consumption

of 24 mol  $h^{-1}$ ), indicating a great biological activity. It is thus not surprising to observe foul taste problems in the water pumped since most of the wells are located in the reduced zone.

The biogeochemical changes occurring in the infiltration flow path are summarized schematically in Figure 7. The processes occurring in the reduced zone are usually detrimental to groundwater quality. The position of wells in an alluvial aquifer with respect to the location of the reduced zone is therefore crucial. Boreholes should be located outside of this zone. However, it is not very easy to predict a priori the location and extent of the reduced zone since it may depend on the water hydraulics, on the possibility of recharge of dissolved oxygen, and on the state of equilibrium or nonequilibrium of the biogeochemical reactions involved. It is therefore important to investigate whether the reduced zone can expand, retract, or migrate as a function of the river quality (O<sub>2</sub>, DOC) and the pumping rate in the well field.

Under the biogeochemical conditions prevailing in September 1990, dissolved zinc in river-borne water is efficiently filtered by bank sediments and/or aquifer alluvions.

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