

# 1 D Geochemical modelling using NETPATH and PHREEQCI (South-West Hungary)

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In order to assess the geochemical reactions during precipitation infiltration an 1 D modelling study was carried out.

The studied aquifer of shallow groundwater is mainly loess and drift sand in Upper Pannonian and Pleistocene formations. Near uniform sample distribution was ensured with almost 250 water samples. The composition of shallow groundwater is typical of hilly areas, with a  $\text{Ca}^{2+}$ - $\text{Mg}^{2+}$ - $\text{HCO}_3^-$  content. Locally, the concentration of pollution-denoting anions ( $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ ) is significant. High concentrations of  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$  and  $\text{Cl}^-$  can be detected in shallow groundwater from the drift sand area, which are connected mainly to settlements.

The NETPATH and PREEQCI softwares were used to study precipitation infiltration tracking and water-rock interaction investigations.

Rainfall composition, "uncontaminated" shallow groundwater data and the mineralogy of aquifer with which the infiltrating waters interact, make it possible to calculate the rate of precipitation infiltration, too. The natural background calculations were based on histograms of  $\text{NO}_3^-$ - $\text{SO}_4^{2-}$ - $\text{Cl}^-$  logarithm concentration-values.

As chloride is a conservative element, it was used to calculate the evaporation factor. The infiltration was about 12-15 % in the loess area, according to the hydrogeochemical modelling. These could be maximum precipitation infiltration values. The approximately 22 % infiltration in the drift sand area is valid.

The water-rock interactions are similar during precipitation infiltration in both regions. The remarkable  $\text{CO}_2$  dissolution and calcite-dolomite dissolution, together with  $\text{N}_2$  gas formation during denitrification, is typical on both sites.

The few differences are the following:

1. there is plagioclase dissolution in the loess area, while quartz dissolves in the drift sand area
2. the calcite dissolution is higher in the drift sand area (because of the higher precipitation infiltration) than in the loess area
3. the K-feldspar dissolution is nearly two times higher in the drift sand territory than in the loess territory
4. ion exchange can be always detected on the drift sand, while in the loess area the water-rock interaction is possible also without ion exchange.

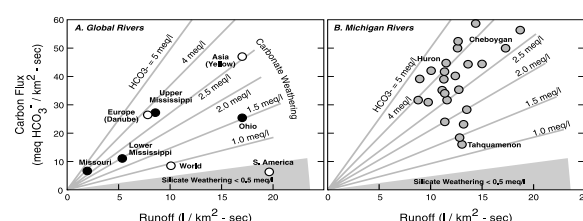
Even after the precise data sorting, the natural background contains some anthropogenic contamination. The water-rock interaction models also bear these potential faults, but the error could not be greater than 10 %. The reliability and accuracy of calculations could be corrected with isotope data.

# Carbonate Equilibria and Mass Transport in Surface Waters

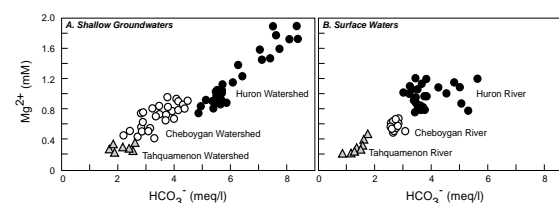
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Factors limiting dissolved inorganic carbon fluxes from watersheds will be very important in predicting the response of earth's surface reservoirs to anticipated changes in biomass and carbon budgets in the next few centuries. The mid-continent region, which has a high proportion of sedimentary bedrock mantled by carbonate-bearing glacial drift, is an ideal field laboratory in which to assess controls on the  $\text{HCO}_3^-$  fluxes. We present results of an ongoing study of watersheds in Michigan. Importantly, these have among the highest dissolved carbonate fluxes per unit area in the world:



The  $\text{HCO}_3^-$  flux from these watersheds is likely related to the  $\text{PCO}_2$  of the soil weathering zone. Surface and groundwater Mg concentrations are excellent conservative tracers of carbonate dissolution. The Ca and Sr mass balances are locally complicated by sources such as  $\text{CaCl}_2$ -rich subsurface brines, gypsum beds, and road salt application. Furthermore, the  $\text{Mg}/\text{HCO}_3^-$  ratio of surface waters relative to groundwaters provides a sensitive indicator of mass balances of carbonate precipitation after groundwaters discharge and degas  $\text{CO}_2$ . Although groundwater  $\text{Mg}/\text{HCO}_3^-$  ratios are nearly constant, surface waters show variable amounts of  $\text{HCO}_3^-$  loss to calcite precipitation:



In general, more than 10-fold supersaturations with respect to calcite are required to cause precipitation. These results suggest that shallow groundwater-stream systems are important in transferring additional carbon from terrestrial environments to the larger ocean reservoir.