Chemical and isotopic composition of soil solutions from cambisols in Styria (Austria) - Seasonality, evaporation and interstitial distribution

W. Schön[1], A. Leis[2], M. Dietzel[1]

[1]Institute of Applied Geosciences, Graz University of Technology, Rechbauerstraße 12, 8010 Graz, Austria,

[2]Institute of Water, Energy and Sustainability, Joanneum Research, Elisabethstraße 18, 8010 Graz, Austria

Introduction

In most natural surroundings soil solutions are primary gained from the uptake of meteoric water. Subsequently infiltration, capillary exchange, bioresponse, evaporation etc. result in complex and individual gas-water-solid systems. Knowledge on the chemical and isotopic evolution of soil solutions and its interstitial distribution is highly relevant for environmental and forensic studies. Therefore we investigated the composition of solids and interstitial solutions of distinct horizons for three cambisols in Styria (Austria) using a wetting and evaporation approach.

Methodology

Sampling

Three cambisols were sampled from localities Edelschrott (A), Obdach (B) and St. Oswald (C) in April and October 2012 down to depths of about 65 cm and subsequently stored in plastic bags to avoid evaporation (Fig.1).
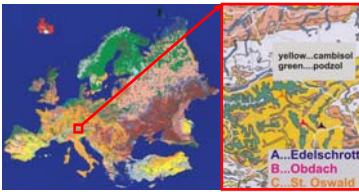

Fig.1: Sampling sites of soils (Anca et al., 2005).

Wetting and evaporation experiments

Wetting experiments were performed by pouring 50 ml deionized water (IASON) with $\delta^{18}O$ and δ^2H values of -348.7 ‰ and -944.2 ‰, respectively, over 0.5 kg soil with a percolation period of 5 min.

For *evaporation experiments* 0.5 kg soil were placed in plastic cups of about 20 cm in diameter to be exposed at T = 20 °C and 37 % relative air humidity for 17 hours (Hama TH 100). Subsequently to both experimental approaches squeezing was conducted.

Extraction of soil solutions

The compaction method was chosen to obtain the interstitial solutions by using 0.5 kg soil, a tempered steel cylinder and a hydraulic squeezing machine (Fig.2).

Pressure steps were (i) 27.4 MPa and (ii) 54.9 MPa corresponding to pF values of 5.43 and 5.73, respectively (Böttcher et al., 1996).
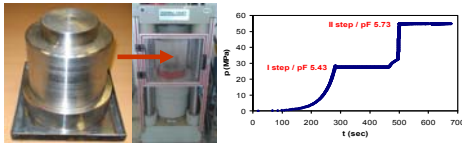

Fig.2: Steel cylinder, squeezing machine and squeezing record.

Analyses

Mineralogical and chemical characterizations of soil samples were done by XRD and XRF analyses. The extracted soil solutions were filtered (0.45 µm), pH and chemical composition were measured by pH meter (inoLab 740) and electrode (Schott BlueLine), IC (Dionex ICS- 3000) and ICP-OES (PE 4300 DV). $\delta^{18}O$ and δ^2H values were measured by using cavity ring-down spectroscopy (Picarro L1115-i isotopic liquid water and water vapor analyzer).

Results and Discussion

Composition of the cambisols

The three sampled cambisols consist mainly of quartz, chlorite, muscovite and plagioclase with minor amounts of kaolinite and vermiculite without any carbonates and significant vertical variability. Grain sizes of soils A and C are dominated by sand fraction (0.063 - 2 mm: 59 and 64 wt.%, respectively), whereas soil B by silt fraction (0.002 - 0.063 mm: 56 wt.%).

Composition of the soil solutions

The pH ranges from 5.8 to 7.8. The soil solutions are dominated by Ca^{2+}, Na^+, K^+, Mg^{2+}, NO_3^-, Cl^- and SO_4^{2-} in decreasing order of concentrations. $\delta^{18}O$ and δ^2H values vary from -11.9 to -4.0 ‰ and -90.4 to -34.4 ‰, respectively. The interstitial solutions from soils A, B and C are generally similar in chemical compositions. In principal, solutes are higher concentrated at pF 5.73 vs. 5.43.

Seasonality

The soil solutions from the three cambisols sampled in April and October show different concentrations due to seasonality. Generally pH values increase with depth. The pH of the soil solutions sampled in October as well as most of the solutes indicate higher values than those from April (Fig.3). A more pronounced decrease in concentration with depth is found in April vs. October for Na^+, K^+, Ca^{2+} and Mg^{2+} at pF 5.43 and 5.73 (Fig.4).
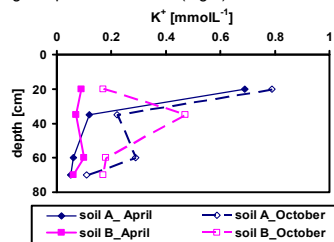

Fig.3: Seasonality - K^+ concentrations of the soil solutions vs. depth for soils A and B (April and October) at pF 5.43.
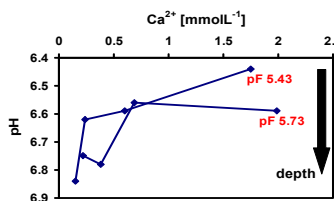

Fig.4: Seasonality - pH vs. Ca^{2+} concentrations of the soil solutions for soil A (April) at pF 5.43 and 5.73.

The $\delta^{18}O$ and δ^2H values of the soil solutions sampled in April trend to isotopically lighter δ-values with increasing depth, whereas for soils solutions from October a trend to heavier δ-values with depth is found (not shown). The soil solutions sampled in October rather represent the isotopic composition of the local precipitation. In contrast, soil solutions sampled in April seem to be affected by evaporation as given by the shift to lower δ^2H values (Fig.5). The *current degrees of evaporation* in % ($\Omega_c = F_e \, 100$) of soil solutions from April were calculated from the isotopic ratios according to equations

$$F_e = 1 - e^{(\delta_e - \delta_i)/\Delta} \quad (1)$$
$$\Delta = (1 - \alpha_{equ}) * 1000 + (1 - h) * (1 - \alpha_{kin}) * 1000 \quad (2)$$

after Mittermayr et al. (2013) for soils A, B and C. Ω_c values were obtained by using the average regional humidity (h = 0.74 %). α_{equ} denotes the equilibrium isotope fractionation factor between water and H_2O vapor (α_{equ} = 1.10495 for $^2H/H$ and 1.01121 for $^{18}O/^{16}O$ at 5°C) and α_{kin} is the kinetic isotope fractionation factor (α_{kin} = 1.0251 for $^2H/H$ and 1.0285 for $^{18}O/^{16}O$). δi and δe are the isotopic compositions of the initial and remaining solution throughout evaporation, respectively.

soil A: Ω_c (^2H) = 6.0 %, Ω_c (^{18}O) = 8.3 %,
soil B: Ω_c (^2H) = 3.6 %, Ω_c (^{18}O) = 4.8 %,
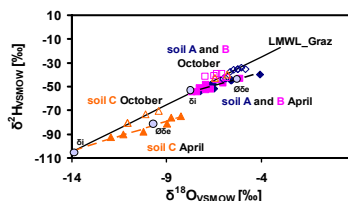soil C: Ω_c (^2H) = 15.2 %, Ω_c (^{18}O) = 18.1 %.

Fig.5: Seasonality - $\delta^{18}O$ and δ^2H values of the soil solutions from soils A, B and C (April and October). Samples from April indicate evaporation (dashed lines), whereas samples from October represent the isotopic composition of the local precipitation.

Evaporation Approach

Evaporation induces generally higher pH and solute concentrations vs. the pristine conditions. $\delta^{18}O$ and δ^2H values of the soil solutions indicate enrichments of heavier vs. lighter isotopes throughout evaporation (Fig.6). *Current average evaporation degrees* for soils A, B and C are calculated with h = 0.37 % and α_{equ} = 1.0852 for $^2H/H$ and 1.0098 for $^{18}O/^{16}O$ at 20°C:

soil A: Ω_c (^2H) = 22.0 %, Ω_c (^{18}O) = 15.5 %,
soil B: Ω_c (^2H) = 5.0 %, Ω_c (^{18}O) = 6.4 %,
soil C: Ω_c (^2H) = 50.3 %, Ω_c (^{18}O) = 32.1 %

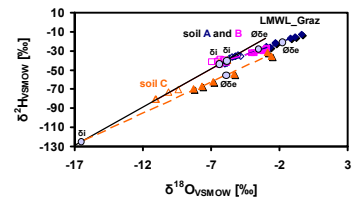**Fig.6**: Evaporation approach - $\delta^{18}O$ and δ^2H values for pristine vs. evaporated soil solutions for soils A, B and C (October) .

Wetting Approach

Obviously, solutes in wetted solutions are generally diluted vs. pristine solutions (Fig.7). The pH in wetted solutions are highest compared to seasonality variability and evaporation approach. $\delta^{18}O$ and δ^2H values for pF 5.73 are heavier vs. those for pF 5.43. At pF 5.73 and 5.43 about 70 and 60 % dilution is calculated from isotopic composition, respectively (Fig.7).
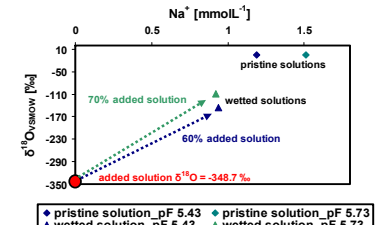

Fig.7: Wetting - $\delta^{18}O$ values vs. Na^+ concentrations for pristine, added and wetted solutions (soil A, October).

Summary and conclusions

Interstitial distribution

- Higher concentrations of solutes at pF 5.73 vs. 5.43 → different surface charcteristics and distinct adsorption mechanisms.
- Increase of pH with depth → Reduction of H^+ ions via silicate weathering and replacement of exchangeable cations.

Seasonality

- Evaporation trend in April → less precipitation and high proportion of evaporation during the winter months.
- Enrichment of lighter vs. heavier isotopes with depth in April → dislocation of isotopic lighter winter precipitation into deeper horizons. (vice versa in October).
- Less correlations of ion concentrations with depth in October vs. April → Soils are more isolated against meteoric impacts during the winter months.

Evaporation approach

- Current evaporation degrees are assessable via isotopic values and given humidities.
- Average evaporation degree is highest for soil C due to the coarse grain size distribution vs. soils A and B.

Wetting approach

- Infiltration of water into micropores is an extrem fast process.
- Even so-called „not available" adsorption- and capillary solutions (pF > 4.2) are significantly affected by wetting.

Outlook

- Individual calculations of evaporation and wetting trends of soil solutions from elemental and isotopic content.
- Developing a conceptual model for the interaction of soil solution and soil matter in respect to the different matrix potentials.
- Impact of the above interaction for environmental and forensic tasks in particular by considering stable isotope values.

References: BÖTTCHER,G.,BRUMSACK,H.-J.,HEINRICHS,H.,POHLMANN,M., 1996, A new high-pressure squeezing technique for pore fluid extractions from terrestrial soils, Water Air and Soil Pollution 94, pp. 289-296
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