

Inhibition of carbon transfer across the vadose zone by 20th century acid rain

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Abstract

Downwards transport of dissolved inorganic carbon (DIC) with infiltrating pore water is a precursor for carbon sequestration to shallow aquifers, or to pedogenic carbonates forming in unsaturated zones or in aquifers further down the flow path. To elucidate controls on the passage of inorganic carbon to the aquifer, we measured seasonal dynamics of water movement, soil gas CO₂, and pore water chemistry in four multi-level profiles through a ~5 m thick sandy unsaturated zone of an agricultural barley field, 10 km south of Ikast, Denmark. We hypothesize that 20th century acid rain deposition has an important effect on today's downwards carbon fluxes and potential for increasing these.

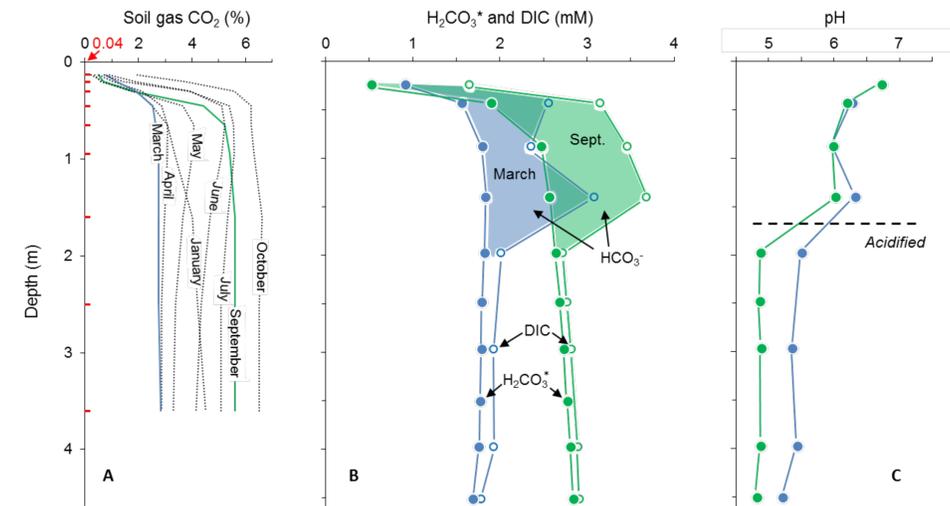


Fig. 1: (A) Soil gas CO₂, (B) inorganic carbon speciation, and (C) pore water pH, in a sandy unsaturated zone under a barley field, 2012. The residence time of water in the unsaturated zone is close to one year.

Vadose zone soil gas CO₂-profiles

Soil gas CO₂ concentrations in the unsaturated zone (Fig. 1A) of 1-3% during winter are observed. The concentrations increase to 4-7% during summer, and stay elevated into the autumn, after harvest of the primary crop (barley).

Gaseous diffusion

CO₂-production in the top soil results in a peak at ~0.5 m depth, which is sustained from April to July. Below the peak depth, CO₂ produced is transported downwards mainly by gaseous diffusion. Upwards diffusion of CO₂ from the deep vadose zone towards the surface takes place from late fall/early winter and continues into March the following year.

Downwards carbon transport

Concentrations of dissolved inorganic carbon of up to 3.0 and 3.6 mM were observed in March and September, respectively (Fig. 1B). However, below ~2 m depth, DIC shows a marked decrease. The DIC-decrease coincides with a decrease in the pore water pH (Fig. 1C), from pH >6, down to pH ~5.

Dissolved inorganic carbon speciation

Speciation of DIC (Fig. 1B) shows that the pore water alkalinity is consumed when pore water passes the acidity front at ~2 m depth. Below the acidity front, DIC is controlled by equilibrium with the transient soil gas CO₂ concentration, with the main DIC species being CO_{2(aq)} and H₂CO₃*, collectively referred to as H₂CO₃*.

Carbon flux across the water table

The aquifer recharge rate is roughly 400 mm/yr. The DIC data in Fig 1B therefore translates into an annual inorganic carbon leaching of 0.7-1.2 moles C/m²/yr. Less than 10% of this, i.e. <0.05 moles C/m²/yr, exchanges across the groundwater table by diffusion into and out of the surficial groundwater.

Dissolved organic carbon (DOC) shows a relationship with depth (Fig. 2), similar to that of pH (Fig. 1C).

DOC leached from the root zone becomes trapped at the acidity front, probably by adsorption to iron oxides. Apparently, little DOC makes its way to the groundwater table. However, the DOC may be an important pH-buffer at the acidity front.

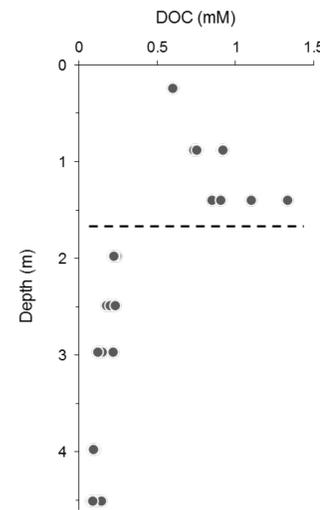


Fig. 2: Profiles of dissolved organic carbon (DOC). Data are from January, July, September and December 2013, and therefore indicate low temporal variability.

What controls the acidity front?

The observed acidity stored in the vadose zone has immediate implication for carbon cycling. But what controls the velocity of the acidity front?

Processes considered include:

- Cation exchange in combination with Al(OH)₃ equilibria¹.
- Slow oxidation of residual pyrite fragments.
- Specific surface adsorption including exchange of organic acids for H⁺.
- Dissolution of Al-SO₄-OH minerals.

Generally, reactions causing the observed slow increase in SO₄ does not result in sharp acidity and alkalinity fronts!

Sulfate deposition by acid rain

SO₄ concentrations increase almost linearly with depth, below the acidity front (Fig. 3).

Acid rain occurred in the region¹ until its mitigation in the 1990's. Acid rain also caused soil acidification along with deposition of SO₄, supplementing that of marine aerosols. The sulfate may have been stored adsorbed to iron oxides and/or precipitated in Al-SO₄-OH minerals.

We propose the observed continuous SO₄ release (Fig. 3) reflects today's mobilization of previously atmospherically deposited and stored sulfate.

The sulfate mobilization therefore relates the observed "fossil acidity" (Fig. 1C) to the 20th century acid rain acidification.

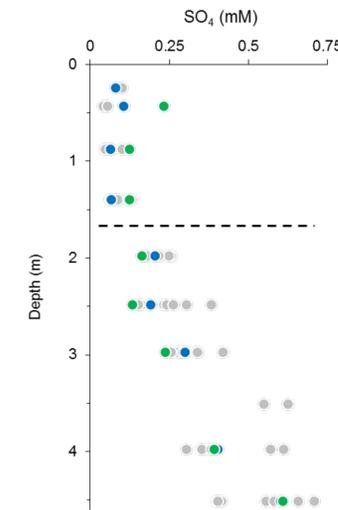


Fig. 3: Concentrations of SO₄ vs. depth. Data stem from nine field campaigns during 2011-2013, hence reflecting temporal invariability. Green and blue dots indicate data from March and September 2012.

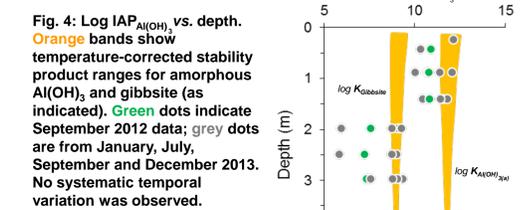
Implications of 'fossil acidity'

No matter what caused the acidity observed below ~2 m depth, the observation has great implications:

- Infiltrating HCO₃⁻ degasses to the atmosphere instead of reaching the groundwater table:
$$\text{HCO}_3^- + \text{H}^+ \rightarrow \text{CO}_2(\text{g}) + \text{H}_2\text{O}$$
- Rules out potentials for carbon sequestration by changed agricultural practices, liming, or otherwise.
- Persistence of acidity: The acidity is present despite years of agricultural liming at the studied field site.
- Al-SO₄-OH minerals and/or surface adsorption may store the acidity for decades to come.

Mineral equilibria

Pore waters are near equilibrium with Al(OH)_{3(aq)} above the acidity front and with gibbsite below the front (Fig. 4). Unfortunately, control by Al-SO₄-OH phases is notoriously difficult to address².



Up-coming modeling

Modeling is ongoing to elucidate the effects of transient water movement and soil gas CO₂ concentrations on carbon fluxes across the vadose zone.

HYDRUS-1D/PHREEQC: HP1

HP1 is a coupled water, gas and solute transport numerical model available as part of HYDRUS-1D. HP1 brings the many generic hydrogeochemical possibilities of PHREEQC into play in the vadose zone, while allowing for transient CO₂ gas production², water movement, and water content controlling gas diffusivity.

The gas diffusivity is an important parameter in the modeling. An estimate was made by a single-point injection-and-withdrawal test was conducted. A known volume of N₂ gas was injected into a soil gas sampler at 3.7 m depth, displacing the naturally O₂ rich soil atmosphere. The back-diffusion of O₂ through the injected N₂ was monitored and interpreted using a numerical model with a spherical grid approximation. Results indicate an effective gas diffusion coefficient for CO₂ of 6×10⁻⁶ m²/s, suggesting both high porosity and tortuosity, and low water content. DECAGON moisture probes, installed over the entire depth of the vadose zone, records a stable water content over the year, suggesting no significant seasonal variation in the gas diffusivity.

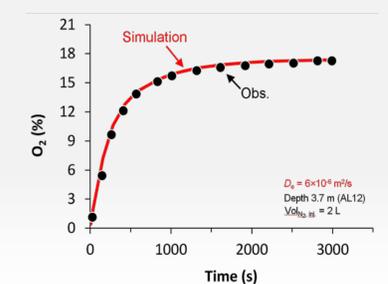


Fig. 5: Estimation of effective diffusion coefficient for CO₂, based on numerical simulation of data for back-diffusion of O₂ subsequent into injected N₂ gas.

