Dynamics and effects of soil CO$_2$ on carbonate dissolution and transport in response to precipitation events

Martin Maier$^1$, Laurin Osterholt$^1$, and Andreas Hartmann$^2$
$^1$Forest Research Institute, Department Soil & Environment, Freiburg, Germany (martin.maier@forst.bwl.de)
$^2$Chair of Hydrological Modeling and Water Resources, Albert-Ludwigs-University of Freiburg, Freiburg, Germany

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What happens?
M. Maier: Soil CO$_2$ effects on carbonate dissolution

Good morning! I will present ideas and experimental results about soil CO$_2$ effects on carbonate dissolution. Let’s start!
Carbonate dissolution depends on soil pH which depends on soil CO₂. Soil air CO₂ can easily dissolve in water at pH>7 as described by Henry’s law.

Dissolution of gaseous CO₂ according to Henry-Dalton law
Field observation:
behavior of soil CO₂ after rain

Some time ago we had a field experiment about soil gas fluxes where we installed CO₂ probes in the soil. We measured soil CO₂ concentration at every minute and observed two different types of reaction to rain in the soil air. An immediate effect after intense rain, and a slower reaction after every rain.

Water infiltration
Soil Aeration
CaCO₃-dissolution

Soil profile measurements

Soil moisture probe

Depth / m
0
1

CO₂ probe (Vaisala GMP343)

(Shown examples from Maier et al. 2010, Eur. J. Soil Science 61; more data available)
So, what happens after a “normal” “slow rain event in a calcarous soil?

1. The top soil gets wet, formerly areated soil pores get blocked.

“Slow” rain event

1. Slow infiltration = reduced aeration
2. Increase in soil CO₂
3. Increase in soil respiration & increase in CaCO₃-dissolution

(Maier et al. 2011, Agric. For. Met 151)
So, what happens after a „normal“ „slow“ rain event in a calcarous soil?

1. The top soil gets wet, formerly aerated soil pores get blocked.
2. Soil CO₂ accumulates until the reduced diffusivity and increased soil CO₂ concentration reach a new steady state.
3. Soil air CO₂ equilibrates with CO₂ dissolved in soil water, and this means the pH decreases, yet only slightly since it is buffered by the dissolution of CaCO₃, which increases

1. Slow infiltration= reduced aeration
2. Increase in soil CO₂
3. Increase in soil respiration & increase in CaCO₃-dissolution

(Maier et al. 2011, Agric. For. Met 151)
Relative drop in CO\(_2\) concentration at 7 cm depth/

First few hours:
1. Fast infiltration & preferential flow = less effect on aeration
2. Mixing of rainwater low in CO\(_2\) with soil water enriched in CO\(_2\)
   \[\rightarrow\] relative undersaturation of new soil water
3. Dips in soil CO\(_2\)
4. Increasing CaCO\(_3\)-dissolution

And after a "fast" rain event?
1. The top soil gets wet quickly, but there is also preferential flow, so that rain water infiltrates quickly into deeper layers.
**Relative drop in CO₂ concentration of initial concentration at 7 cm depth / %**

### First few hours:
1. Fast infiltration & preferential flow = less effect on aeration
2. Mixing of rainwater low in CO₂ with soil water enriched in CO₂
   - relative undersaturation of new soil water
3. Dips in soil CO₂
4. Increasing CaCO₃-dissolution

### And after a „fast“ rain event?
1. The Top soil gets wet quickly, but there is also preferential flow, so that rain water infiltrates quickly into deeper layers.
2. The percolating rainwater is CO₂ depleted relatively to the soil water and will thus „draw“ CO₂ molecules from the surrounding soil air.
3. Dips in soil CO₂ concentration can be observed due to this effect. The stronger the rain, the more preferentially percolating water, the stronger dips in CO₂
4. And this means that more CaCO₃ is dissolved.
The total amount of Ca\(^{2+}\) mobilized due to CaCO\(_3\) dissolution is not affected by slow or fast rain event, but the localization where exactly the Carbonate is dissolved is affected.

**First few hours:**

1. Fast infiltration & preferential flow = less effect on aeration
2. Mixing of rainwater low in CO\(_2\) with soil water enriched in CO\(_2\)
   
   -> relative undersaturation of new soil water
3. Dips in soil CO\(_2\)
4. Increasing CaCO\(_3\)-dissolution
If this interpretation was true, we should be able to reproduce this effect also in the lab. So we set up an experiment with soil mesocosms. One with intact soil structure, and one repacked mesocosm.
Intact Mescosm

Re-Packed Mescosm
And we ran experiments similar to those in the field, measuring soil CO$_2$ concentrations, soil moisture, water from suction cups, and an electrical conductivity of the draining water.
And we observed the same dips in soil CO₂ concentrations as in the field, with stronger dips during intense rainfall events.
And we also saw that much more \text{Ca}^{2+} was washed from the re-packed soil column, especially during the first experiments. The surfaces of the preferential flow paths seem thus less susceptible to mobilize \text{Ca}^{2+}, maybe, because most \text{Ca}^{2+} has been washed from this pore surfaces already.

(Freiberg, 2019, modified)
Thank you for watching!

If you have questions or comments you’ll find me in the chat on Friday, 8 May 2020, 10:45-12:00, or please find my e-mail via the EGU!

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