24/7 Monitoring of soil gas pCO_2 concentrations in large scale ERW experiments with low cost electronics

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Abstract

In our endeavor to measure the climate relevant effects of rock weathering in agriculture we have been setting up several field and greenhouse experiments over the last three years. During this work we started experimenting with low cost electronic sensors in 2022 with the goal to monitor the soil gas CO_2 concentration (pCO_2) in our enhanced rock weathering (ERW) experiments, mainly in lysimeters in fields and greenhouses.

In this article we document our latest sensor design which gives us reasonably good pCO_2 measurements as well as the steps that got us to this design. We furthermore share a preview of our pCO_2 data and compare these with the CDR estimates we recently derived from soil leachate alkalinity measurements. So far, we haven't observed a good match between these two parameters which likely indicates that leachate alkalinity and soil pCO_2 data alone do not suffice to understand all carbon related processes in the soil. Our main observation is that whether or not the soil pCO_2 changes after rock dust amendment, and if it does whether it increases or decreases, seems to mostly depend on the soil type rather than the type of rock dust. This could explain why studies where only one or two soil types are tested result in very different conclusions.

In our main experiment with 4 soils and 4 types of rock dust the majority of soil-rock variations tends to move towards an increase in soil pCO_2 although only a few of them are significantly different from their control. In our secondary experiment where the same rock dust was applied to 7 different soils, we see almost the opposite as now 5 out of 7 variations are significantly different from their control, showing 2/3 increase/decrease of the soil pCO_2. We will continue monitoring soil pCO_2 to see how these trends might evolve over time and whether a correlation between soil water alkalinity and soil pCO_2 still emerges.

Despite giving away the ending already, we hope this story is still an entertaining and interesting read. Follow us through the jungle of building scientific instruments from scratch and trying to make them work in greenhouse as well as in outdoor settings.

Note 1: What you are about to read is a hopefully entertaining mashup of a photo album of our prototyping experiences along with the reasoning of why we do this and an overview of the data we have generated so far. This is not a scientific article, although we certainly strive to do serious scientific work at all times.

Note 2: According to feedback from scientists we are doing something unusual with our pCO_2 based approach - which is intentional. Only if one does things differently will he or she be able to achieve different results. We all know the challenge of measuring the carbon dioxide removal effects of enhanced rock weathering at scale in agriculture has not yet been solved. Our goal is to uncover new potential MRV approaches using novel concepts. Measuring the pCO_2 is one of the things that might help, but nobody knows yet if this will actually be a solution, or even a part of it. Although we don't actually measure the CDR, the pCO_2 metrics might at least help to understand the carbon fluxes and balances inside our experiments which could bring us one step closer to MRV. In essence, we will either fail completely - as predicted by some of these scientists - or we will find some surprising new insights. We are ready for both outcomes, **let's enjoy the journey anyway.**

Introduction: Why measure soil gas CO_2 concentrations in the context of CDR?

Carbon dioxide removal (CDR) through enhanced rock weathering involves spreading fine rock dust on agricultural fields. By adding rock dust to the soil we are actively changing the carbon cycles in that environment. The amount of “rerouted” carbon (=captured CO_2 that is turned into HCO_3^- in the pore water of rock dust treated soil) is about one order of magnitude smaller than the natural annual carbon cycle in the soil. We have shown this in our blog post [The Annual Carbon Cycle on 1 m^2 of Cropland - With Enhanced Weathering]().

Our soil pCO_2 approach is more complex than it might seem due to the extensive carbon party that nature holds in the soil. A variety of plants, bacteria, fungi and insects are simultaneously feeding off and/or emitting various kinds of carbon. Because of this activity the concentration of CO_2 in the soil gas (sometimes also called “soil air”) is much higher (we have seen thousands to ten thousands of ppm) than in the ambient air above the ground (420 ppm) which is exactly one of the reasons why we put the rock dust there in the first place: it is much easier to find the next carbon dioxide molecule for the weathering reactions when a hundred times more CO_2 is around.

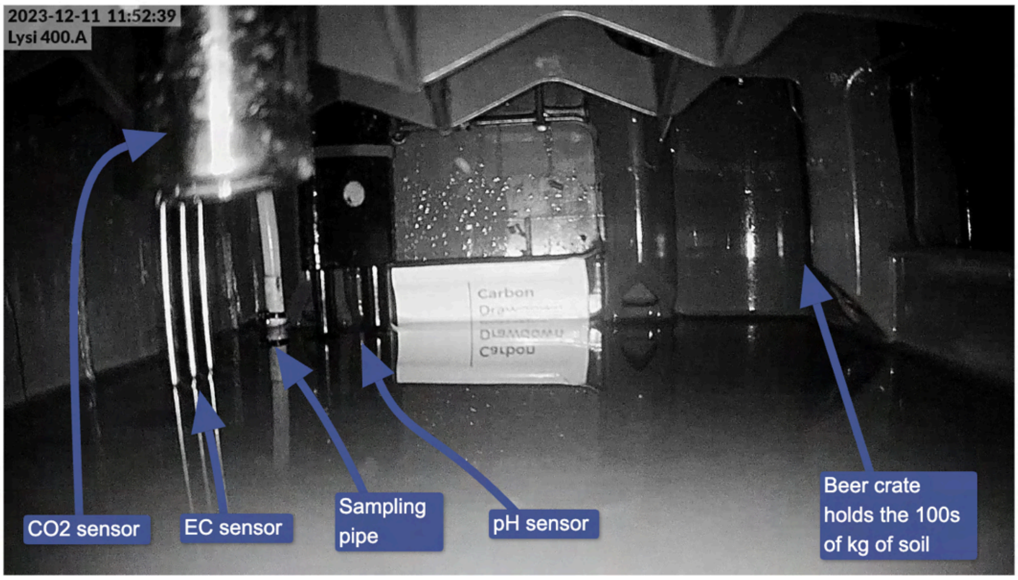
The CO_2 efflux from the soil into the ambient air above the ground is coupled to the CO_2 concentration in the soil via [Fick’s 1st law](). The efflux has a linear relationship to the concentration (twice pCO_2 causes twice the CO_2 efflux, given everything else is the same). So by looking at the CO_2 concentration in the soil we should also be able to estimate the CO_2 efflux from the soil. This law seems to hold up pretty well in our greenhouse experiment, but let’s keep the soil CO_2 efflux measurements with our fluxmeter army for one of our next articles.

As you are about to see, the major step forward of our approach for pCO_2 measurements in soils is that we are “monitoring” this metric with high density intervals (between every 10 minutes and 1 hour) instead of taking a measurement every few days or weeks. This allows us to uncover the intra-day changes and distinguish them from trends that occur over days, weeks and seasons - of which there are plenty.

Will this high frequency “monitoring”-based improvement in pCO_2 measurements be good enough to enable us to estimate the CDR effect of rock dust?-We don’t know, the only way to find out is to try it. At least from a “first principles thinking” perspective it seems to make sense to look at the CO_2 itself if you want to remove CO_2 from the atmosphere (instead of only looking at ERW proxies like dissolution rates, alkalinity or cation concentrations, etc.).

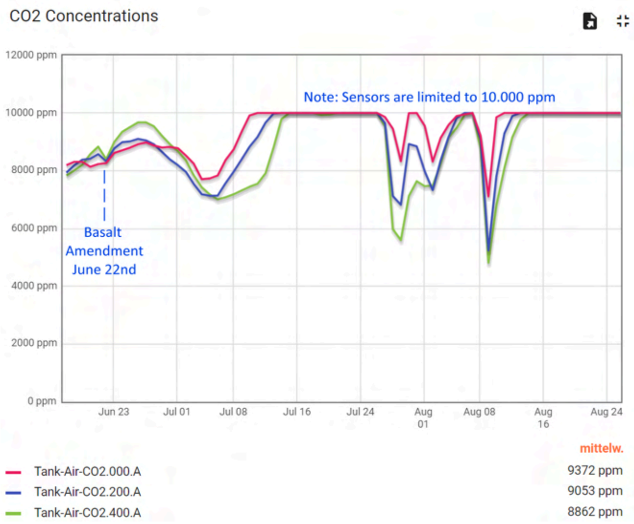
The history of our pCO₂ sensors: How it all began

Our first experiment with CO_2 sensors involved three off-the-shelf air-CO_2 sensors (LoRaWAN wireless sensors) that we built into the water collecting tanks at the bottom of 60 cm of soil of our large XXL lysimeters in May 2022. This is a photo from one of the cameras in the lysimeter tanks, the CO_2 sensor is the metal pipe on the top left.



Extra-Insight: Have you noted our logo without the blue C trademark on the sticker in these tank photos? Well, turns out an infrared camera night-light does not properly light up a blue logo. 🙄 *And now all this is buried at 80cm depth and we can't change it.*

Although these CO_2 sensors were limited to a max of 10,000 ppm, they did show lower CO_2 concentrations in the bottom tank of basalt treated lysimeters merely weeks after the basalt amendment in June 2022. The periods in July-August with values below 10,000 ppm were likely caused by summer drought (dry soil) which reduced bio-activity and hence also CO_2 respiration.

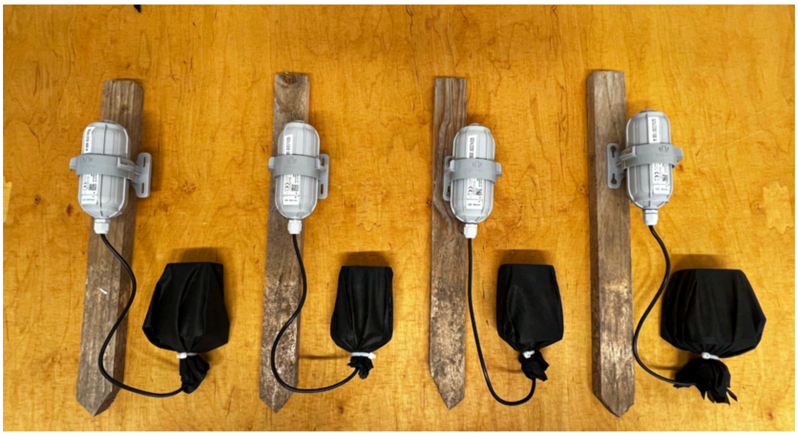


Red: Untreated control; blue: 200 t/ha basalt treatment; green: 400 t/ha basalt treatment

Such nice, clear, easy and obvious results - we should have stopped right there… But instead this encouraged us to carry on and investigate further.

Approach #1: Soil Gas CO_2 Sensor “Model P”

These promising pCO_2 measurements in the water tank below the soil columns made us wonder if we could detect a similar signal within the soil itself. So in August 2022 we created our first soil CO_2 concentration sensors, again from off-the-shelf air CO_2 sensors (we used the Seeedstudio Sensecap CO_2 LoRaWAN Gen 1) which we buried 15 cm below the XXL lysimeters’ soil surface. The basic idea was to create a small “chamber” around the CO_2 sensor so that it did not come in direct contact with the soil whilst still allowing the soil gas to freely enter and equilibrate with this chamber. For that purpose we used small upside-down plastic containers for the chamber so that no water could enter the chamber from above. And if the water levels would rise inside the soil, the chamber would create an air bubble around the sensor which would also save it from drowning. A root fleece over this plastic container made sure the plants’ roots, insects or worms could not enter the chamber whilst soil gas could easily pass through.



To validate our homemade solution, a soil air specialist from an environmental lab brought his high-end soil CO_2 measurement instrument onto our field and we found that our sensors were accurate in the order of plus/minus 10%. This part of the story is extensively documented in our working paper from March 2023 (page 18ff).

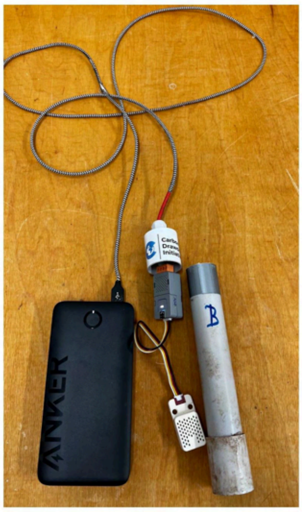
In our 2023 greenhouse experiment we are using 97 of the same Seeedstudio Sensecap CO_2 LoRaWAN Gen 1 sensors based on the Sensirion SCD30 CO_2 module (works up to 40.000 ppm), which were effectively the last ones available on the global market. Over weeks we hamstered these from many online shops, buying up their remaining stock. The vendor had discontinued this old model and switched to the cheaper SCD40 sensor for the new one. This updated sensor only goes up to 10.000 ppm, which is fine for most CO_2 sensor applications but not good enough for our needs of pCO_2 measurements in soils. So, from here on we had to move from off-the-shelf devices to building our own systems.

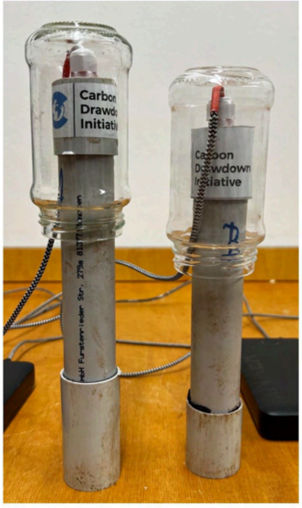
Greenhouse lysimeters with CO_2 sensors: The gray pill-shaped tubes contain controller, antenna and battery, the cable leads to the sensor buried at x cm in the soil.

Approach #2: Soil Gas CO_2 Sensor "Model Z"

We talked about our pCO_2 sensor building efforts to our friend Christian Zeh, an experienced "maker". He subsequently designed and built the first four Carbon Drawdown soil CO_2 sensors, based on a plastic tube, 3D-printed stuff, the already well tested Sensirion SCD30 CO_2 sensor and a small ESP32-based micro controller (plus some cloud based IT data pipeline using MQTT and PRTG). This had several advantages: We had a much smaller chamber in the soil (less need to disturb soil), we had full control over measurement intervals and the total cost per piece was only about 60 EUR, less than half of the price of the LoRaWAN sensors we had used before. Compared to these LoRaWAN sensors, however, this design also had two downsides: We needed a permanent power supply (USB-C) and we needed a wifi connection. Although both these requirements were no limitation in our field and greenhouse, they might be in common field settings.

These prototypes #2 worked fine in the field for a few weeks until one after the other died. When we disassembled them we found the cause: Despite extensive insulation efforts water had gotten into the electronics along the power cable that enters the case from the top. We discarded the electronics and rebuilt it with a new controller and SCD30 sensors we had at hand, but this time we placed a Barilla pasta sauce glass as "roof" over the device. Which gave prototype #3 a much longer lifespan. By using a huge power bank instead of a power connection we could now also move around our fields for measurements. The power bank kept the sensor working for 10 days until a recharge was required. The firmware we used was "tasmota-sensors.bin" which only required a bit of configuration to get it up and running.





Approach #3: Soil Gas CO_2 Sensor "Model S"

We still wanted something "simpler", manufacturing-wise. The next prototype #4 also used ultra cheap plastic tubes as well as the SCD30 sensor. This time the microcontrollers (ESP32-based M5Stack Core 2) were placed in a protective box together with the power supply. Cables in protective flexible tubes connected this box with the sensor tubes.

Even though we got reasonable CO_2 data WHEN it worked, we couldn't get this to work reliably for more than a few days at a time and we had to go out there and fix things very often. In the natural outdoor setting the long but delicate cables and plugs went on and off all the time, leading to a redesign of the same basic concept and prototype #5:

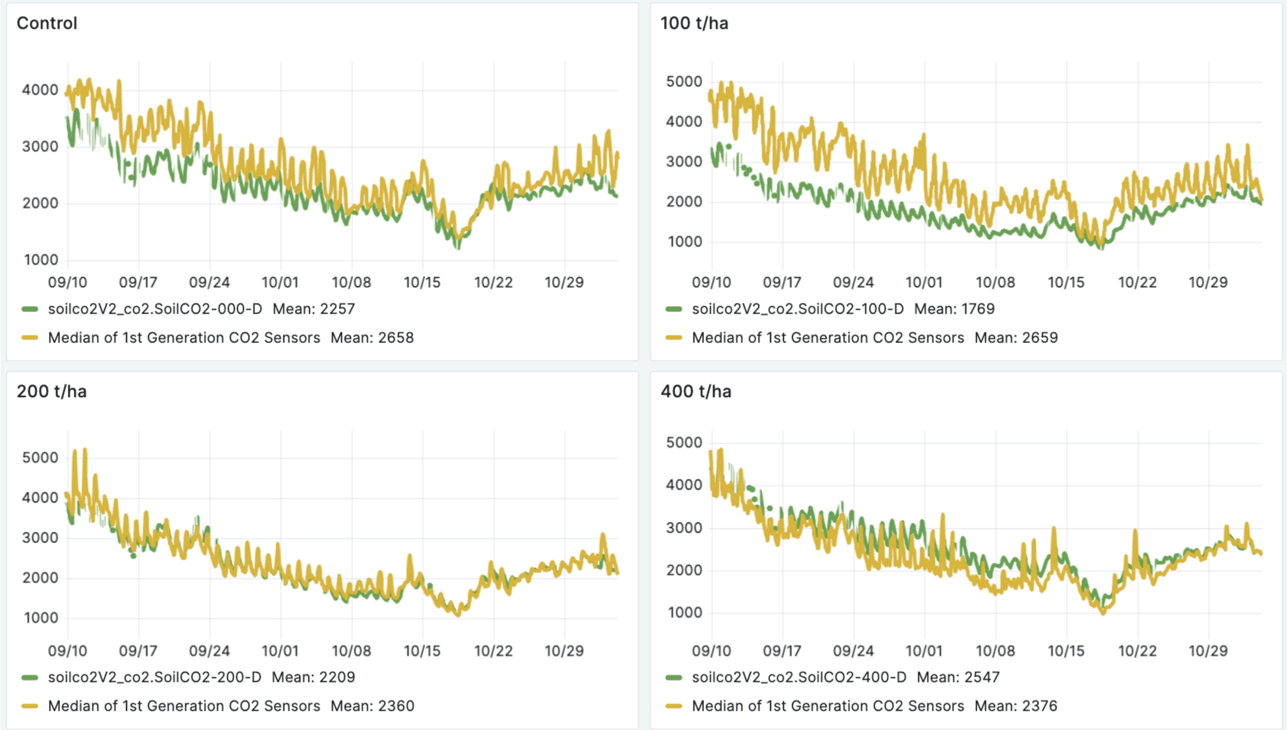
This time we glued the microcontroller, the weather proof “tough” model of the M5Stack Core 2, directly to the tube (100% waterproof) leaving only the well insulated USB cable to run through the outdoors. The chamber at the bottom is about 10 cm high and has holes to the sides and to the bottom so the chamber air can equilibrate with the soil air. Most of the dead space in the pipe is filled with material from a pool noodle (closed pore foam) in order to avoid too much headspace and calibrate all probes to the same air volume inside.

All Model S prototypes use a firmware software that we have developed ourselves based on M5Stack UiFlow. It connects to the also self-developed data pipeline of our greenhouse experiment which handles more than 4 million data points per day.

This setup worked fine for several months, until we had a few days of almost -10 °C frost with lots of snow in October 2023 where 3 of the 4 sensors stopped working and died. OK, building sensor stuff for the great outdoors is really challenging. Unsurprisingly, all our electronics experiments in the climate-controlled greenhouse have much longer lifespans.

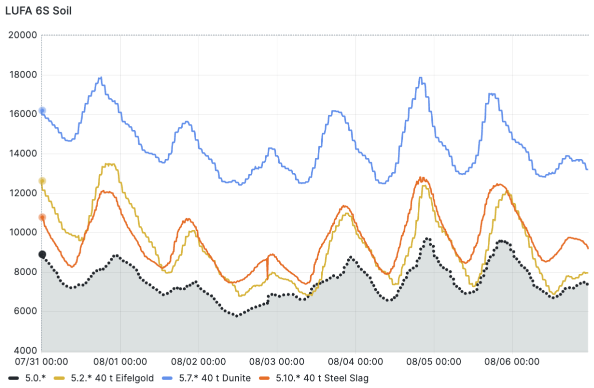
	Model P	Model S	Difference
Control	2658	2257	-15%
100 t/ha	2659	1769	-33%
200 t/ha	2360	2209	-6%
400 t/ha	2376	2376	0%

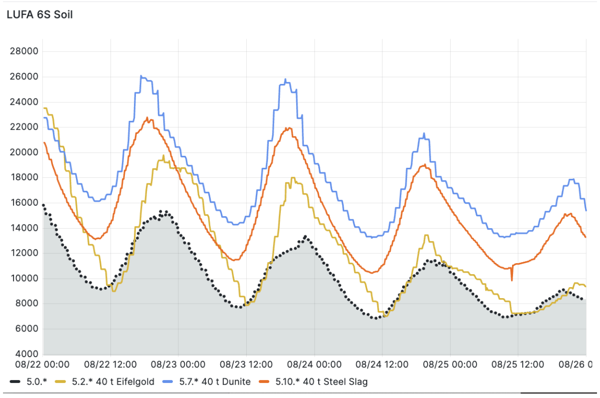
Here is a comparison of data from the older Model P and newer Model S sensors in the XXL Lysimeters over 2 months. The green line (Model S) is only based on one sensor while the yellow line (Model P) is the average of 4 replicas. Except for the 100 t/ha treatment (top right) the new sensors' data is quite close to the median of the 4 replicas of the older sensors. Considering the fact that the older sensors (truthed by fancy scientific equipment in 2022) had 12 months more time to settle in the pots these results are rather good.



Why ongoing pCO_2 measurements provide superior data quality to a few data points every few days

Consider the following graphs of soil pCO_2 measurements in the greenhouse in a control series and 3 amended series (showing medians of 4 replicas each) during two weeks in the summer of 2023. The daily maximum can be up to 50% higher than the daily minimum and the shape of the daily curves can be quite different from one day to the next (e.g. due to weather/sun/temperature). This clearly shows that if one measures pCO_2 (or a similar and related parameter such as CO_2 efflux) only every x days at a specific time he/she would not be able to resolve daily fluctuations from actual changes in the carbon system since one would not know which part of the intra-day curve was measured at a specific measurement moment.

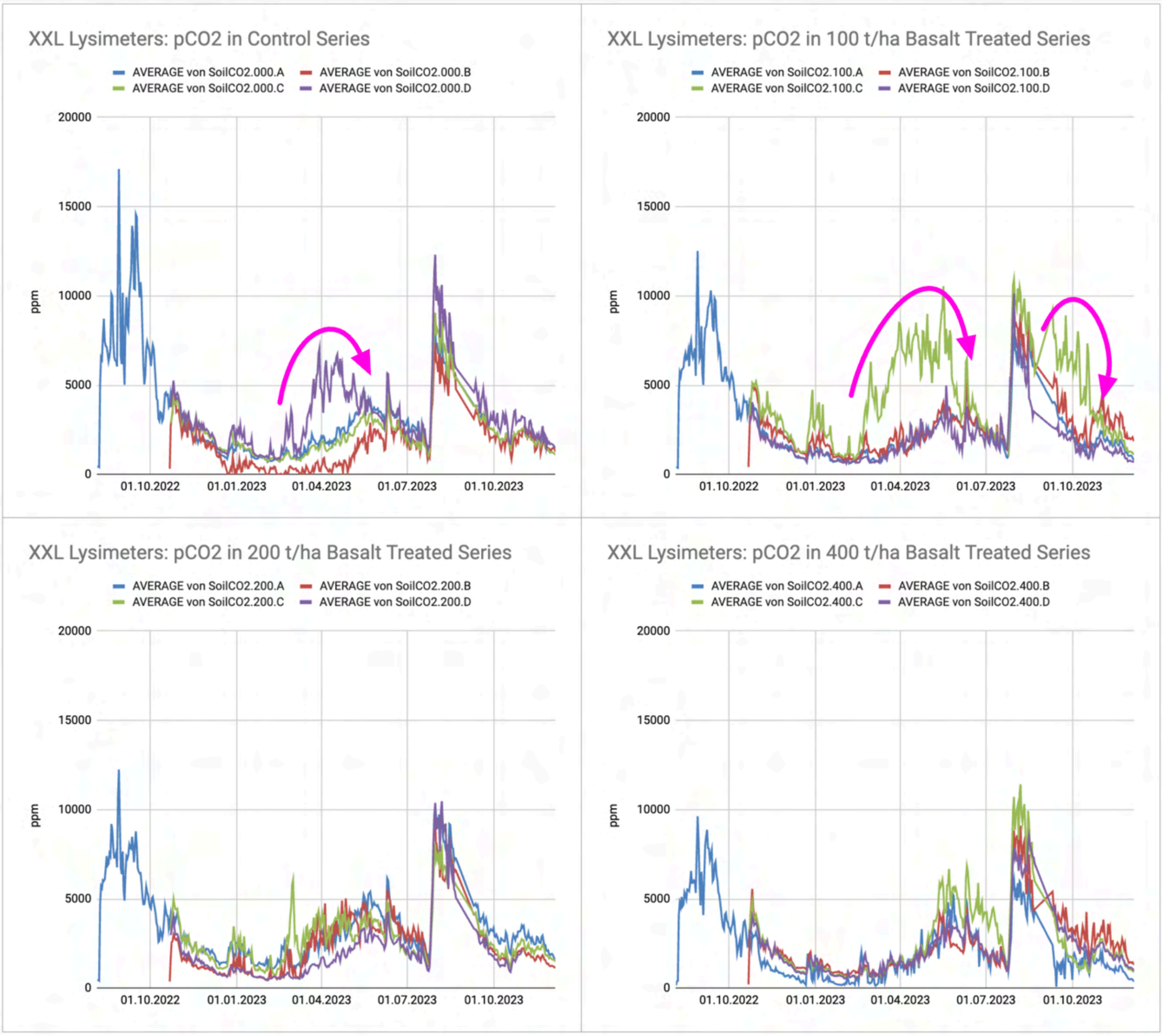




The “sampling theorem” basically states that the measurement frequency for a signal must be at least twice the change rate of this signal. The above graphs show a mix of fluctuations, some of which clearly have a smaller than daily frequency. Only continuous 24/7 measurements with an interval below 1-2 hours will allow us to measure the actual CO_2 concentrations in the soil with good accuracy. Just taking a few scheduled measurements with intervals longer than 1-2 hours will not make it possible to assess what is actually happening with the pCO_2 in the soil.

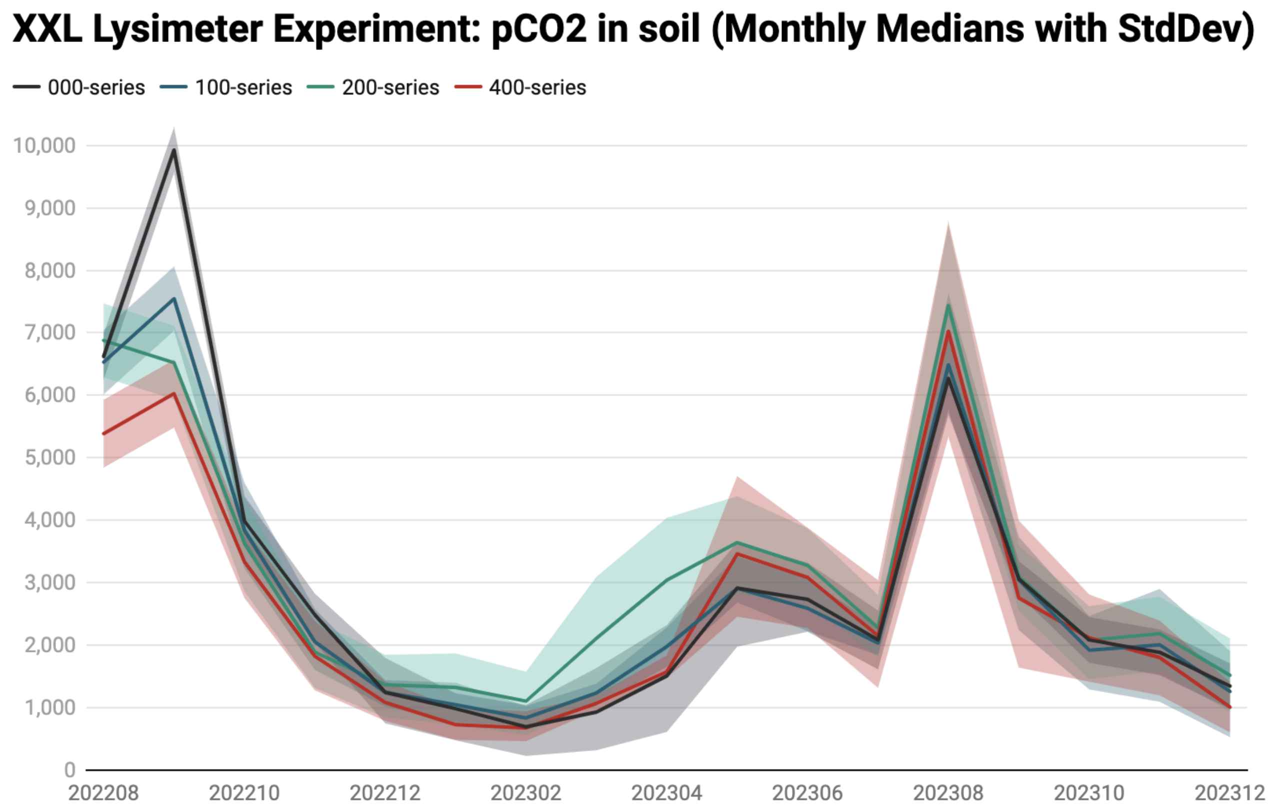
Soil Gas CO_2 concentrations from the XXL Lysimeter Experiment

We have the longest running pCO_2 data for the XXL lysimeter experiment, shown below as daily medians for each of the 16 pCO_2 sensors (note: there is a 3 week data gap in late August/early September due to technical problems).



While most of the time the sensors in the four replicas align pretty well, especially in 2022, sensors 000.D and 100.C are off in the spring of 2023, sensor 100.C again in fall 2023 (pink arrows). We do not know why.

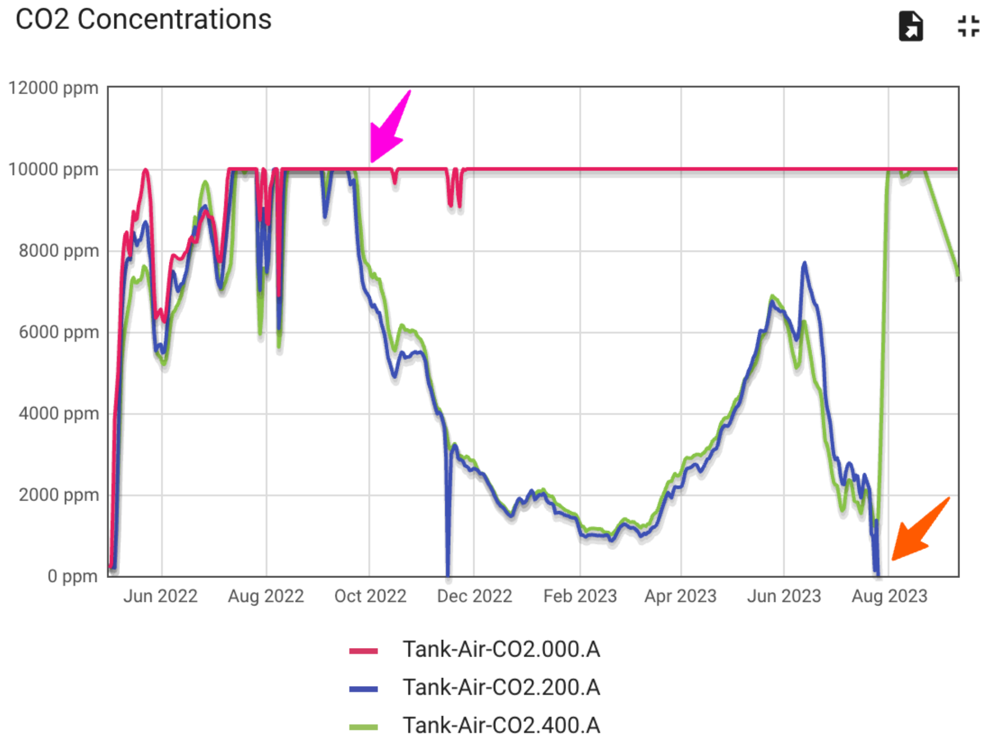
As these anomalous excursions of sensors 000.D and 100.C do not seem to reflect true pCO_2 values, we removed data from these two sensors in the subsequent analysis. The following graph with pruned data shows monthly medians of the control series and three treated series, each having 3-4 replicas, over 16 months with their ranges of standard deviations.



In 2022 we regularly irrigated the XXL lysimeters which resulted in rather steady trends and relatively small uncertainty ranges. In 2023 the XXL lysimeters only received natural rainfall, so two dry spells in June/July and September/October with a strong rain event in between caused a strong pCO_2 peak in August. Not having constant irrigation seems to have caused a less stable signal with much bigger uncertainty in 2023 compared to 2022.

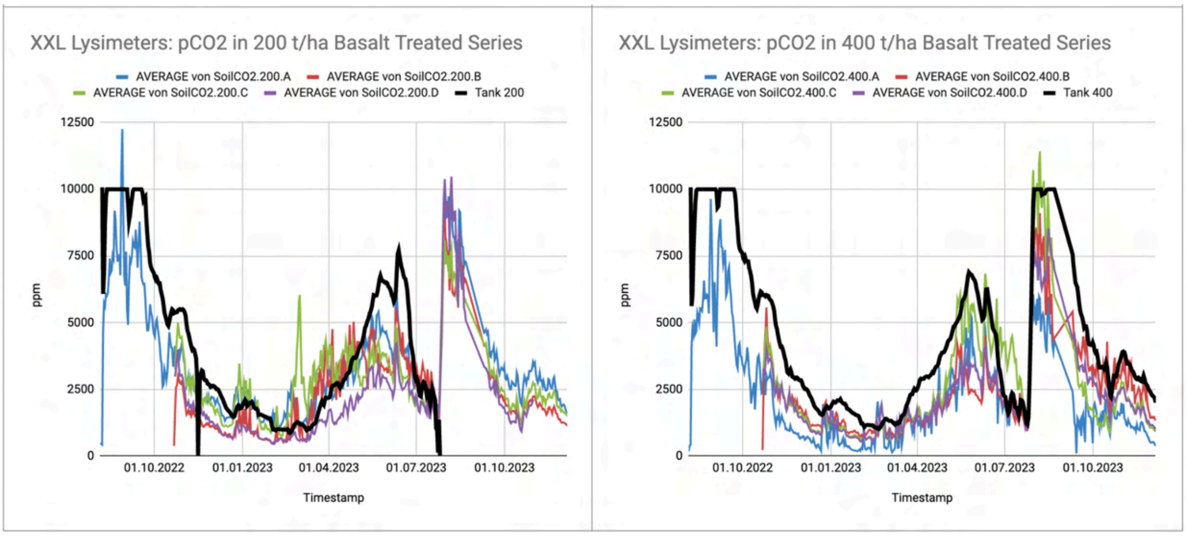
During the summer of 2022 (rock dust was applied in June 2022) the soil pCO_2 in the treated pots was always significantly below the controls' soil pCO_2. It is thereby remarkable that the CO_2 levels were lower the more basalt had been applied, in accordance with our initial observations of the pCO_2 levels in the leachate water tanks below the soil columns. But from October 2022 onwards we can hardly see any significant difference between the soil pCO_2 of controls and treatments. At least we have proof that we were able to create 16 very similar replicas, though.

Let's return to the pCO_2 concentrations in the XXL lysimeters' bottom tank for leachate collection, whose initial data sent us on this soil pCO_2 sensor building journey. The following graph shows the hourly CO_2 concentration in the lysimeter bottom tanks over 14 months since installation.



Unfortunately, the sensor in the control (000.A, red) seems broken from October 2022 onward (pink arrow) as since then it continuously shows its maximum reading of 10,000 ppm (electronics are still alive, but sensor is broken). In August 2023 also the sensor in the 200 t/ha treatment broke down (blue line, orange arrow). Note: downward spikes are mostly caused by transient data pipeline issues.

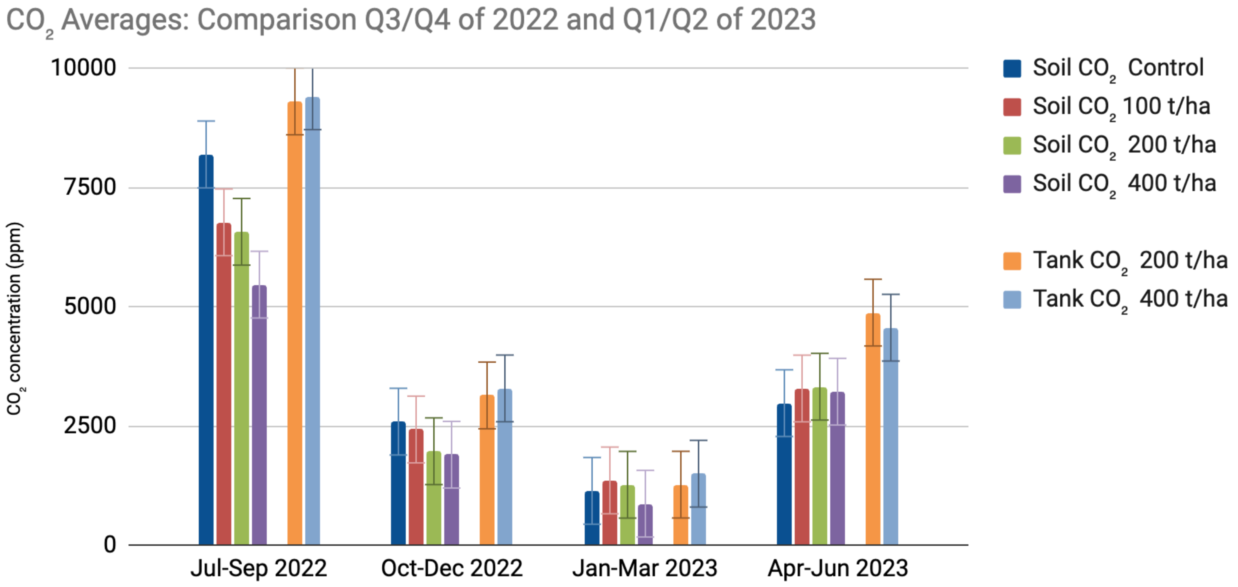
What is interesting is a comparison of the pCO_2 data from the two tank sensors (black lines) to the soil pCO_2 sensors installed at 15 cm depth in the following graph:



The pCO_2 signal from the tank sensors tends to be fluctuating less on shorter timescales and and seems to reflect higher CO_2 readings for longer than the soil pCO_2 sensors, likely because they are further away from the surface so it takes longer for the higher CO_2 concentrations in the bottom tank to equilibrate with the atmospheric air. Regardless of these small differences, the pCO_2 curves measured in the soil and in the tank look very similar.

While the differences between controls' and treatments' soil pCO_2 measurements in Q3 and Q4 in 2022 remain visible, there is no difference between the tank CO_2 averages over the time we have data for - except for the first 2-3 months (May-Jul) as shown above.

Similar to the soil pCO_2 data in the previous graph, there was not much difference after the summer of 2022 between the 200 t/ha and 400 t/ha treatments as the following graph shows (soil CO_2 data are averages of 4 replicas, tank CO_2 has only one sensor in one replica). So again, no indication of a CO_2 change by double the rock amendment after the first few months.


CO_2 Averages: Comparison Q3/Q4 of 2022 and Q1/Q2 of 2023

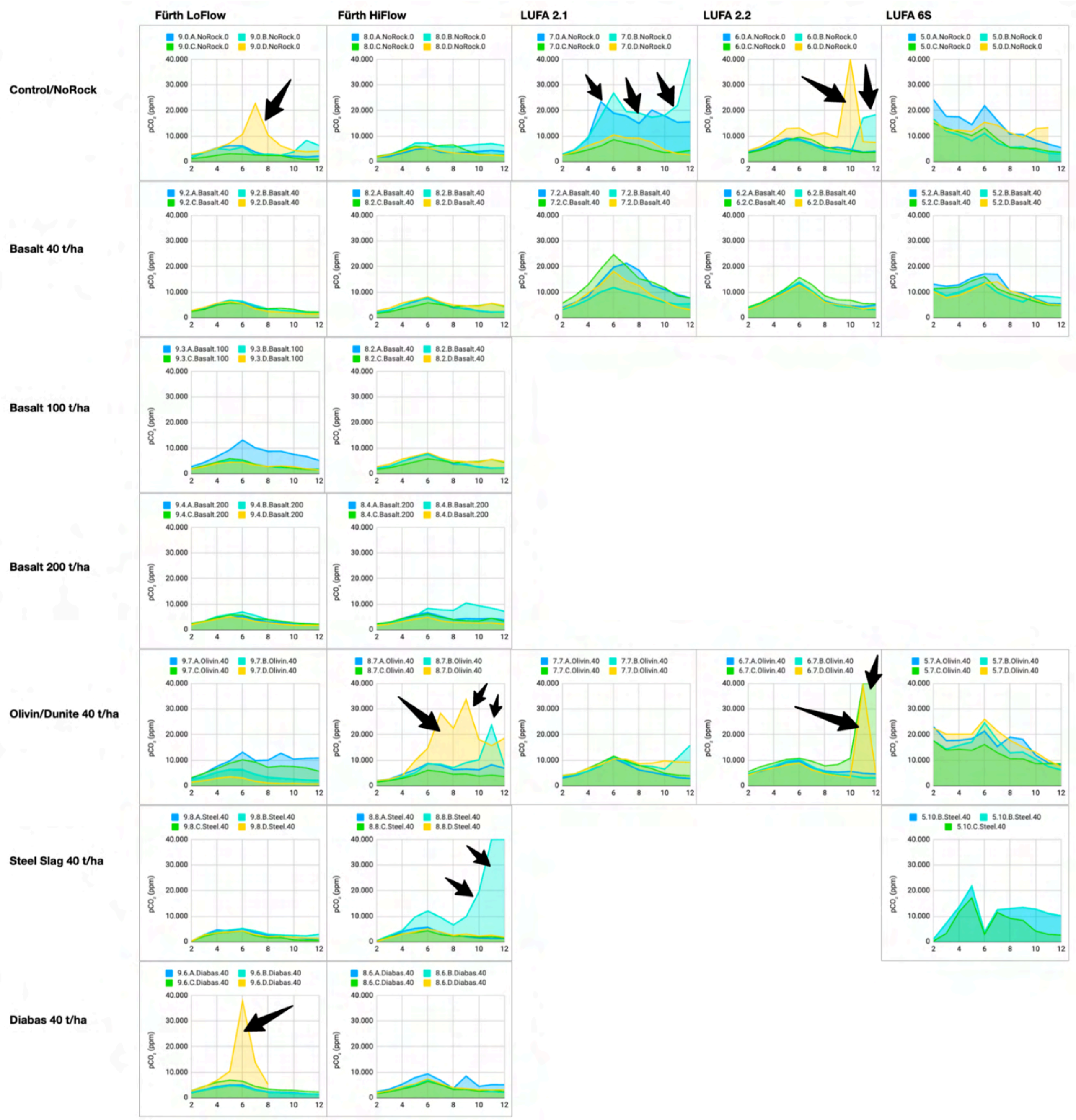
A possible explanation of the fact that we see a significant signal in both soil pCO_2 and leachate tank pCO_2 during those first months after application, is that due to summer temperatures and plenty of irrigation a lot of the very fine rock dust weathered. The lack of distinct differences in soil pCO_2 between control and treatments throughout 2023 could reflect the fact that after this initial 'burst' of dissolution of the rock dust's finest particles during optimum conditions, dissolution of the remaining larger particles goes more slowly, especially during the colder winter months.

In our paper from March 2023 we share data from Lithos' ICP-MS analysis of soil samples which show that some rock dust dissolution can indeed be recognised 8 months after application. However, a rock weathering signal in the form of increased cation concentrations or much higher bicarbonate contents has not yet shown up in the soil leachate water.

Both soil pCO_2 and leachate tank pCO_2 measurements in the XXL lysimeters seem to leave us with a potential CDR related signal in the very first few months after rock dust application - despite the noisy outdoor environment. Maybe it was random, we can't be sure if this is a general characteristic of ERW based on the above presented limited data of a single experiment, but at least it caused us to look further into this.

Soil Gas CO_2 concentrations from the Carbdown Greenhouse experiment

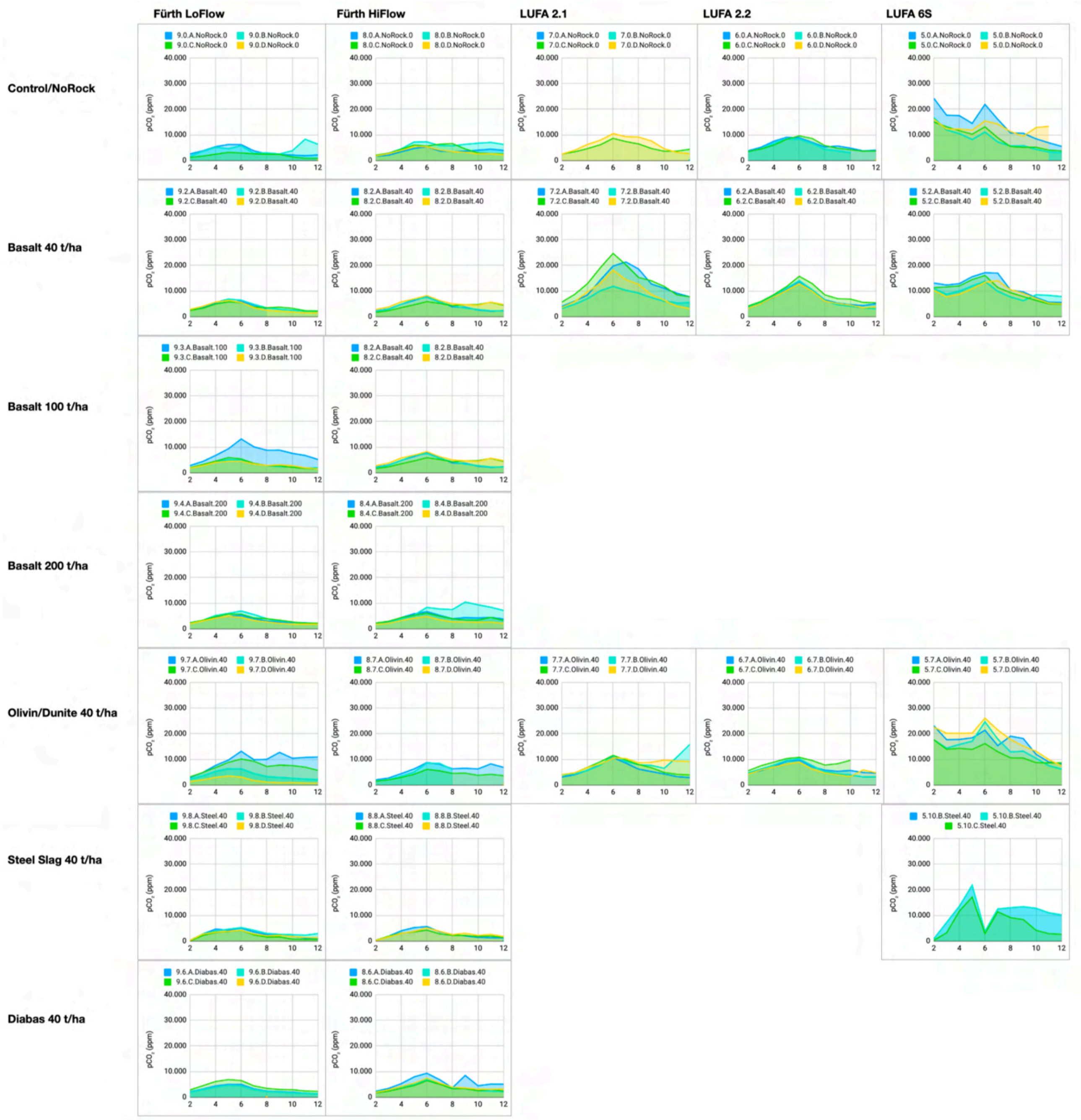
Let’s take a look now at the soil pCO_2 data from our greenhouse experiment. Here are graphs with continuous measurements from our pCO_2 sensors from the moment they were placed in the lysimeter pots (end of January 2023) until Dec 9th 2023. Our main treatments that combine 4 soils with 4 ERW materials have 4 replica pots each. Below we show the monthly median soil pCO_2 data of all 4 replicas of each treatment combination (from left to right = soil types; vertical = ERW material added):



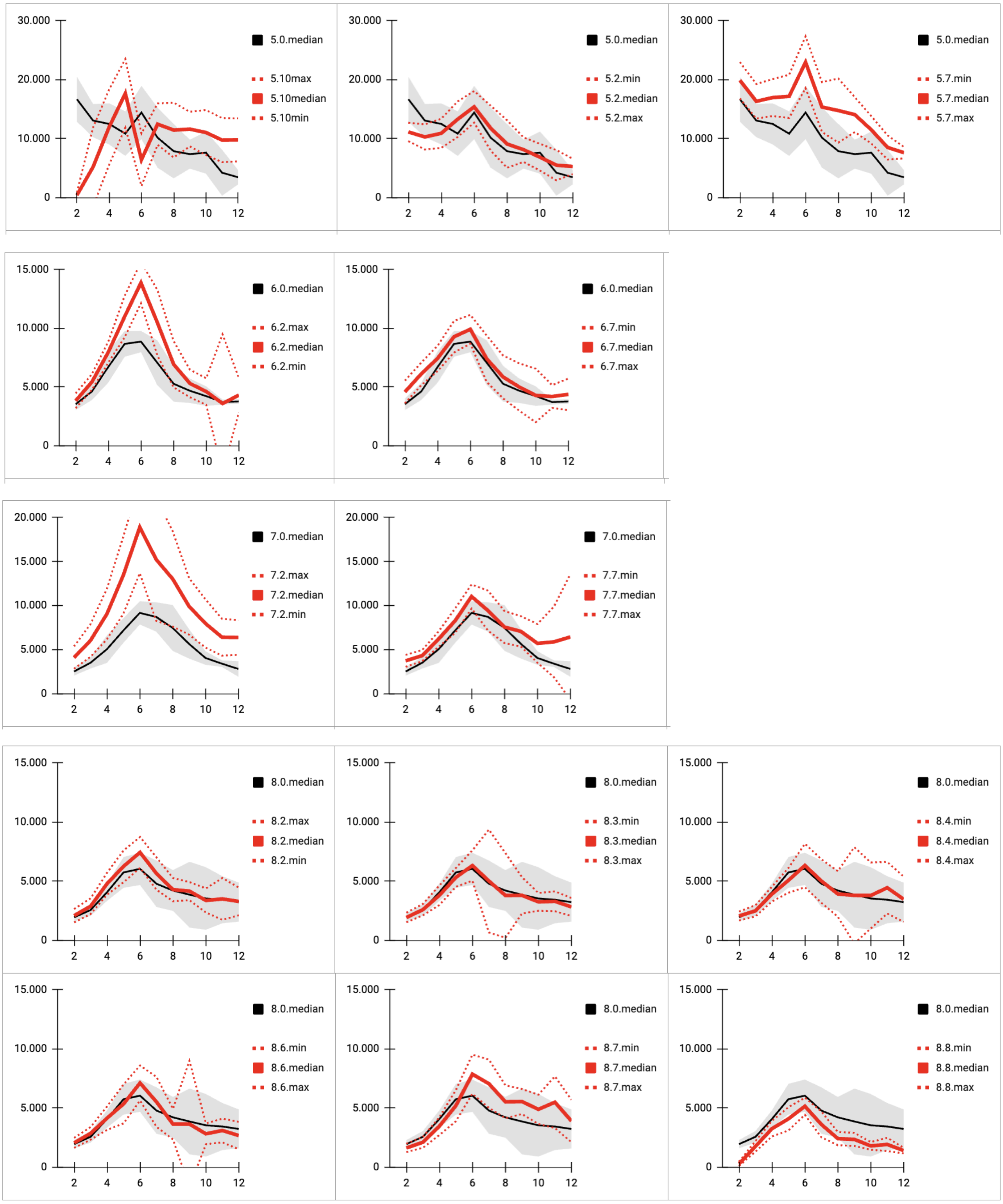
The arrows indicate extreme outliers of a sensor from its respective replicas set, in total this happened for 11 of 88 sensors. These sensors were removed for the following data analysis.

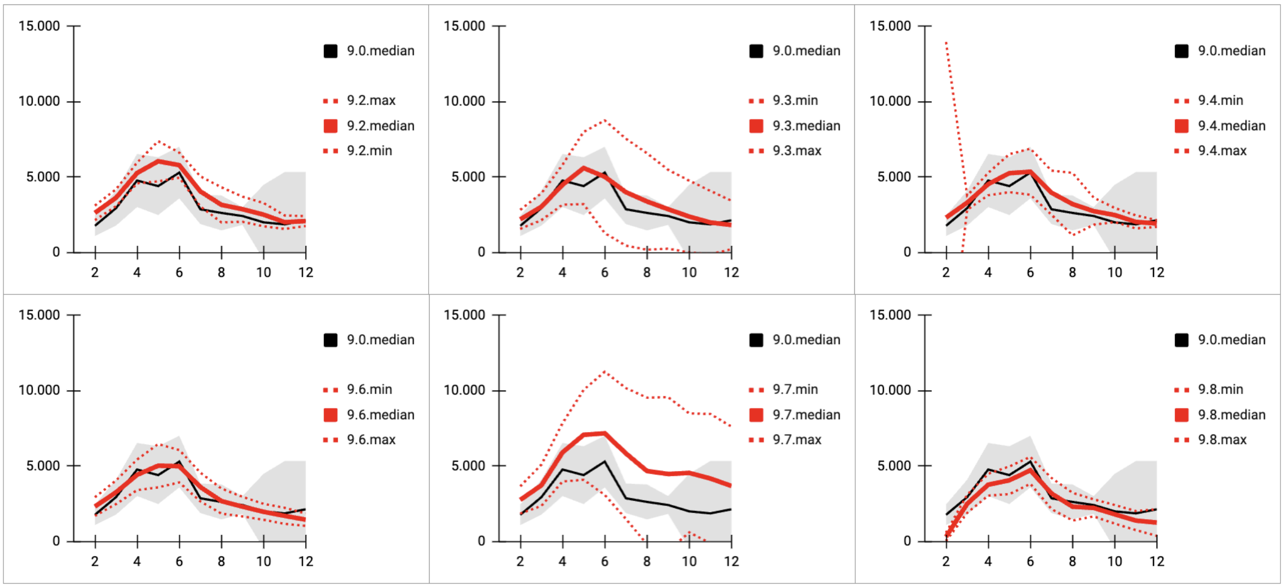
We do not know why some sensors show different values and in most cases just for some time. Some even hit the 40,000 ppm upper sensor range limit over some time. We think this is in part caused by what we call “clogging”: The soil in the pot and/or around the sensors’ chambers is clogged (e.g. by too much water?), so the CO_2 cannot flow out. In other cases this seems to be sensor malfunction, e.g. for 9.6.D (lower left) which stopped sending data after the peak. The interesting thing is that in some instances our CO_2 efflux measurements did not show a “clogging signal” at the same time (i.e. no significantly reduced efflux), which rather points to a sensor malfunction/problem and not an actual extreme CO_2 accumulation in the pot.

These leaves us with this pruned data:



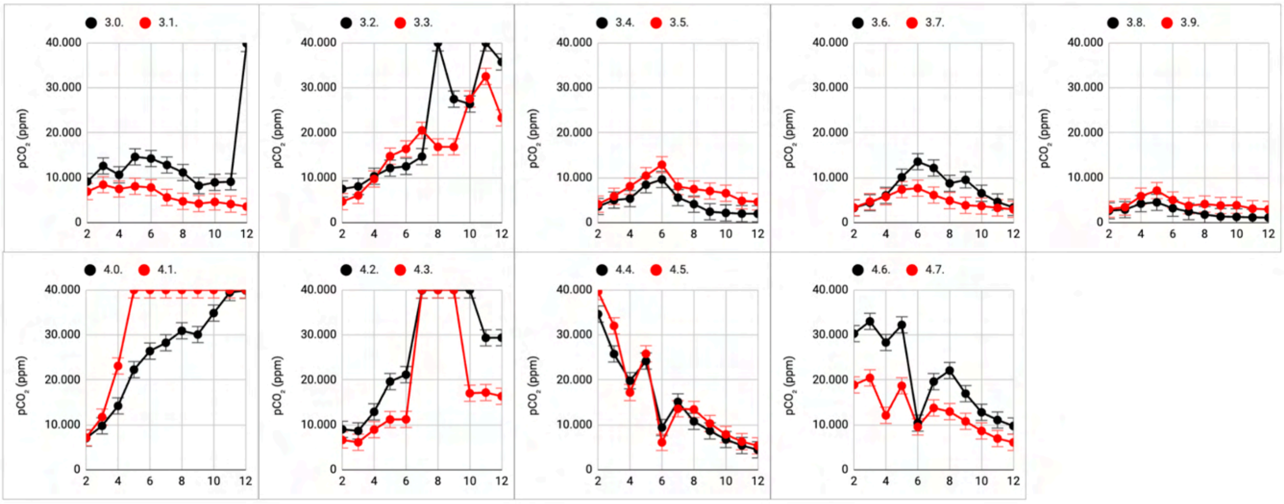
With the pruned data we now compare the pCO_2 of each treatment to its respective control pCO_2 for all variants with up to 4 replicas, starting with table 5 (LUFA 6S soil), followed by table 6 (LUFA 2.2 soil), table 7 (LUFA 2.1 soil), table 8 (Fürth 1 soil HighFlow), and finally table 9 (Fürth 1 soil). In each graph, the black line represents the monthly median pCO_2 value of the 3 or- 4 control pots (x.0, 4 replicas) with the standard deviation (± 1 sigma) uncertainty range indicated by a gray area. The red lines are the monthly median pCO_2 value of the treatments (3-4 replicas) with the dashed lines showing again the standard deviations (± 1 sigma).





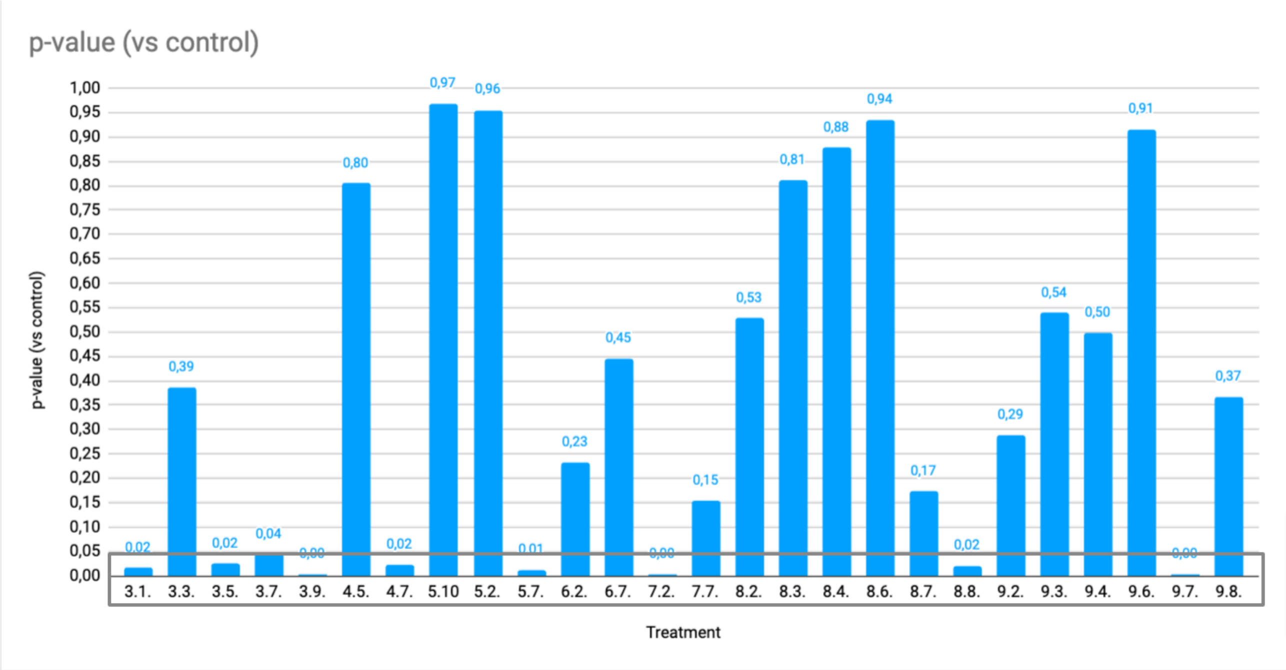
Soils: 5.x=LUFA 6S; 6.x=LUFA 2.2; 7.x=LUFA 2.1; 8.x=Fürth 1 (Highflow); 9.x=Fürth 1
Amendments: x.2/4=Basalt; x.6=Diabas; x.7=Dunite; x.8/10=Steel Slag

We also have soil pCO_2 data for tables 3 and 4 which comprise 10 soil samples from farms in Orthenau Kreis and Franconia (both in southern Germany) all treated with 40 t/ha basalt. Due to the limited number of pCO_2 sensors, however, we could only monitor 9 of these 10 treatments, and only with one sensor for a control and one for a soil-rock combination each. In the graphs below we show the soil pCO_2 evolution in these pots of table 3 and 4, again with black lines representing controls and red lines treatments. As we only have one sensor per variant in one replica, we show the average standard deviation of all 4-replica-variations on tables 5 to 9, which is 1,800 ppm.



Since 4.0 and 4.2/4.3 seem to have clogged-pot or sensor issues for some of the time, their data is compromised and we will not further discuss these treatments.

As a means of understanding whether or not a treatment differs significantly from their respective control we carried out a t-test analysis of all sensor data. The below p-values are calculated with two sample t-tests with unequal variance, i.e. values inside the gray box below 0.05 indicate that this soil-rock combination is a distinct set from its control.



When we look at the pCO_2 measurements of the treatments vs. their respective controls we observe the following:

- Significant increase for 3.5 and 3.9 (both basalt treated), 5.7, 7.2, and 9.7 (.7 is Dunite, .2 is Basalt),
- Significant decrease for 3.1, 3.7, 4.7 (all basalt treated), and 8.8 (steel slag),
- No statistically significant difference for all other treatments (17 of 26 = 68%) compared to their control.

The following graphs compare the 2023 changes in average pCO_2 between treatments and control of the more intensely monitored tables 5 to 9 with the percentage changes in accumulated alkalinity (treatment vs. control) in 2023, see our blog post on how this was calculated. Each data point is represented together with the respective uncertainties on the difference in accumulated alkalinity and average pCO_2 compared to its control. When a dot is above 0% it shows an increase in alkalinity in the leachate, a good indicator for CDR happening in this experiment. The area of the graph where an increase in soil pCO_2 coincides with increased leachate alkalinity is marked blue, red areas mark the quadrant where increased soil pCO_2 is coupled with a decrease in leachate alkalinity.

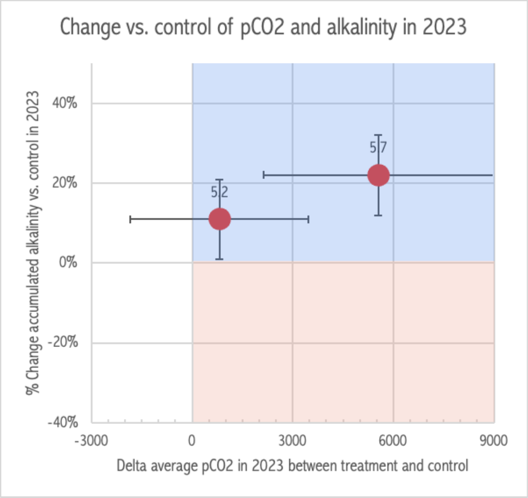


Table 5 on LUFA 6S soil

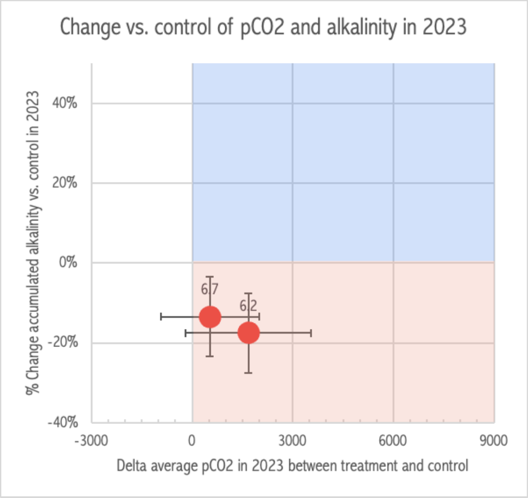


Table 6 on LUFA 2.2 soil

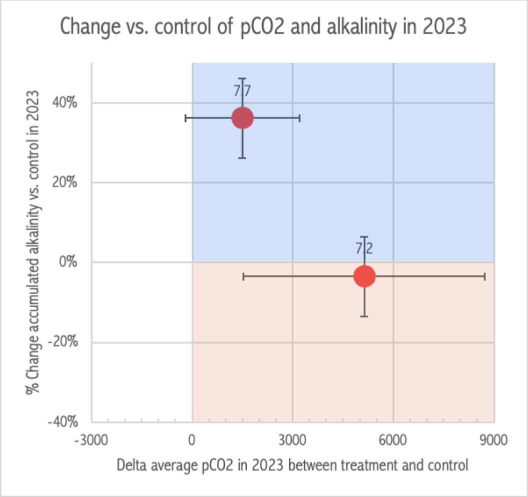


Table 7 on LUFA 2.1 soil

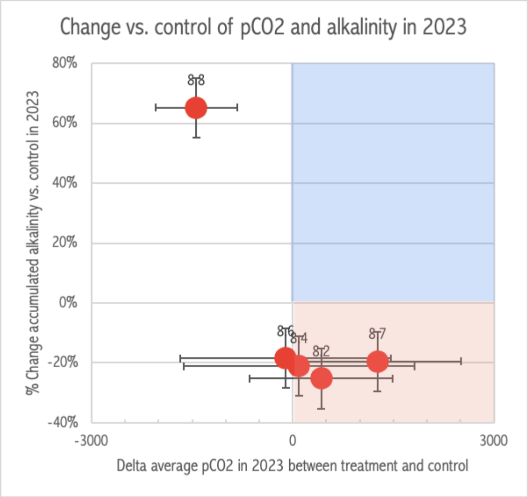


Table 8 on Fürth 1 soil (High flow irrigation)

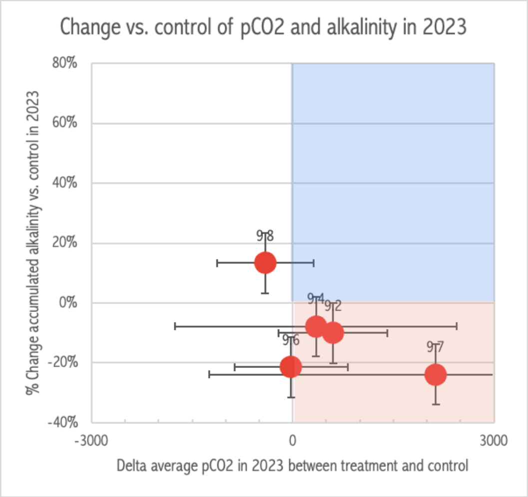


Table 9 on Fürth 1 soil

Of the 16 soil-rock dust treatments for which we have both TA and pCO_2 data, 14 show a significant change in accumulated alkalinity compared to their control (vertically either above or below 0% including error bars, ranging from -20% to +65%). But only 4 of the 16 treatments show a significant change in pCO_2 compared to their control, with a range of change in pCO_2 from minus 1500 ppm up to plus 6000 ppm.

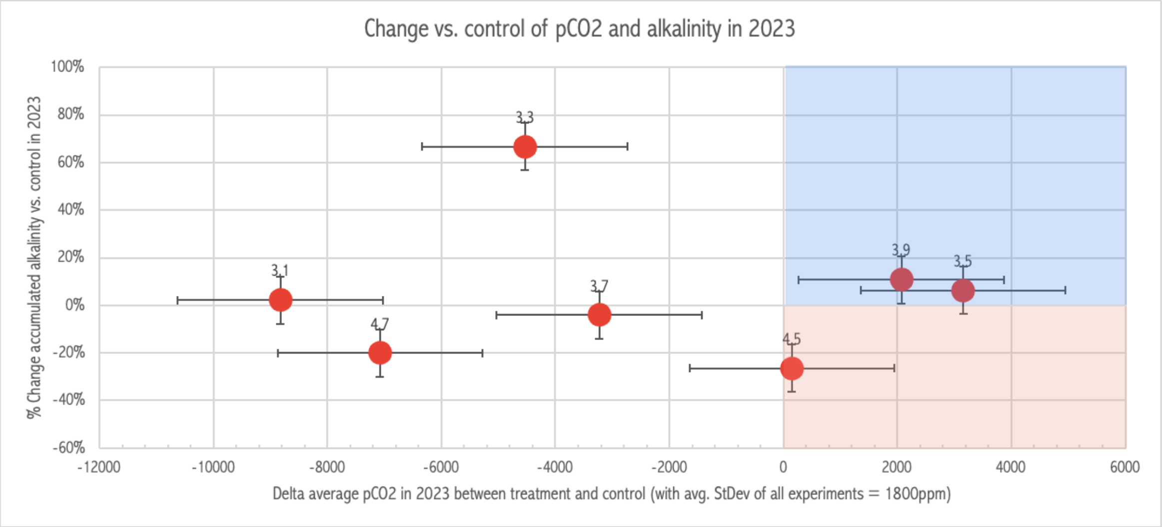
The three treatments with significant changes in both their alkalinity and pCO_2 signal are discussed below:

- 5.7 (LUFA 6S soil with dunite) shows increased removal of CO_2 as bicarbonates in the leachate water which goes hand in hand with an increase in soil pCO_2.
- A similar trend can be observed for 7.7 (LUFA 2.1 soil with dunite) although here the increase in leachate alkalinity is much higher, and the pCO_2 increase is less pronounced than in 5.7.
- 8.8 (steel slag on Fürth soil with Highflow) is the only treatment that shows a significant decrease of pCO_2. It also shows the highest increase of alkalinity in the leachate, however this is probably in part due to dissolution of calcium carbonates present in this material.

From these data it seems that adding ERW materials to soils overall tends to increase the soil pCO_2 in comparison to the same soil without any treatment (most dots are on the right side of the y-axis). This ERW effect might reflect an increase in biological activity upon addition of nutrients from rock dust dissolution and may include both more CO_2 root respiration from increased plant growth as increased CO_2 release from decay of biomass in the soil. Time and further research will tell whether this increase in soil pCO_2 is temporary, and whether it might be (over)compensated by increased removal of carbon as bicarbonates (alkalinity) in soil water. When we look at the soil pCO_2 and leachate alkalinity trends without strictly looking at their standard deviation ranges one soil (LUFA 6S, table 5) seems to show a positive relationship between alkalinity increase and pCO_2 increase, suggesting that both changes to the carbon cycle are correlated. All other soils suggest an inverse relationship of less soil pCO_2 correlating to more leachate alkalinity which could indicate that in these soils ERW is better able to reduce the soil CO_2 concentration.

The observation that nearly all variants tend to show a higher soil pCO_2 after the rock amendment (dots in red or blue quadrant) will likely lead to an increased CO_2 efflux (Fick's 1st law). This seems to be a bit counterproductive as we want to reduce carbon dioxide, but we should not forget that this is just one part of the soil carbon cycle and we need to also look at changes in other carbon pools to be able to assess the total effect. Only steel-slag-treated variations 8.8 and 9.8 show a lowering of pCO_2, which is again counterintuitive as this amendment contains 27% calcite which weathers fast but is less efficient in capturing CO_2 upon its dissolution than silicate minerals such as olivine.

Now let's have a look at the changes in soil pCO_2 and accumulated alkalinity that we observed between control and treatments during 2023 for the 7 soil-rock variations on tables 3 and 4.



Tables 3 and 4

The graph shows the high variability of the effects you get for both alkalinity change and pCO_2 change over 11 months when you apply the same rock dust on different soils. For pCO_2 we see a huge range of changes from minus 9,000 ppm up to plus 3,000 ppm (bigger than the range observed on tables 5 to 9) the change in leachate alkalinity ranges from minus 30% to plus 70% (similar to the range observed on tables 5 to 9). When compared to the same graphs from tables 5 to 9 which represent the combination of 4 soils with 4 rock dusts, we get quite a different pCO_2 picture. Now the majority of the soil-rock variations (5 out of 7) show soil CO_2 concentrations that are statistically different from their control, as opposed to 4 out of 16. And the shift in soil pCO_2 after rock dust amendment is no longer towards an increase as we saw for most of the variations before: on these two tables 3 soil-rock combinations actually have a significant pCO_2 decrease and only 2 a significant increase (significance refers to the p-values above).

Based on the above preliminary data, it is hard to argue for an MRV method that uses soil pCO_2 to assess CDR resulting from ERW. This parameter does not seem to sufficiently represent all changes in the carbon related soil processes. It looks like that any potential CDR effect resulting from ERW has only limited visibility in soil pCO_2 compared to the natural background which by itself is quite dependent on the soil type. And although the TA-derived CDR approach seems to result in a better CDR signal, with this parameter we also only “see” a subset of the soil processes that affect the carbon cycle. There are a number of other soil processes that influence the fate of the ERW products and the soil’s carbon cycle. For example, some of the cations from the rock dissolution might not yet be visible in leachate as they could still be stuck in the ca(r)tion park. Upcoming analysis of the different soil pools and estimation of the rock dust dissolution will help shed more light on this soon.

Only if we build a more complete understanding of the rock-induced changes in carbon fluxes and balances in the pot will we be able to understand how these findings might fit into the complete ERW picture.

This brings us to one of the next articles in our greenhouse series, the upcoming article about our CO_2 efflux measurements.

Summary

The combined measurements from our outdoors XXL lysimeter experiment over 20 months and indoor large scale greenhouse experiment over 11 months offer an ERW related soil pCO_2 dataset that is unique and extensive, both in terms of measurement frequency (every 10 minutes to 1 hour), 24/7 time coverage as in the number of soil-rock combinations (11 soils and 4 rock dusts).

Based on these preliminary data we can make the following conclusions and observations:

- High frequency soil pCO_2 monitoring over prolonged periods of time is necessary in order to be able to distinguish effects due to rock amendment from the many natural inter/intra day fluctuations.
- CO_2 concentrations measured simultaneously inside the bottom leachate tank and at 15 cm depth in the soil of the XXL lysimeters show very similar patterns.
- In the XXL lysimeters we amended our backyard Fürth soil in April 2022 with basalt at exceptionally high application doses of 100 t/ha, 200 t/ha and 400 t/ha. In the following months the pCO_2 in both the soil and leachate tanks was lower at higher application rates. Since late autumn 2022, however, the pCO_2 trends of the 4 variations have converged again. The initial distinction between the different treatments might reflect quick weathering of the finest rock dust particles during optimal conditions (summer temperatures and frequent irrigation) during the first months of the experiment.
- In the greenhouse, our main experiment comprises the combination of 4 different rock dusts with 4 soils. Although the soil pCO_2 data from the majority of these treatments tend towards increased concentrations, only 4 out of 16 are statistically different from their respective control, with 3 rock-soil combinations showing an increase in pCO_2 and one combination a decrease.
- Our secondary greenhouse experiment involves the addition of the same basalt rock dust to 9 different soils - and it shows quite different results. The valid pCO_2 data from 7 of these 9 soil-rock combinations have 2 combinations with statistically significant increases in soil pCO_2 whilst 3 others have a distinct pCO_2 decrease.
- Looking at the very different results from these two sets of greenhouse experiments we conclude that the soil type seems to have a much bigger influence on any changes in soil pCO_2 that might arise from ERW than the type of rock dust.
- Rock dust amendment effects can vary from nearly no change in pCO_2 to both a significant increase or decrease of this parameter. With this knowledge it becomes apparent how ERW studies where only 1 or 2 soil types are being tested might come to very different conclusions with regards to the effects on pCO_2.
- There does not seem to be any correlation between the changes in soil pCO_2 signal and the leachate alkalinity of a soil treated with an ERW material. The pCO_2 signal currently does not seem to be a good proxy for CDR as it is, quite frankly, mystifying.

With TA in the soil water leachate and pCO_2 in the soil we are obviously not covering the whole set of CO_2 related processes in the soil. We likely also need rock dissolution estimates, CO_2 efflux measurements, biomass data, etc. There is more to this and it needs further investigation. But we keep our pCO_2 sensors running, and will even add another 80 new ones in January. For this report, we 'only' had data from 97 pCO_2 sensors in 31 soil-rock variations, giving us limited insights into the 100 soil-rock variations we have in the greenhouse. But our fluxmeter monitoring of the soil CO_2 efflux actually covers all 100 variations and will improve this visibility. Stay tuned!

Note: Data used for this article will be published together with data from our upcoming articles soon.