Unravelling carbon cycle flows using the three stable isotopes of oxygen in atmospheric CO_2

measurements with a new laser absorption spectrometer

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If you want to skip or go back to a section you can do this by clicking on the hyperlinks, which you can recognize as underlined text.

1. Introduction

1. Atmospheric CO_2 – anthropogenic emissions and seasonal variations
2. Net Ecosystem Exchange (NEE)
3. $\Delta^{17}O$ of atmospheric CO_2 – a potential tracer for gross primary production
4. The 2018 drought in North-Western Europe

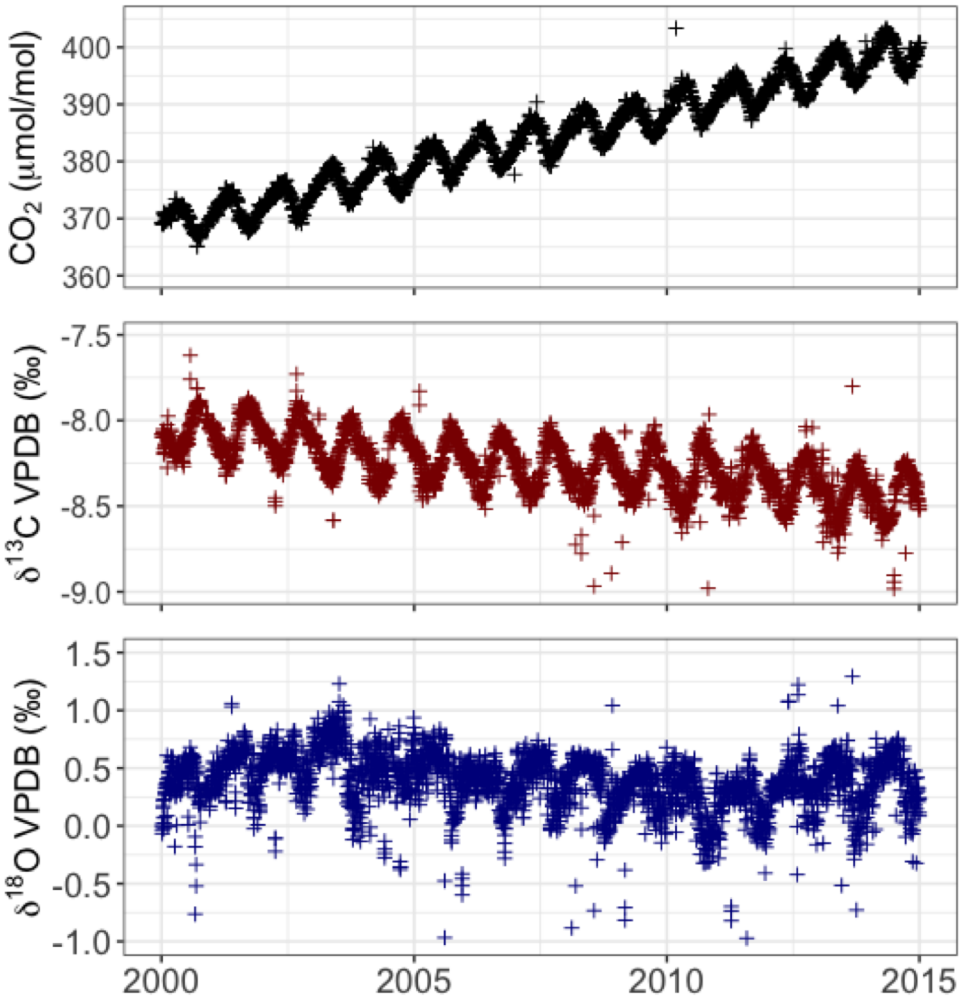
1.1 Atmospheric CO_2 – anthropogenic emissions and seasonal cycles

CO_2 mole fractions show an **increasing trend** over time, due to **anthropogenic activities** such as fossil fuel emissions and land use change. A **seasonal cycle**, with lower mole fractions during the Northern Hemisphere (NH) summer, is also observed, mainly caused by **land biosphere activity**.

The $\delta^{13}C$ record shows the same processes as the CO_2 mole fraction record: the **decreasing trend** can be explained by the increase of CO_2 in the atmosphere as the results of **fossil fuel emissions**, which have a relatively depleted $^{13}C/^{12}C$ composition. The **seasonal cycle** with more enriched values during the NH summer is due to the preference of **C3 plants** for the lighter ^{12}C isotope for photosynthesis.

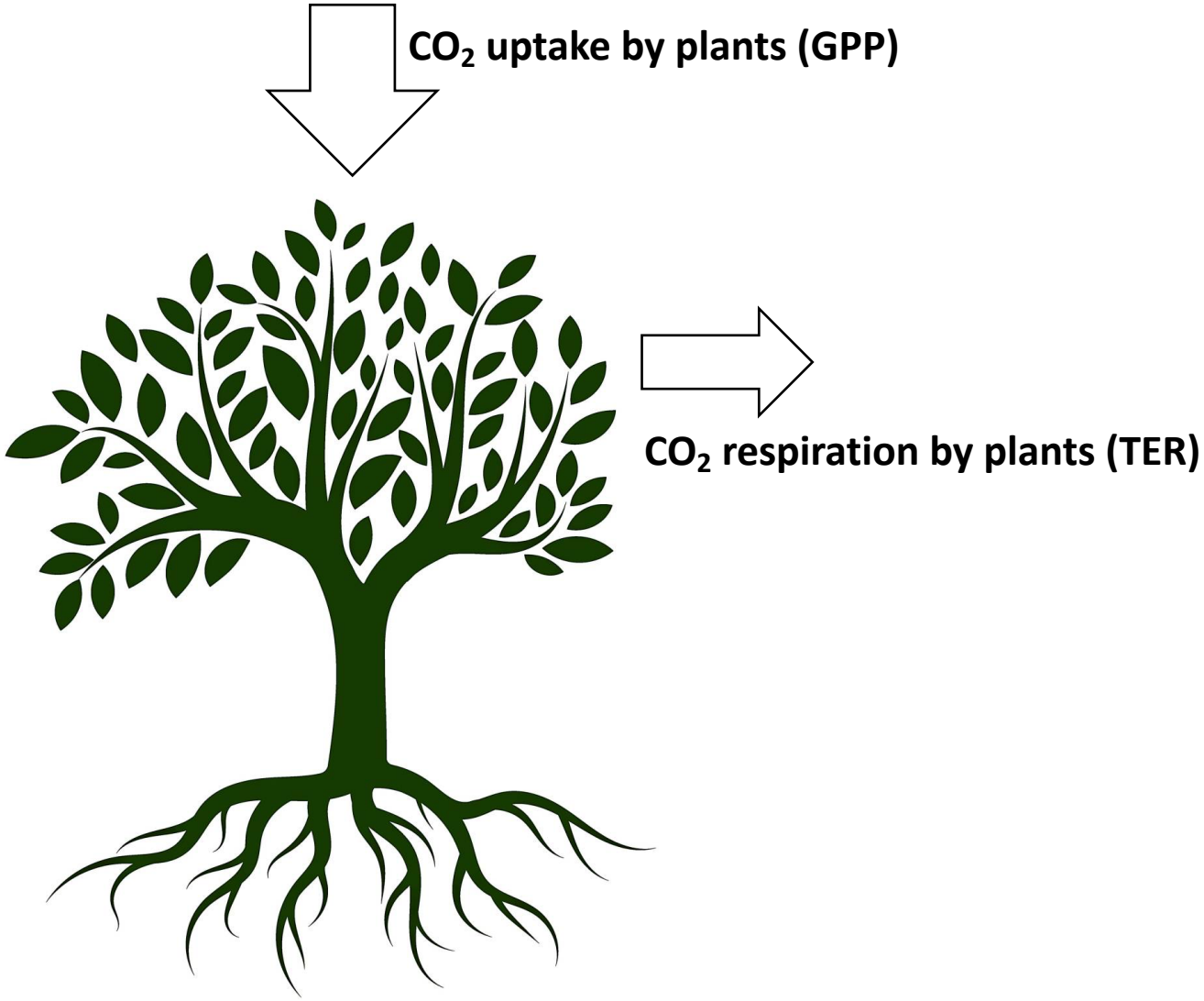
The $\delta^{18}O$ composition of atmospheric CO_2 is mainly influenced by the isotope exchange with water. The seasonal cycle, with in general more depleted values in summer can be explained by the difference in $\delta^{18}O$ composition between ocean water (very stable, close to 0 ‰) and meteoric water (variable, more depleted). During growing seasons atmospheric CO_2 equilibrates with water in plants, hence the influence of meteoric water on the atmospheric CO_2 composition is higher.

Mauna Loa Flask measurements



Source: NOAA ESRL GMD

1.2 Net ecosystem exchange



The net ecosystem exchange (NEE) is the imbalance between the CO_2 uptake of plants, or gross primary production (GPP) and the amount of CO_2 that is respired by plants, known as the terrestrial ecosystem respiration (TER).

NEE = GPP – TER

The NEE has been positive over the last decades, meaning that the **biosphere** acts as a **sink** for atmospheric CO_2 (Ballantyne et al., 2012).

Extreme climate events, such as **droughts**, have shown to change the imbalance between GPP and TER this much that ecosystems can turn into CO_2 **sources** instead of sinks (Ciais et al. 2005).

1.3 $\Delta^{17}O$ of atmospheric CO_2 - a potential tracer for GPP

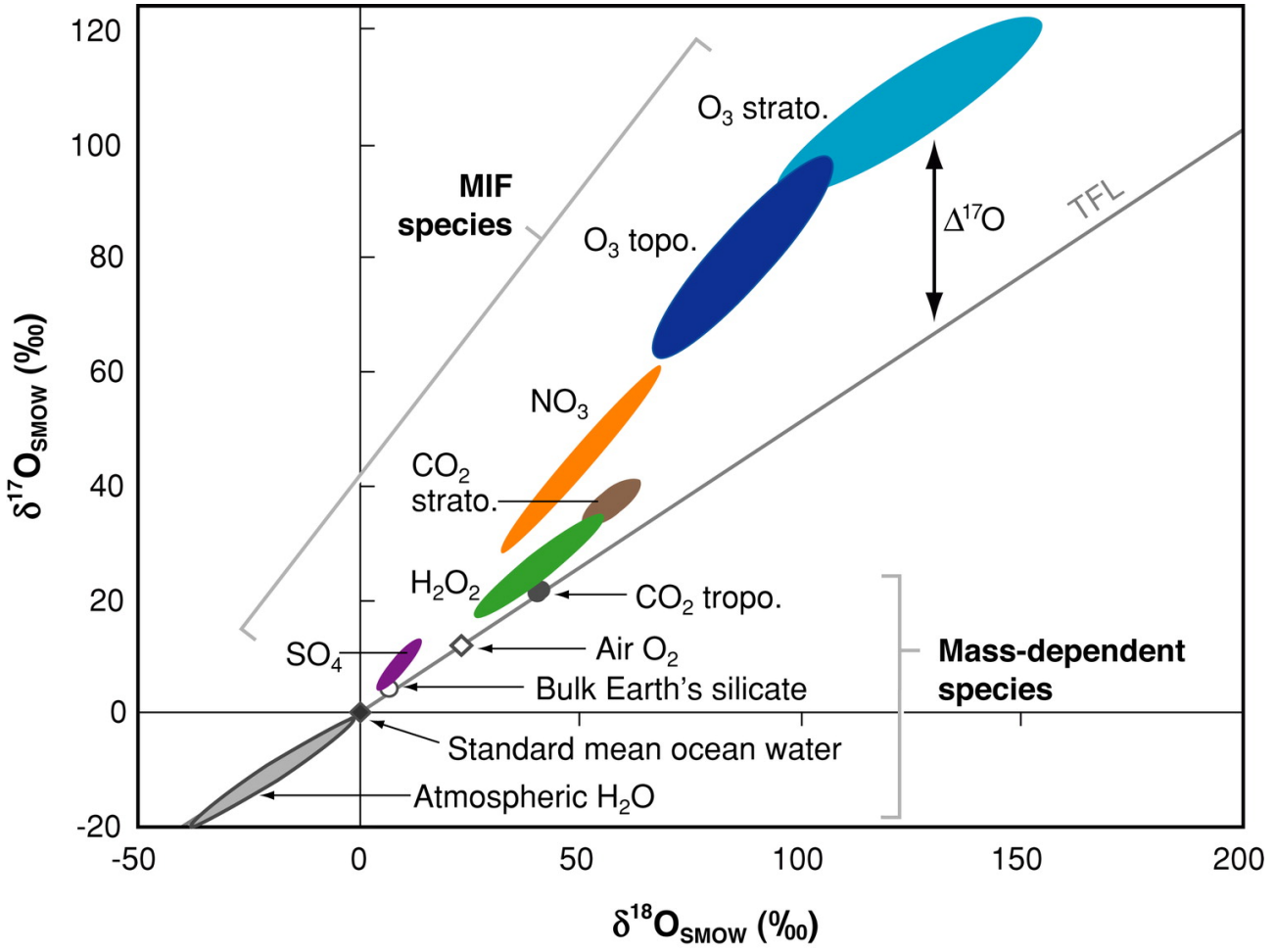
The $\delta^{17}O/\delta^{18}O$ ratio in **water** is very stable (close to 0.5) as the result of the fixed $\delta^{17}O$ - $\delta^{18}O$ relation in **mass-dependent fractionation** processes. Equilibration of CO_2 with water follows mass dependent fractionation, so the $\delta^{17}O/\delta^{18}O$ ratio in **tropospheric CO_2** is very close to 0.5 as well.

Stratospheric CO_2 carries a more deviating $\delta^{17}O/\delta^{18}O$ ratio as the result of **mass-independent fractionation** processes occurring during the formation of ozone.

The $\Delta^{17}O$ can be defined as the deviation from a fixed $\delta^{17}O$-$\delta^{18}O$ relation:

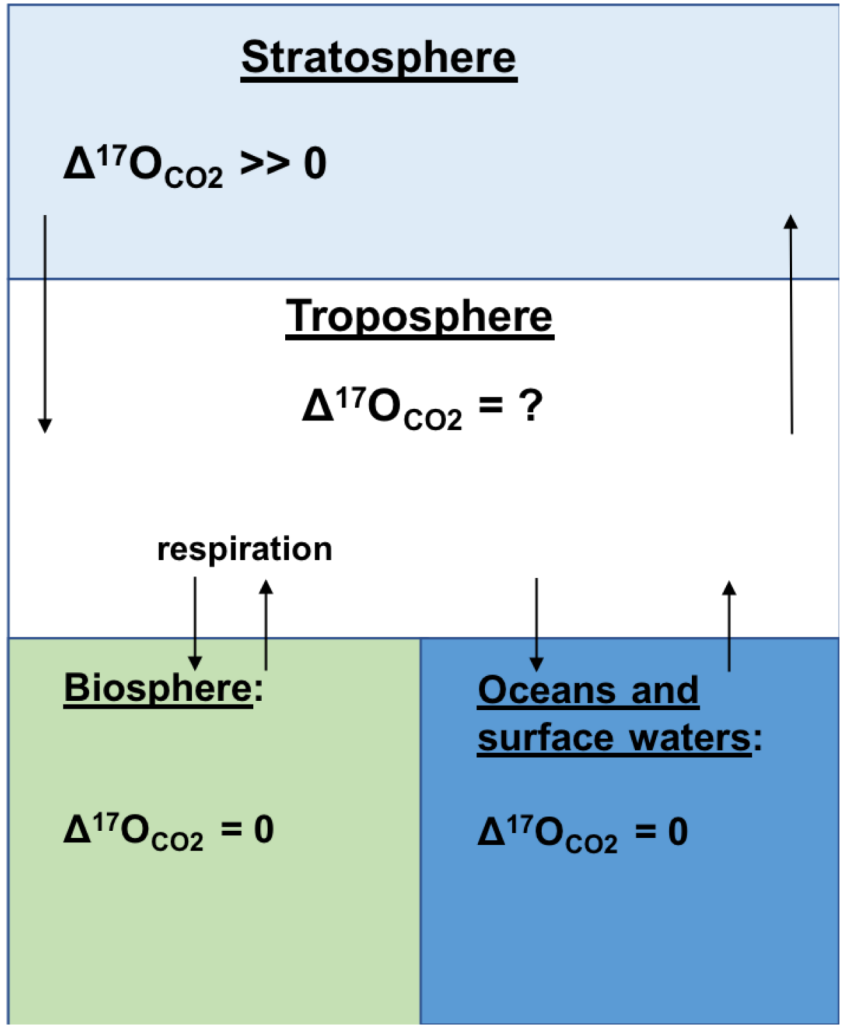
$$\Delta^{17}O = \ln(\delta^{17}O +1)-\lambda*\ln(\delta^{18}O +1)$$

For atmospheric CO_2 we use a λ of 0.5229, following measurements of CO_2 equilibrated with water by Barkan and Luz (2012).



Thiemens MH. 2006.
Annu. Rev. Earth Planet. Sci. 34:217–62

1.3 $\Delta^{17}O$ of atmospheric CO_2 - a potential tracer for GPP



Simplified box model of CO_2 fluxes relevant for $\Delta^{17}O_{CO2}$ variations in the troposphere. Adapted from Luz et al., 1999

The $\Delta^{17}O$ of tropospheric CO_2 is (mainly) the result of:

- Intrusion of CO_2 from the stratosphere → increase of the $\Delta^{17}O$
- Equilibration of CO_2 with water, occurring over oceans and surface waters, but mainly in plants → setting the $\Delta^{17}O$ to 0

This causes the $\Delta^{17}O$ of tropospheric CO_2 to be, in general, **higher in winter and close to 0 is spring/summer**.

Extreme weather events such as **droughts** can reduce the uptake of CO_2 by plants, and can therefore appear as periods with **elevated $\Delta^{17}O$ values** in measurement series.

1.4 The 2018 drought in North-Western Europe

Smith et al. (2020):

- **Enhanced heat and solar radiation leading to enhanced carbon uptake during spring, when soil moisture was still available**
- **Eventual cancellation of carbon uptake due to unavailability of soil moisture**

PHILOSOPHICAL TRANSACTIONS B

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Research

Cite this article: Smith NE *et al.* 2020 Spring enhancement and summer reduction in

Spring enhancement and summer reduction in carbon uptake during the 2018 drought in northwestern Europe

Naomi E. Smith[1], Linda M. J. Kooijmans[1], Gerbrand Koren[1], Erik van Schaik[1], Auke M. van der Woude[1,2], Niko Wanders[3], Michel Ramonet[4], Irène Xueref-Remy[4], Lukas Siebicke[5], Giovanni Manca[6], Christian Brümmer[7], Ian T. Baker[8], Katherine D. Haynes[8], Ingrid T. Luijkx[1] and Wouter Peters[1,2]

PHILOSOPHICAL TRANSACTIONS B

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Research

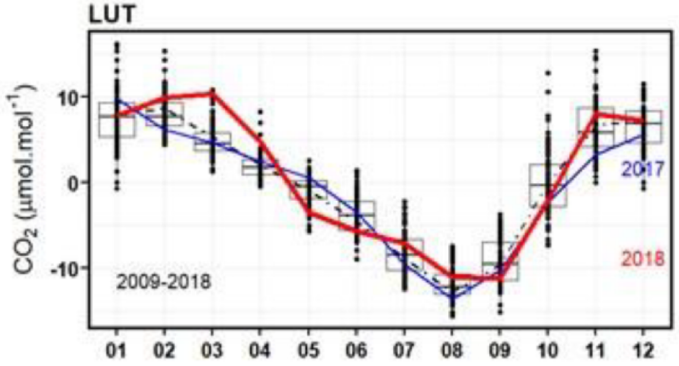
Cite this article: Ramonet M *et al.* 2020 The

The fingerprint of the summer 2018 drought in Europe on ground-based atmospheric CO_2 measurements

M. Ramonet[1], P. Ciais[1], F. Apadula[25], J. Bartyzel[33], A. Bastos[35], P. Bergamaschi[20], P. E. Blanc[15], D. Brunner[26], L. Caracciolo di Torchiarolo[18], F. Calzolari[17], H. Chen[4], L. Chmura[33], A. Colomb[28], S. Conil[7], P. Cristofanelli[17], E. Cuevas[19], R. Curcoll[14], M. Delmotte[1], A. di Sarra[34], L. Emmenegger[26],

CO_2 seasonal cycle at Lutjewad:

Red= 2018
Blue=2017
Black= statistical summary of period 2009-2018



Link to special issue: 'Impacts of the 2018 severe drought and heatwave in Europe: from site to continental scale'

Photo: Philip Kraaijenbrink

2. Methods and sampling site

1. Stable Isotopes of CO_2 Absorption Spectrometer (SICAS)
2. The atmospheric measurement station Lutjewad
3. Sampling methods
4. Stability of oxygen isotopes in sample flasks

2.1 Stable isotopes of CO_2 absorption spectrometer (SICAS)

Aerodyne dual laser optical spectrometer (CW-IC-TILDAS-D)

Two interband cascade lasers operate in the mid infrared region at 2350 cm^{-1} and 2310 cm^{-1}

Absorption of CO_2 isotopologues takes place in a 0.16 L sample cell, total cell path length is 36 m

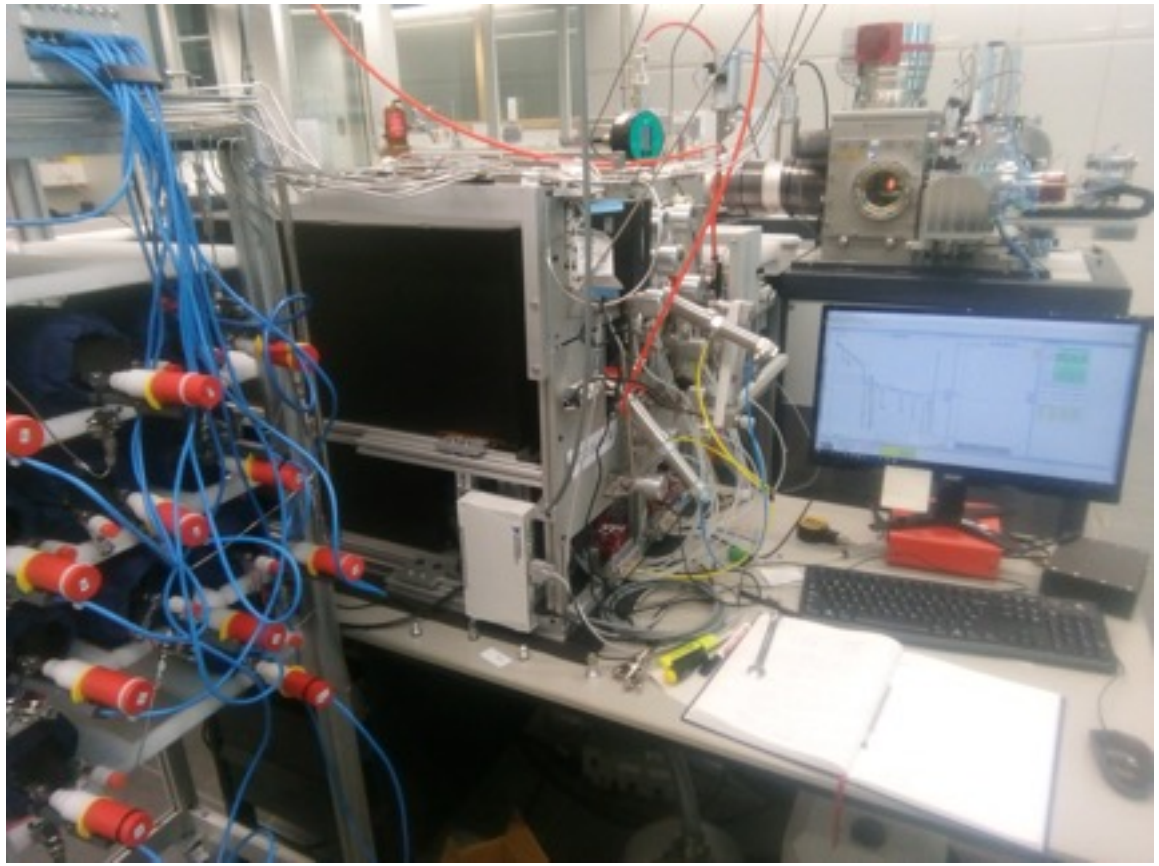
Measures $\delta^{13}C$, $\delta^{18}O$ and $\delta^{17}O$ of atmospheric CO_2 directly on dry air samples

Combined uncertainties for presented measurement period: $\delta^{13}C$=0.05‰, $\delta^{18}O$=0.07‰ and $\Delta^{17}O$=0.05 ‰

Operates in static mode, suitable for flask measurements

A paper on the performance and calibration methods of the instrument is accepted an will soon be published in Atmospheric Measurement Techniques under the following title:

Simultaneous measurement of $\delta^{13}C$, $\delta^{18}O$ and $\delta^{17}O$ of atmospheric CO_2- performance and assessment of a dual-laser absorption spectrometer (Steur et al.)



The Aerodyne dual laser optical spectrometer, in the CIO lab with on the left the sample flasks rack

2.2 Atmospheric measurement station Lutjewad

The Lutjewad station, set up in 2000 by the Center of Isotope Research, is situated at the coast of the Wadden Sea, in the **North of the Netherlands**



Northern winds → Middle European background signal

Southern winds → Anthropogenic and biogenic sources and sinks

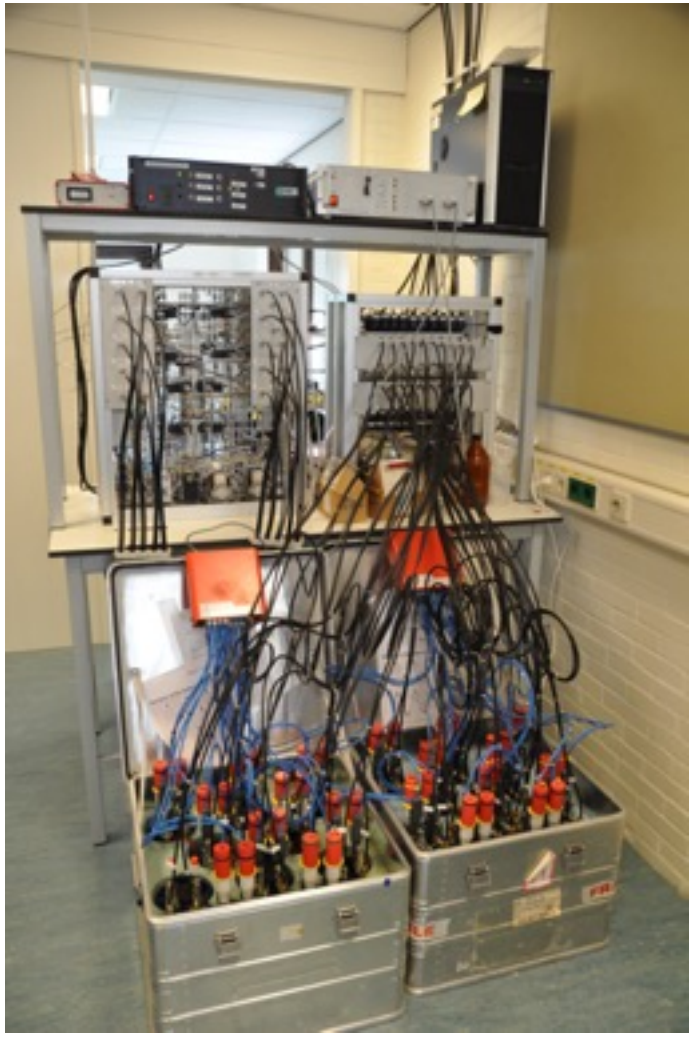
From a **60 m tall tower**, air is continuously sampled and measured for trace gas concentrations, including CO_2, CO and CH_4

ICOS class 2 station

For stable isotope measurements, flasks are sampled every 3 days using an automated sampling system

2.3 Sampling method

Sample flasks

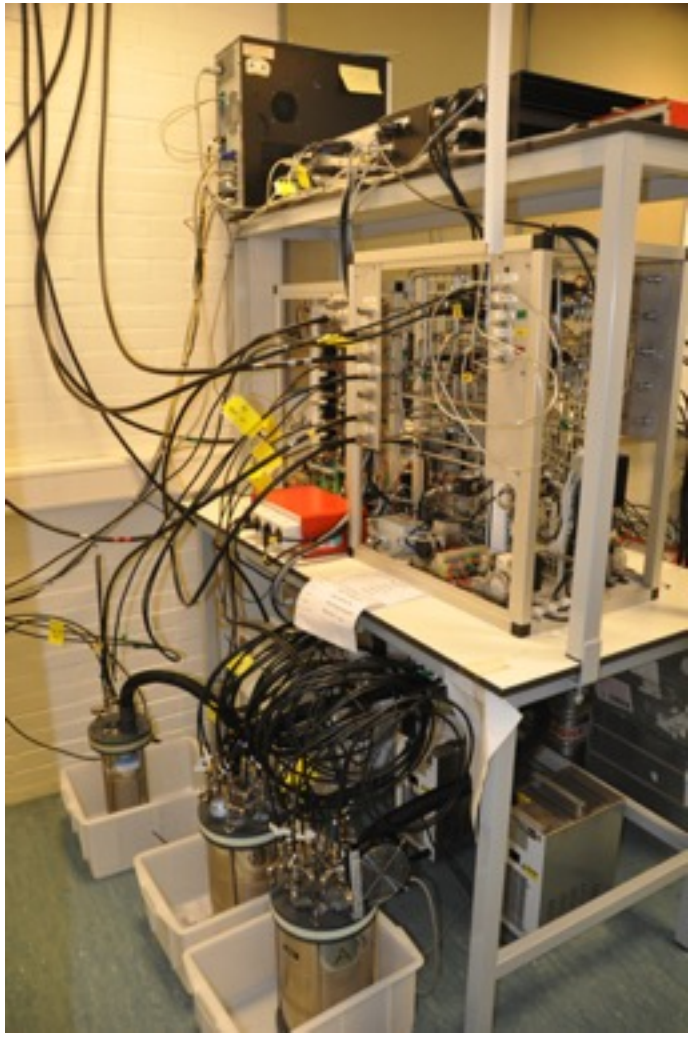


Flasks are all connected and continuously flushed with dry sample air

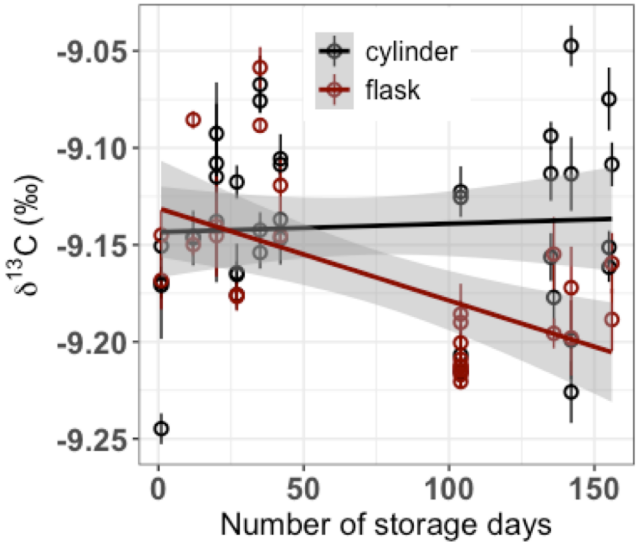
Sample air is dried at -80° C, with two cooling systems that are alternated to prevent clogging

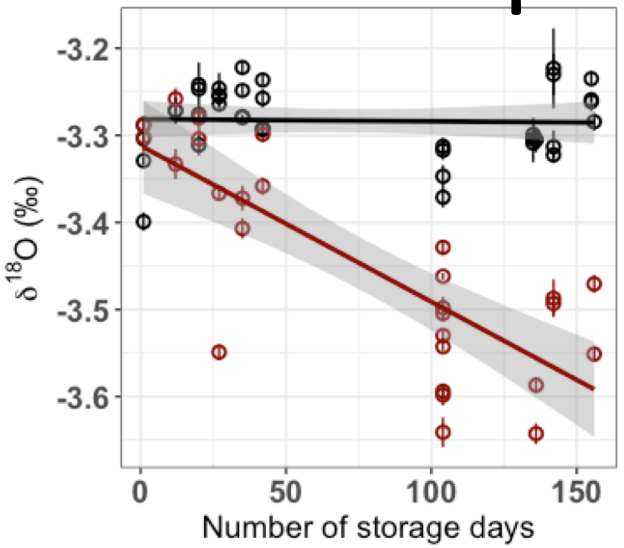
The automated system takes samples by closing one flask at noon every three days

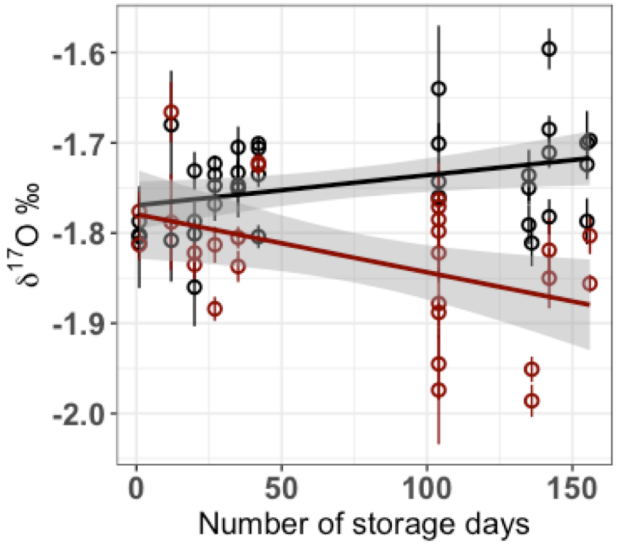
Dryers

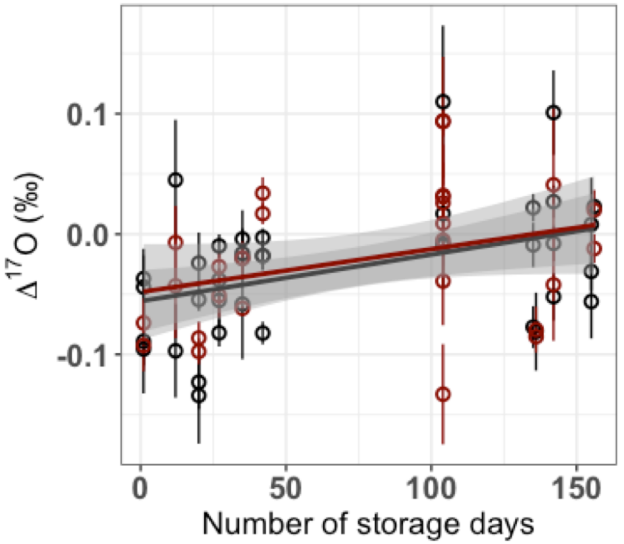


2.4 Stability of oxygen isotopes in glass sample flasks









Stability of CO_2 isotopes in sample flasks was tested by filling 10 flasks with well-known air from a cylinder

Flasks and the cylinder were measured at different moments over a time period of ~150 days

The stability of the $\delta^{13}C$ isotopes is quite high: not more than 0.05‰ drift

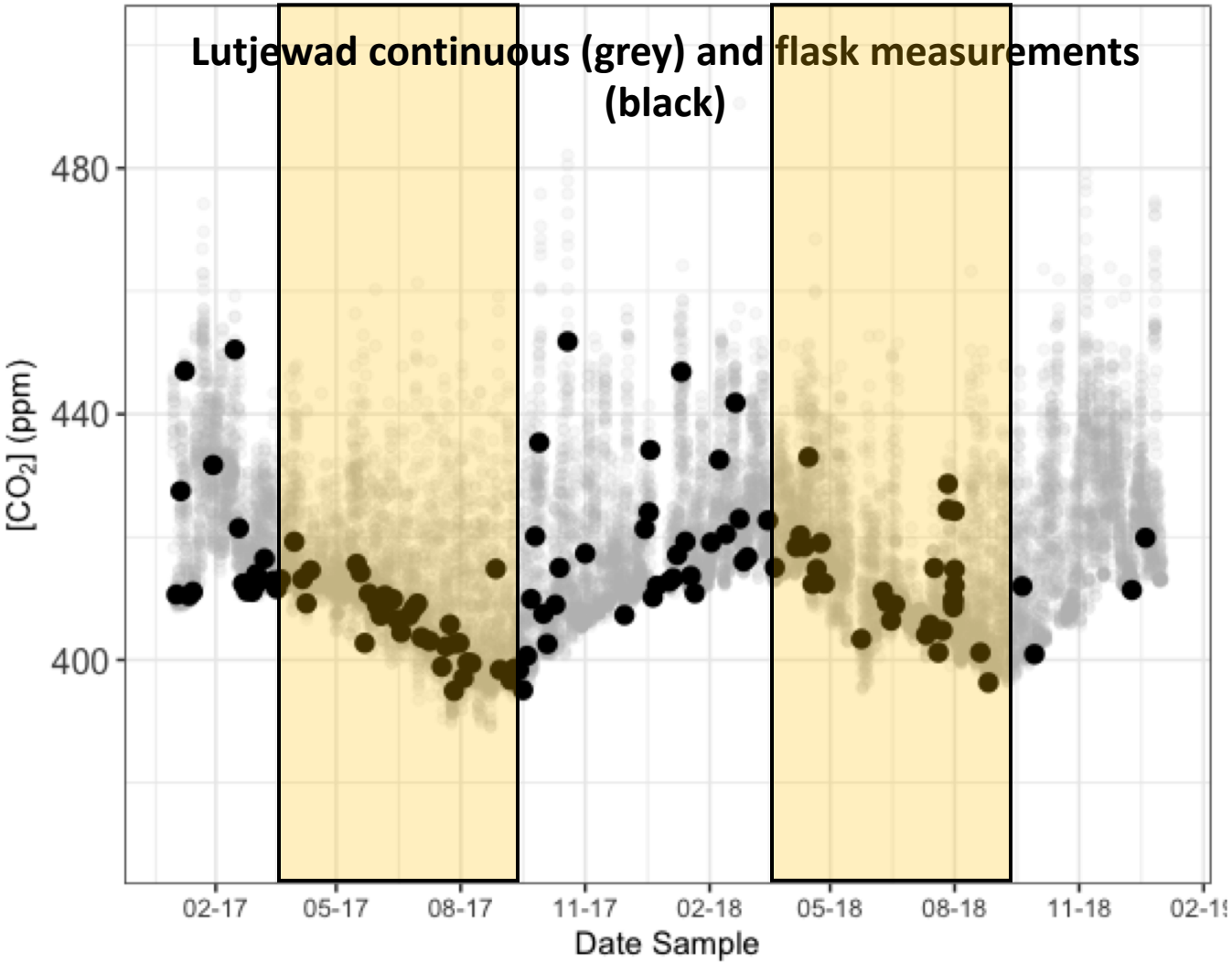
Stability of the $\delta^{18}O$ and $\delta^{17}O$ is lower: 0.3 and 0.1‰ drift respectively

Stability of the $\Delta^{17}O$ is not affected by the instability of the oxygen isotopes (the drift towards more enriched values can be explained by instrumental drift of the $\delta^{17}O$ measurements)

3. Measurement results of Lutjewad for the period 2017-2018

1. CO_2 concentration measurement results
2. $\delta^{13}C$ measurement results
3. $\delta^{18}O$ measurement results
4. $\Delta^{17}O$ measurement results
5. Lutjewad during the 2018 drought period

3.1 CO_2 concentration measurements results

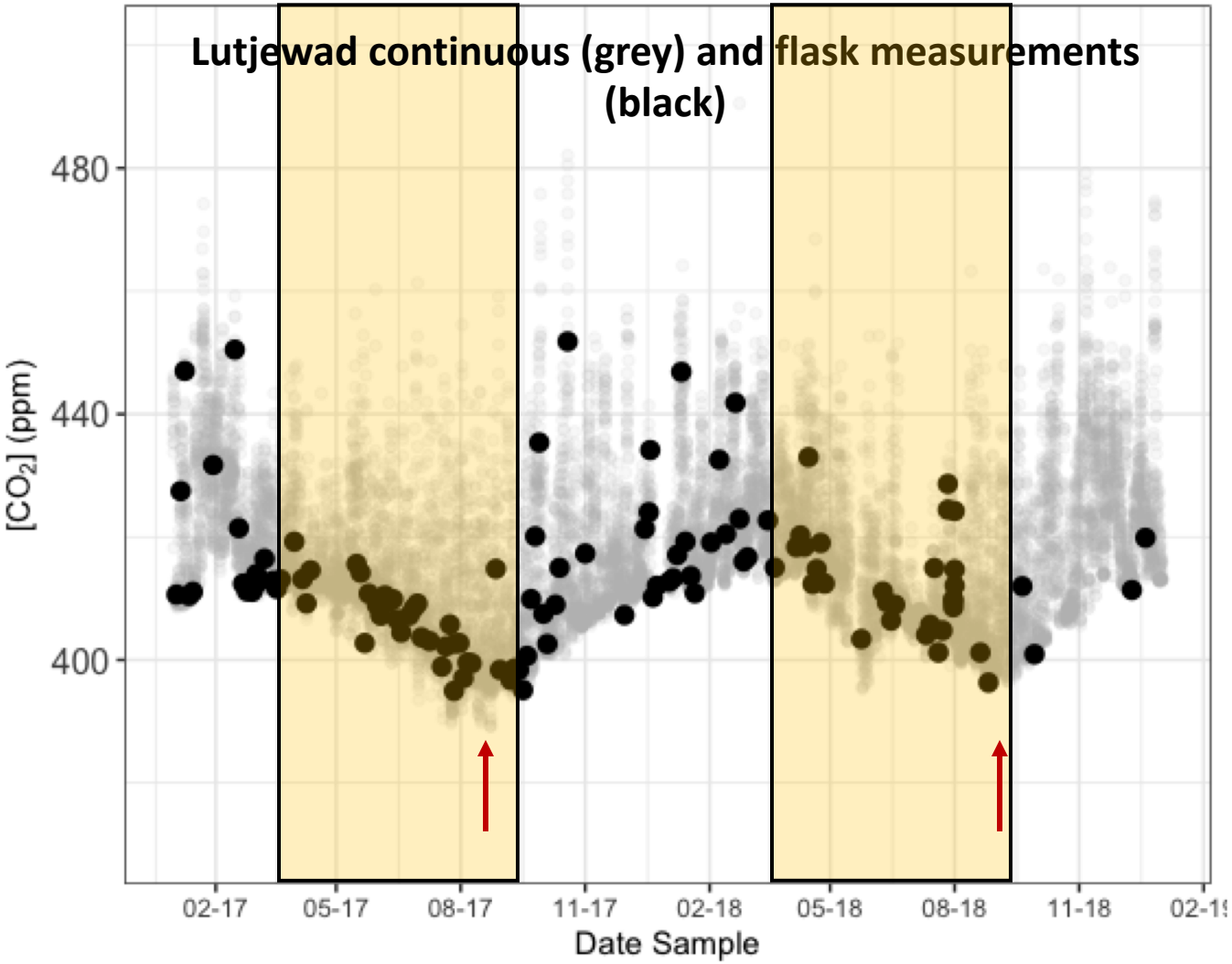


Lutjewad CO_2 concentration measurements from continuous and flask samples

Spring and summer periods are marked in orange

Main differences between 2017 and 2018:

3.1 CO_2 concentration measurements results



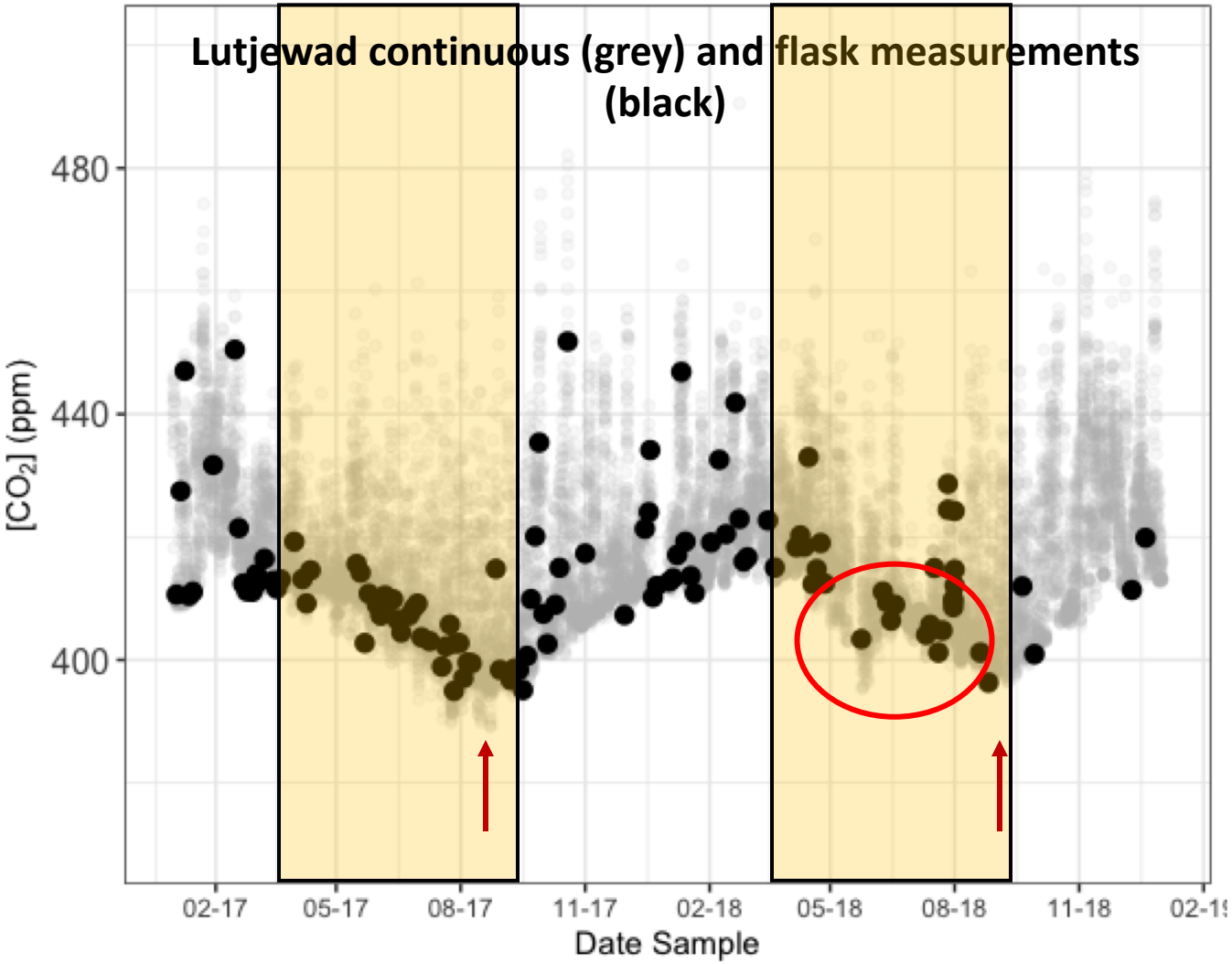
Lutjewad CO_2 concentration measurements from continuous and flask samples

Spring and summer periods are marked in orange

Main differences between 2017 and 2018:

Timing lowest CO_2 concentration in late summer

3.1 CO_2 concentration measurements results



Lutjewad CO_2 concentration measurements from continuous and flask samples

Spring and summer periods are marked in orange

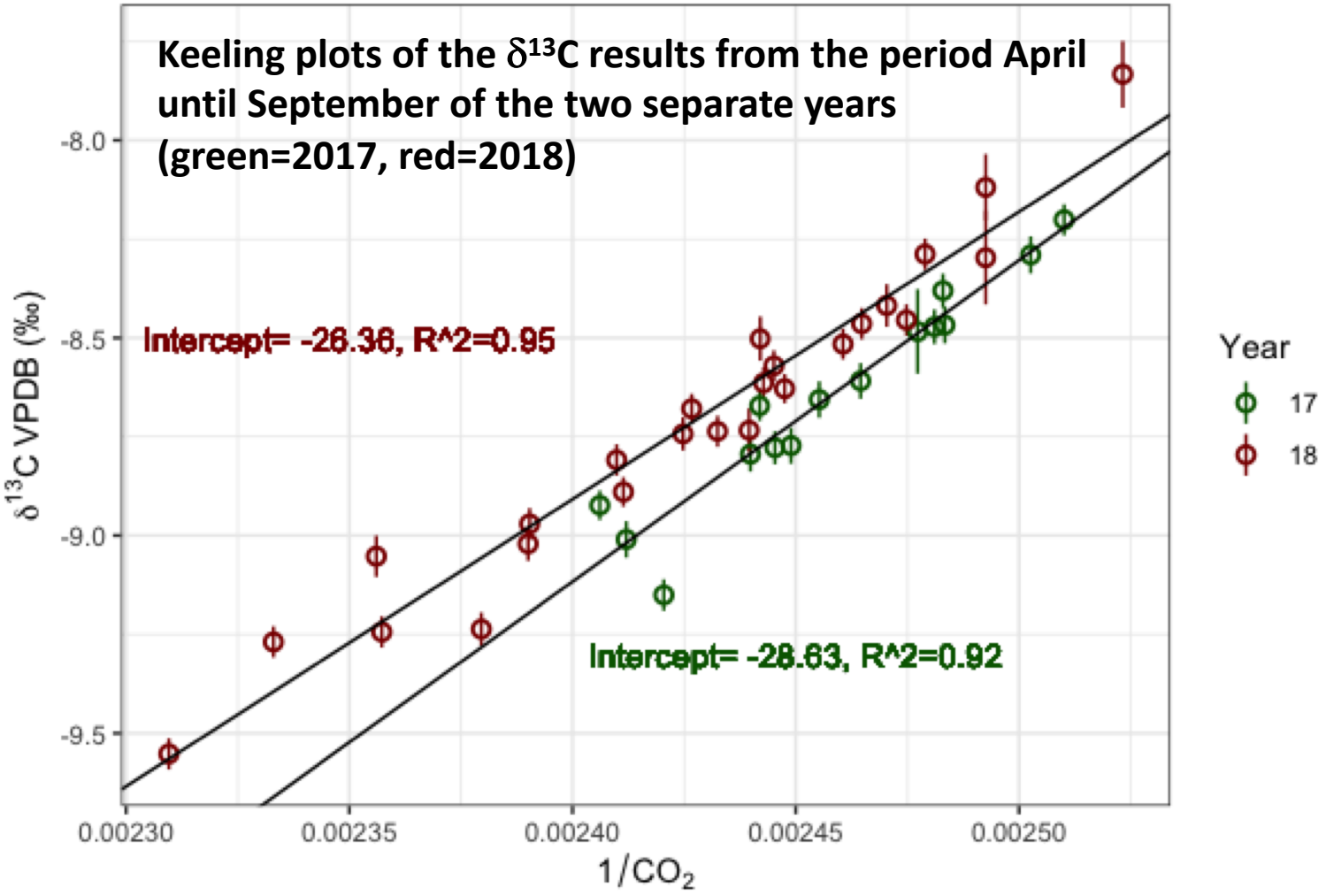
Main differences between 2017 and 2018:

Timing lowest CO_2 concentration in late summer

Inversion of decreasing CO_2 concentration trend in 2018

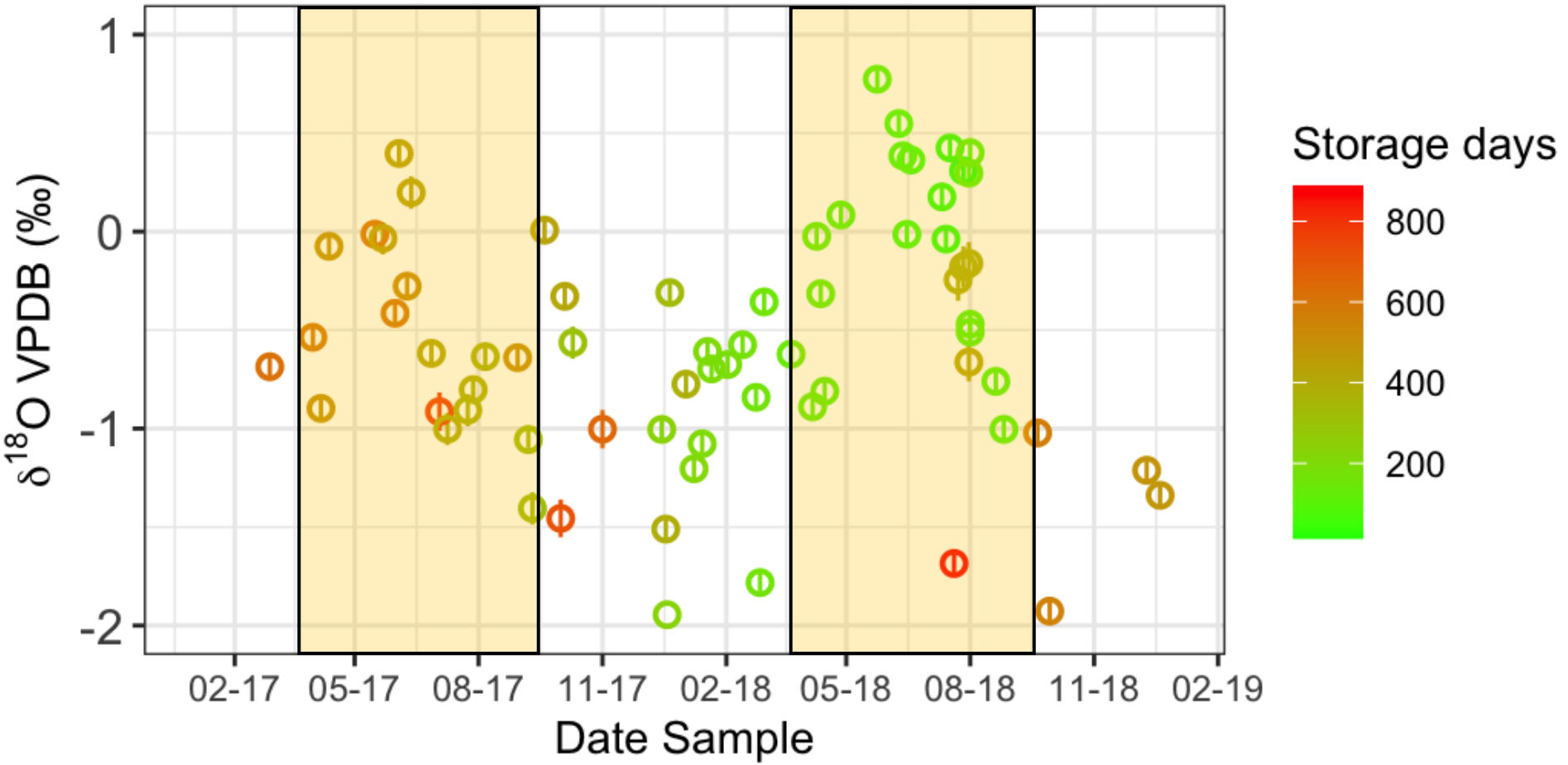
3.2 $\delta^{13}C$ measurement results

The stable isotope data shown in the results section were filtered to remove fossil fuel dominated samples. Curious how? Click here!



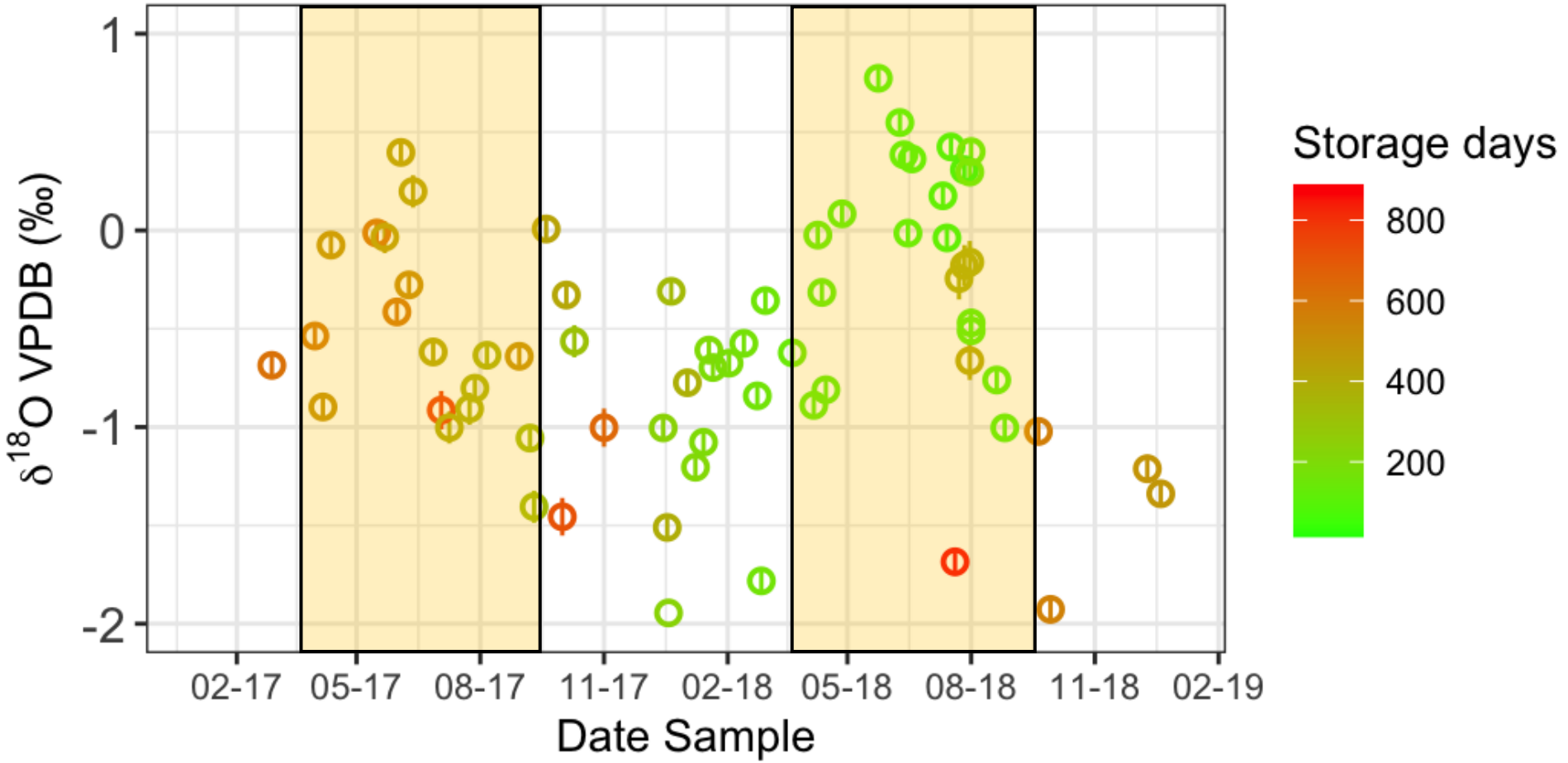
- Significant differences in source signatures between periods April-September of 2017 and 2018
- The more enriched value in 2018 indicates to increased water use efficiency of plants due to the drought, which also leads to a decrease of the discrimination against the heavier $^{13}CO_2$ isotope (Peters et al., 2018)

3.3 $\delta^{18}O$ measurement results

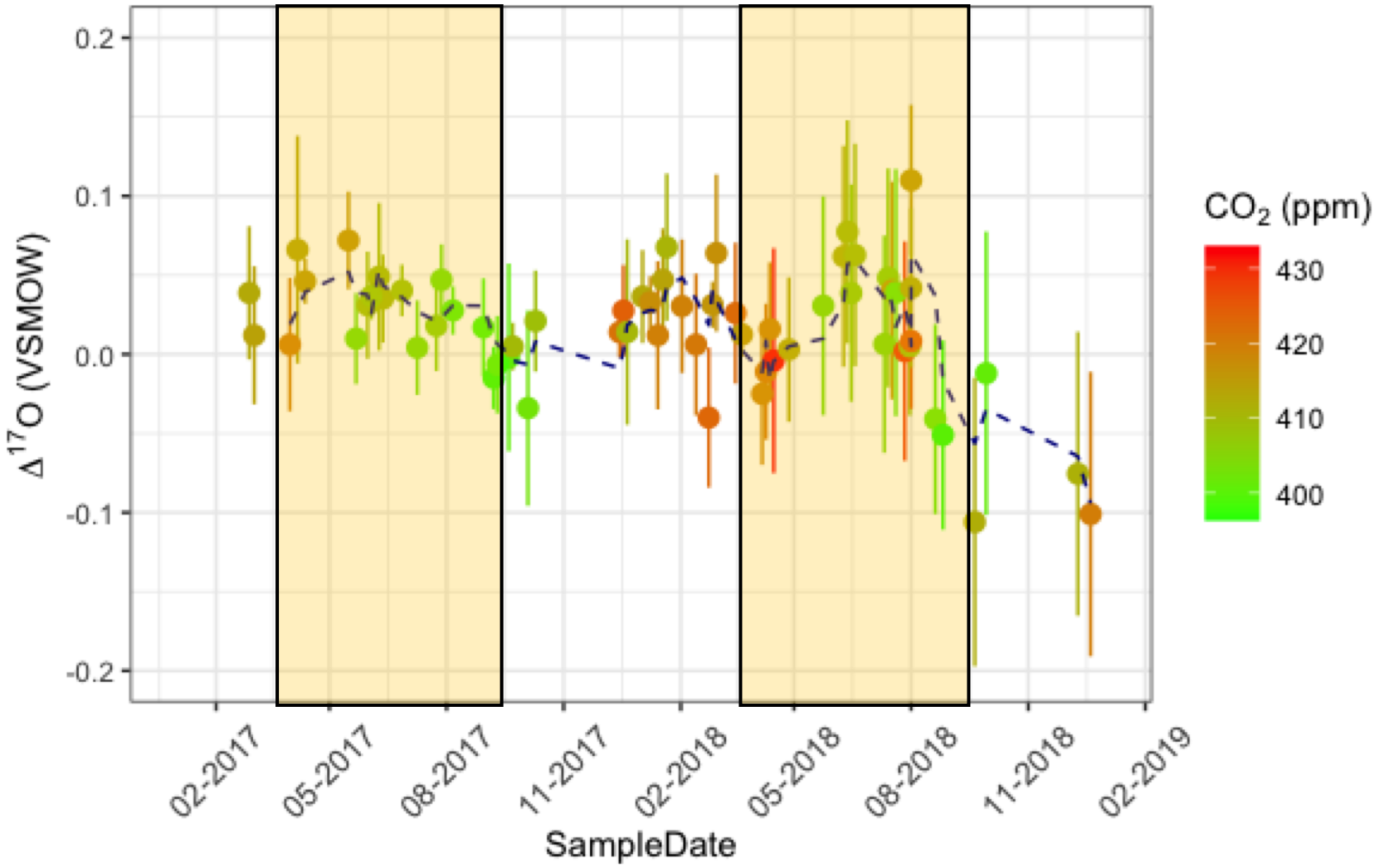


3.3 $\delta^{18}O$ measurement results

When analyzing these data, we should take into account the sometimes very high storage times (color of markers in the graph) and differences in storage times between samples



3.4 $\Delta^{17}O$ measurement results



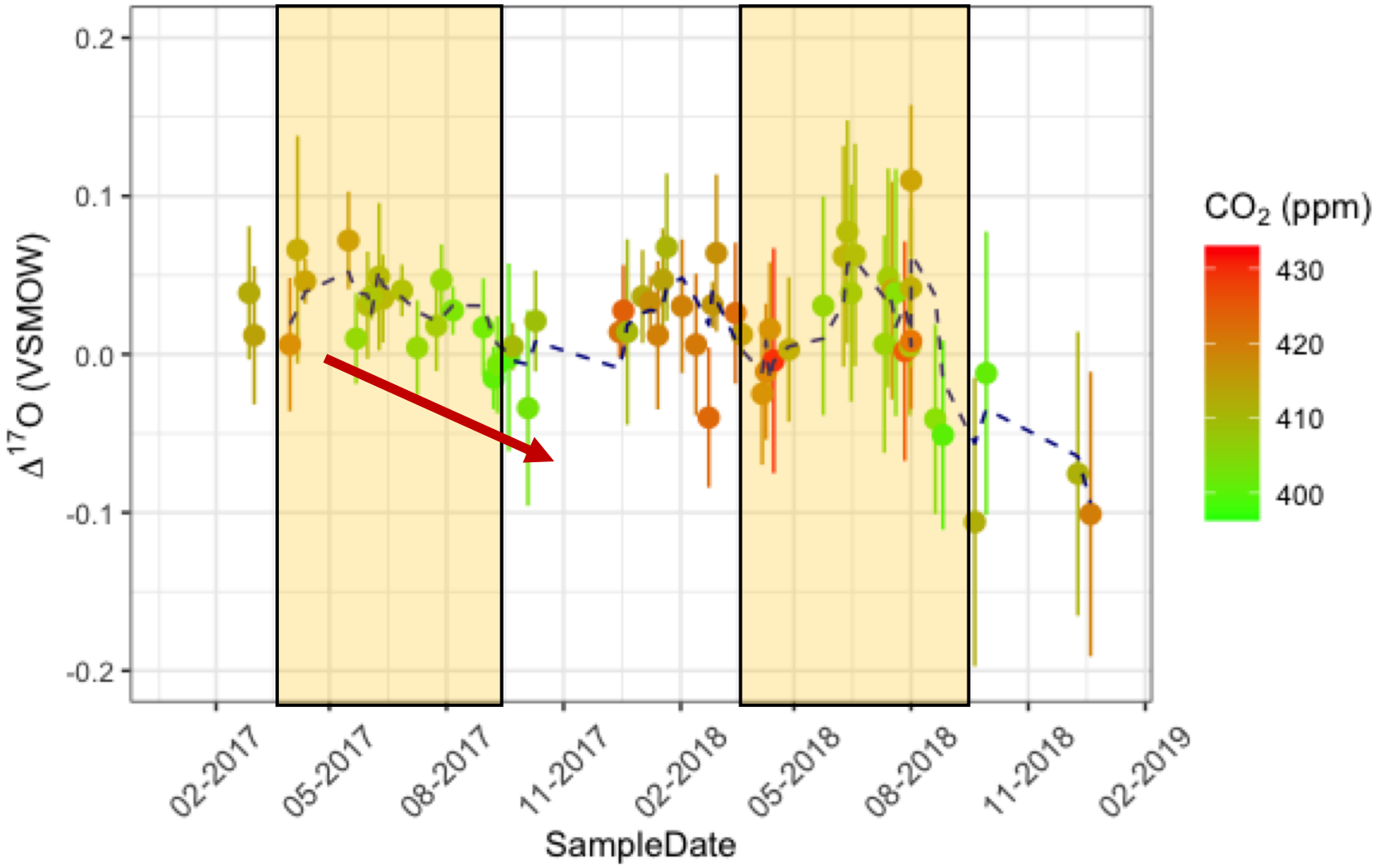
The Lutjewad $\Delta^{17}O$ record shows a clear seasonality with an amplitude of ~0.05‰

The values agree well with the predicted value for the global mean of 0.06 ± 0.03‰ from the modelling study by Hofmann et al. (2017)

The timing and amplitude of the 2017 Lutjewad (53.24°N) seasonal cycle agrees with the model simulation by Koren et al. (2019)

Click here for the simulation by Koren et al. (2019)

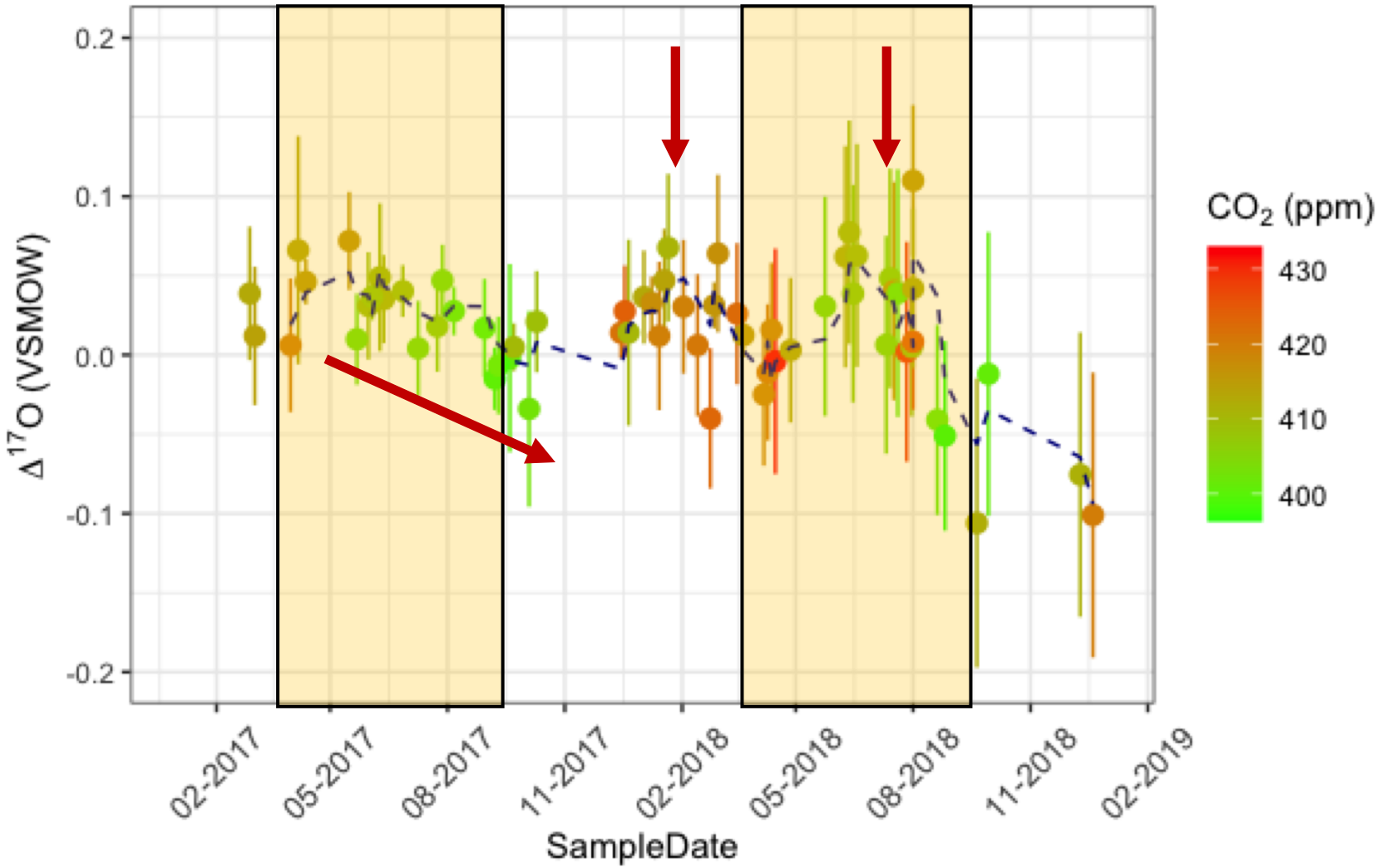
3.4 $\Delta^{17}O$ measurement results



Difference between the $\Delta^{17}O$ trend in 2017 and 2018:

- 2017 follows sinusoid with decreasing values over the whole summer period

3.4 $\Delta^{17}O$ measurement results



Difference between the $\Delta^{17}O$ trend in 2017 and 2018:

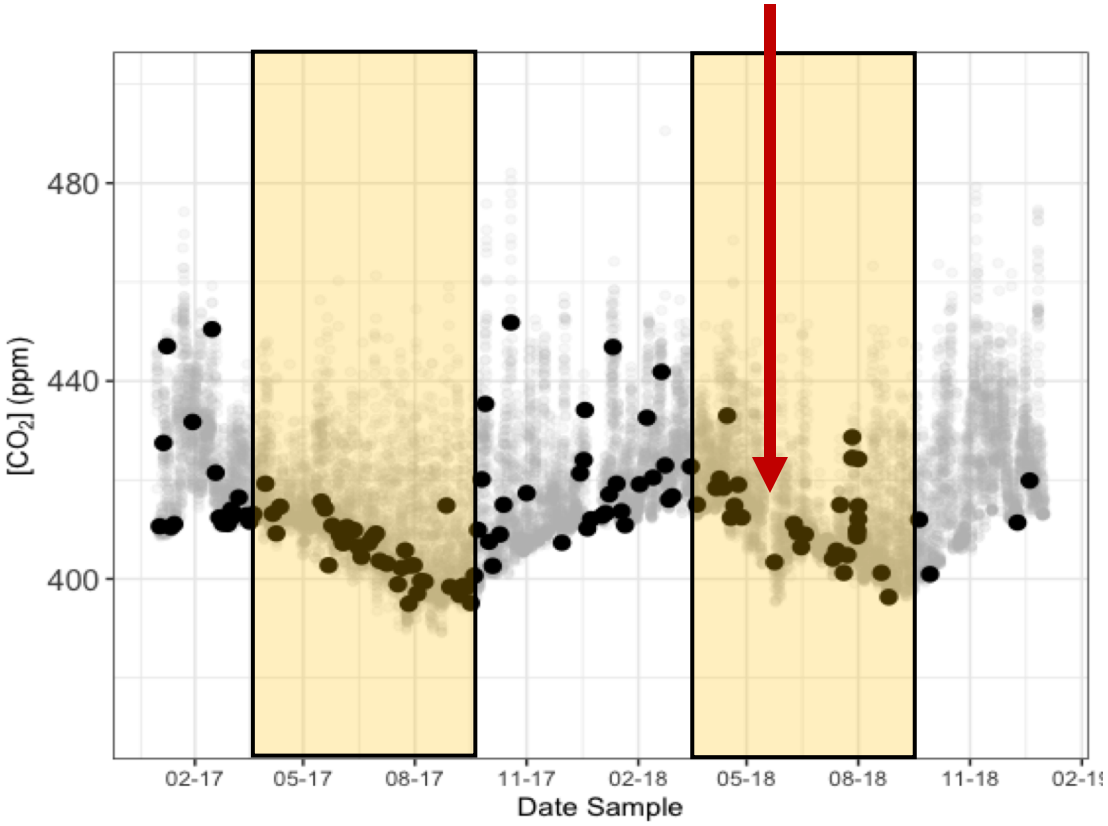
- 2017 follows sinusoid with decreasing values over the whole summer period
- 2018 shows two peaks: one in winter, and one in late summer

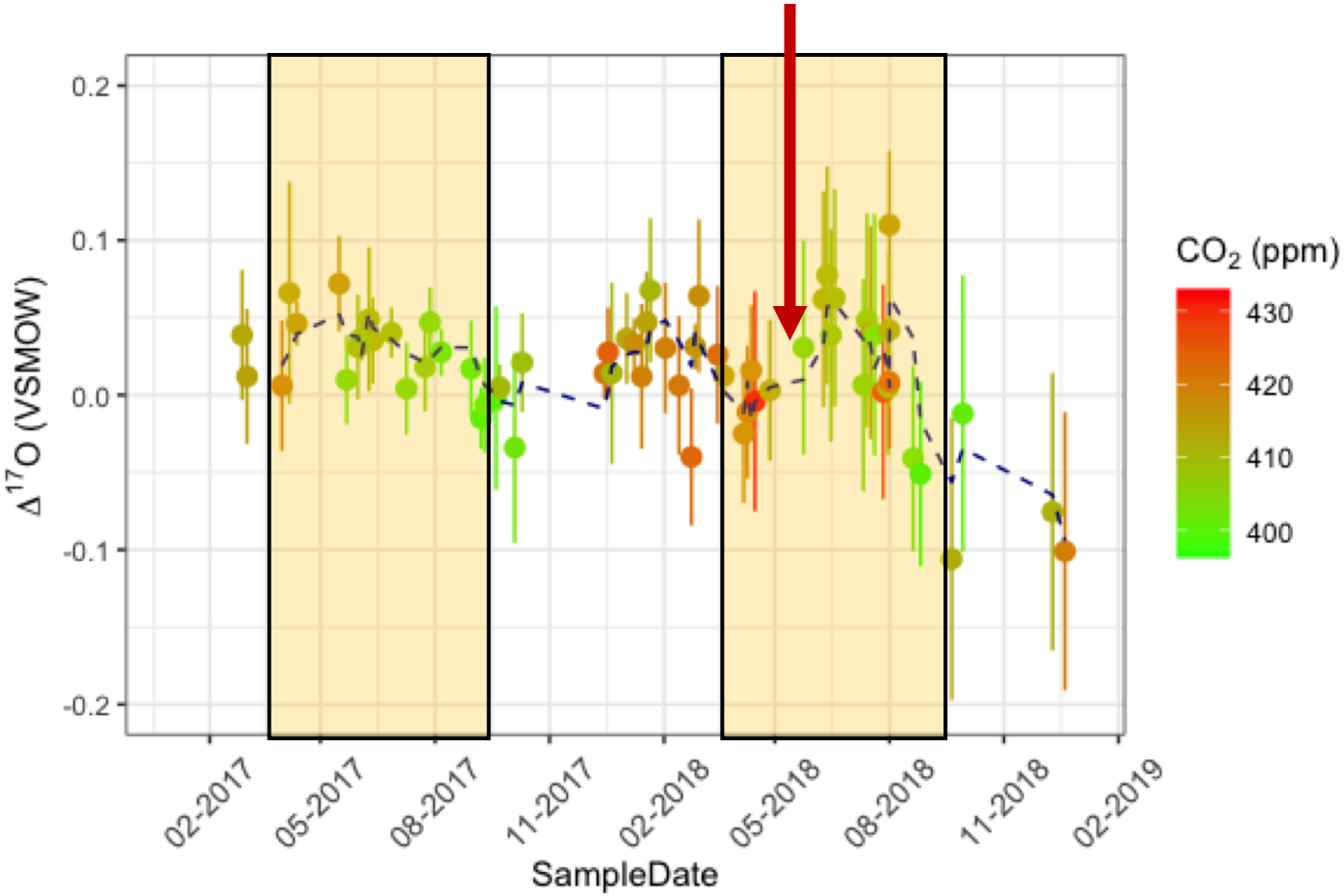
3.5 Lutjewad during the 2018 drought period

Switch from carbon sink to source due to unavailability of soil moisture

Coincides with

Increase of $\Delta^{17}O$ values during summer period due to decrease of plant activity





3.5 Lutjewad during the 2018 drought period

Period March to May 2017 and 2018 differs strongly in CO_2 decrease rate, with a stronger CO_2 decrease in 2018 than in 2017

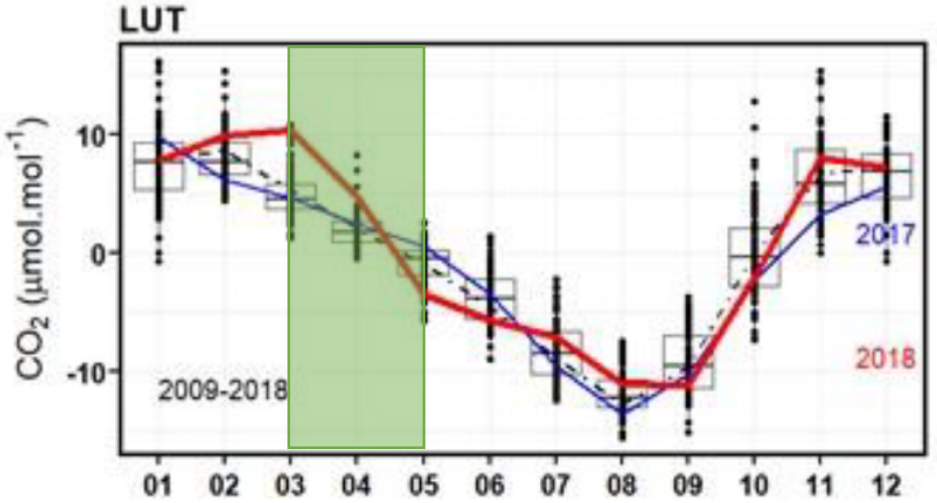
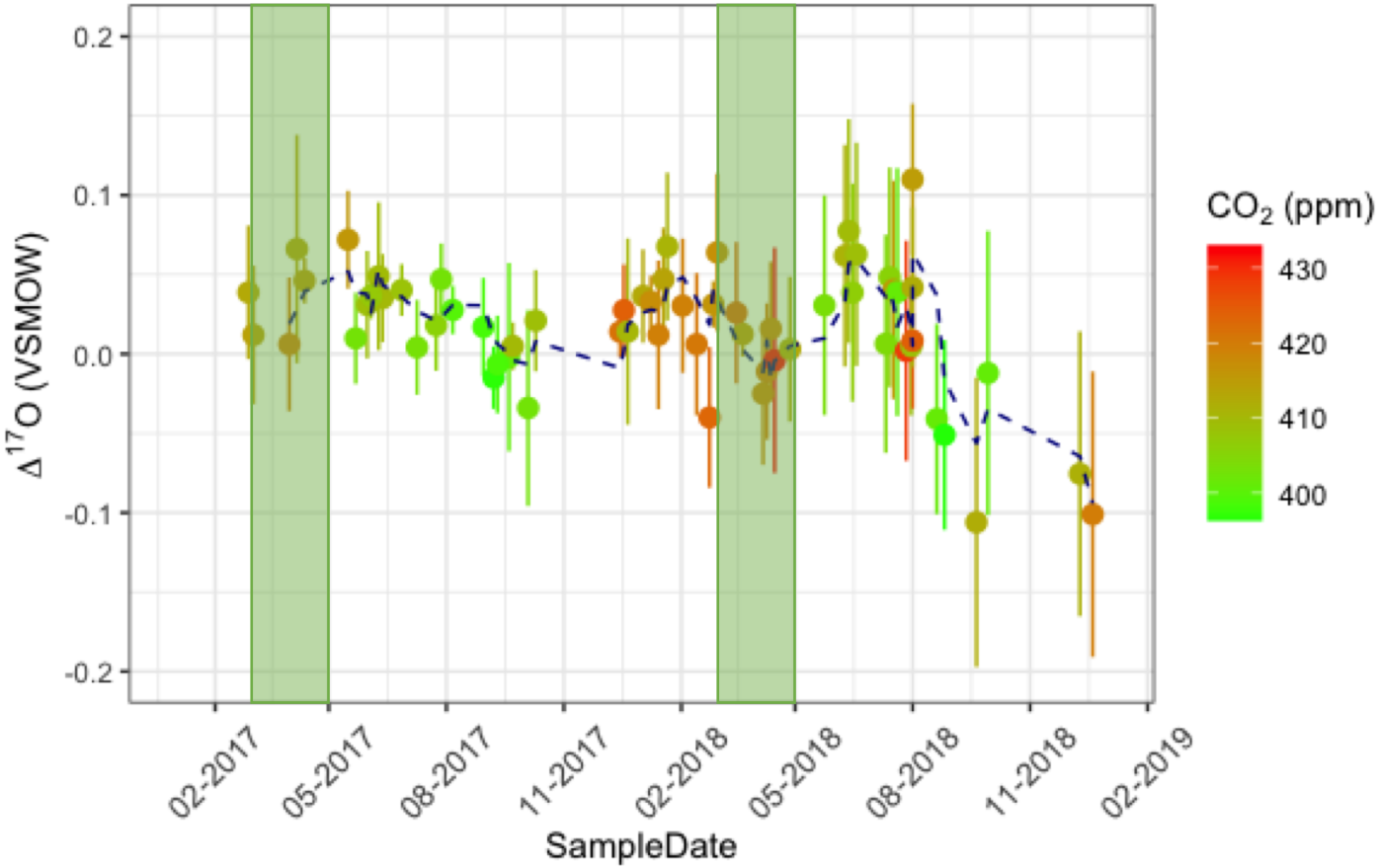


Figure from Ramonet et al., 2020. Seasonal cycles observed at Lutjewad. Red=2018, blue=2017 and black=2009-2018 measurement period

The 2017 and 2018 $\Delta^{17}O$ record from March to May differ in direction: 2017 shows increasing values and 2018 shows decreasing values



3.5 Lutjewad during the 2018 drought period

Period March to May 2017 and 2018 differs strongly in CO_2 decrease rate, with a stronger CO_2 decrease in 2018 than in 2017

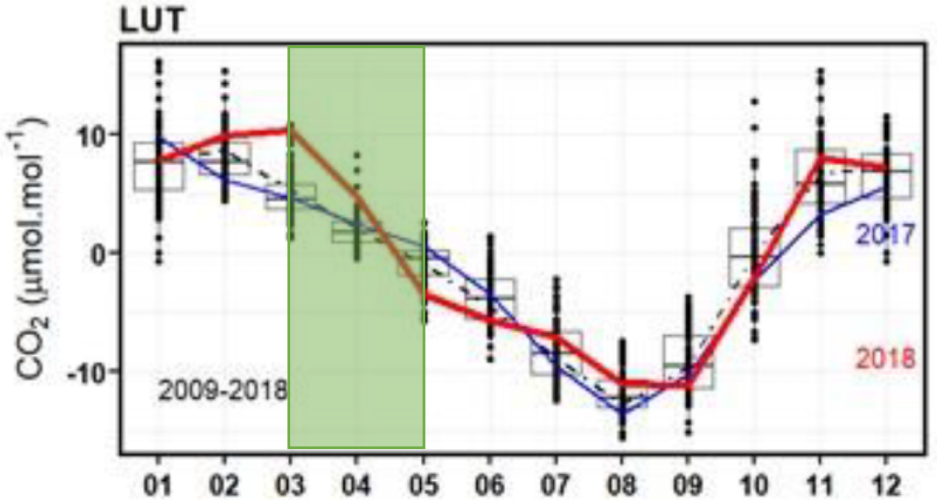
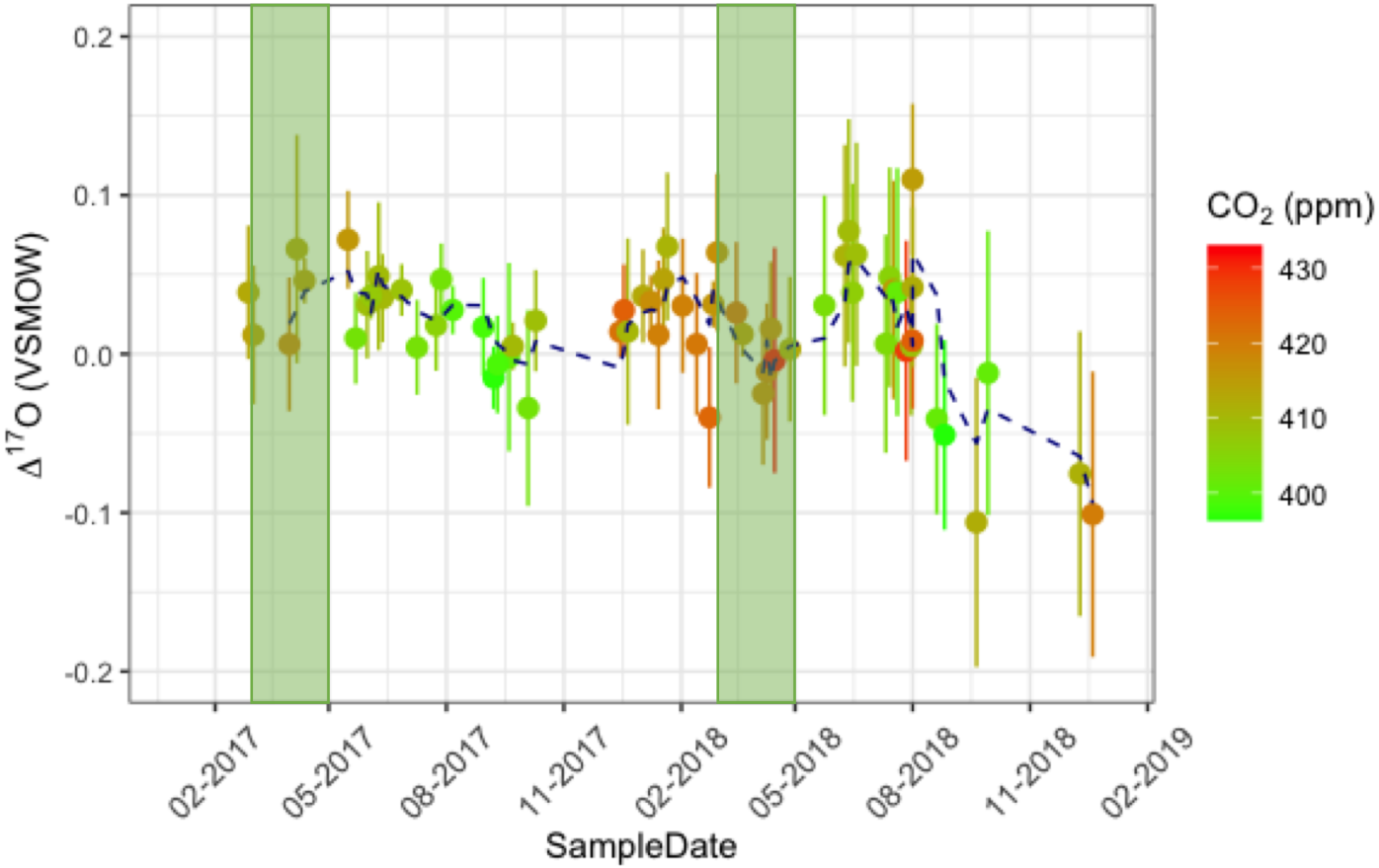


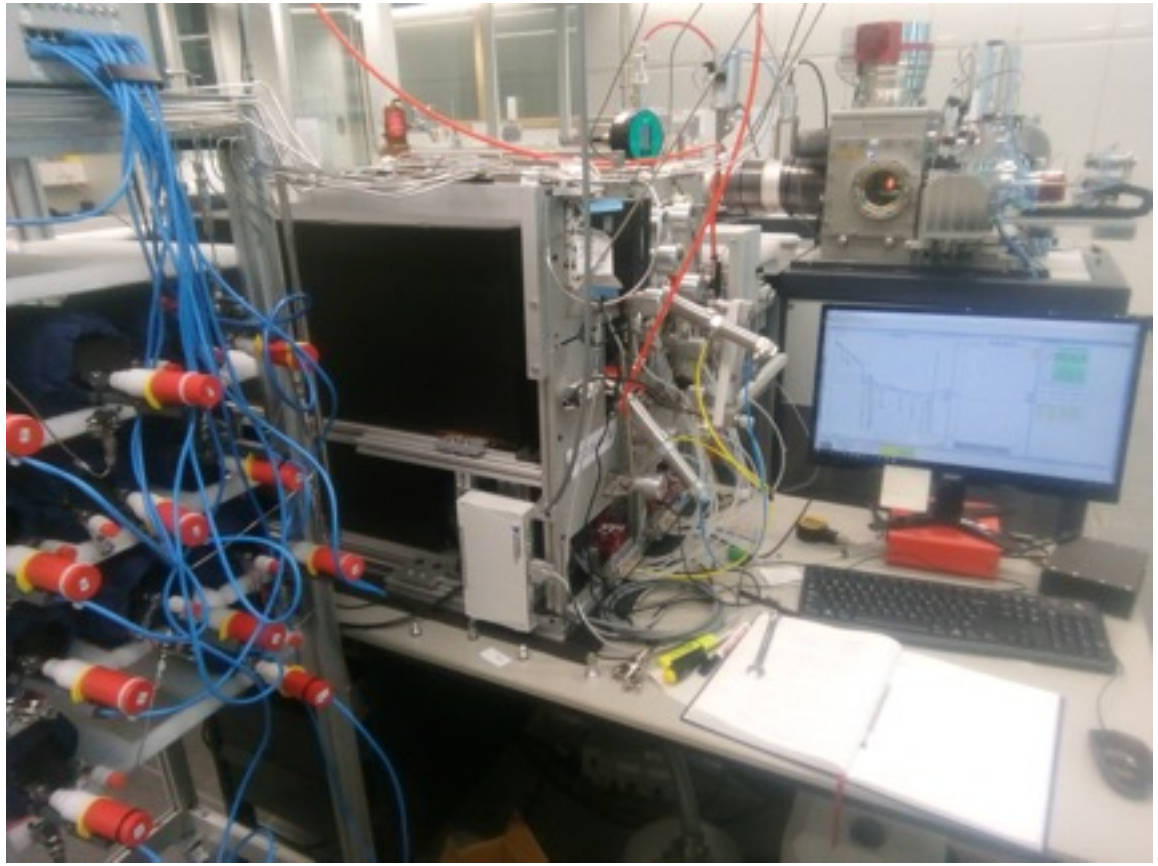
Figure from Ramonet et al., 2020. Seasonal cycles observed at Lutjewad. Red=2018, blue=2017 and black=2009-2018 measurement period

Anomalous biosphere activity due to the drought is clearly visible in Lutjewad 2018 record, and this can be used in models to quantify the GPP

The 2017 and 2018 $\Delta^{17}O$ record from March to May differ in direction: 2017 shows increasing values and 2018 shows decreasing values



4. Conclusions and outlook

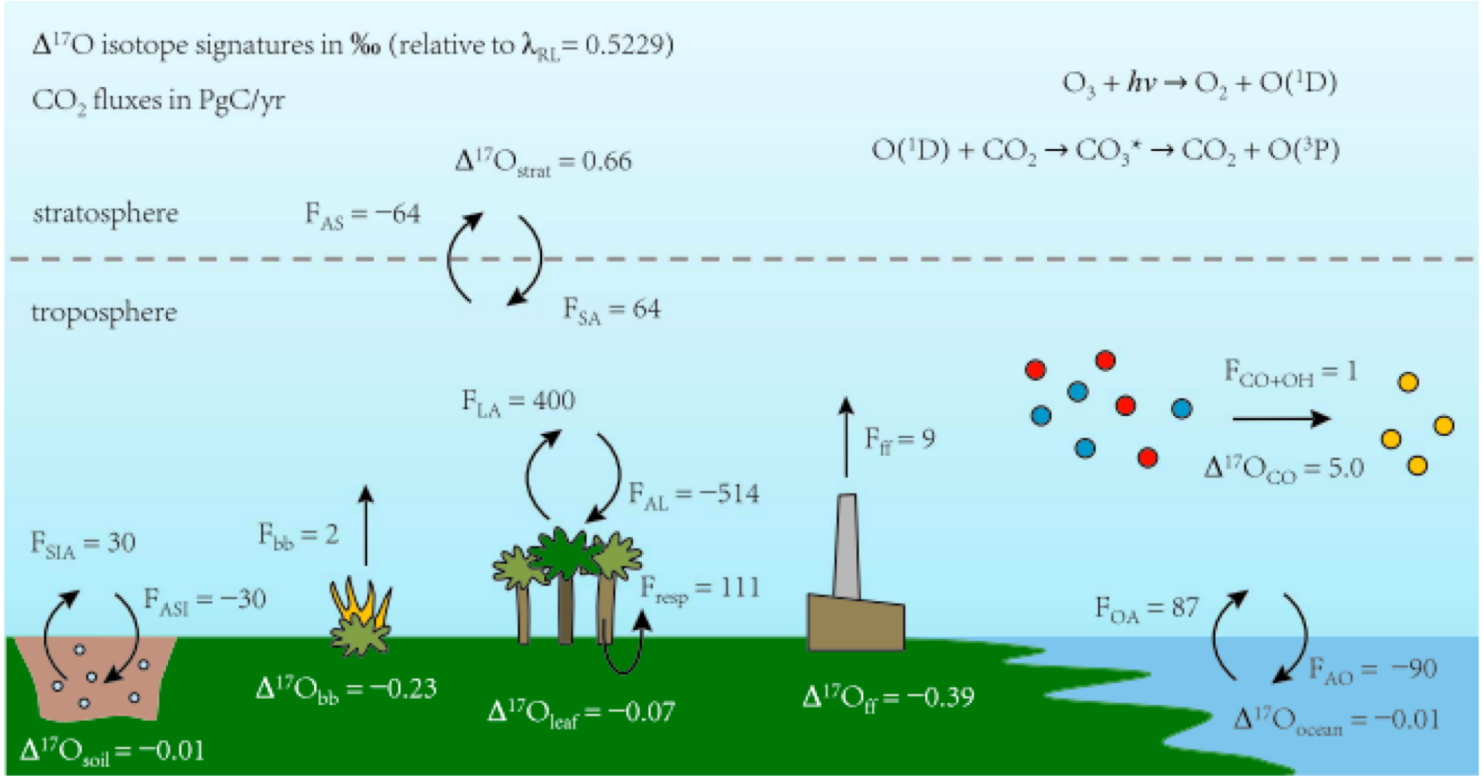


The Aerodyne dual laser optical spectrometer, in the CIO lab with on the left the sample flasks rack

- With our Aerodyne dual laser optical spectrometer it is now possible to measure the $\delta^{13}C$, $\delta^{18}O$ and $\delta^{17}O$ of atmospheric CO_2, directly on dry air samples.
- A 2-year long record - from 2017 to 2018 - of Lutjewad was here presented including continuous and flask measurements of CO_2 concentrations and flask measurements of $\delta^{13}C$, $\delta^{18}O$ and $\Delta^{17}O$
- Oxygen isotopes is flask samples drift over time, making the $\delta^{18}O$ record hard to interpret as the result of high storage times. The $\Delta^{17}O$ measurements were not significantly affected by the drift over a period of 150 days.

4. Conclusion and outlook

- The Lutjewad $\Delta^{17}O$ of 2018 shows significant anomalies from the 2017 record due to the drought that occurred over North-Western Europe.
- An early decrease of $\Delta^{17}O$ values due to enhanced biosphere activity and an increase in $\Delta^{17}O$ values in summer can be identified in the 2018 record.
- Our $\Delta^{17}O$ measurements can be used to validate and improve climate models that incorporate biosphere activity for the determination of atmospheric CO_2 by including better estimates of GPP and TER in changing environmental conditions.



Conceptual overview of processes influencing the atmospheric $\Delta^{17}O$, as used for the model developed by Koren et al. (2019). Figure from Koren et al., 2019.

Thank you for your attention

When you go further you find some extra slides giving extra info or background to this presentation.

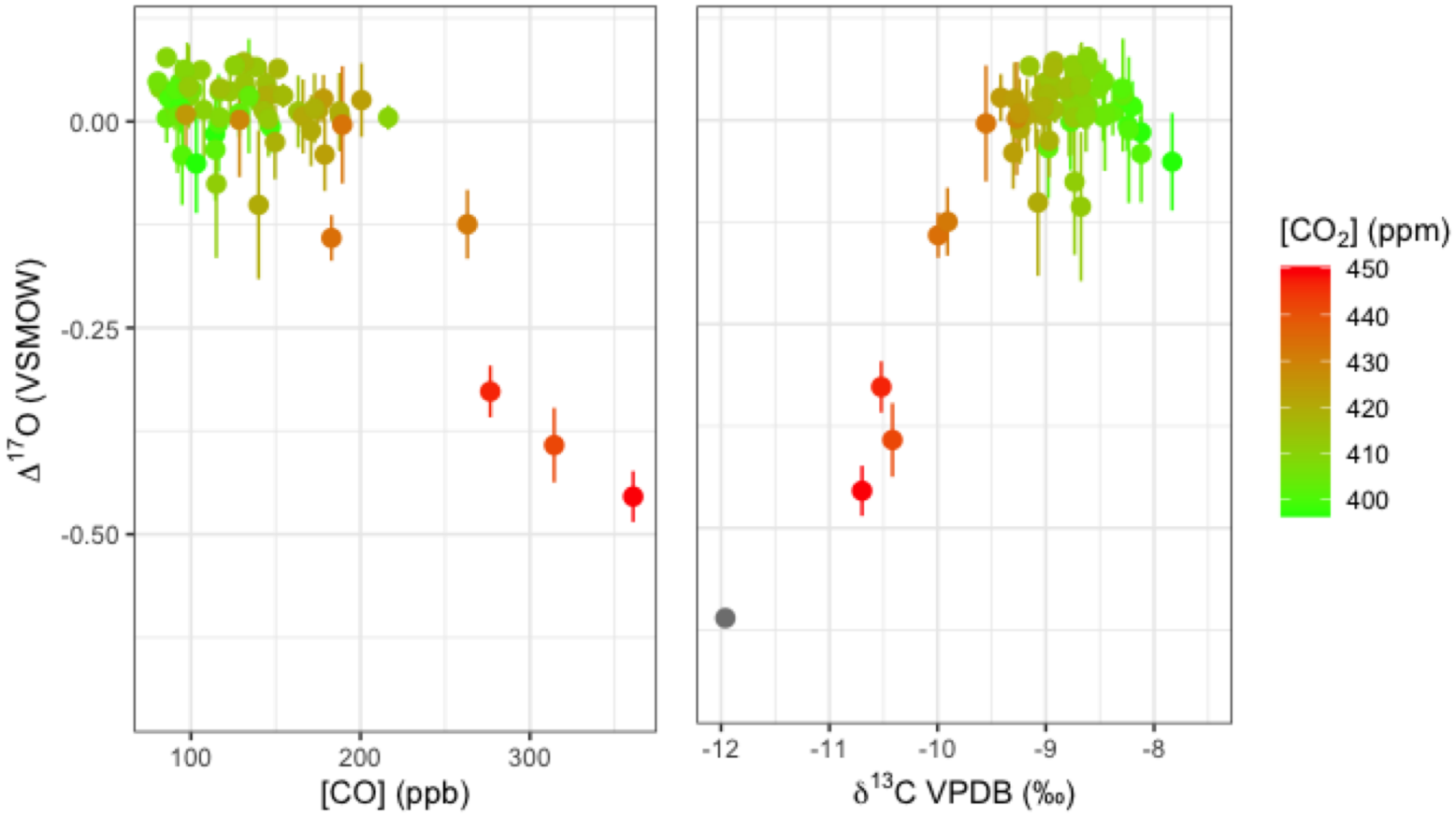
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3.2 Filtering out fossil fuel dominated samples

$\Delta^{17}O$ signatures of CO_2 from several combustion process were measured in a study by Horváth et al. (2012) where they found a value between -0.30 and -0.32 ‰ for combusted natural gas and propane-butane gas and car exhaust. We expect therefore more depleted $\Delta^{17}O$ values in samples that are dominated by fossil fuel combustion processes.

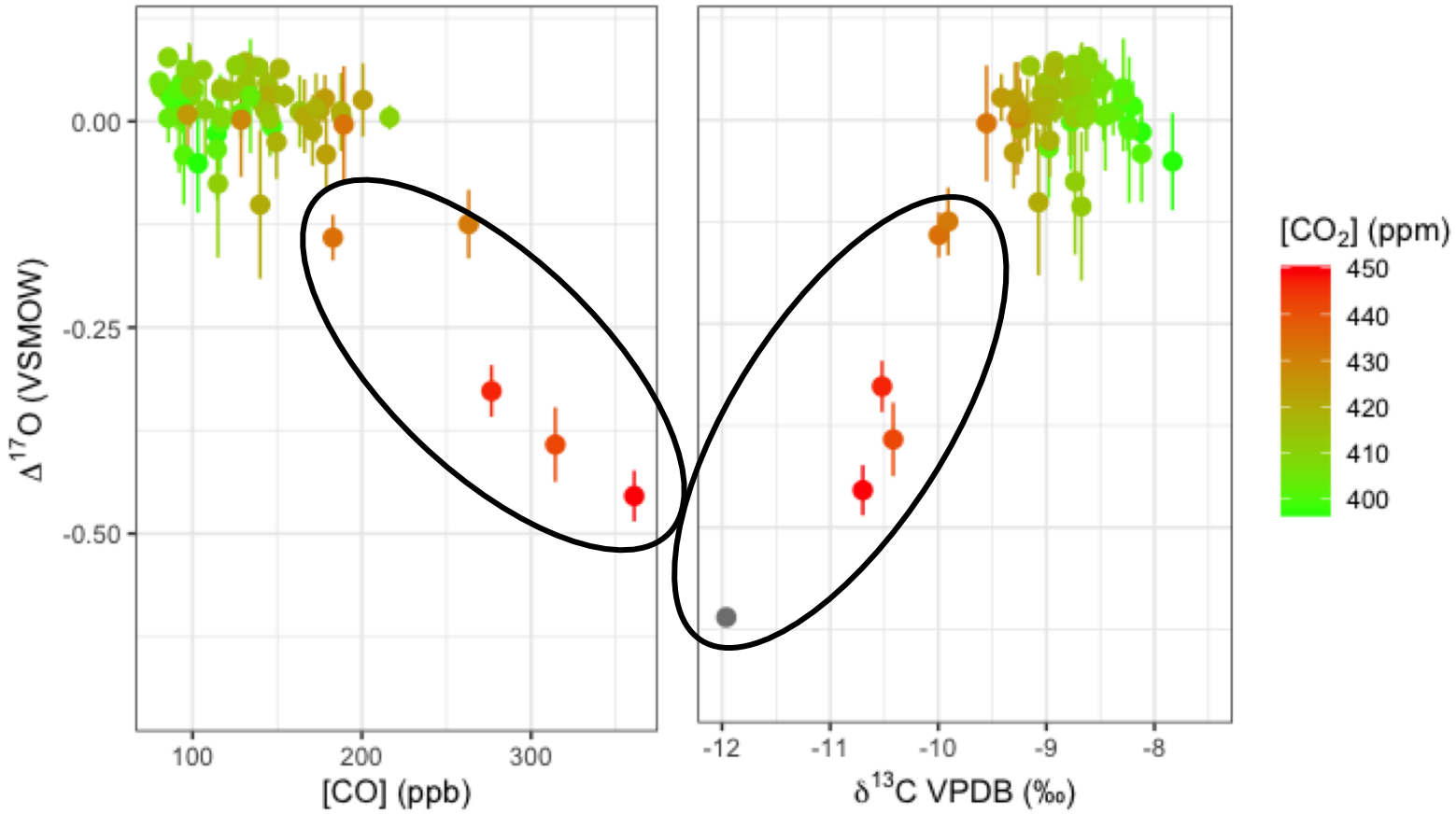
Although the CO_2 concentration in these samples are far out of the reach of the CO_2 concentration range of our calibration gases (not higher than 425 ppm), and the absolute values have therefore high uncertainties, a general trend of more depleted values for fossil fuel dominated gases can be observed in the Lutjewad measurements.



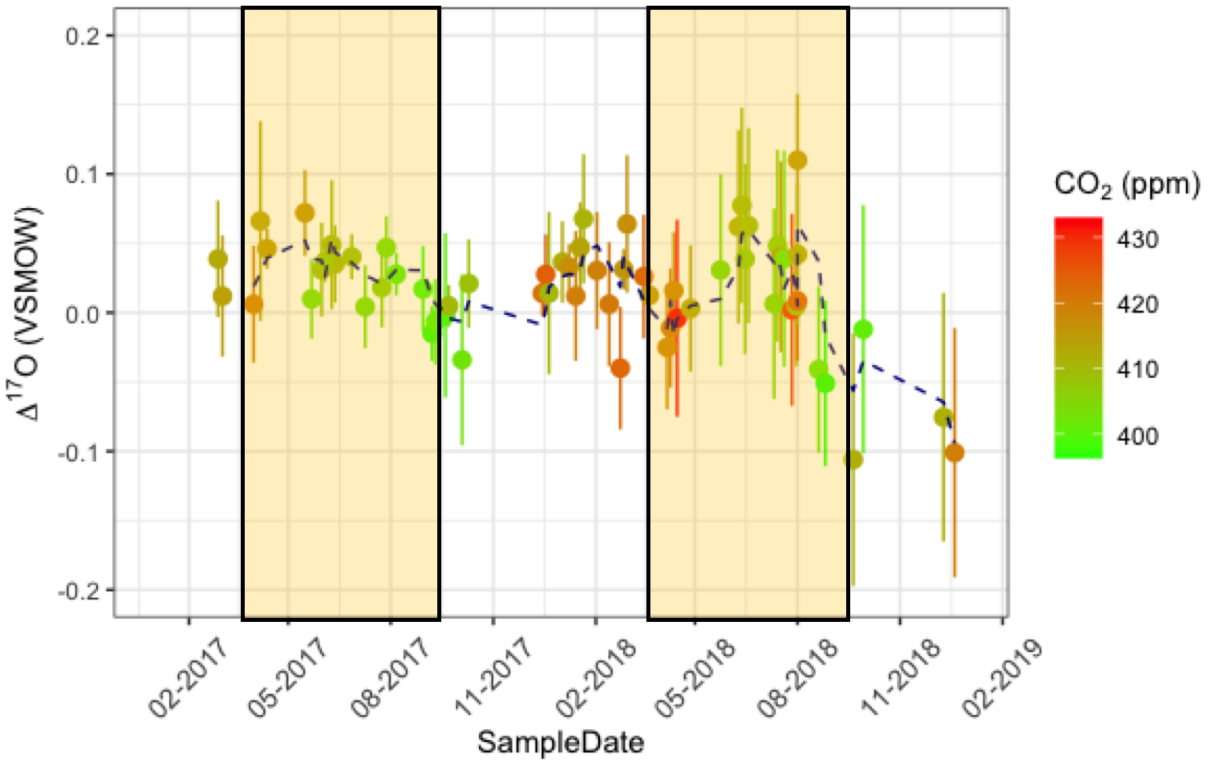
3.2 Filtering out fossil fuel dominated samples

Samples showing a clear correlation between $\Delta^{17}O$ values, high CO concentrations and a depleted $\delta^{13}C$ value are filtered out to acquire a record of $\Delta^{17}O$ values that is dominated by the biosphere component.

Click here to get back to the stable isotope measurement results!

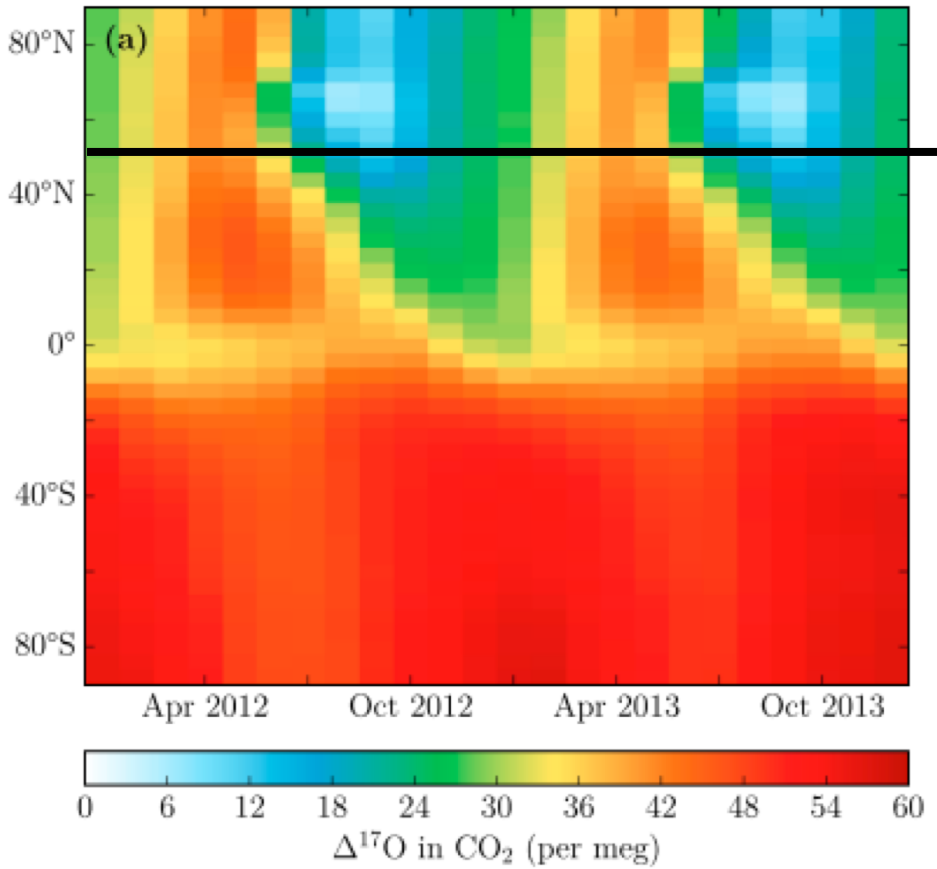


3.4 Comparison Lutjewad $\Delta^{17}O$ results and model simulation



Seasonal cycle at Lutjewad is ~0.05‰, agrees with model simulation of the same latitude by Koren et al. (2019)

Click here to get back to the $\Delta^{17}O$ measurement results!



Latitude Lutjewad is 53°24'00.0"N

Hovmöller diagram of $\Delta^{17}O$ in CO_2 from monthly average of simulated $\Delta^{17}O$ in CO_2 for the lowest 500 m of the atmosphere using TM5 model, from Koren et al. (2019)