



BACHELOR THESIS

Isotopic composition of CO emitted by plants under the influence of light and temperature



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Abstract

In this study, the influence of light and temperature on plant emitted carbon monoxide has been investigated. This was done by using a dynamical sampling method directly connected to a CO isotope measurement system. Plant material was put into a quartz reactor and was either irradiated with light or the reactor was heated in an oven. Emission rates and isotopic composition of C and O isotopes have been determined. Light experiments have been performed with fresh leaves and dried leaves. All plants showed emission of CO when irradiated with solar simulated light. Fresh plants showed an average $\delta^{13}\text{C}$ value of 43.67 ± 3.64 ‰ and an average $\delta^{18}\text{O}$ of 26.14 ± 4.25 ‰. Drying of the plants decreased the $\delta^{18}\text{O}$ value. Additionally the influence of UV was investigated by blocking UVB with a glass plate or blocking UVA and UVB with a transparent plastic plate. These tests showed that blocking UVA and UVB decreases the emission and increases the $\delta^{13}\text{C}$ value. Temperature increase to 30 - 50 °C also induced CO emission from leaves. The results of the temperature experiments showed large variability in terms of emission rate and isotopic composition. It is suggested that temperature but also the storage time of plant material increases the $\delta^{13}\text{C}$ value.

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Chapter 1

Introduction

1.1 Emissions of trace gases

The main components of the Earth's atmosphere are nitrogen (approx. 78%) and oxygen (approx. 21%), other significant components are water and argon (Pidwirny and Budikova [2006]). These are however not the only components in the atmosphere. There are also components that make up less than 1% of the Earth's atmosphere, the so called trace gases. Examples include carbon monoxide (CO), hydrocarbons (HCs), nitrogen oxides (NO_x) and sulphur oxides (SO_x) (Müller [1992]). It has been shown that trace gases play an important role in atmospheric chemistry (Hansen et al. [2007]). One of the trace gases that has been identified as important for atmospheric chemistry is carbon monoxide (CO). This trace gas is the topic under investigation in this study.

1.2 Importance of CO

Earth's climate and the temperature are controlled by the natural greenhouse effect of greenhouse gases in the atmosphere. The most important greenhouse gases are CO₂, CH₄ and N₂O (Solomon [2007]). CO is not a direct greenhouse gas because its absorption of infrared irradiation is not high enough. It does however have some important indirect greenhouse effects. CO reacts relatively fast with OH radicals in the atmosphere, in this reaction CO₂ is formed (full reaction CO+OH → CO₂+H₂ (Crutzen and Zimmermann [1991])). The annual emission of CO is about 2600 Tg, though the average mole fraction is only ~ 100 ppb (Brenninkmeijer et al. [1999], Pathirana et al. [2015]). About 60% of the atmospheric CO is being removed through oxidation. In the reaction with OH the CO is competing with CH₄, because CH₄ also reacts with OH radical. For methane the OH is one of the major sinks. Due to this an increase of atmospheric CO could lead to a longer lifetime of CH₄ in the atmosphere and an increase of CH₄ concentration (Daniel and Solomon [1998]). This is important because CH₄ is an important greenhouse gas. Additionally, CO can also increase the ozone concentrations due to oxidation of the CO (Smithson [2002]).

1.3 CO sources and sinks

Most sources of atmospheric CO are known to be anthropogenic, these human sources are car exhaust fumes, biomass burning, deforestation and fossil fuel use. There are also natural sources of CO. The largest are photochemical reactions in the troposphere and oxidation of methane in the atmosphere. Additionally, oceans and vegetation have shown to be a source of carbon monoxide (Smithson [2002], Tarr et al. [1995], Kanakidou and Crutzen [1999]).

There are several sinks for CO, the main one is oxidation with OH radicals in the atmosphere. But there is also a small sink effect caused by deposition on the ground and diffusion into the stratosphere (Bruhn et al. [2013]). Contributions of the sources and sinks of CO are shown in Table 1.1.

Table 1.1 – CO sources, abundance and isotopic composition. Table from [Brenninkmeijer et al. \[1999\]](#)

Sources	Source (Tg/yr)	$\delta^{13}\text{C}$ (‰) V-PDB	$\delta^{18}\text{O}$ (‰) V-SMOW
Fossil fuel combustion	300 - 550	-27.5	12.25
Biomass burning	300 - 700	-21.3	~ 16.3
CH ₄ oxidation	400 - 1000	-52.6	~ 0
NMHC oxidation	200 - 600	-32.2	~ 0
Biogenic	60 - 160		
Oceans	20 - 200	-13.5	
Total Sources	1800 - 2700		
Sinks	Sinks (Tg/yr)		
Reaction with OH	1400 - 2600		
Soil uptake	250 - 640		
Loss to stratosphere	~ 100		

1.4 CO emission from plant material

It has been shown that living plant material emits CO due to photo- and thermal degradation ([Tarr et al. \[1995\]](#)). Senescent, dead brown leaves and leaf litter were also shown to emit carbon monoxide ([Schade et al. \[1999\]](#)). Several studies have already investigated this phenomenon. It has been shown that emission of carbon monoxide increases linear with light-intensity ([Tarr et al. \[1995\]](#)), and that the UV-spectrum plays a major for this emission ([Bruhn et al. \[2013\]](#)). Next to this CO emission also increases with increasing temperature ([Derendorp et al. \[2011\]](#)). In IPCC 2001, the global burden of CO is very uncertain. Photo-induced CO emission from living plants has been taken into account but this estimation is based on solely the visible part of solar irradiation ([Bruhn et al. \[2013\]](#)). Current estimation of the magnitude of direct emission of plants is 50 - 200 Tg/yr ([Smithson \[2002\]](#)).

1.5 Stable isotopes

Atoms that belong the same chemical element but have a different atomic mass are isotopes. The nuclei of these atoms have the same amount of protons but they have different amount of neutrons. Looking at concentration and flux measurements of carbon monoxide, budgets of this trace gas can be determined. Isotope measurements can give additional information on this trace gas ([Derendorp et al. \[2011\]](#)).

The stable carbon isotopes in carbon monoxide are ¹²C (98.89%) and ¹³C (1.11%). For oxygen the stable isotopes are ¹⁶O (99.76%), ¹⁷O (0.04%) and ¹⁸O (0.20%). Isotope values are usually expressed as a delta value, this delta value is defined as a relative isotope enrichment of a sample gas compared to a reference.

$$\delta_{s,ref} = \frac{R_s - R_{ref}}{R_{ref}} \cdot 1000\text{‰} \quad (1.1)$$

This delta value is expressed in parts per-mille (‰), the R is the isotope ratio, the abundance of the heavier isotope to the lighter isotope. In carbon monoxide the isotope ratios of interest in this study are ¹³C/¹²C for carbon and ¹⁸O/¹⁶O for oxygen.

Every source of CO emission has a combination of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ which gives an isotopic signature, isotopic signatures can be distinct for an CO source. For some sources the range can overlap in $\delta^{13}\text{C}$, $\delta^{18}\text{O}$ can then be a better tracer ([Pathirana et al. \[2015\]](#)).

By looking at the stable isotopic composition, CO cycles could be better constrained and the processed of the photo- and thermal degradation could be better understood. Signatures of different sources of CO can be found in [Table 1.1](#).

Looking at the stable isotopes from plant emitted carbon monoxide has only been performed once by [Vijverberg \[2015\]](#). Isotopic composition for living plant material ranged between -43.1 and -29.6 ‰ with an average of $-36.3 \pm 5.8\text{‰}$ for $\delta^{13}\text{C}$. For $\delta^{18}\text{O}$ the values ranged between 37.9 and 42.3 ‰ with an average of $39.6 \pm 2.0\text{‰}$.

1.6 This study

This study focuses on plant emitted carbon monoxide. There is still much uncertainty in the research of the emission of carbon monoxide from different sources. Only one study has been performed before on the isotopic composition of plant emitted carbon monoxide (Vijverberg [2015]), this study was without the influence of light. In this study the influence of light, including the UV-spectrum, has been investigated. Light experiments have been performed on fresh and dried leaves. The temperature in the reactor was observed to increase due to the light. Additional temperature experiments were thus performed, to determine whether the emission of CO was due to temperature increase or light. Temperature experiments were performed solely with fresh leaves and did not include the influence of light. An isotope analysis was performed on the plant emitted CO. This was done by using a dynamic sampling system where green or dried leaves were put in a quartz reactor. The leaves were either irradiated with light from a sunlight simulation lamp (Osram Vitalux 300W) or the entire reactor was put into an oven for heating. The influence of light, UV and temperature on the emission rate of CO and isotopic composition were determined.

Chapter 2

Experimental setup

2.1 General Setup

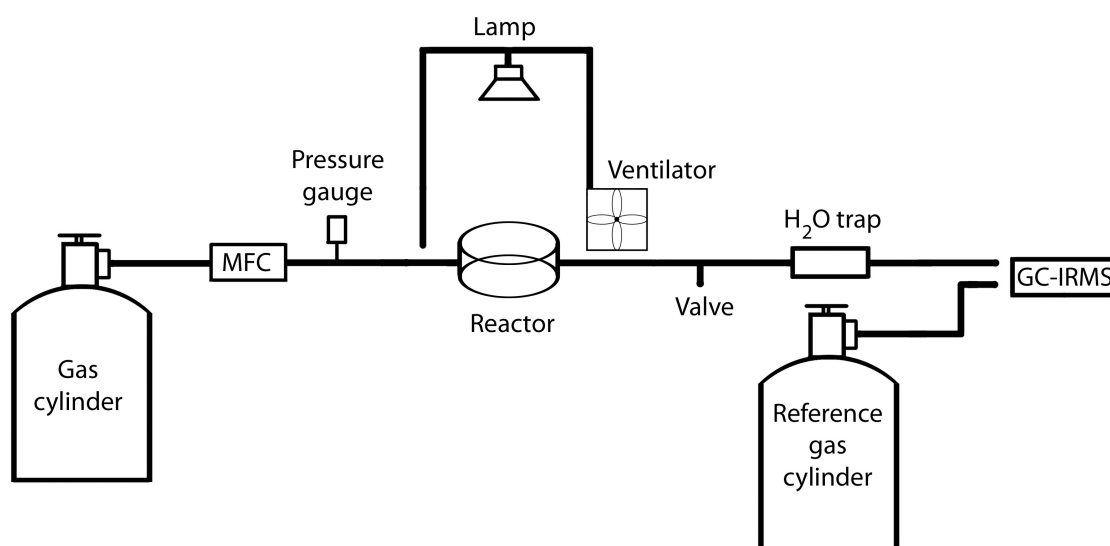


Figure 2.1 – Schematic of the setup used for performing light experiments. For temperature experiments the lamp and ventilator were removed, instead the reactor was put into a dark oven with controllable temperature.

In this study two types of experiments were performed, light experiments and temperature experiments. For determining CO emission from plant material under the influence of light and temperature a dynamic sampling method was used. This sampling method used ‘on-line’ measurements. This means no air samples had to be taken separately, but the air sample would go directly to a CO isotope measurement system for analyses (see Figure 2.1 for a schematic of the setup used for light experiments). Plant material was put into a quartz reactor connected to a cylinder filled with gas. This cylinder was filled with normal dried atmospheric air. The influence of UV was also investigated, for this reason a quartz reactor was used because normal glass would block (parts) of the UV spectrum.

The gas from the cylinder was constantly flowing through the setup. By using a mass flow controller (MFC) the flow rate was controlled, the flow used was 60 ml/min. To guaranty that the pressure in the reactor did not change, a pressure gauge was placed before the reactor to monitor the pressure in the system.

The other side of the reactor was connected to a CO isotope measurement system. For the analyses of an air sample (described in Section 2.6) the system uses 100ml of air. This air was taken from the sample with a flow of 20ml/min. The remaining air sample will leave the setup through a valve and is released to the room. Between the connection of the reactor and the IRMS

the air went through a drying trap, filled with magnesium perchlorate. An Osram Vitalux (300W) sunlight simulation lamp was hanging above the reactor to irradiate the plant material with the entire spectrum of light. Because the light also heats up the reactor, a ventilator was used to keep the temperature from increasing too much. For temperature experiments the lamp and ventilator were removed, instead the reactor was put into a dark oven with controllable temperature.

The main components of the setup are:

- Cylinder with dry atmospheric air.
- A mass flow controller, Analyt type GFC17.
- Pressure meter
- Quartz reactor (Irradiation surface 34.21 cm², volume 82.1 cm³)
- Lamp Osram Vitalux (300W)
- Ventilator
- Oven
- Magnesium perchlorate
- CO isotope measuring system (Section 2.6)

2.2 Light source

Sunlight contains ultraviolet light(UV). UV is electromagnetic radiation with a wavelength from 10 nm to 380 nm, wavelengths which are shorter than the wavelength of visible light. Sunlight at ground level consists of 53% infrared light, 44% visible light and 3% ultraviolet. Ultraviolet light has been classified in different subtypes, divided by the wavelength, see Table 2.1.

Table 2.1 – Types of ultraviolet light.

Name	abbreviation	Wavelength (nm)
Ultraviolet A	UVA	315 - 400
Ultraviolet B	UVB	280 - 315
Ultraviolet C	UVC	100 - 280

In sunlight more than 95% of the UV light consists of UVA and a small part of UVB. The light source that has been used for the UV experiments was an Osram Vitalux lamp (300W). This lamp has an UVA and UVB content that is comparable with sunlight. The radiative power of this lamp is 13.6 W for UVA and 3.0 W for UVB. All UV-experiments have been performed at the same distance between lamp and reactor of 56.4 cm. Taking the lamp as a point source would give an intensity of 75.05 W/m² for the entire spectrum, 3.40 W/m² for UVA and 0.75 W/m² for UVB.

2.3 Plant material

Most of the plant material that was used for the experiments was collected from the surroundings of Utrecht University. One plant, *Polypodium vulgare*, was collected from the Utrecht University Botanical garden. Only the green leaves from plants were used. For all the light experiments the plant material was picked within 2 hours before every experiment. For some of the temperature experiments the *Lolium perenne* (grass) that was used was picked in the morning and then used for a entire day of testing. Because the start of this study was in February, not all trees or plants had leaves. Due to this the leaves that were tested were the small young leaves. For this reason also a comparison is made between a young leaf of *Hedera helix Baltica* (hedera) and an older one. For some experiments dried leaves were used. Plant material was dried in different ways. *Prunus*

laurocerasus was put into an oven of 50°C for 12 hours, while *Lolium perenne* was tested after drying at room temperature for 8 days. The young leaves of *Hedera helix Baltica* were dried for two weeks at room temperature, *Thuja occidentalis* three weeks, *Sambucus nigra* and *Phyllostachys aurea* were dried at room temperature for one month. Emission of CO from the plant material was expressed per dry weight of the leaf, plant material was weighted with an Mettler H10 balance. In previous studies it has been shown that stable isotopic compositions are different for C3 and C4 plants Liu et al. [2005]. C3 and C4 plants differ in their photosynthetic pathway. In this study only C3 plants were tested. For the full list of plant material see Appendix A.

2.4 Types of Experiments

In this study light experiments and temperature experiments have been performed with different types of plant material.

Light experiments

For the light experiments two types of lamps have been tested. Only when the plant was irradiated with the Osram Vitalux 300W lamp it showed observable emission of CO, only these results are presented. Temperature in the reactor increased drastically when irradiated by the Vitalux lamp. Therefore a ventilator was placed next to the reactor to decrease the effect of heating by the lamp. With this setup most of the experiments were performed.

For comparing the different plants, their emission rate and isotopic composition were determined. The height of the lamp was constant, so the intensity of irradiation was the same during all the experiments. Tests with each plant were only performed once, except for fresh grass where three tests were performed. Two types of hedges (*Hedera helix Baltica* and *Hedera hibernica Arbori*) were tested and from *Hedera helix Baltica* an older and younger leaf obtained from the same branch.

To see what the influence of the UVA and UVB were on the emission and isotopic composition of the carbon monoxide UV was blocked in two ways. A glass plate was placed on top of the reactor to block UVB, tests were performed in the same procedure. A visible light transparent plastic plate was placed on top of the reactor in between tests of a sequence to block UVA and UVB. The blocking of the UV was determined by using a Waldmann UV meter. The full list of light experiments can be found in Appendix A.

Temperature experiments

It was shown that the Vitalux lamp also increased the temperature in the reactor (also see Appendix C.1). To see if the emission of the CO would come from the irradiation of the lamp or because of the heating, temperature experiments were performed. In these tests the reactor was heated by putting the reactor into an oven at a set temperature. Temperatures of these tests varied between 30 °C and 50 °C. The temperature of the oven and the temperature in the reactor were not the same (see also Section 3.7). For the temperature experiments, mainly grass was tested. Two tests were also performed with hedges, but these tests did not show enough emission to give reliable values. During the temperature experiments more plant material could be put into the reactor because leaves covering each other would not influence the test. For these experiments the reactor was fully covered in aluminium foil to exclude the factor of light. In these temperature tests a difference was also made between grass that was picked fresh for each experiment and grass that was picked in the morning, kept in a plastic bag and then tested during the entire day. At first this was only done to eliminate the difference between picking the grass at different times of the day. These tests showed that the time between picking the grass and testing the grass also has an influence on the emission rate and isotopic composition. The full list of temperature experiments can be found in Appendix B.

An overview of the types of experiments that have been performed can be found in Table 2.2. Most of the experiments were performed with grass. This was done because different plant material show a lot of fluctuation. To neutralize this fluctuation, a bundle of grass was tested each time. This bundle consisted of older and younger grass, so an average would be tested.

Table 2.2 – Overview of the types of experiments performed.

Setup	Additional information	Time of irradiation or temperature	Plant material
Light experiments			
300W lamp without ventilator	Plant severely damaged by temperature	18-23 min	Hedera
26W lamp, at two different heights. (56.4 cm and 41.1 cm)	Showed not enough emission.	18-23 min, 41 – 46 min and 63 – 68 min	Hedera
300 W lamp with ventilator	Lamp was at fixed height for every test (height 56.4 cm).	18-23 min and 41 – 46 min	14 different types of fresh plants 6 dried plants
300 W lamp with ventilator and glass plate on top of the reactor	Lamp was at fixed height for every test (height 56.4 cm). No UVB irradiation.	18-23 min and 41 – 46 min	Grass
300 W lamp with ventilator and plastic plate	Lamp was at fixed height for every test (height 56.4 cm). Plate put on top inbetween tests. No irradiation of UVA and UVB	18-23 min and 41 – 46 min	Grass
Temperature experiments			
Reactor was put into an oven to change the temperature. Temperatures between 30 and 50°C	Oven temperature and temperature in reactor are different. Reactor was completely covered with aluminium foil so no light would affect CO emission.	18-23 min (System heating) and 41 – 46 min (system at approx. constant temp)	Hedera, fresh grass and grass that was stored for longer time

2.5 Procedure of an experiment

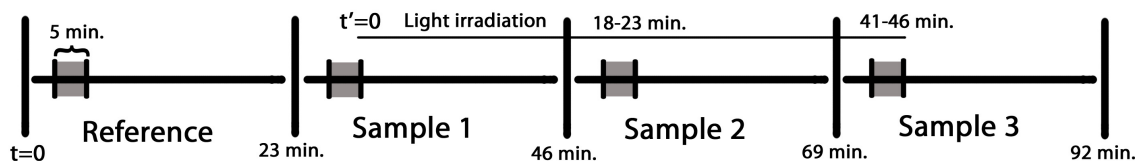


Figure 2.2 – Time scheme of an experiment. IRMS is started at $t=0$, first the reference gas is tested. After the first sample is taken without irradiation, the lamp and ventilator are switched on ($t'=0$). Second sample is taken after 18-23 minutes of irradiation and third sample after 41-46 of irradiation.

The CG-IRMS system analyses one air sample in 23 minutes, 5 minutes of this is when the air sample is taken from the setup. For performing the light and temperature experiments, irradiation or heating could for this reason be performed during the analysis of the previous experiment. The time scheme of an experiment is shown in Figure 2.2

For each experiment, the following procedure was performed.

1. The reactor is opened and cleaned with laboratory paper.
2. The quartz reactor is connected to the gas cylinder and IRMS system.
3. The gas cylinder is opened. A flow of 60ml/min flows through the setup.
4. The plant material is put in the quartz reactor and then the reactor is closed. Temperature is now at room temperature (In the lab approx. 22.5 °C).
5. The connection to the IRMS is flushed with gas from the cylinder.
6. The IRMS is started ($t=0$) and takes a sample of the reference gas. (To determine if IRMS is working correctly and from this reference the amount of CO emission and isotopes can be determined). In the time the reference gas is being taken and analysed (23 min), the reactor is flushed with the cylinder gas with dry atmospheric air.
7. IRMS takes the first sample of the setup with the light turned off (5min).
8. After the IRMS took the first sample, the lamp and ventilator are switched on ($t'=0$).
9. Two samples are taken, one between 18 and 23 minutes of irradiation, and one at 41 to 46 minutes of irradiation.
10. After the third sample is taken, the UV light is switched off and the reactor is being cooled by the ventilator.
11. A next experiment can be done when the reactor is back to room temperature. The reactor is back to room temperature in 15 minutes with a closed reactor. Opening the reactor makes the cooling go faster.

The temperature experiments were performed in the same way as the UV experiments. The difference is in step 8, here the light is not switched on but the reactor is put into an oven and in step 10 it is taken out of the oven.

For every experiment at least 3 air samples were analysed. The first sample is the sample when the reactor is flushed and there is the emission of the plant without influence of light or temperature. Because a gas cylinder is constantly flowing through the setup most of the time the first test did not show any emission of the plant (only grass that was kept for a longer time showed emission in the first sample, see Section 4.2.3). With influence of radiation or temperature there was enough emission to be measurable. This means that you can see from the first sample if the reactor has sufficiently been flushed after opening. If the concentration of the first sample was comparable to the concentration of an empty reactor with cylinder gas flowing, it was assumed the reactor was

flushed enough.

For light experiments the second and third sample were both irradiated. There was almost no difference in CO mole fraction and delta values of the stable isotopes between the second and third sample, for presenting the data the average was taken from these tests.

In the temperature experiments, at the second sample the reactor is still being heated by the oven and in the third sample the reactor was heated (Section 3.7). This means that only the third test showed the emission of the plant at the temperature the oven was set to. In the result section only the results of the third sample will be presented.

2.6 CO isotope measurements

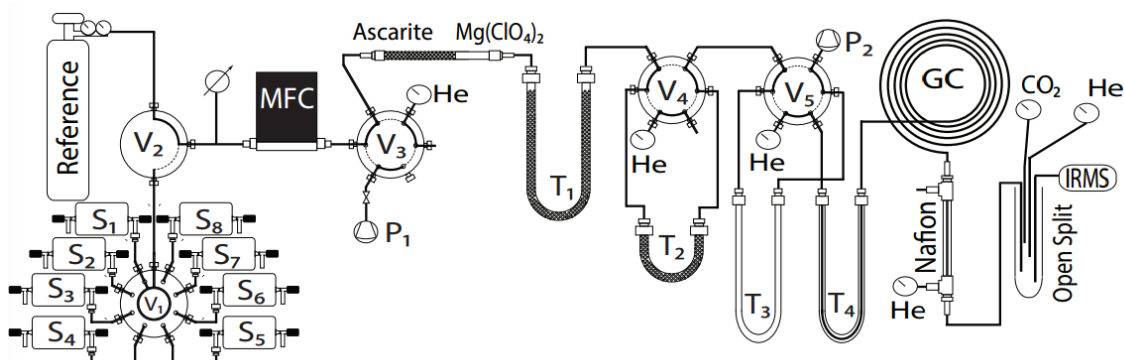


Figure 2.3 – Schematic of the GC-IRMS from Pathirana et al. [2015].

The instrument used in this study to analyse air samples is described in Pathirana et al. [2015] this is the so called continuous-flow isotope-ratio mass spectrometer (GC-IRMS), a diagram of the system is shown in Figure 2.3 from Pathirana et al. [2015]. Difference is that in this study no flask samples are being analyzed, but a dynamic system is used as described in Section 2.1. This setup is connected to the GC-IRMS system on one of the automated multi-sampling units for analysis, which can analyse an air sample for CO or CO₂ in 23 minutes.

The system consist of different components. First, the air sample is injected at constant flow through a mass flow controller. After this it goes through a chemical trap containing ascarite and magnesium perchlorate. In this chemical trap CO₂ and H₂O are being removed from the air sample. Afterwards the sample goes to a cryogenic trap and condensable gases at liquid nitrogen temperature, CO₂ and N₂O are removed here. Subsequently the CO is selectively oxidized to CO₂ using the Schütze reagent, a technique developed by Stevens and Krout [1972]. Using this technique makes it possible to measure CO at very low concentrations. During this procedure the isotopic compositions of C and O isotopes is preserved. Because high precision mass-spectrometry is often developed for CO₂ measurement, by converting the CO to CO₂, standardized techniques and isotope calibration scales can be used.

The oxidized CO₂ is now trapped in a collection trap, while other gases are being removed using a vacuum pump. Finally the sample is goes to an IRMS system that measures the mole fractions and delta values of C and O isotopes.

Chapter 3

Calculating values

3.1 Emission rate

In this study the emission of CO from plant material in different situations is being determined. This emission is expressed as an emission rate; the amount of CO emission in a certain time. The emission rate is divided over the dry weight of the plant material, to correct for the amount that is tested. This makes it possible to compare different plants. The emission rate has the unit [ng_{co}/gDW_h]. This emission rate is determined by using a dynamic system. The setup is constantly flushed with cylinder gas filled with dry atmospheric air with a flow rate of 60ml/min. When a concentration increase in ppb is measured by the IRMS, the flow rate of the gas flowing through the system needs to be taken into account for determining the emission over a certain amount of time. For calculating this emission rate the following equation is being used (Vigano [2010]).

$$ER = \frac{f \cdot \Delta c \cdot M_{CO}}{M_{air} \cdot DW} \quad (3.1)$$

ER = Emission rate [ng_{co}/gDW_h]

f = flow rate [l/h]

Δc = concentration increase [ppbv]

M_{air} = Molar mass air in one litre of air

M_{CO} = Molar mass CO = 28 [g/mol]

DW = Dry weight of plant material [g]

In the experiments in this study the following values were used; f = 3.6 [l/h] and M_{air} = 22.4 [l/mol] at standard temperature and pressure (0°C and 100kPa).

3.2 Isotopic values

Relative differences in isotopic ratios can be determined far more precise than absolute isotope ratios. Due to this, the delta notation for reporting stable isotopes was introduced. This delta value is defined as a relative isotope enrichment of a sample gas compared to a reference gas. This notation provides a way that small relative differences in samples and references can be expressed. The delta notation is defined as:

$$\delta_{s,ref} = \frac{R_s - R_{ref}}{R_{ref}} \cdot 1000\text{‰} \quad (3.2)$$

This delta value is expressed in parts per-mille (‰), the R is the isotope ratio, the abundance of the heavier isotope to the lighter isotope. In carbon monoxide the isotope ratios are ¹³C/¹²C for carbon and ¹⁸O/¹⁶O for oxygen. A positive delta value means that in the sample there are more heavy isotopes compared to the reference, a negative delta value means more lighter isotopes compared to the reference.

In the IRMS system the delta values are determined relative to a reference gas, in order to compare different delta values, the reference gas needs to be the same. This is not always the case,

due to this delta values are usually expressed relative to an international standard so different delta values can be compared. To convert delta values from one scale to another the following equation is used.

$$\delta_{Svs.IS} = \delta_{Svs.R} + \delta_{Rvs.IS} + 0.001 \cdot \delta_{Svs.R} \cdot \delta_{Rvs.IS} \quad (3.3)$$

$\delta_{Svs.IS}$ is here the delta value of the sample relative to the international standard, calculated from the sample relative to the reference gas $\delta_{Svs.R}$ and the reference gas relative to the international standard $\delta_{Rvs.IS}$.

International standard for $\delta^{13}C$ is Vienna PeeDeeBelemnite (V-PDB) and for $\delta^{18}O$ Vienna Standard Mean Ocean Water (V-SMOW) (Pathirana et al. [2015]).

3.2.1 Calculating isotopic values relative to the international standard

The system of the IRMS is being monitored by constantly analysing a reference gas, with a known mole fraction for CO and isotopic composition against the international standards (V-PDB or V-SMOW). Before every experiment, the reference gas was measured. The average value of the reference gas determined during this study can be found in Appendix D. In the IRMS system the software that is used reports the delta of the sample versus the laboratory working gas. Also the reference gas is reported against the working gas. Due to this to get the sample relative to the international standards the values need to be converted using Equation 3.3 twice.

First to calculate the sample vs. the reference gas.

$$\delta_{Svs.R} = \frac{(\delta_{Svs.WG} - \delta_{Rvs.WG}) \cdot 1000}{1000 + \delta_{Rvs.WG}} \quad (3.4)$$

Subsequently the sample is calculated against the international standard.

$$\delta_{Svs.IS} = \delta_{Svs.R} + \delta_{Rvs.IS} + 0.001 \cdot \delta_{Svs.R} \cdot \delta_{Rvs.IS} \quad (3.5)$$

Because in the analysing system the CO is oxidated to CO₂, a correction in the calculation for the $\delta^{18}O$ had to be performed. This is the following correction from Pathirana et al. [2015]

$$\begin{aligned} \delta^{18}O_{Svs.IS:CO} &= 2\delta^{18}O_{Svs.IS:CO_2} - \delta^{18}O_{Schütze \text{ reagent}} \\ &= 2\delta^{18}O_{Svs.IS:CO_2} - (2\delta^{18}O_{Rvs.IS:CO_2} - \delta^{18}O_{Rvs.IS:CO}) \end{aligned} \quad (3.6)$$

3.2.2 Values of the reference gas

The following values of the reference gas against the international reference have been used for calculation:

Mole fraction CO = 185.4 [ppb]

$\delta^{13}C_{refvs.IS} = -29.44 \text{ ‰}$

$\delta^{18}O_{refvs.IS} = 8.47 \text{ ‰}$

$\delta^{18}O_{WG-CO_2vs.IS} = 4.69 \text{ ‰}$

3.3 Blank measurements

To correct for emission under irradiation of the empty reactor, the same procedure of tests was performed for an empty reactor. This showed that there was some emission of CO when the reactor was under irradiation. To correct for this emission an average of three tests of an empty reactor with irradiation was made. The average emission and isotopic composition of the emission can be found in Table 3.1.

For the temperature experiments also an empty reactor was tested. This test was at an oven temperature of 45°C. This test did not show any emission of CO, or changes in the isotopic compositions. The temperature experiments where only corrected for the first test were the reactor with plant material was still outside the oven. The values of the empty reactor in the oven can be found in Table 3.2.

Table 3.1 – Average emission of the empty reactor under irradiation.

Emission empty reactor (ppbv)	SD	$\delta^{13}\text{C}$ (‰)	SD	$\delta^{18}\text{O}$ (‰)	SD
4.70	0.94	-38.82	2.47	22.94	3.65

Table 3.2 – Testing influence of temperature on CO emission of the setup. Temperature of the oven was set at 45°C.

	CO Concentration (ppbv)	$\delta^{13}\text{C}$ (‰)	$\delta^{18}\text{O}$ (‰)
Reactor outside oven	195.35	-27.33	11.36
In oven 18- 23 min	192.35	-27.29	11.28
In oven 41 – 46 min	192.44	-27.51	11.13
In oven 64 – 69 min	194.07	-27.61	11.18

3.4 Correcting for the empty reactor emission

The same sequence of tests was performed with an empty reactor, an average of the emission from these measurement was determined and used for correction. To determine the isotopic composition of the CO emission from the plant material, tests with the plant material had to be corrected with these blank tests. This correction is done as follows.

The sample of a test gives the final mixing ratio of CO which consist of the initial mixing ratio (empty reactor) and the added mixing ratio from plant material.

$$c_f = c_i + c_s \quad (3.7)$$

Where:

c_f = Final mixing ratio [ppb CO]

c_i = Initial mixing ratio [ppb CO]

c_s = Source mixing ratio [ppb CO]

To calculate the isotopic composition of the plant material the following calculation has to be done

$$\delta^{13}C_f \cdot c_f = \delta^{13}C_i \cdot c_i + \delta^{13}C_s \cdot c_s \quad (3.8)$$

With

$\delta^{13}C_f$ = Final delta value ‰

$\delta^{13}C_i$ = Initial delta value ‰

$\delta^{13}C_s$ = Source delta value ‰

The same calculation can be done for oxygen by replacing $\delta^{13}C_x$ with $\delta^{18}O_x$. When there are two data points the isotopic composition of the source can be calculated by combining 3.7 with 3.8 to:

$$\delta^{13}C_s = \frac{\delta^{13}C_f \cdot c_f - \delta^{13}C_i \cdot c_i}{c_f - c_i} \quad (3.9)$$

For light experiments the correction is performed twice, once for correction of the emission of the blank measurements, and once for the first test of the sequence. This is to ensure that only the emission from the plant due to light is taken into account.

For temperature experiments, the correction is only performed once since there was no extra empty reactor emission due to temperature of the system. The tests are only corrected for the first sample.

3.5 Error calculation

To take the measurement limitations into account for the calculated emission rate and delta values, a propagation of uncertainty had to be performed.

To get the standard deviation of two numbers with an uncertainty ($A + \sigma_A$ and $B + \sigma_B$) that are being subtracted or added the following calculation is performed.

$$f = A + B \quad (3.10)$$

$$\sigma_f = \sqrt{\sigma_A^2 + \sigma_B^2} \quad (3.11)$$

When two numbers are being multiplied or divided the standard deviation is calculated as follows.

$$f = A \cdot B \quad (3.12)$$

$$\sigma_f = |f| \sqrt{\left(\frac{\sigma_A}{A}\right)^2 + \left(\frac{\sigma_B}{B}\right)^2} \quad (3.13)$$

The calculation above is valid if the errors are not correlated. In the case of these experiments the errors were strongly correlated, which led to a strong overestimation of the final error. The final errors reported here were obtained by a Monte-Carlo simulation performed by Elena Popa. In principle, errors are applied to the input variables, and the calculation is made a large number of times (eg. 10000 times). The results of the repeated calculation give a mean and a standard deviation, this standard deviation is taken as the final error.

From a higher emission rate of CO, the isotopic compositions could be determined more accurately which results in a decreased error (Figure 3.1). Figure 3.1 shows that an emission rate of ~ 100 ng/h (or higher) uncorrected for the weight of the plant material is needed to get a reasonable error. Additionally the figure shows that there is a limit to the value that the standard deviation can decrease to.

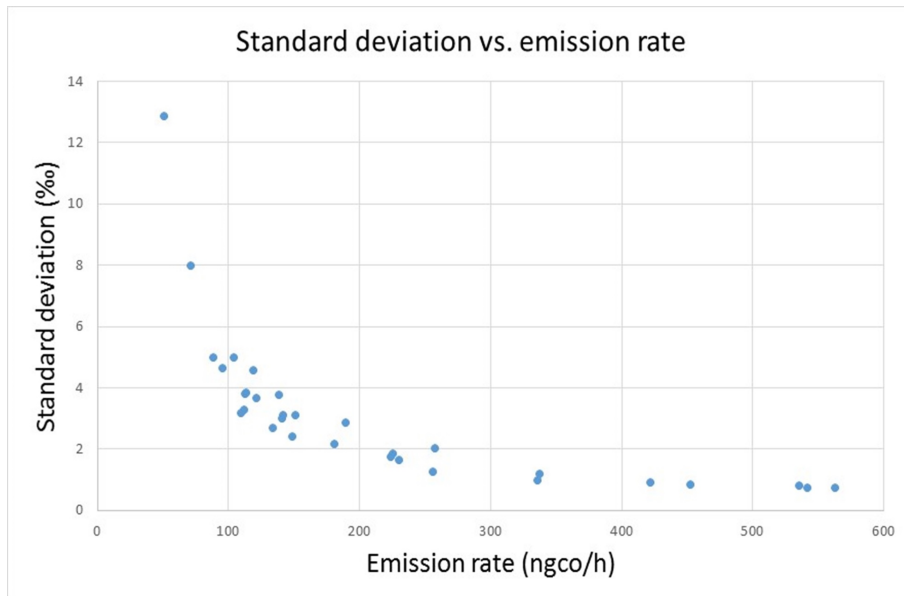


Figure 3.1 – Standard deviation compared to the emission rate, uncorrected for dry weight of the plant. A higher emission rate results in a decreased error.

3.5.1 Uncertainties in the system

In the measurements the following values of the reference gas, calculated by a calibration of the system, were considered.

$$\begin{aligned} CO &= 185.4 \pm 1.0 \text{ [ppb]} \\ \delta^{13}C_{\text{Rvs.IS}} &= -29.44 \pm 0.22 \text{ ‰} \\ \delta^{18}O_{\text{Rvs.IS}} &= 8.47 \pm 0.23 \text{ ‰} \end{aligned}$$

For determining the uncertainties of the measurement during this study, the standard deviation was determined from all the reference measurements performed before every experiment.

$$\begin{aligned} \sigma_{CO} &= 0.1 \text{ [ppb]} \\ \sigma_{\delta^{13}C} &= 0.2 \text{ ‰} \\ \sigma_{\delta^{18}O} &= 0.2 \text{ ‰} \end{aligned}$$

3.5.2 Uncertainties in the blank measurements

In this study it was shown that the setup itself also emitted CO under the influence of Light. To correct for this emission the average of three tests (n=3) of an empty reactor under the influence of light was made. To get the uncertainty of this average, the standard deviation of the mean is calculated with Equation 3.14.

$$SD_f = \frac{\sigma_f}{\sqrt{n}} \quad (3.14)$$

n = Number of measurements

3.6 Temperature increase in reactor due to light

To see how much the temperature increased in the reactor due to the light, a temperature test was performed with an empty reactor. In this test the gas cylinder was flowing and the ventilator switched on. In this temperature test one of the sides of the reactor was not connected and a Fluke 51 II thermometer was put inside the reactor.

This temperature test showed that the reactor would get to a maximum temperature of 34.6°C. This was after 42 minutes of irradiation during which the temperature was stable for the last 12 minutes. The cooling of the reactor was also tested. During the cooling the light was switched off, cylinder gas was flowing and ventilator switched on. This showed that the reactor is back to room temperature in 15 minutes when the reactor remained closed. Exact numbers can be found in Appendix C.1.

In light experiments also a plastic plate was put on top of the reactor. To see if this would affect the temperature in the reactor also a temperature test was performed with the plastic plate and when it was removed. This test shows that the plastic plate decreased the temperature with approximately 3°C. This test can be found in Appendix C.2.

3.7 Temperature measurement of the reactor in the oven

Temperature was also determined in the empty reactor when it was heated by the oven. These measurements showed that during the sample of 18-23 min the reactor was still heating and the temperature is about 6°C lower than the temperature of the oven. Between the sample of 18-23 and 41 -46 min the temperature has risen with another 1.5°C (exact temperature measurement can be found in the Appendix C.3). This means that temperature inside the reactor is approximately 5°C lower than the oven.

3.8 Flushing the reactor

To determine how long it would take to flush the reactor, a test was performed when the reactor was not attached to the gas cylinder. Now air from the room went through the reactor and was analysed. After this sample was taken the reactor was attached to the gas cylinder and for the

duration of analyses the air sample by de IRMS the reactor was being flushed (18 min). This showed that for a small difference in CO concentration, flushing the reactor for 18 minutes (the time of analysing 1 air sample by the IRMS) is enough between measurements (see Table 3.3). This shows that flushing the reactor during the measurement of the reference gas(23 min) is enough. From this test one can also see what the normal values are of an empty reactor with the cylinder gas are.

Table 3.3 – Results from flushing the reactor. Flushing the reactor for 23 minutes is sufficient for the experiments performed.

	CO Concentration (ppbv)	$\delta^{13}\text{C}$ (‰) V-PDB	$\delta^{18}\text{O}$ (‰) V-SMOW
Room air	178.31	-26.678	12.25
Flushing of 18- 23 min	200.03	-28.040	11.08
flushing of 41 – 46 min	200.64	-27.979	11.06
Flushing of 64 – 69 min	199.80	-27.868	11.09

Chapter 4

Results

4.1 Light experiments

4.1.1 Comparison of different plants

For comparing the different plants, their emission rate and isotopic composition were determined. The height of the lamp was constant, so the intensity of irradiation was the same during all the experiments. Tests with each plant were only performed once, except for fresh grass for which three tests were performed. Two types of hederas were tested and from one of the hederas an older and younger leaf were used that were obtained from the same branch.

Emission rate

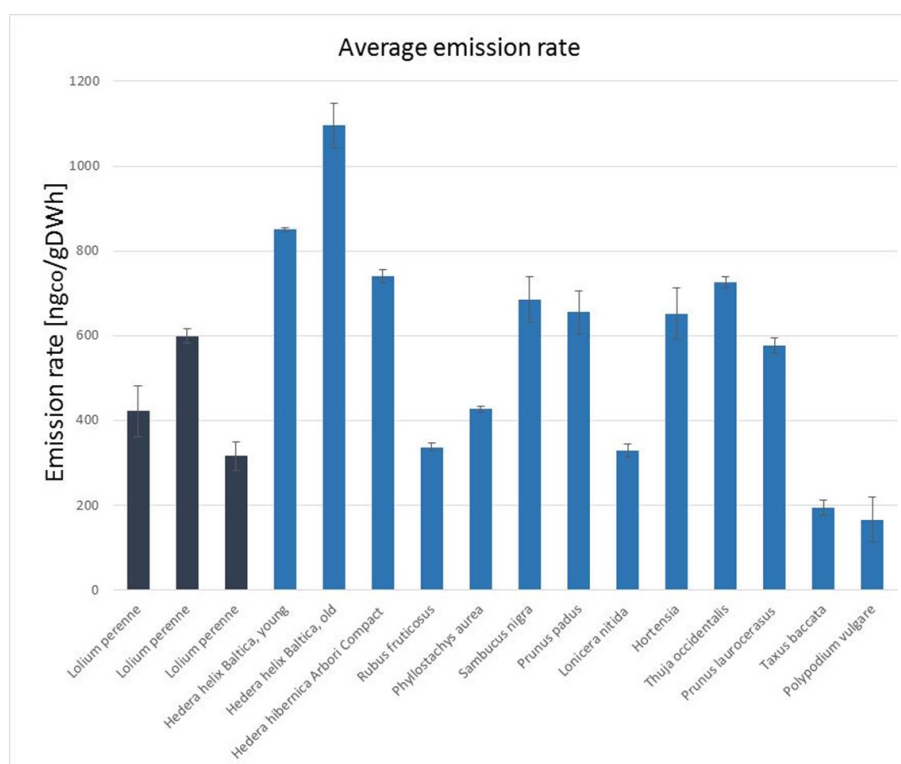


Figure 4.1 – Average emission rate of different plants under irradiation.

In one sequence of testing a plant, two samples were taken with the influence of irradiation. In Figure 4.1 the results of the average emission rates from these two samples of the different plants are presented, the errors are the standard deviation of the average.

The first thing the figure shows is that all the plants emit CO under the influence of irradiation. This emission fluctuates a lot. The figure shows that *Polypodium vulgare* has the lowest emission rate of $166.84 \pm 53.54 \text{ ng}_{\text{CO}}/\text{gDWh}$. The older leaves from the *Hedera helix Baltica* emit the most CO, with an emission rate of $1095.46 \pm 53.62 \text{ ng}_{\text{CO}}/\text{gDWh}$.

Three tests were performed with grass. These tests showed a big fluctuation in the emission rate, the difference between lowest and highest value is $282.35 \text{ ng}_{\text{CO}}/\text{gDWh}$. The reason for this fluctuation is probably the way grass is put into the reactor. With all the other plants, the leaves are not covering each other but were put next to each other in the reactor, while with the grass this was not the case and blades were covering each other. Because of this probably not all the grass blades were irradiated which could lead to less emission of CO.

$\delta^{13}\text{C}$

The isotopic composition of carbon isotopes emitted by the different plants was between the value of $-37.05 \pm 1.12 \text{ ‰}$ for *Lonicera nitida* and $-51.35 \pm 0.36 \text{ ‰}$ for *Thuja occidentalis*. The average of all the plants comes to a value of $-43.67 \pm 3.64 \text{ ‰}$. In Figure 4.2 the $\delta^{13}\text{C}$ values is shown against CO emission rate. Again, the isotopic composition values are the average of the two samples that are taken during the testing sequence of one plant. In these results the value for *Polypodium vulgare* is left out, this was done because the emission of CO (before correcting for the weight of the dried leaf) was too low to determine the isotopic compositions accurately. Looking at the different values shown, there does not seem to be a connection between emission rate and isotopic composition.

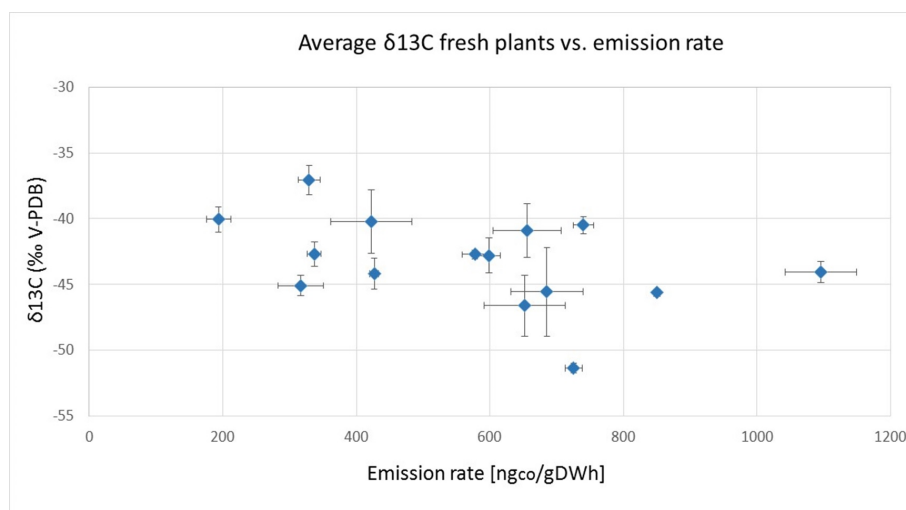


Figure 4.2 – Average $\delta^{13}\text{C}$ plotted against the average emission rate per plant.

$\delta^{18}\text{O}$

Values for $\delta^{18}\text{O}$ vary between $19.97 \pm 1.05 \text{ ‰}$ for *Hedera helix Baltica*(young) and $33.30 \pm 0.29 \text{ ‰}$ for *Lolium perenne* (grass). The average of all the plant comes to a value of $26.14 \pm 4.25 \text{ ‰}$. Plotting the isotopic composition against emission rate does not show an connection (Figure 4.3), which means the amount of emission does not affect the isotopic composition. Also when the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ are plotted together there does not seem to be a connexion between the two, so these do not affect each other (Figure 4.4).

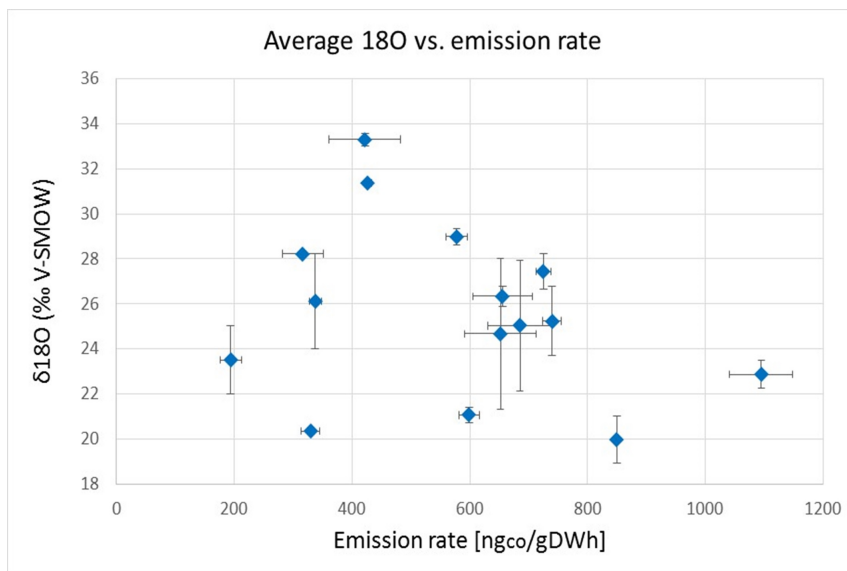


Figure 4.3 – Average $\delta^{18}\text{O}$ plotted against the average emission rate per plant.

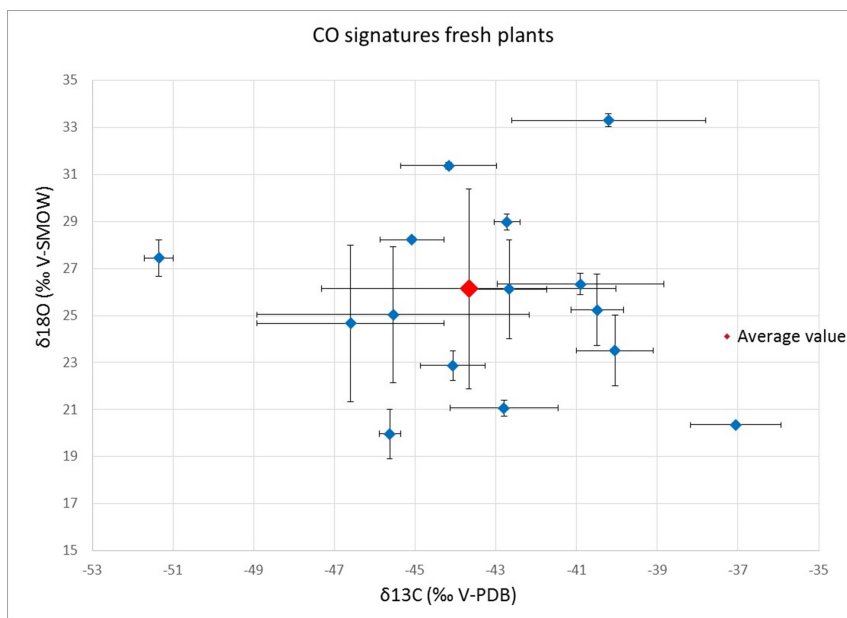


Figure 4.4 – CO isotopic signatures of different plants from light experiments.

4.1.2 Dried and fresh plants

In this study several different plants were tested fresh. Six of these plants were also tested when dried. The results of these six plants will be presented here.

Emission rate

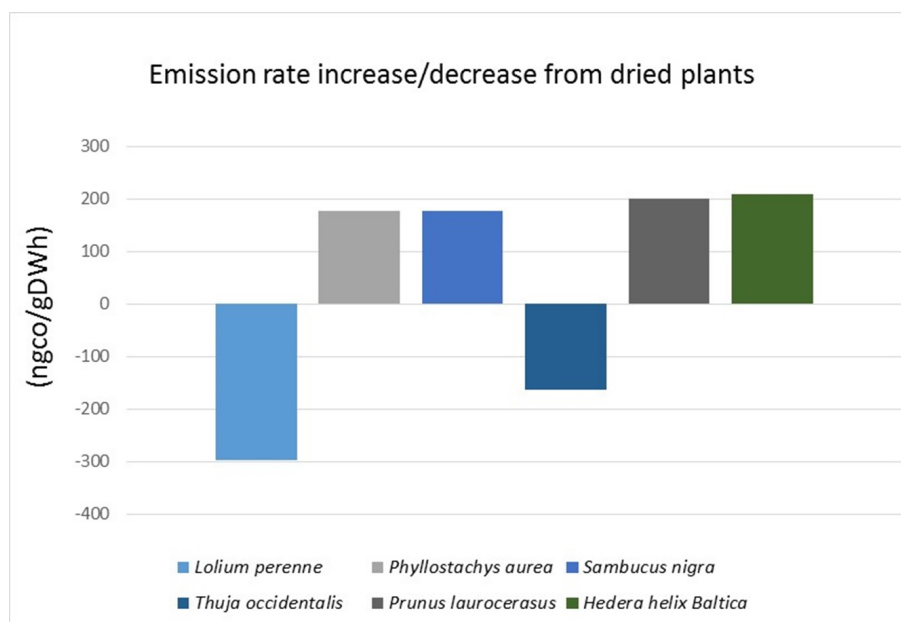


Figure 4.5 – Difference in emission rate after drying the leaves. A negative value means that the plant emitted less after drying, a positive value means the plant emitted more after drying.

The drying of the plants affected the emission of CO in different ways. Although still all the dried plants emitted CO under irradiation, the drying led to decrease in emission for *Lolium perenne* and *Sambucus nigra*, while for the other plants the emission increased after drying (Figure 4.5).

Note needs to be taken of *Phyllostachys aurea* because after drying the leaf curled, so less surface of the leaf was irradiated, still *Phyllostachys aurea* emitted more after drying.

Isotopic composition

Table 4.1 represents the average delta values for C and O isotopes for the dried and fresh plants. Drying the plants does not seem to affect the $\delta^{13}\text{C}$ value, while for $\delta^{18}\text{O}$ for all the plants decreased.

Table 4.1 – Average isotopic compositions of fresh and dried plant material.

	Average $\delta^{13}\text{C}$ (‰) V-PDB	SD	$\delta^{18}\text{O}$ (‰) V-SMOW	SD	n
Fresh	-45.37	3.19	25.64	4.48	6
Dried	-46.98	4.99	19.23	4.21	6

4.1.3 Blocking of UVB by a glass plate

By putting the glass plate on top of the reactor the UVB (320-290nm) spectra was blocked so it becomes possible to see the influence of the remaining light on the isotopic signatures. Tests with the glass plate were only performed with grass. A big fluctuation was seen in the emission rate of fresh grass. Because of this fluctuation in measurements it was impossible to say something about the influence of blocking UVB on the emission rate of the grass. The emission of the grass was high enough to determine the isotopic compositions.

Table 4.2 – Average results of blocking UVB using a glass plate. Tests were performed with grass.

	Average $\delta^{13}\text{C}$ (‰) V-PDB	SD	Average $\delta^{18}\text{O}$ (‰) V-SMOW	SD	n
No glass plate	-42.69	2.44	27.53	6.15	3
Glass plate(no UVB)	-39.37	5.58	26.05	2.57	2

The values presented in Table 4.2 suggest that the glass plate increased the $\delta^{13}\text{C}$ value but the deviation also increased. This is due to the fact that there were only two test performed with the glass plate. These two test had a difference of 8 ‰ for $\delta^{13}\text{C}$ which increased the standard deviation (see also Appendix A for the values). To see if blocking UVB had an influence more tests have to be performed with a wider selection of plants.

4.1.4 Blocking of UVA and UVB by a plastic plate

To see what the effect was from the UV, tests were performed while UVA and UVB were blocked. This was done by placing a plastic transparent plate on the reactor. This plate blocked both UVA and UVB light but let (most of) the visible light through. Additionally the way of testing was adjusted as well. This was done because of the high fluctuation between different test performed with grass. Now the same grass was used for the test with the plate on top and a test without the plate. Two tests were performed, but the sequence in these test were inversed to exclude that previous irradiation would affect the emission. In test 1 the first sample was the plant without any light on the plant, second sample with light including UV and the third sample the UV was blocked. In test 2 the second sample the UV was blocked and the third was light including the UV. In Table 4.3 the results of the experiment with the plastic plate are presented.

Table 4.3 – Results of blocking UVA and UVB by using a plastic plate. Tests were performed with grass.

	Emission rate (ng _{co} /gDW _h)	SD	$\delta^{13}\text{C}$ (‰) V-PDB	SD	$\delta^{18}\text{O}$ (‰) V-SMOW	SD
Test 1 UV	670.97	29.48	-41.02	0.77	28.90	1.48
Test 1 no UV	310.83	26.64	-31.48	1.31	26.73	2.94
Test 2 no UV	417.55	25.62	-28.95	0.96	28.71	2.18
Test 2 UV	518.60	26.17	-37.47	0.85	27.29	1.70

The results in Table 4.2 show that both light, without UV, as UV increased the emission of CO. In test 1 the emission rate increased from 283.22 to 670.97 ng_{co}/gDW_h. In test 2, where the sequence was reversed, the emission rate decreased from 391.21 to 518.60 ng_{co}/gDW_h.

Additionally the values show that there is a definite change in the isotopic composition of carbon isotopes when UVA and UVB are blocked. It becomes clear that after putting the plastic plate on top of the reactor the delta value for $\delta^{13}\text{C}$ increased. When the test was performed in reverse order one can observe that by removing the plastic plate the $\delta^{13}\text{C}$ value for carbon decreased. The average values of the two tests with the full light spectrum is for $\delta^{13}\text{C}$ -39.24 ± 2.51 ‰ and when UVA and UVB is blocked -30.21 ± 1.78 ‰.

4.1.5 Overview of the light experiments

An overview of all the isotopic signatures of the UV experiments is shown in Table 4.4 and Figure 4.6. The values in this table and figure are all averages for the experiments performed.

Table 4.4 – Overview of the results from the light experiments.

	Average $\delta^{13}\text{C}$ (‰) V-PDB	SD	Average $\delta^{18}\text{O}$ (‰) V-SMOW	SD	n
Fresh plants	-43.67	3.64	26.14	4.25	15
Subset fresh plants used for drying	-45.37	3.19	25.64	4.48	6
Dried plants	-46.98	4.99	19.23	4.21	6
Fresh grass	-42.69	2.44	27.53	6.15	3
Fresh grass UVB blocked	-39.37	5.58	26.05	2.57	2
Fresh grass, used for UVA and UVB blocking	-39.24	2.51	28.10	1.14	2
Fresh grass UVA and UVB blocked	-30.21	1.78	27.72	1.40	2

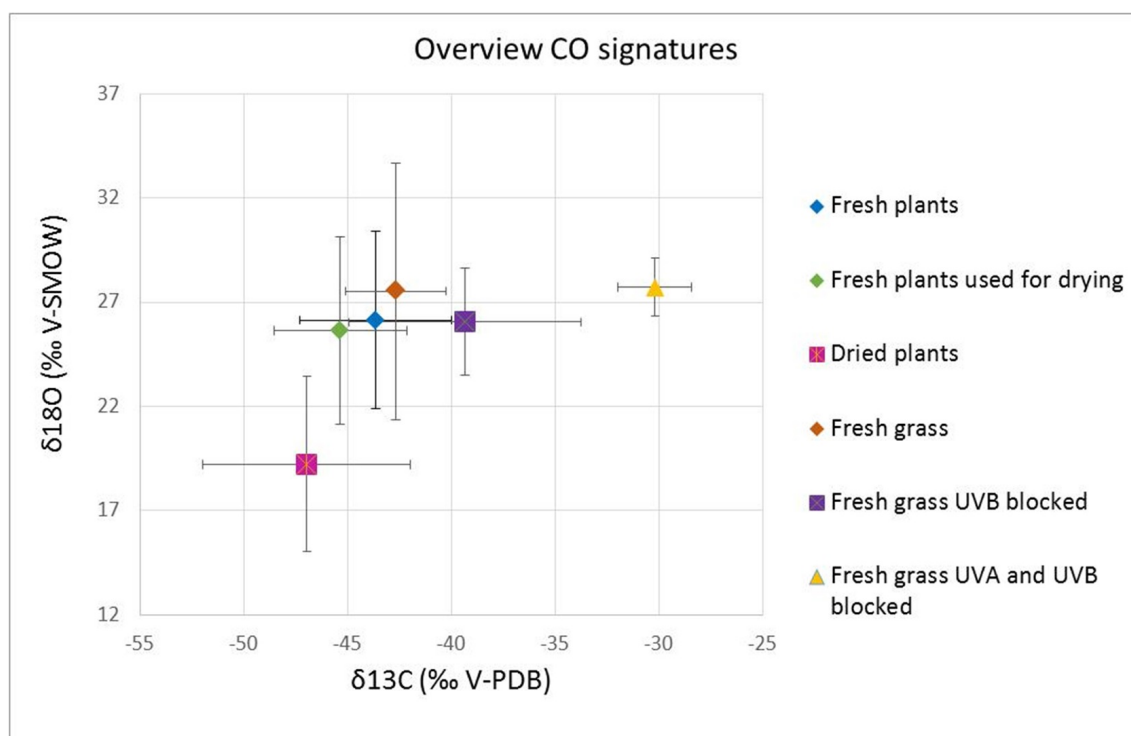


Figure 4.6 – Overview of the CO signatures from the light experiments.

4.2 Temperature experiments

To see if the emission of the CO in light experiments would come from the irradiation of the lamp or from of the heating in the reactor, temperature experiments were performed. Temperatures of the oven in these tests varied between 30 °C and 50 °C. Temperature inside the reactor was approximately 5 °C lower.

4.2.1 Freshly picked grass

The different test performed with grass showed that a higher temperature increases the emission of CO (Figure 4.7a). There is however a lot of fluctuation in the emission rate at the same temperature. Two tests that were performed on different days at the same temperature of 40°C, the emission rate had a difference of 240.7 ng_{co}/gDWh.

The $\delta^{13}\text{C}$ values from the fresh picked grass also show a lot of fluctuation (Figure 4.7b). Two tests that were performed on different days at the same temperature gave a value difference of 12 ‰. Although the values fluctuate a lot it does seem like the $\delta^{13}\text{C}$ value is decreasing with the temperature. Because of the high fluctuation this is very uncertain.

Also for $\delta^{18}\text{O}$ the tests suggest that the value increases with increasing temperature (Figure 4.7c). Although one test at 40°C does not seem to follow this rule.

4.2.2 Freshly picked hедера

Next to grass also two temperature tests were performed with hедера. In these tests more plant material was put into the reactor than with light experiments. These tests only showed at a temperature of 50°C an emission rate of 41.41 ng_{co}/h (uncorrected for the weight). This value is not high enough to determine accurate values for the isotopic composition.

4.2.3 Testing the same grass in one day

With these tests the grass was picked in the morning, during the day it was kept in a plastic bag at room temperature in the lab (approx 20°C). The time between the start of every experiment was approximately one and a half hour. The first test of the day was at the higher temperature because heating the oven took a lot of time. The tests were done on two separate days. One the first day tests with different temperatures at 45, 40 and 35°C. On the second day tests at the same temperature of 50°C with a test at 35°C in between.

One day different temperatures

Results of these tests can be found in Table 4.5 and Figure 4.7. Still with these test the emission rate follows the rule of higher emission at higher temperature. The $\delta^{13}\text{C}$ values seems to decrease with the temperature this is the same as with the grass that was picked fresh. For $\delta^{18}\text{O}$ the values seem to decrease with increasing temperature, which contradicts with the freshly picked grass.

Table 4.5 – Results of temperature experiments with stored grass. The temperature given is the temperature of the oven.

	Temperature (°C)	Emission rate (ng _{co} /gDWh)	SD	$\delta^{13}\text{C}$ (‰) V-PDB	SD	$\delta^{18}\text{O}$ (‰) V-SMOW	SD
Fresh	45	175.68	16.79	-46.00	2.11	15.22	2.96
1.5 hour after fresh test	40	107.22	18.81	-42.59	3.71	17.79	5.56
3 hours after fresh test	35	70.89	16.49	-41.43	6.70	18.68	7.84

One day same temperatures

To see if the time the grass was stored between collecting and measuring had an influence tests were performed at the same temperature. First one test at 50 °C followed by a test at 35 °C and subsequently another test at 50 °C.

Table 4.6 – Results of temperature experiments with stored grass. The temperature given is the temperature of the oven.

	Temperature (°C)	Emission rate (ng _{co} /gDWh)	SD	$\delta^{13}\text{C}$ (‰) V-PDB	SD	$\delta^{18}\text{O}$ (‰) V-SMOW	SD
Fresh	50	429.55	18.35	-50.12	0.93	28.37	1.47
1.5 hour after fresh test	35	54.51	15.55	-41.43	9.33	19.34	12.90
3 hours after fresh test	50	242.56	15.53	-43.41	1.34	24.63	2.28

Values of these tests can be found in Table 4.6. From these test it appears that keeping the grass indeed influences the amount of emission from the plants. Additionally it changes the isotopic composition. By keeping the grass for longer time the emission at 50°C decreased from 429.6 to 242.6 ng_{co}/gDWh. In the other tests the sequence of the test were performed from a higher temperature to a lower temperature and those test showed that the emission decreased. This test makes clear that not only the temperature had that influence but keeping the grass also had an influence on the emission of CO.

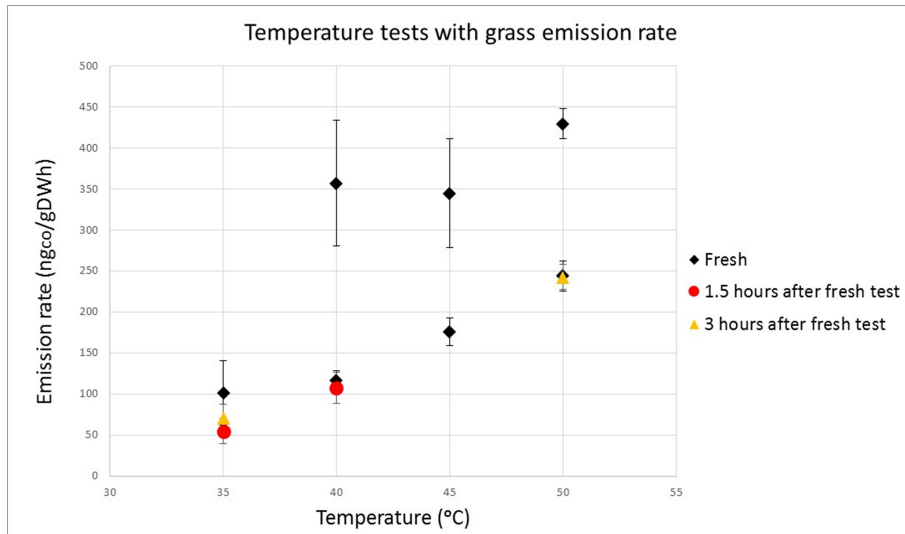
The same thing holds for the isotopic compositions. The data from Table 4.5 suggest that decreasing the temperature the $\delta^{13}\text{C}$ value increase. In Table 4.6 The first test at 50 °C had a value of $\delta^{13} = -50.12 \pm 0.93$ ‰ and the second test (3 hours later) had a value of -43.41 ± 1.34 ‰. This suggest that not only the temperature increased $\delta^{13}\text{C}$, but also time between collecting and measuring influences this value.

For $\delta^{18}\text{O}$ Table 4.6 shows that time between collecting and testing the grass also influenced the isotopic composition. Decreasing the temperature decreased the $\delta^{18}\text{O}$ value but also time decreased this value.

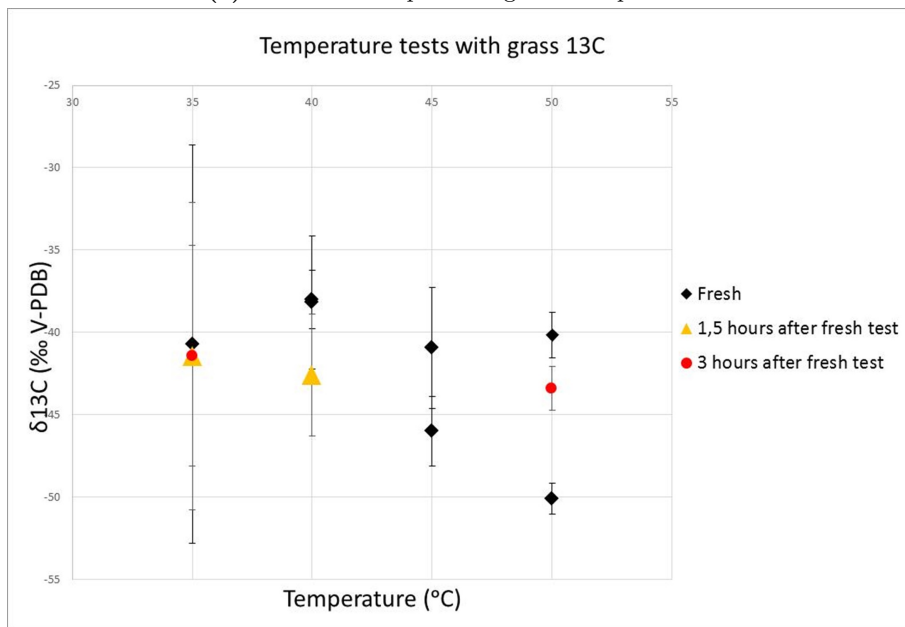
The tests for $\delta^{18}\text{O}$ are contradictory. Fresh tests suggested that increasing temperature also increases the $\delta^{18}\text{O}$ value. This is also suggested by the test that were performed with the same grass in one day at the same temperature. While the tests with grass that was longer kept, tested at different temperatures, show an decrease with increasing temperature and an increase over time.

First sample for longer stored grass

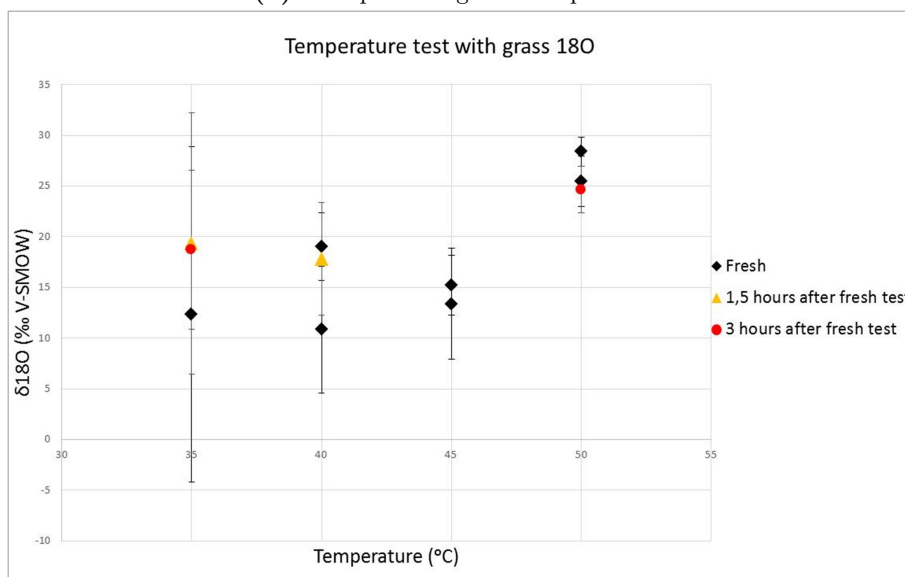
Additionally something interesting showed in the first sample from these tests. Fresh grass did not show emission without influence of light or temperature. Grass that was kept for a longer time did show an emission in the sample without the influence of light or temperature. These tests were still corrected for the first sample.



(a) Emission rate plotted against temperature.



(b) $\delta^{13}\text{C}$ plotted against temperature.



(c) $\delta^{18}\text{O}$ plotted against temperature.

Figure 4.7 – Results from all temperature experiments. The temperature given is the temperature of the oven.

Chapter 5

Discussion

5.1 Light experiments

Light experiments

Looking at the isotopic signatures of plant emitted CO has only been performed in one previous study (Vijverberg [2015]). In that study tests were performed on living plant material without the influence of light. The isotopic signatures presented in Vijverberg [2015] varied between -43.1 and -29.6 ‰ with an average of -36.3 ± 5.8 ‰ for $\delta^{13}\text{C}$. $\delta^{18}\text{O}$ values ranged between 37.9 and 42.3 ‰ with an average of 39.6 ± 2.0 ‰. Comparing with this previous study would not lead to valid conclusions because different type of experiments were performed.

In the current work irradiating different fresh plant types with solar like irradiation, including UV, showed that all the plants tested emitted CO. The emission rate for the different plants vary between 166.84 and 1095.46 ng_{co}/gDWh. The isotopic compositions of $\delta^{13}\text{C}$ ranged between -37.05 and -51.35 ‰ with an average value of -43.67 ± 3.64 ‰. The $\delta^{18}\text{O}$ values were between 19.97 and 33.30 ‰ with an average value of 26.14 ± 4.25 ‰. The amount of CO emitted does not influence the isotopic signatures. Next to this the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values do not seem to influence each other. In the comparison between dried and fresh plants, increase and decrease in emission was found. In a previous study it was shown that photo-production of CO emission from leaf litter was higher than from living plant material (Tarr et al. [1995]). It cannot be stated whether dried or fresh leaves emit more from this study.

Drying of the leaves did not seem to affect the $\delta^{13}\text{C}$, but there was a change in $\delta^{18}\text{O}$. After drying the average value of the same plants decreased from a values of 25.64 ± 4.48 ‰ to a value of 19.23 ± 4.21 ‰. A decrease of $\delta^{18}\text{O}$ appeared with every plant. Atmospheric $\delta^{18}\text{O}$ has the value of 23.5 ± 0.3 ‰ (Kroopnick and Craig [1972]). From drying the leaves one could expect that the $\delta^{18}\text{O}$ value would get more closely to atmospheric $\delta^{18}\text{O}$ level. This because there is no H₂O inside the plant where the binding oxygen atom could come from. This means that the binding oxygen atom would come from atmospheric O₂. This was not the case in tests performed, this suggests that the binding oxygen atom might come from another plant chemical.

Additionally it is important to consider that in this study the emission rate was expressed per dry weight of the leaf. This correcting for the weight was thus the same for the fresh and dried plants. In other studies the emission was expressed per surface of the leaf. It was noted that for some plants in this study the surface of the leaf decreased by drying the leaf. When the emission is expressed per surface of the leaf, it is possible that the dried leaf is corrected for a smaller surface. This could lead to a increase in emission. Moreover the weight of thicker leaves, such as *Hedera helix Baltica* and *Prunus laurocerasus*, is larger per surface than for the thinner green leaves.

UV blocked experiments

Tarr et al. [1995] showed that UVB is important in CO emission from plant material. Because there was a big fluctuation in light experiments between different grass samples nothing can be concluded about the influence of blocking UVB on the emission of CO. Next to this, blocking the UVB did not seem to affect the isotopic composition of C and O isotopes. More tests with different plants should be performed to verify whether this is actually true.

In the experiments in which UVA and UVB were blocked something can be said about the emission rate. This is because in these tests the plastic plate was placed on top(or removed) of the reactor between second and third sample. The tests were thus with the same grass. This showed that the emission rate increased when UVA and UVB were not blocked and the emission decreased when UVA and UVB were blocked. Additionally also the isotopic composition of carbon isotopes changed. $\delta^{13}\text{C}$ increased from an average value $-39.24 \pm 2.51 \text{ ‰}$ when UV wasn't blocked to a value of $-30.21 \pm 1.78 \text{ ‰}$ where UV was blocked. A change was not observed in the $\delta^{18}\text{O}$ value.

5.2 Temperature experiments

Temperature tests were performed at first to determine whether the increase of emission of CO was due to light or because the temperature increase in the reactor. During light experiments temperature increased to a maximum value of 34.6 °C. Because of this temperature experiments at a temperature of 40°C are compared. For grass the highest emission rate at a temperature of 40°C was $357.12 \pm 76.12 \text{ ng}_{\text{co}}/\text{gDWh}$. This is higher than the lowest emission rate from a light experiment performed with grass which had a value of $316.49 \pm 34.05 \text{ ng}_{\text{co}}/\text{gDWh}$. Nevertheless it is assumed that UV in the light experiments had a bigger influence than the temperature. This is because there is a lot of fluctuation between light experiments performed with grass because blades of grass were covering each other. Next to this blocking UVA and UVB also made the emission decrease significantly, while the blocking only changed the temperature in the reactor with 2°C. Additionally, temperature test performed with hedera showed almost no emission at a temperature of 50 °C. This is a higher temperature than what the reactor would get from a light experiment. While during light experiments, hedera was the plant that emitted the most CO. Suggested is that temperature might have a bigger influence on the thinner leaves. Emission due to temperature was noted in tests performed with grass but not from the thicker leaves from hedera. Next to this the thicker leaves also didn't lose any moisture during testing while this did happen with the green leaves, which might also influence the emission and isotopic composition.

The average $\delta^{13}\text{C}$ values of fresh grass tested at 40 °C was $-38.10 \pm 0.12 \text{ ‰}$. This is a bit higher than fresh grass in light experiments that had an average value of $-42.69 \pm 2.44 \text{ ‰}$. Strangely it is lower than the light experiment in which the UVA and UVB is blocked which gave a value of $-30.21 \pm 1.78 \text{ ‰}$. This is not expected because in the temperature test the reactor was dark.

Looking at what the influence of temperature was on CO emission, the emission rate increased with increasing temperature. For the isotopic compositions it is suggested, from the fresh tests, that increasing temperature decreases $\delta^{13}\text{C}$. For $\delta^{18}\text{O}$ it is suggested that increasing temperature also increased $\delta^{18}\text{O}$. Due to a lot of fluctuation in the results this very uncertain. More test would have to be performed ideally with a wider selection of plants.

Also the time between collecting and measuring seemed to affect the emission and isotopic composition from plant emitted CO. From the tests performed it seemed that keeping the grass for a longer time increases the $\delta^{13}\text{C}$ value. For $\delta^{18}\text{O}$ the tests contradicted each other and no suggestion can be made. Moreover grass that was kept for a longer time did show an emission in the sample without the influence of light or temperature. This was not the case with fresh collected grass. Additionally the longer kept grass showed less effect of emission from temperature.

5.3 Improving the experiment

It was shown that a higher emission of CO decreased the errors in the tests. An emission rate of ~ 100 ng/h (or higher) uncorrected for the weight of the plant material is needed to get a reasonable error. In this study the comparison of different plants was only performed with one test per plant. To improve the reliability of the values of the emission rate and the isotopic signatures more tests should be performed with the same type of plant. In this study it is stated that UV irradiation decreased the $\delta^{13}\text{C}$ value. Tests would have to be performed with the lamp at different heights, so the effect of different intensities of irradiation could be compared. The sequence (one sample without irradiation, two samples with irradiation) that has been used in this study for UV seems to be a good way to test. The differences between values with an irradiation of 18 - 23 min are comparable to the values of an irradiation of 41-46 min.

Temperature tests of grass showed very different values, the cause of this difference is not known. Testing other plants or changing the time between collecting and testing might show what causes this difference. For the temperature tests a better way of heating the reactor should be used, in this study only values of the third sample were at the right temperature.

Chapter 6

Conclusion

The influence of light and temperature on plant emitted CO was investigated. The emission rate and isotopic composition of C and O isotopes were determined. Under the influence of light all the plants showed an emission of CO. Freshly collected plant material gave an average value of -43.67 ± 3.64 for $\delta^{13}\text{C}$. The average of $\delta^{18}\text{O}$ was determined to a value of 26.14 ± 4.25 . Drying of the plant material did not have a clear effect on the emission of CO and the $\delta^{13}\text{C}$. The drying did decrease the $\delta^{18}\text{O}$. Blocking UVB with a glass plate did not have a clear effect. Blocking UVA and UVB with a plastic plate decreased the emission of CO and increased the $\delta^{13}\text{C}$ value from a value of -39.24 ± 2.41 ‰ to 30.21 ± 21 ‰. From temperature experiments it is concluded that the light increased most of the emission in light experiments. Increasing temperature also increased the emission. Suggested is that increasing temperature decreased the $\delta^{13}\text{C}$ and increases $\delta^{18}\text{O}$. This is uncertain due to a lot of fluctuation. The time between collecting and measuring plant material also showed an effect. Emission from the grass that was stored for longer time was noted without the influence of temperature or light. Additionally the effect of temperature seemed to decrease when grass was stored longer. The $\delta^{13}\text{C}$ value seemed to increase and $\delta^{18}\text{O}$ showed unclear changes.

Appendix A

Light experiments

Table A.1 – The results from the light experiments except the experiments were UVA and UVB were blocked. All the values are the average of two samples.

Fresh plant material	Emission rate (ng _{co} /gDWh)	SD	$\delta^{13}\text{C}$ (‰) V-PDB	SD	$\delta^{18}\text{O}$ (‰) V-SMOW	SD
<i>Lolium perenne</i>	422.21	60.87	-42.80	1.34	21.07	0.34
	598.84	17.03	-45.08	0.80	28.23	0.11
	316.49	34.05	-40.21	2.40	33.30	0.29
<i>Hedera helix Baltica, young</i>	850.03	5.00	-45.63	0.26	19.97	1.05
<i>Hedera helix Baltica, old</i>	1095.46	53.62	-44.06	0.80	22.87	0.63
<i>Hedera hibernica Arbori</i>	739.87	15.29	-40.49	0.65	25.24	1.52
<i>Rubus fruticosus</i>	337.27	10.19	-42.67	0.93	26.12	2.10
<i>Phyllostachus aurea</i>	426.81	6.52	-44.17	1.19	31.37	0.14
<i>Sambucus nigra</i>	685.26	53.88	-45.54	3.37	25.03	2.88
<i>Prunus padus</i>	655.66	50.94	-40.91	2.06	26.34	0.44
<i>Lonicera nitida</i>	329.50	16.00	-37.05	1.12	20.35	0.06
<i>Hortensia</i>	652.35	60.55	-46.60	2.32	24.67	3.33
<i>Thuja occidentalis</i>	725.41	13.13	-51.35	0.36	27.44	0.78
<i>Prunus laurocerasus</i>	577.56	18.44	-42.72	0.32	28.98	0.35
<i>Taxus baccata</i>	193.67	18.37	-40.05	0.95	23.51	1.51
<i>Polypodium vulgare</i>	166.84	53.54	ND		ND	
Average value			-43.67	3.64	26.14	4.25
Dried plant material						
<i>Lolium perenne</i>	301.32	2.12	-50.15	1.02	17.79	2.13
<i>Phyllostachus aurea</i>	603.14	38.14	-43.10	0.29	19.99	0.85
<i>Sambucus nigra</i>	1011.43	51.60	-50.52	0.30	17.65	1.25
<i>Thuja occidentalis</i>	561.77	74.59	-51.36	2.25	23.45	0.87
<i>Prunus laurocerasus</i>	777.70	12.04	-38.81	0.27	23.90	0.36
<i>Hedera helix Baltica, young</i>	1059.53	62.62	-47.92	0.15	12.62	0.40
Average value			-46.98	4.99	19.23	4.21
UVB blocked						
<i>Lolium perenne</i>	403.44	27.11	-43.31	1.12	24.23	0.12
	668.01	100.85	-35.43	1.51	27.86	0.78
Average value			-39.37	5.58	26.05	2.57

Table A.2 – Results of blocking UVA and UVB by using a plastic plate. Tests were performed with *Lolium perenne*.

	Emission rate (ng _{co} /gDWh)	SD	$\delta^{13}\text{C}$ (‰) V-PDB	SD	$\delta^{18}\text{O}$ (‰) V-SMOW	SD
Test 1 UV	670.97	29.48	-41.02	0.77	28.90	1.48
Test 1 no UV	310.83	26.64	-31.48	1.31	26.73	2.94
Test 2 no UV	417.55	25.62	-28.95	0.96	28.71	2.18
Test 2 UV	518.60	26.17	-37.47	0.85	27.29	1.70

Appendix B

Temperature experiments

Table B.1 – All the results from the temperature experiments. The values are those from the third sample of an experiment.

Fresh	Temperature oven (°C)	Emission rate (ng _{co} /gDWh)	SD	$\delta^{13}\text{C}$ (‰) V-PDB	SD	$\delta^{18}\text{O}$ (‰) V-SMOW	SD
<i>Lolium perenne</i>	35	101.31	39.55	-40.71	12.10	12.37	16.54
	40	357.12	76.32	-38.19	4.02	10.83	6.24
	40	116.38	12.31	-38.01	1.79	19.00	3.35
	45	344.70	66.36	-40.94	3.67	13.38	5.49
	45	175.68	16.79	-46.00	2.11	15.22	2.96
	50	243.82	18.41	-40.16	1.38	25.45	2.46
1.5 hours after fresh test							
<i>Lolium perenne</i>	35	54.51	15.55	-41.43	9.33	19.34	12.90
	40	107.22	18.81	-42.59	3.71	17.79	5.56
3 hours after fresh test							
<i>Lolium perenne</i>	35	70.89	16.49	-41.43	6.70	18.68	7.84
	50	242.56	15.53	-43.41	1.34	24.63	2.28

Appendix C

Temperature measurements

C.1 Temperature from lamp

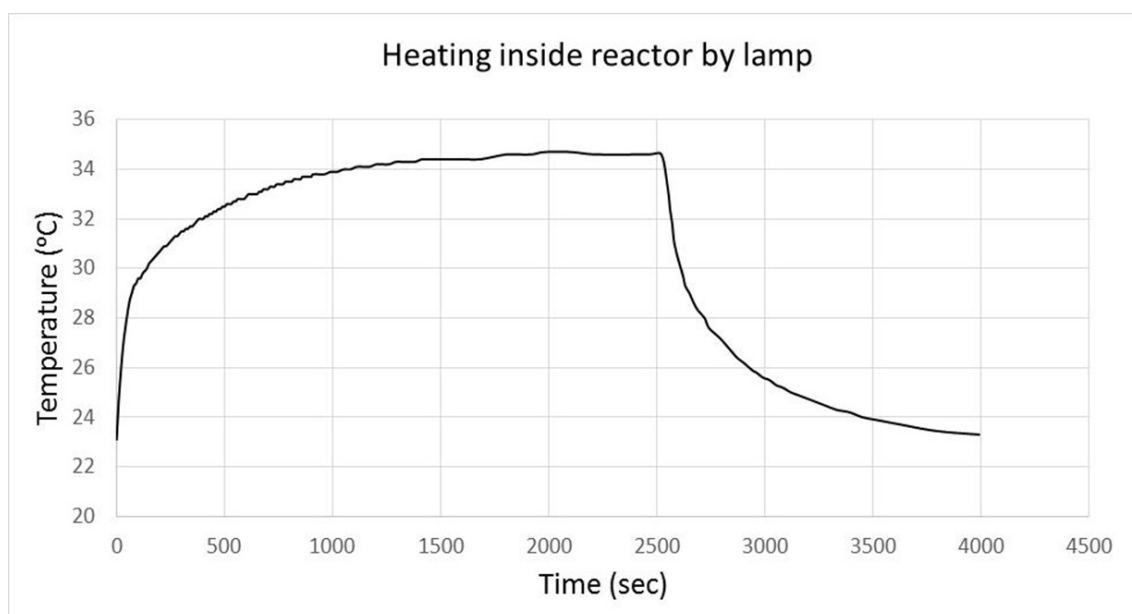


Figure C.1 – Heating of the reactor by switching the Vitalux 300W lamp on, during this test cylinder gas was flowing and also the ventilator was on. After 2520 sec (42 minutes) the light was switched off.

C.2 Temperature from lamp with plastic plate

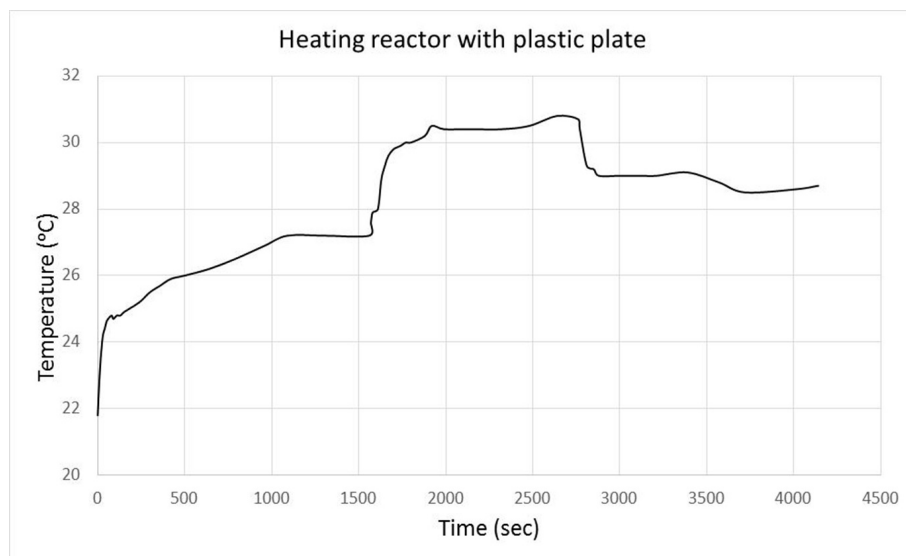


Figure C.2 – Heating of the reactor with a plastic plate on top. After 26 minutes (1560 seconds) the plastic was removed and after 46 minutes (2770 seconds) the plastic was again placed on top of the reactor.

C.3 Temperature from oven

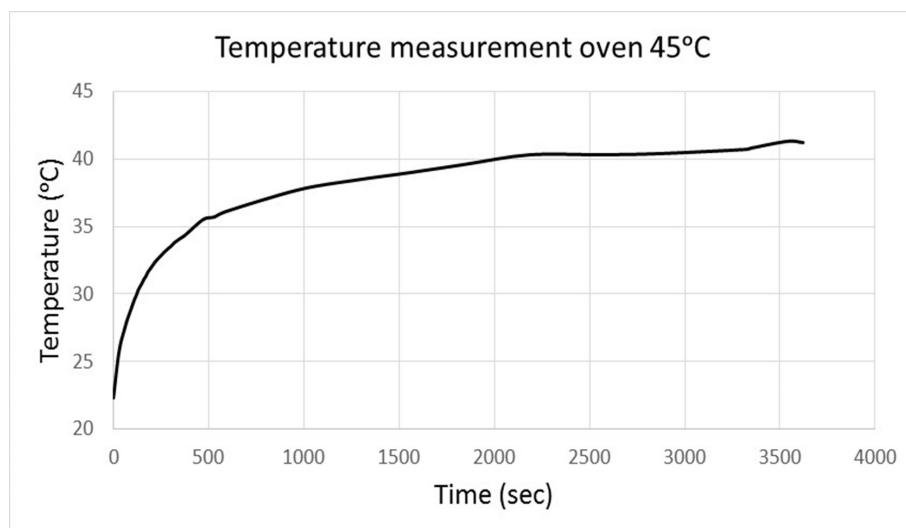


Figure C.3 – Heating of the reactor by the oven.

Appendix D

Reference gas values during experiments

Table D.1 – Average values of the reference gas during experiments.

Peak value	SD	$\delta^{13}\text{C}_{Rvs.WG}$ (‰)	SD	$\delta^{18}\text{O}_{Rvs.WG}$ (‰)	SD
5.91	0.11	-28.69	0.21	-0.003	0.11

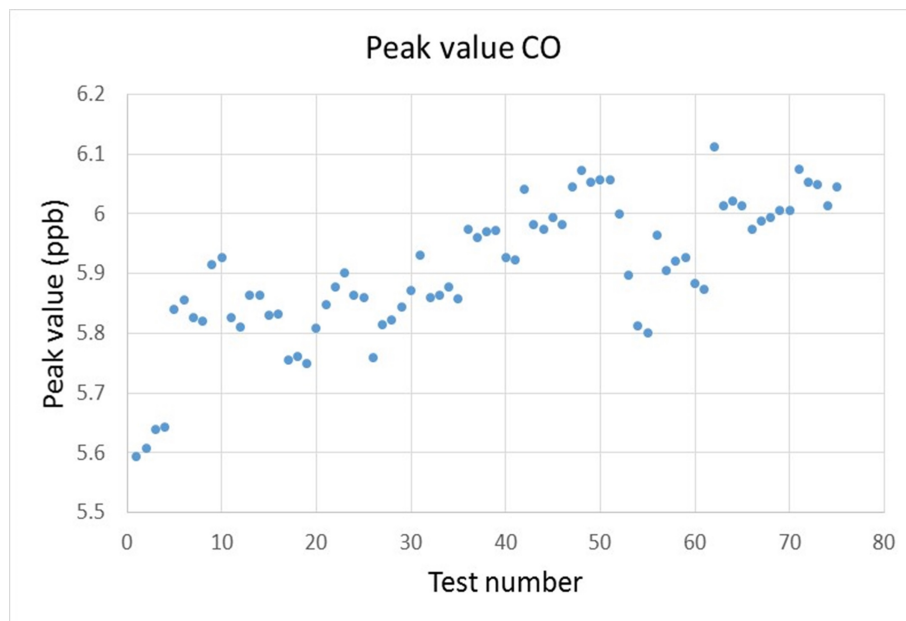


Figure D.1 – Peak values of the reference gas during experiments.

Bibliography

- Brenninkmeijer, C., Röckmann, T., Bräunlich, M., Jöckel, P., and Bergamaschi, P. (1999). Review of progress in isotope studies of atmospheric carbon monoxide. *Chemosphere-Global Change Science*, 1(1):33–52.
- Bruhn, D., Albert, K. R., Mikkelsen, T. N., and Ambus, P. (2013). Uv-induced carbon monoxide emission from living vegetation. *Biogeosciences*, 10(6).
- Crutzen, P. J. and Zimmermann, P. H. (1991). The changing photochemistry of the troposphere. *Tellus B*, 43(4):136–151.
- Daniel, J. S. and Solomon, S. (1998). On the climate forcing of carbon monoxide. *Journal of Geophysical Research: Atmospheres*, 103(D11):13249–13260.
- Derendorp, L., Quist, J., Holzinger, R., and Röckmann, T. (2011). Emissions of h₂ and co from leaf litter of sequoiadendron giganteum, and their dependence on uv radiation and temperature. *Atmospheric environment*, 45(39):7520–7524.
- Hansen, J., Sato, M., Kharecha, P., Russell, G., Lea, D. W., and Siddall, M. (2007). Climate change and trace gases. *Philosophical Transactions of the Royal Society of London A: Mathematical, Physical and Engineering Sciences*, 365(1856):1925–1954.
- Jiang, W., Peng, S., Hao, Q., and Liu, T. (2002). Carbon isotopic records in paleosols over the pliocene in northern china: implication on vegetation development and tibetan uplift. *Chinese Science Bulletin*, 47(8):687–690.
- Kanakidou, M. and Crutzen, P. J. (1999). The photochemical source of carbon monoxide: Importance, uncertainties and feedbacks. *Chemosphere-Global Change Science*, 1(1):91–109.
- Kroopnick, P. and Craig, H. (1972). Atmospheric oxygen: isotopic composition and solubility fractionation. *Science*, 175(4017):54–55.
- Liu, W., Ning, Y., An, Z., Wu, Z., Lu, H., and Cao, Y. (2005). Carbon isotopic composition of modern soil and paleosol as a response to vegetation change on the chinese loess plateau. *Science in China Series D: Earth Sciences*, 48(1):93–99.
- Müller, J. F. (1992). Geographical distribution and seasonal variation of surface emissions and deposition velocities of atmospheric trace gases. *Journal of Geophysical Research: Atmospheres*, (97):3787–3804.
- Pathirana, S., van der Veen, C., Popa, M., and Röckmann, T. (2015). An analytical system for stable isotope analysis on carbon monoxide using continuous-flow isotope-ratio mass spectrometry. *Atmospheric Measurement Techniques*, 8(12):5315–5324.
- Pidwirny, M. and Budikova, D. (2006). Atmospheric composition. *Fundamentals of Physical Geography*.
- Schade, G. W., HOFMANN, R.-M., and Crutzen, P. J. (1999). Co emissions from degrading plant matter. *Tellus B*, 51(5):889–908.

- Smithson, P. A. (2002). Ipcc, 2001: climate change 2001: the scientific basis. contribution of working group 1 to the third assessment report of the intergovernmental panel on climate change, edited by jt houghton, y. ding, dj griggs, m. noguer, pj van der linden, x. dai, k. maskell and ca johnson (eds). cambridge university press, cambridge, uk, and new york, usa, 2001. no. of pages: 881. price£ 34.95, us 49.95, *isbn*0 – 521 – 01495 – 6(*paperback*).£90.00, *us*130.00, *isbn* 0-521-80767-0 (*hardback*). *International Journal of Climatology*, 22(9):1144–1144.
- Solomon, S. (2007). *Climate change 2007-the physical science basis: Working group I contribution to the fourth assessment report of the IPCC*, volume 4. Cambridge University Press.
- Stevens, C. and Krout, L. (1972). Method for the determination of the concentration and of the carbon and oxygen isotopic composition of atmospheric carbon monoxide. *International Journal of Mass Spectrometry and Ion Physics*, 8(4):265–275.
- Tarr, M. A., Miller, W. L., and Zepp, R. G. (1995). Direct carbon monoxide photoproduction from plant matter. *Journal of Geophysical Research: Atmospheres*, 100(D6):11403–11413.
- Vigano, I. (2010). Aerobic methane production from organic matter.
- Vijverberg, S. (2015). Effect of stressing on the isotopic composition of plant-emitted carbon monoxide. Bachelor thesis.

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