INTERNSHIP REPORT

ON

CHARACTERISATION OF GREENHOUSE GAS EMISSIONS AND SOIL PROPERTIES IN THE CAIRNGORMS

By

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1. Introduction

1.1. Objective of the Internship

This internship aimed to couple measurements of greenhouse gas fluxes with soil mineralogy and geochemical analyses for the Cairngorms, as part of the larger characterization of the impact of land use change in the area.

I was joined by Angela Roberts, another undergraduate student, for both sections of this internship and the majority of the work was completed together. The project was supervised by Alexandra Turchyn.

1.2. Scope and Methodology

The internship consisted of both fieldwork and lab work components. Over a 2 week period, we covered 20 plots across different sites in the Cairngorms, conducting monitoring tasks and taking a range samples and measurements on each plot. The key samples we took for analysis were soil samples stored in glass vials, from which the gas concentration in the headspace of the vials was analysed in Cambridge. Additional soil samples were collected at each of these points for mineralogical and compositional analysis. 151 soil samples were taken in total. Flux chamber measurements were also carried out in the field to record CH_4 and CO_2 flux on several plots, although the extent of this was limited by battery failure in the gas analyser.

In the lab, a range of methods including mass spectroscopy, x-ray diffraction, gas analyses and soil separation were used to analyse the collected soil samples. Our analyses focused on variation between plots and between plot types rather than within individual plots.

1.3. Links to other projects

This works links to a wider project by the Centre for Landscape Regeneration, whose research in the Cairngorms includes work to evaluate the impact of conservation efforts on greenhouse gas emissions. They work closely with the Cairngorms Connect partnership, who focus on long-term conservation and restoration across over 600 km^2 in the Cairngorms national park.

2. Details of Internship Work

2.1 Structure of the Internship

There were two main phases to the internship work – a period of fieldwork in Scotland, and then a period of lab analysis in Cambridge. The fieldwork was conducted in the Cairngorms, based out of Aviemore, joining Liam Wakefield who regularly does fieldwork in the region collecting data for his PhD project. This was followed by two weeks in Cambridge to analyse the collected samples and data.

2.1.1 Field Work

Two weeks, from the 16th-30th July, were spent in Scotland, collecting samples and taking measurements at 20 plots, mostly on land within the Cairngorms Connect partnership. The two days preceding this, the 14th and 15th, were spent preparing for fieldwork by cleaning vials, flushing them with nitrogen, and learning how to use the Aeris Mira, the instrument used for gas flux measurements.

In Scotland, we travelled to 2-3 sites each day. At each plot, we collected 5-10 soil samples and several tree cores, as well as assisting Liam with tasks such as emptying litterfall traps, downloading monthly data from sensors and recording flux measurements from respiration collars on the ground and tree stems. We had also aimed to take several flux measurements as time series at each site, however were unable to do this at a large number of sites due to equipment failure.

2.1.2 Laboratory Work

After taking stock of and organising the samples we had collected, the first week was spent analysing the gas concentration in the headspace of soil samples, preparing samples to be run through the GC-MS for elemental composition and isotope data and starting to work on X-ray diffraction (XRD) of the samples. The rest of the lab work period was spent preparing samples for XRD, doing initial analysis of XRD data, further refining the analysis through Rietveld Refinement, attempting to separate the clay fraction of the samples, and analysing the data.

2.2 Framework for Sample Collection

In order to investigate the relationship between plot type and greenhouse gas emissions, data on the gas fluxes from different plot types and corresponding soil samples needed to be collected. Two types of sample were collected: soil samples for gas analysis taken in glass vials filled with nitrogen, with 5 ml of 1M NaOH to stop microbial activity in the soil, and separate samples of the same soils for mineralogical analysis, stored in small centrifuge tubes. We intended to take flux chamber measurements using an Aeris Mira to measure the gas flux to and from different plots, however battery issues meant that only the first five plots could have

flux measurements made, and at these we measured ~50 different 7 minute flux measurements.

In the Cairngorms, we were joining Liam Wakefield for fieldwork he does regularly for his PhD – he manages 20 'micro' GEM plots[1] and spends two weeks every month collecting various data from each one. These plots cover a variety of different land use types and soil types, and therefore provide a suitable framework for ensuring a range of samples are collected. The 20 plots are divided into 4 categories: natural colonisation, mature thinning, old growth and grazed heathland. These reflect the different forestry conditions of each plot and the different ways land has been managed in the area.

Each plot consists of a 20m x 20m square, with a litterfall trap and soil core at each of 9 points on a uniform grid across the plot, a Bluetooth temperature and humidity sensor on the three points across a diagonal of the square, and a set of respiration collars in the ground going outwards from the center of the plot.

The soil cores had been in place for several months, and were being removed in July so that they could be analysed for the root growth. Since the cores were already not of a constant volume, taking soil samples from the base of them was a time-efficient method of collecting soil samples at depth at uniform points across a plot.

Fig. 1 - The Aeris Mira in use in a Mature Thinning (MT) plot

The number of soil samples taken at each plot varied. Initially 5 vials and 5 centrifuge tubes were taken on every plot, however this was adjusted during the course of the fieldwork to ensure there were enough vials remaining. On a small number of plots, the webbing holding the soil cores had degraded and they could not be removed from the soil, so <5 centrifuge tubes and <3 vials were taken.

Greenhouse gas fluxes were measured in situ by placing a small chamber on the ground and connecting it to the Aeris Mira. Fluxes depend on a variety of factors, which for methane include the presence of methanogens and methanotrophs, organisms which produce and consume methane, respectively. Taking several of these measurements on each plot would give us an opportunity to investigate any correlation between the plot type and the emissions or consumption of greenhouse gases.

Fig. 2 – On the way to a natural colonisation plot

Fig. 3 - An old growth plot, with litterfall traps visible on the right-hand side of the photo

2.3 Analysis of Samples and Data

The methods and instruments used to analyse the samples are as follows:

- A Picarro Isotopic Analyzer was used for concentrations and isotope ratios of CH_4 and CO_2 in the headspace of soil samples
- Gas Chromatography-Mass Spectrometry (GC-MS) was used for carbon and nitrogen composition and isotope data for each sample
- X-Ray Diffraction (XRD) for mineralogical data

2.3.1 Flux Chamber Measurements

The flux chamber measurements we could take were limited due to the battery failure of the Aeris Mira. This meant that the number of measurements taken each day gradually decreased over the first week, before the instrument became unusable due to a faulty battery. However, it seems possible that there is variation between different plot types, as shown in Fig.4. Further fieldwork would be needed to investigate this further.

[redacted]

Fig. 4 - [redacted]

2.3.2 CH_4 and CO_2 Measurements from Samples

A Picarro G2201-I Analyzer was used to determine isotopic CO_2 and CH_4 concentrations in soil samples. This revealed that a large proportion of the samples had elevated CO2 levels, suggesting ongoing respiration in the sample vials and hinting that microbial activity had not been sufficiently stopped. Additionally, although the majority of samples were stored in vials filled with nitrogen, some vials had not been filled with nitrogen and so soils were stored in atmospheric conditions in these vials. To correct for this, the standard atmospheric concentration of methane was subtracted from the values measured. However, some samples that had been stored in atmospheric conditions had < 2 ppm CH_4, so when the correction was applied their concentrations became negative. It is unclear why this happened even in samples where microbial activity appears to have been successfully prevented. Fig. 5 shows the corrected results from this analysis after samples with elevated CO_2 had been removed. Many samples had elevated CO_2 concentrations, so the sample numbers in Fig. 5 are low. Although Fig. 5 suggests that soils on Grazed Heath plots had lower methane concentrations, this is because of negative values which do not make sense, and with n=3 further sampling would be needed to confirm any difference with the other site types.

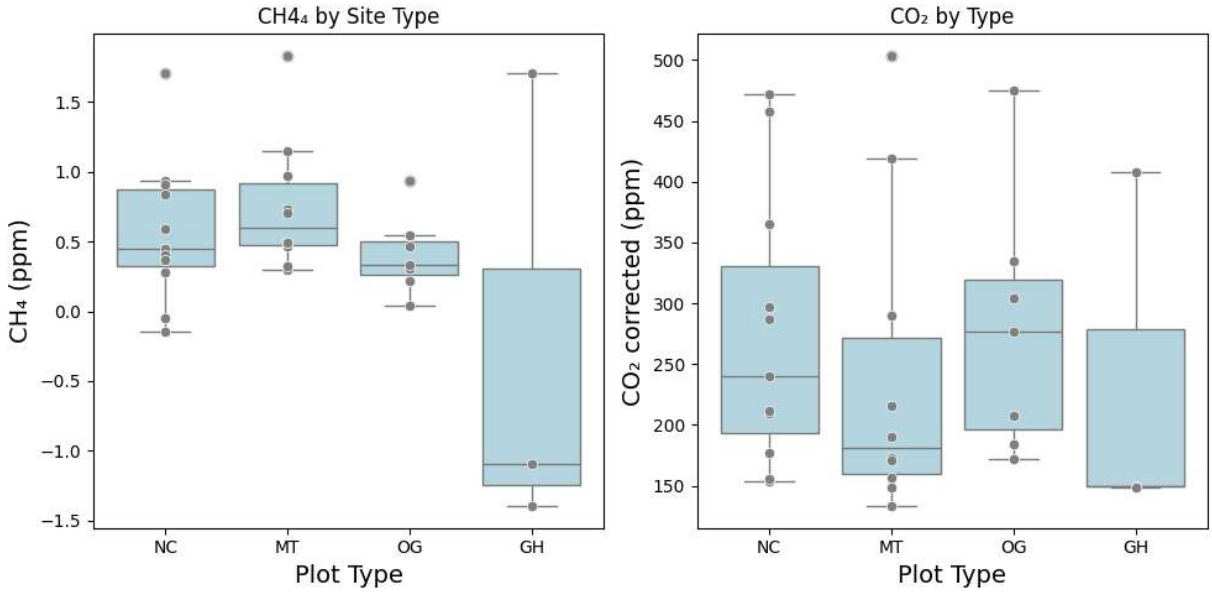

Fig. 5 - CH_4 and CO_2 concentrations for samples from Natural Colonisation (NC), Mature Thinning (MT), Old Growth (OG) and Grazed Heath (GH) plots

2.3.3 Isotopic and compositional analysis of soils

An initial run of 8 samples of 2, 5 and 10 mg from samples from different sites was analysed to establish which weight of sample should be used for all the samples. The weight of sample introduced to the mass spectrometer for isotope analysis must be balanced with the gas dilution factor to ensure that both carbon and nitrogen can be accurately measured within the range of the machine.

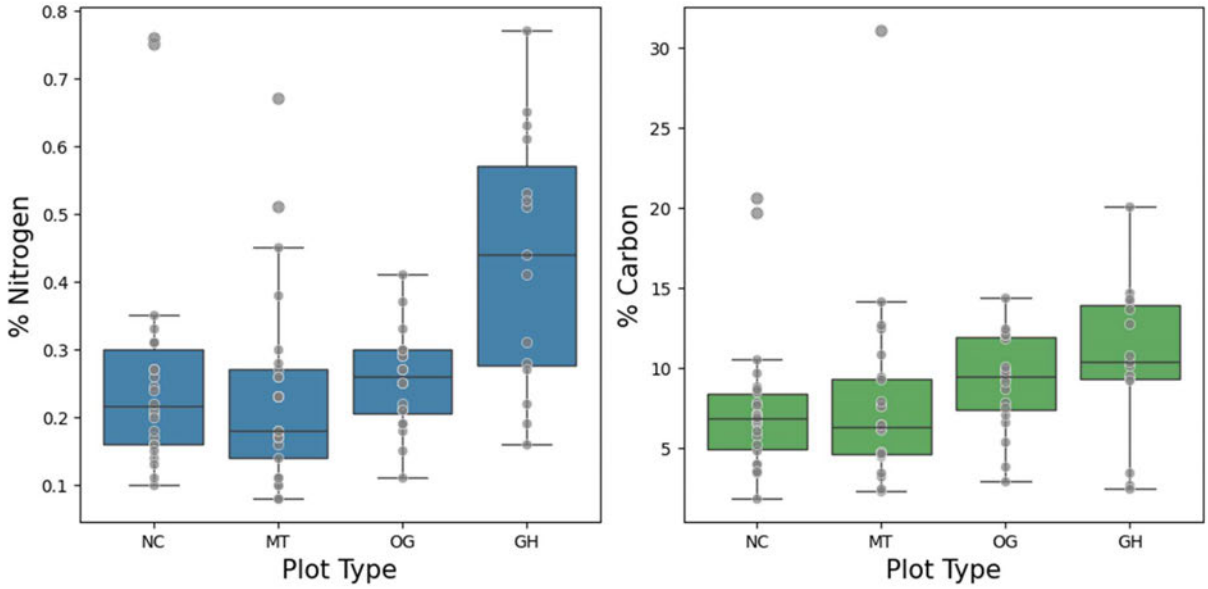

Fig. 6 - Weight % nitrogen and carbon of samples from the four different plot types

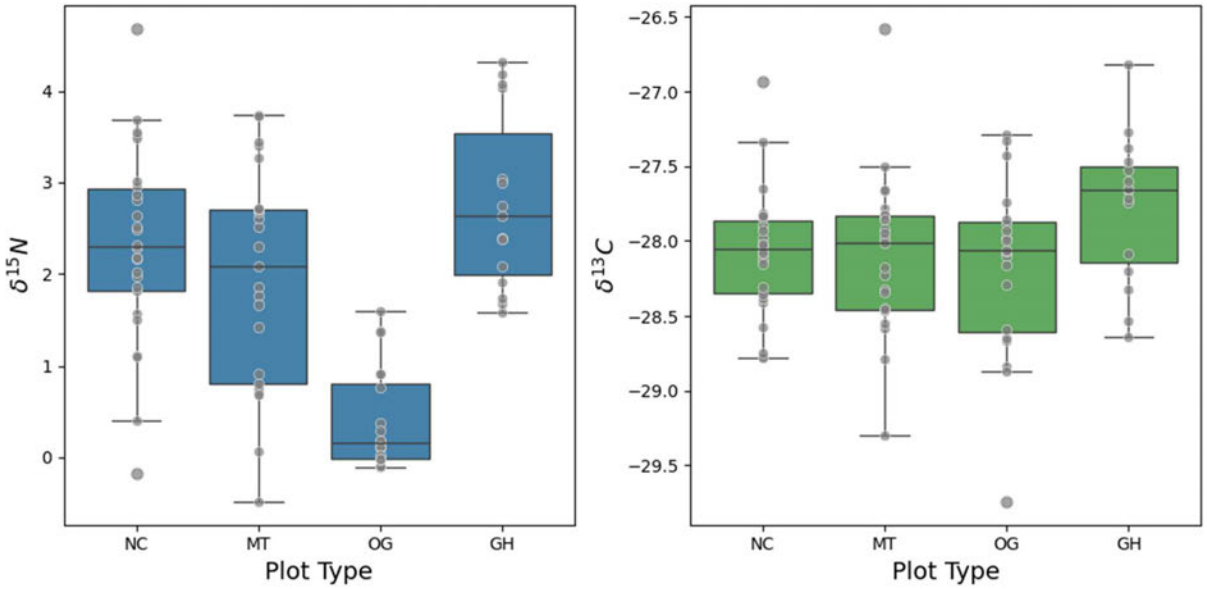

Fig. 7 - $\delta^{15}N$ and $\delta^{13}C$ of samples from the four different plot types

Once the weight was determined, the remaining samples were weighed and analysed. Fig. 6 shows the weight % of nitrogen and carbon found in different plot types. The data suggest that grazed heath sites have more weight percent nitrogen and carbon and so are more organic soils.

Fig. 7 shows the isotope data obtained from this analysis. These are given in delta notation, which measures the 13C/12C or 15N/14N isotope ratio against a standard and reports it in units of parts per thousand (permil, ‰).

2.3.4 X-Ray Diffraction

X-Ray Diffraction (XRD) measures the Bragg diffraction angle in a sample and this can be used to identify the mineral phases present in the sample, by comparing the peaks in each sample's diffraction spectrum to a reference database of known compounds. An initial analysis gives a semi-quantitative indication of which phases are present, and a technique called Rietveld refinement can then be used to more precisely match sample spectra to the known peaks of the phases and produce quantitative data.

Our samples consisted of a combination of quartz, feldspars, and clay minerals. We were primarily interested in the clay minerals, as these vary more between samples and could provide more information to differentiate different soils. However, our samples often had a high proportion of quartz, which causes clay mineral peaks to appear small and less defined. We therefore performed an initial, semi-quantitative analysis of a sample from every plot, and then in the remaining time performed Rietveld refinements for a smaller selection of samples. In addition, we attempted to separate the clay fraction of a subset of samples, to reduce or remove the quartz peaks in their spectra.

Although the XRD software can suggest the spectra that most closely match the peaks in a sample, it is essential to have some knowledge of which compounds it makes sense to see within the context of the sample. The software often recommended synthetic compounds, specific organic solvents or rare minerals which could not have been in these soils as likely matches, because some of their peaks matched some of the peaks produced by our samples. For more uncertain situations, consulting literature about the region can also be helpful for mineral identification.

Rietveld Refinement relies on correct identification of all phases present in a sample. For many samples, attempting to do the refinement revealed that the phases had not been fully or correctly identified so it took further work to reevaluate which phases were present. Table 1 shows some results from Rietveld refinement,

showing the quartz and feldspar (albite and orthoclase) proportions, and some common clay minerals. Illite and muscovite are reported together since they are structurally similar and difficult to distinguish through XRD alone.

	Mineral %						
Site	**Quartz**	**Albite**	**Orthoclase**	**Illite /Muscovite**	**Vermiculite**	**Phlogopite**	**Chlorite**
Insh MT 9	58.0(.5)	24.5(.4)	11.9(.4)			3.7(.4)	
Insh OG 9	57.2(.5)	23.7(.4)	17.6(.4)			1.5(.3)	
Insh NC 9	59.0(.6)	30.5(.5)	10.5(.4)				
Feshie MT 9	65.3(.7)	18.2(.5)	4.8(.3)	6.8(.5)	3.6(.2)		
Feshie OGA	63.5(.5)	26.4(.4)	7.2(.2)		2.4(.1)		
Feshie NC 1	57.8(.5)	23.5(.4)	6.0(.3)	9.2(.4)	3.5(.2)		
Balmoral 1	32.4(.5)	32.6(.7)	22.9(.4)		4.8(.1)		3.5(.3)
Marr 1 9	62(1)	9.0(.4)	9.0(.6)	17(1)			2.6(.4)
Rothie MT 5	56(1)	20(1)	12.8(.4)	5.0(.5)	5.6(.6)		
Marr 2 7	70.1(.8)	8.5(.4)	7.8(.6)	12.2(.8)			
Glen NC 4	50.1(.8)	27.9(.6)	8.1(.4)	14(1)			
Glen MT 9	58.1(.7)	18.4(.5)	10.4(.3)	7.5(.7)	1.6(.1)	4.0(.3)	

Table 1 – Weight % of minerals in a set of samples, with the uncertainty for each value given in parentheses

2.3.5 Clay Separation

In order to get more information about the clay mineral composition of samples, we attempted to separate the clay fraction of 16 samples. This required disaggregating a soil sample in water using an ultrasonic bath, allowing it to settle over time and then removing a section of the mixture at a specific depth using a pipette. Different depths correspond to specific settling velocities and therefore specific sizes of particle.

The available ultrasonic bath was small so this could only be done on a limited selection of samples in the time we had available. This method yielded mixed results and although most samples had most quartz removed a minority retained a significant proportion of quartz.

2.4 Limitations within sample collection and analysis

There were several limitations which affected both fieldwork and the analysis of samples during this project. These have been discussed in the above sections where relevant and are summarised here.

- The battery of the Aeris Mira failed during the first week of fieldwork, meaning flux measurements could only be taken on 5 days. The number of measurements that could be taken decreased each day during this period.
- Taking vials of soil and not immediately measuring them was experimental and would have been more successful if we had used more NaOH in each vial to more effectively prevent microbial activity, which changed the concentrations of CH_4 and CO_2 between taking samples in the field and measuring them in Cambridge.
- We did not have enough time to fully analyse all samples through XRD or to separate the clay fraction from each sample. With additional time, other analysis methods could also have been attempted.
- Less results than expected through both forms of gas analysis meant we had limited data to compare mineralogical and element/isotope composition data to and could draw very limited conclusions about the effect of plot type on greenhouse gas emissions.

3. Recommendations

The most useful next step for this project would be to return to the plots we visited or similar sites and obtain additional flux measurements. At present, it remains difficult to draw any potential correlations with data obtained from samples.
Additionally, if the fieldwork were repeated, more NaOH (for example 10ml) should be used in each vial to ensure that microbial activity is more effectively prevented.

If more data were to be collected to support the data presented here, stronger conclusions could be drawn about how plot type affects greenhouse gas emissions. This information could inform decisions on land management and, at a larger scale, decisions about land management and restoration could have a significant impact on emissions.

Due to time limitations, we focused our analyses on differences between plots rather than examining variation within plots. If further XRD analysis could be carried out, the variability of soil composition within plots could be investigated, and the same could be done with more flux chamber measurements.

4. Conclusion

The fieldwork was largely successful in that we covered all the plots, took over 150 samples and all routine monthly tasks were completed. The main limitation was the battery failure of the Aeris Mira. We had also taken equipment for taking water samples to the Cairngorms, but no surface water was present on or near any of the plots. If surface water had been present, we would have been able to take a different type of sample and obtain an additional dataset.

Due to the failure of the Aeris Mira and adding insufficient NaOH to sample vials, we struggled to obtain data on gases. It was difficult to know in advance how much NaOH was necessary and it's clear that we underestimated. On the other hand, there was no correlation between sample collection date and CO_2 or CH_4 concentration, which demonstrates that collecting these sorts of samples in the field and waiting until the fieldwork is over to analyse them in a lab can produce valid measurements provided that appropriate steps are taken to prevent microbial activity. Additionally, some details of how to take the samples were successfully changed in the field to adjust for problems encountered, for example adapting a centrifuge tube to act as a small funnel to channel soil from the larger opening in the syringe to the smaller opening of the vial.

During the lab work phase of the project, we gathered a significant amount of data through multiple methods, although the limited timeframe meant we couldn't carry this out fully (for example, performing Rietveld Refinements on XRD data from all plots). We also did not have time to fully analyse isotope data or explore reasons why this might vary between plot types.

Overall, throughout the internship problems encountered were countered and adjusted to well where possible and a significant amount of data was gathered, with most analytical methods being successful. The conclusions drawn from the current data are limited, but the internship was successful in many aspects and further fieldwork and analysis could rectify the limitations of the project as it stands.

References

[1] Malhi, Y. *et al.* (2021) 'The Global Ecosystems Monitoring Network: Monitoring Ecosystem Productivity and carbon cycling across the Tropics', *Biological Conservation*, 253, p. 108889. doi:10.1016/j.biocon.2020.108889.