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Atmospheric measurement of point source fossil fuel CO₂ emissions

J. C. Turnbull^{1,2}, E. D. Keller¹, W. T. Baisden¹, G. Brailsford³, T. Bromley³, M. Norris¹, and A. Zondervan¹

¹National Isotope Centre, GNS Science, Lower Hutt, New Zealand

²CIRES, University of Colorado at Boulder, Boulder, CO, USA

³NIWA, Wellington, New Zealand

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Correspondence to: J. C. Turnbull (j.turnbull@gns.cri.nz)

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We use the Kapuni Gas Treatment Plant to examine methodologies for atmospheric monitoring of point source fossil fuel CO₂ (CO₂ff) emissions. The Kapuni plant, located in rural New Zealand, removes CO₂ from locally extracted natural gas and vents that CO₂ to the atmosphere, at a rate of ~ 0.1 Tg carbon per year. The plant is located in a rural dairy farming area, with no other significant CO₂ff sources nearby, but large, diurnally varying, biospheric CO₂ fluxes from the surrounding highly productive agricultural grassland. We made flask measurements of CO₂ and ¹⁴CO₂ (from which we derive the CO₂ff component) and in situ measurements of CO₂ downwind of the Kapuni plant, using a Helikite to sample transects across the emission plume from the surface up to 100 m.a.g.l. We also determined the surface CO₂ff content averaged over several weeks from the ¹⁴C content of grass samples collected from the surrounding area. We use the WindTrax plume dispersion model to compare the atmospheric observations with the emissions reported by the Kapuni plant, and to determine how well atmospheric measurements can constrain the emissions. The model has difficulty accurately capturing the fluctuations and short-term variability in the Helikite samples, but does quite well in representing the observed CO₂ff in 15 min averaged surface flask samples and in ~ 1 week integrated CO₂ff averages from grass samples. In this pilot study, we found that using grass samples, the modeled and observed CO₂ff emissions averaged over one week agreed to within 30 %. The results imply that greater verification accuracy may be achieved by including more detailed meteorological observations and refining ¹⁴C sampling strategies.

1 Introduction

Emissions of fossil fuel carbon dioxide (CO₂ff) are the main driver of the post-industrial increase in atmosphere CO₂ mole fraction (IPCC, 2007; Tans et al., 1990). Knowledge of the sources and magnitude of CO₂ff emissions is critical to improving our under-

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standing of Earth's carbon cycle and climate system. Large point sources (electricity generation and large-scale industry) make up roughly one third of all CO₂ff emissions (IPCC, 2007). These point sources are the first CO₂ff emissions sector to be regulated under various national and international carbon tax and cap and trade schemes (e.g. Australian Government, 2013; Government of India, 2010). Point sources are also the most likely candidates for emissions reduction by carbon capture and sequestration (IPCC, 2007).

The success of regulatory schemes depends on the ability to demonstrate that emissions targets are actually achieved. Regulating emissions without monitoring “is like dieting without weighing oneself” (Nisbet and Weiss, 2010). Currently, point source emissions are determined using “bottom-up” estimates from self-reported inventory data. Emissions estimates are typically obtained from the volume of fossil fuel (coal, oil or natural gas) consumed and carbon content of that fuel (Andres et al., 2012; Gurney et al., 2009). Uncertainties in the calculated emissions arise from uncertainties in the amount of fuel used, which may include transcription errors and errors in collating the data, and from uncertainties in the carbon content of the fuels themselves. In some countries, smokestack CO₂ emissions are directly measured (e.g. CEMS in the US), with a likely uncertainty of 20 % (Ackerman and Sundquist, 2008). In upcoming regulatory environments, it is also possible that deliberate falsification of reported emissions will occur. Thus there is a need for independent, objective measurements of these emissions both to improve the accuracy of the reported emissions, and to provide independent monitoring as we move into a regulatory environment.

Atmospheric measurements of recently added fossil fuel CO₂ mole fraction can be combined with knowledge of atmospheric transport in a “top-down” approach to infer the CO₂ff emission flux, providing an emission estimate with quantifiable uncertainties, that is independent from the bottom-up approaches. In the top-down approach, two key components are needed: measurements of CO₂ff mole fraction and a model of the atmospheric transport.

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CO₂ff cannot be directly measured in the atmosphere, since CO₂ff is but one component of the total CO₂ mole fraction. The CO₂ background mole fraction is ~ 400 parts per million (ppm) and increasing by 1–2 ppm yr⁻¹ primarily due to global CO₂ff emissions (IPCC, 2007; Conway et al., 2011). Large diurnal and seasonal cycles are superimposed on this, mainly due to the seasonally and diurnally varying exchange with the terrestrial biosphere by photosynthesis and respiration as well as biomass burning (IPCC, 2007). Ocean exchange of carbon, although having a gross flux of similar magnitude, is of lesser importance over the land areas where most CO₂ff emissions occur. The CO₂ mole fraction at a given site will also vary with meteorology as different air masses are advected to the location and as vertical mixing varies through time. When the CO₂ff mole fraction added by a point source is large relative to the variability in the CO₂ background, CO₂ measurements alone may be sufficient to determine added CO₂ff mole fraction. However, in many cases, variability in CO₂ background is large relative to the added CO₂ff mole fraction. This is particularly important when there is a strong biospheric carbon flux nearby. Loh et al. (2009) used the WindTrax Lagrangian particle dispersion model to evaluate atmospheric measurements of point source CO₂ and methane emissions at a local scale. They showed that the method could be useful for methane, where the emissions were large relative to the methane background variability, but was more difficult for CO₂, where background variability was a dominant source of uncertainty.

CO₂ derived from fossil sources is entirely free of the isotope ¹⁴C, which is removed by radioactive decay with a half-life of 5730 yr (Karlen et al., 1968). All other sources of CO₂ contain ¹⁴C at levels close to that of the current atmosphere (Randerson et al., 2002; Turnbull et al., 2009). Thus measurements of the radiocarbon content of CO₂ ($\Delta^{14}\text{CO}_2$) can be used to quantify the CO₂ff mole fraction (Suess, 1955; Tans et al., 1979). In the current atmosphere, 1 ppm of added CO₂ff decreases $\Delta^{14}\text{CO}_2$ by 2.6 % (Turnbull et al., 2011a).

$\Delta^{14}\text{CO}_2$ can be determined directly from measurements of ¹⁴C in CO₂ extracted from flask samples of air (e.g. Turnbull et al., 2007; Graven et al., 2007). The ¹⁴C content

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of CO₂ is also maintained in carbon assimilated by plants so that the average $\Delta^{14}\text{C}$ of the assimilated CO₂, and hence the overlying atmosphere at the time of uptake can be determined from the ¹⁴C content of plant materials (e.g. Hsueh et al., 2007; Palstra et al., 2008). CO₂ assimilation rates vary with local climatic weather conditions, plant type, and plant growth phase, meaning that a complex weighting function may be needed to describe the averaging period (Bozhinova et al., 2013). CO₂ can be absorbed into basic (sodium hydroxide, NaOH) solution from the atmosphere, and this is another commonly used method to obtain time-integrated average $\Delta^{14}\text{C}$ in the atmosphere (e.g. Levin et al., 2010; Currie et al., 2009; van der Laan et al., 2010).

A number of studies have used correlate tracers to estimate CO₂ff. In this method, a trace gas that is co-emitted with CO₂ff, such as carbon monoxide (CO), is monitored in the atmosphere. If the emission ratio of CO : CO₂ff is known, then CO₂ff can easily be determined (Levin and Karstens, 2007). CO is much more readily measured than $\Delta^{14}\text{CO}_2$, so this method can obtain CO₂ff mole fractions at higher resolution (Vogel et al., 2010; Turnbull et al., 2011b). Unfortunately, the emission ratio CO : CO₂ff is imperfectly known, variable by combustion efficiency and method, and large power plants typically emit little or no CO (USEPA, 2012). Other correlate tracers have been considered, including sulphur hexafluoride (Turnbull et al., 2006), perchloroethylene (Miller et al., 2012), and acetylene (LaFranchi et al., 2013), but most of these tracers are only indirectly associated with CO₂ff combustion sources, so are likely not appropriate for monitoring of individual point source emissions. Further, the amount of correlate trace gases emitted directly from the point source may vary widely depending on the fuel used, combustion process, and “scrubbing” of pollutant gases before they are emitted to the atmosphere. Hence $\Delta^{14}\text{CO}_2$ remains the most robust method for quantifying CO₂ff across a range of environments.

Once the CO₂ff mole fraction is measured, the emission flux can be modeled or estimated by using a description of atmospheric transport from the emission source to the measurement location. This has been performed at various scales using techniques ranging from a simple mass balance model for urban scale emissions (Turnbull

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et al., 2011b), to a Lagrangian particle dispersion model for regional scale (Turnbull et al., 2011a), to tracer : tracer flux estimates using radon (Van der Laan et al., 2010). Modeling studies have demonstrated that long-term trends in regional CO₂ff emissions could be determined from a combination of $\Delta^{14}\text{C}$ observations and regional or global modeling (Levin and Rödenbeck, 2007). Monitoring of CO₂ff from point sources has not previously been attempted, but other species emitted by point sources have been monitored in the atmosphere. Mass balance modeling has been successfully used to monitor ozone from large power plants (Trainer et al., 1995; Ryerson et al., 2001). This method uses aircraft sampling at high temporal resolution across transects downwind of the point source, and a simple description of plume dispersion to quantify emissions. It can estimate emissions to within $\sim 50\%$ under consistent wind conditions when emissions are large relative to the background mole fraction. More commonly, Lagrangian atmospheric transport modeling is used to both identify emission sources and to quantify those emissions. Point source emissions of numerous pollutant species have been evaluated using this method, including SO₂, NO_x and particulates (e.g. Dresser and Huizer, 2011; Ghannam and El-Fadel, 2013). These studies are focused on air quality impacts, and there is little detailed information about the quality of total flux estimates in the models.

Here we examine methodologies for atmospheric monitoring of point source CO₂ff emissions. Our experimental site is a small, isolated industrial CO₂ff emission source in rural New Zealand. Our focus is on CO₂ff quantification from $\Delta^{14}\text{CO}_2$ measurements, examining two different sampling methods: snapshot flask sampling in the atmosphere, and time-integrated sampling from grass. We use a Lagrangian plume dispersion model run forward in time to predict the CO₂ff mole fraction from the known emissions and meteorological data. We then compare the predicted and observed CO₂ff mole fractions to examine the different methods.

Our goal is to evaluate the methods from both scientific and application perspectives, considering:

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- Measurement cost and complexity. How easily can the sampling method be deployed at field sites, and how difficult is the measurement?
- What sampling methods are most compatible with the strengths of the current generation of atmospheric transport models? Models imperfectly simulate atmospheric transport, and emissions detection will be more or less robust depending on how the model is used.
- What are the uncertainties in the estimate of the CO₂ff emission flux, and how could these uncertainties be reduced?

2 Methods

2.1 Sampling location and point source description

Our experimental site is the Kapuni Gas Treatment Plant, located in rural New Zealand and run by Vector (Fig. 1). The Kapuni plant processes natural gas extracted from nearby onshore natural gas wells in the Taranaki Basin. Natural gas from this field contains ~ 40 % CO₂. At the Kapuni plant, the CO₂ is stripped from the natural gas and vented to the atmosphere at a rate of ~ 0.1 TgCyr⁻¹ (NZMED, 2010). This equates to average emissions of about 3300 gC s⁻¹. The emissions are small relative to many industrial facilities and power plants around the world, for example, the world's largest power plant (Taichung, Taiwan) emits ~ 300 000 gCs⁻¹ (Ummel, 2012; Wheeler and Ummel, 2008). We recognize that there will be differences in applying the results of our study to larger emission sources.

The Kapuni plant is located in a rural dairy farming area, with no other significant CO₂ff sources nearby. The Agri urea plant located 500 m west the Kapuni plant does emit a small amount of CO₂, but this is approximately 1 % of the Kapuni plant emissions (NZMED, 2010). We avoid sampling close to local roads, and also note that traffic counts are low (one vehicle every ~ 10 min), so the overall contribution of traffic CO₂ff

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in our measurements is expected to be minimal. There is a small CO₂ff source from residential heating using natural gas and from farm vehicle exhaust, but farm and residential power is typically from mains electrical supply, with no local CO₂ff emissions. The farmland is highly productive grassland, with large, diurnally varying, biospheric CO₂ fluxes. The surrounding terrain is relatively flat, with elevations within two km of the Kapuni plant varying by about 10 m. There are some trees of ~ 20 m height to the south and west of the plant, and a dip to lower elevation directly to the east where a stream flows (Fig. 1).

2.2 Sampling methods

2.2.1 Kite platform

A Helikite (a patented combination of helium balloon and kite, Allsopp Helikites Limited) was used to sample air from the surface up to 100 m above ground level, downwind of the Kapuni plant, on 26 October 2012. The Helikite was fitted with a GPS (Garmin 60CSx) to determine location at 1 s time resolution. A tether sonde (Graham Digital Design, Amberley, New Zealand) with an anemometer was used to measure wind speed and wind direction, temperature and pressure at 10 s resolution. Transmissions of data were received at a ground station providing real time height and wind data. The anemometer cups tangled with the tether line for short periods during the measurement campaign, identified as zero wind speeds, and we exclude these periods from our dataset. 300 m of 4 mm OD polyethylene (Leda Extrusions, New Zealand) tubing was attached to the kite tether close to the tether sonde, bringing air from the kite to our mobile lab. A diaphragm pump (KNF, model # N186.1.2KN.18) was placed halfway along the inlet line on the ground to improve flow rate.

The inlet line ran to a cavity ring down to a spectrometer (CRDS, Picarro model G1301) inside a mobile laboratory. The CRDS provided real time mole fractions for CO₂ in the air arriving from the intake on the Helikite. Individual observations were made every ~ 2 s, and measurement precision for CO₂ is better than 0.1 ppm. The CO₂

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measurements are referenced to the World Meteorological Organization WMO X2007 CO₂ mole fraction scale to within 0.05 ppm, and one-minute averages of transfer gases have also been determined to a standard deviation on replicates of 0.05 ppm. Methane (CH₄) was simultaneously measured but is not discussed here, since CH₄ sources in the area are complex. The transit time from the inlet to the mobile lab was determined from timed puffs of (high CO₂) human breath, and determined as 173 s. The flask filling and CO₂ mole fraction measurements are adjusted for this time delay and matched to the GPS and meteorological measurements, which were operating on the same timestamp.

Previously evacuated glass flasks (0.8–2 L volume) were filled by opening a valve directly upstream of the CRDS unit without reducing sample flow to the CRDS. The air was dried using magnesium perchlorate and then passed through a diaphragm pump to fill the flasks to a pressure of 2 bar absolute. Flask fill times varied from 2 to 6 min, depending on the flask volume. We determine the CO₂ mole fraction in the flask sample as a weighted average of the CO₂ mole fraction measured on the CRDS made during the flask filling time. The weighting function for the flask fill was obtained by logging the pressure increase in a flask, as a function of time, for the flask sampling pump (KNF, model N814KNE) and scaling the resulting function by flask size. The weighting function was then approximated by fitting a polynomial to the pressure change through time, which well approximates the fill rate ($r^2 = 0.99$).

2.2.2 Surface flasks

Five surface samplers were also deployed on 26 October 2012 at one location upwind of the Kapuni plant and four locations downwind and beneath the Helikite track. For each sampler, the air is drawn in through an inlet line (6 mm OD, polyethylene) from an intake 3 m off the ground. A deflated 4 L tedlar bag is slowly filled at a designated flow rate from a manifold operating at a preset overpressure. In this case, three liters of air was collected over 15 min. Each sampler was preprogrammed to purge the sample lines for one minute and then collect a 15 min sample once every 18 min. After sampling

was complete, a small aliquot was used to determine the CO₂ mole fraction on the CRDS, and then the air sample was transferred into a pre-evacuated glass flask using the flask pump and pressurization method described above. A subset of these surface samples were selected for Δ¹⁴CO₂ analysis.

2.2.3 Grass samples

When plants photosynthesize CO₂, the ¹⁴C/¹²C ratio of that CO₂ is altered only by isotopic fractionation during photosynthesis (Suess et al., 1955). The ¹⁴C/¹²C fractionation can be quantified from the ¹³C/¹²C fractionation (δ¹³C), and Δ¹⁴C for CO₂ and plant material is normalized to a δ¹³C of -25‰ (Stuiver and Polach, 1977). Thus the Δ¹⁴C of the plant material can be considered identical to the photosynthesized CO₂, integrated over the period of plant growth.

A number of studies have shown that plant material records the broad spatial patterns of Δ¹⁴CO₂ in the modern atmosphere, using corn leaves (Hsueh et al., 2007; Riley et al., 2008), wine ethanol (Palstra et al., 2008), and rice grains (Shibata et al., 2005). Several of these studies compared the observations with model predictions, and achieved reasonable agreement at the continental and regional scales, mostly reflecting the spatial pattern of CO₂ff emissions. However, the exact Δ¹⁴C measured will depend on the growth period of the plant, variations in photosynthetic uptake during the growth period (e.g. weather conditions) and how the plant allocates the photosynthesized carbon amongst different parts of the plant (Bozhinova et al., 2013). The resulting sample integrates over variable rates of photosynthesis but can generally be viewed as an integrator of the daytime photoperiod Δ¹⁴CO₂.

We collected samples of grass from farmland around the Kapuni plant on 15 August 2012 and 24 October 2012. The farmland in this region is divided into small paddocks (fenced fields), and each paddock is grazed by the dairy cow herd for one day every 18–25 days. The grass grows ~ 20 cm during the regrowth period, and regrazing occurs before any flowering has begun. We sampled grass from paddocks that had

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been grazed 1–2 weeks previously, so our samples likely represent an average over 1–2 weeks. As all growth is in vegetative phase, allocation of carbon to the leaves is likely consistent across the growth period, but there will be some variability in uptake with weather patterns, which we do not account for. We make the simplifying assumption that the leaf samples represent the daytime average for the one week period preceding sampling. Sample locations were determined using a handheld GPS, and locations close to obstructions such as hedges and buildings were avoided, as were sites close to roads.

2.3 ¹⁴C measurement and CO₂f determination

CO₂ was cryogenically extracted from the flask samples by slowly flowing the air over a Russian doll type liquid nitrogen trap (Brenninkmeijer and Röckmann, 1996). In the case of grass samples, pieces of grass were acid washed (0.5 M HCl at 85 °C for 30 min) to remove any adhering material, then rinsed to neutral and freeze dried, prior to sealed tube combustion with copper oxide and silver wire at 900 °C. The resulting CO₂ was cryogenically purified. CO₂ from either sample type was then reduced to graphite with hydrogen over an iron catalyst, using methods adapted from Turnbull et al. (2007). The ¹⁴C content was measured using accelerator mass spectrometry at GNS Science (Baisden et al., 2013).

Measurement uncertainty in each sample was derived from three sources: counting error of ¹⁴C atoms in the sample, counting error in the standards used for calibration, and additional variability amongst those standards. While counting errors in the measurement process are governed by Poisson statistics, we regard the variability in excess of counting errors as being representative of a systematic uncertainty in the measurement and/or sample preparation. Since these three error sources are assumed independent, they are added in quadrature. All samples in each experimental dataset (two grass sampling experiments, and one flask experiment) were measured in the same AMS measurement wheel. Therefore, we do not include additional uncertainty due to wheel-to-wheel scatter in secondary standards (Turnbull et al., 2007;

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Graven et al., 2007). The grass samples were measured to 1 000 000 ¹⁴C counts or until the graphite target was exhausted, resulting in overall, single sample precision of 1.1–1.5 ‰. Anticipating large CO₂ff contributions in the flask samples, they were counted to 650 000 counts or until the graphite target was exhausted. This, combined with poorer AMS stability during the flask sample wheel measurement (as derived from the scatter of the calibration standards) resulted in overall uncertainties of 2.0–2.5 ‰. Between 4 and 10 secondary standards were also measured in each wheel, and the scatter of these secondary standards within each wheel is, in all cases, consistent with their assigned uncertainties.

CO₂ff is determined from the Δ¹⁴C of the grass or flask sample, taking advantage of the fact that CO₂ff contains zero ¹⁴C (Δ¹⁴C = –1000 ‰), whereas all other CO₂ sources have Δ¹⁴C close to that of the atmosphere. The CO₂ff added relative to a clean air background measurement can be determined using mass balance (Levin et al., 2003).

When the CO₂ content of the observed sample is known, as for our flask samples, CO₂ff is calculated from

$$\text{CO}_{2\text{ff}} = \frac{\text{CO}_{2\text{obs}}(\Delta_{\text{obs}} - \Delta_{\text{bg}})}{\Delta_{\text{ff}} - \Delta_{\text{bg}}} - \beta \quad (1)$$

following Eq. (3) in Turnbull et al. (2009). CO₂obs is the CO₂ mole fraction in the observed sample, Δ_{obs} and Δ_{bg} are the Δ¹⁴C of the observed sample and background sample, respectively. Δ_{ff} is the Δ¹⁴C of CO₂ff, and is assigned to be –1000 ‰. Δ_{bg} for the flask samples was determined from surface flasks collected upwind of the Kapuni plant (Fig. 1) on the same day, at about the same time of day.

β is a small correction term to account for the fact that the Δ¹⁴C of CO₂ from other sources may be slightly different from that of the atmosphere, and may include contributions from heterotrophic respiration, oceanic CO₂ sources and nuclear-industry-produced ¹⁴C. Here, we set β to zero, and justify this choice for each possible contribu-

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tion. The background sample was collected close to our observational sampling sites in both space and time, so that at our site a few tens of kilometers from the ocean, it is likely that ocean CO₂ exchange has altered $\Delta^{14}\text{C}$, but this alteration occurred in both background and observed samples. There is no nuclear industry activity in New Zealand and only a handful of reactors elsewhere in the Southern Hemisphere (Graven and Gruber, 2011), so we assume there is no nuclear industry bias in our samples. Of most importance is the effect of heterotrophic respiration occurring throughout the landscape. This is expected to have equally impacted both background and observed $\Delta^{14}\text{C}$, and hence the heterotrophic respiration correction is implicitly included in the background. We tested how important this assumption might be, using the Biome-BGC model v4.2 (Thornton et al., 2002, 2005), calibrated to New Zealand pasture (Baisden and Keller, 2013). The Biome-BGC model is an ecosystem process model that simulates the biological and physical processes controlling cycles of carbon, nitrogen and water of vegetation and soil in terrestrial ecosystems. Important inputs include weather conditions at a daily time step and site-specific information such as elevation, soil composition and rooting depth. The model has a set of 43 ecological parameters that can be customized for a particular ecosystem. In previous work, using pasture clipping data from several sites distributed across New Zealand, we adjusted selected model parameters to fit modeled pasture growth to the data to obtain a national model of pasture production for both dairy and sheep/beef pasture at a grid scale of ~ 5 km (Keller et al., 2013). We ran the dairy model for the grid location that includes the Kapuni processing plant to arrive at an estimate for the respiration CO₂ flux and its $\Delta^{14}\text{C}$ at the sampling sites. We assume a boundary layer flushing time of one day at our site, and using the Biome-BGC estimates, β due to the heterotrophic respiration flux could be 0.2–0.4 ppm. This is the maximum bias if the heterotrophic respiration flux occurs at the observation site but not in the background, an unlikely scenario.

In the case of the grass samples, the CO₂ content of the sampled air is unknown, so CO₂ff was calculated using the slightly different formulation reported as Eq. (6) in Turnbull et al. (2009), which requires that the CO₂ of the background air (CO₂bg) be

known.

$$\text{CO}_{2\text{ff}} = \frac{\text{CO}_{2\text{bg}}(\Delta_{\text{obs}} - \Delta_{\text{bg}})}{\Delta_{\text{ff}} - \Delta_{\text{obs}}} - \beta' \quad (2)$$

The grass Δ_{bg} values were from samples collected ~ 20 km to the north of the Kapuni plant in similar dairy farmland, on the same day as the observed samples were collected. The background CO_2 mole fraction was estimated as 390 ppm, from measured values at Baring Head, New Zealand at the same time (Currie et al., 2009; dataset extended to 2012). A 4 ppm error in the choice of CO_2 observed (Eq. 1) or background (Eq. 2) value equates to a 1 % error in the determined $\text{CO}_{2\text{ff}}$ mole fraction, small relative to the measurement and atmospheric transport uncertainties. β' is also a bias correction, formulated slightly differently to β , but accounting for the same biases. We also set this value to zero.

2.4 Atmospheric transport model

WindTrax (Thunder Beach Scientific, Nanaimo, Canada) is a Lagrangian stochastic particle dispersion model, designed for modeling short-range atmospheric dispersion (horizontal distances of less than 1 km from source). The physics are described by Flesch et al. (2004) and Wilson and Sawford (1996). We run the model in forward mode, in which $\text{CO}_{2\text{ff}}$ emissions are assumed known and gas concentrations or mole fractions at any given location are unknowns to be determined. We set the model to release 10^5 particles from the simulated stack at every time step, enough to reduce model uncertainty to satisfactory levels (the more particles released, the lower the uncertainty in model predictions). Each particle is transported according to the model physics and specified meteorological conditions. Concentration sensors are placed at the observation locations, and the model outputs a prediction of $\text{CO}_{2\text{ff}}$ mole fraction at each sensor for each time step. The wind speed and direction (along with other atmospheric conditions), combined with the prescribed emission rate, determine the predicted $\text{CO}_{2\text{ff}}$ mole fraction at that location and time. We then compare the model prediction with the

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observed mole fractions. Alternatively, the model can be run in backward mode to predict the emissions from the observed CO₂ff mole fractions, but this is computationally more expensive, and forward mode allows us to also investigate the broader patterns of the predicted plume dispersion. It is important to note that the model is statistical, not deterministic, so the outcome of model runs will vary even with the same initial conditions and parameters. This is a source of model error that is quantified at each time step. The terrain elevation varies by about 10 m across our sampling area, and this is not accounted for in our model simulations.

Daily emissions were provided by the Kapuni plant operator, Vector (P. Stephenson, personal communication, 2013). We assume constant emissions for each 24 h period, although emission rates may vary by up to 3 % during that time. Emission rates were 3100–3750 g C s⁻¹ in the two weeks of August 2012 preceding the day when the first grass samples were collected, 2700–3,500 g C s⁻¹ during the two weeks prior to grass sample collection on 25 October 2012, and 3200 g C s⁻¹ on 26 October 2012 when the flask samples were collected. Emissions are from two stacks, both 35 m high, and ~ 10 m apart. In the model, we assume that the stacks are close enough in space to be modeled as a single point source. We release the emissions from the known stack height of 35 m a.g.l. We also tested an alternative scenario where emissions were released from a height of 45 m a.g.l., 10 m higher than the actual stack height, to account for buoyant rise of the warm, moving plume (Briggs, 1975). This value was determined using the known emission temperature (80–85 °C) and stack diameter (0.6 m), and a velocity estimated from the CO₂ emission rate. Under the unstable atmospheric conditions during our measurement campaigns, the difference in effective stack height did not make a significant difference in our results.

For the flask samples, we use a model time step of approximately 10 s, commensurate with the wind data collected from the Helikite at 10 s resolution and fed into the model. We note that previous studies have shown that WindTrax performs best over much longer averaging periods (Flesch et al., 2004), on the order of 10–30 min, and using the model with very short time intervals (i.e. less than 1 min) is problematic, as

the relationships built into the model assume atmospheric equilibrium, which might not be the case at such short time scales. Our results should be interpreted with caution, as they might reflect the inability of the model to resolve atmospheric instability and rapid fluctuations at such fine time scales.

5 In the case of the grass samples, 10 min time steps were used with wind data from the stationary meteorological station installed close to the site (Fig. 1). Wind information was not available from the local site for the August grass growth period; instead we used the meteorological data obtained for the week directly following the grass sampling. We justify this by comparing data from the two weeks at a long-term station
10 ~ 20 km away in Hawera, which provides hourly temperature and pressure data. This long-term station data could not be used as a proxy for wind speed and direction at our Kapuni site because the particular locations and orientations of the two sites relative to Mt Taranaki result in large differences in wind direction between the two sites. However, we found that the weeks preceding and following our August grass sampling had
15 similar wind patterns at Hawera.

In the absence of detailed measurements of turbulence and atmospheric stability, a general stability category was specified in WindTrax using the Pasquill–Gifford classes (Pasquill, 1961; Gifford, 1961). The Monin–Obukhov length L (a meteorological measurement of stability) was then calculated by the model along with other related
20 variables. As the measurements necessary for a more exact quantification were not made, we assumed “slightly unstable” conditions for the flask samples, and “moderately unstable” conditions for the grass sampling. The meteorological conditions during the grass sampling periods may more correctly match neutral to slightly unstable conditions, but we found that under these conditions, the model underestimated the
25 observed plume dispersion.

The model output was sampled at the location and corresponding time step(s) for each sample. As the Helikite moved during the flask filling procedure, the modeled sensor was moved both horizontally and vertically according to the location obtained from the GPS on the kite. For the simulation with the grass samples, the model was

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sampled at the GPS location and 1.5 m above ground level to avoid surface effects. We found that grouping several model sensors around the GPS location and then averaging their output was more accurate than using just one; in all results reported for the grass samples, we used four sensors placed at the corners of a square 30.5×30.5 m, with the actual sample location in the center. The model output was averaged over all daytime time steps for the week prior to grass sampling to arrive at a final predicted CO_{2ff} mole fraction.

3 Observational results

3.1 CO₂ measurements

During the Helikite sampling period on 26 October 2013, the measured CO₂ mole fraction varied from 360 ppm at ground level to 592 ppm in samples within the Kapuni emission plume (Figs. 2 and 3). The emission plume moved during the four-hour sampling period, so that our Helikite observed the plume at different locations across the north-south transect at different times. The plume also moved in the vertical, and was more dispersed at some times than at others.

In Fig. 3, strong photosynthetic drawdown can be seen in the ~ 7 m above the surface, with CO₂ mole fractions as low as 360 ppm, about 30 ppm of drawdown. Above 7 m, the CO₂ background can be estimated from the lowest CO₂ mole fractions observed (Fig. 3). This background varied from 390–395 ppm with height, and also evolved during the four-hour measurement time. CO₂ mole fraction in the up-wind surface flask samples (collected three meters above ground) varied from 386.3 to 387.4 ppm over the four hour measurement period.

We determine the CO₂ enhancement over background (Δ CO₂) in each CRDS or flask sample by subtracting the estimated height-dependent CO₂ background value (Fig. 3) from the observed CO₂ mole fraction. In this method, uncertainty in the background mole fraction propagates directly to uncertainty in the CO₂ enhancement. The

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CO₂ measurement uncertainty is small relative to the background uncertainty, so the total uncertainty in the enhancement for this dataset is determined from the range of background CO₂ values, and is ± 15 ppm in the lowest 7 m, and ± 2.5 ppm above 7 m. This level of uncertainty is quite significant for most of the measurements, except those

5 where the enhancements are very large. The median CO₂ mole fraction for samples taken above 7 m was 397 ppm, so that the majority of measurements are difficult to distinguish from the CO₂ background of 390–395 ppm.

3.2 CO₂ and CO₂ff from ¹⁴C in flasks

CO₂ff in the flask samples ranged from 0.6 to 52 ppm, with one-sigma uncertainties of

10 1.3 ppm (Fig. 4). Background $\Delta^{14}\text{C}$ is not changed by CO₂ drawdown, and hence was less variable than background CO₂. Δ_{bg} varied from 39.2 ± 2.6 to 43.9 ± 2.8 ‰, (these values do not differ significantly, $p = 0.39$).

We compare the ¹⁴C-derived CO₂ff with ΔCO_2 using the ratio $\Delta\text{CO}_2:\text{CO}_2\text{ff}$ ($R_{\text{CO}_2:\text{CO}_2\text{ff}}$) (Fig. 5). If the CO₂ emitted from the Kapuni plant is entirely fossil-derived,

15 then ΔCO_2 should be equal to CO₂ff, and $R_{\text{CO}_2:\text{CO}_2\text{ff}}$ equal to one. We find that for the 15 Helikite samples, $R_{\text{CO}_2:\text{CO}_2\text{ff}} = 1.3 \pm 0.4$ ppm ppm⁻¹, suggesting that there may be a contribution of non-fossil CO₂ in the Kapuni emission plume. However, when we increase the CO₂ background values by 3 ppm (within the range of background variability), we find $R_{\text{CO}_2:\text{CO}_2\text{ff}} = 1.0 \pm 0.3$ ppm ppm⁻¹ (blue points in Fig. 5), indicating that the

20 plume CO₂ is entirely fossil derived. The variability in $R_{\text{CO}_2:\text{CO}_2\text{ff}}$ is therefore likely predominantly due to uncertainties in determining the flask ΔCO_2 and background CO₂, and also to uncertainties in CO₂ff which are important in the lower mole fraction samples. The emitted plume appears to be entirely fossil-derived, within the uncertainties of our measurements.

3.3 CO₂ff from grass samples

The derived CO₂ff in the grass samples for the two sampling dates of 14 August and 24 October 2012 are shown in Fig. 6. Grass samples were measured to $\Delta^{14}\text{C}$ precision of 1.1 to 1.5 ‰. This equates to 0.6 to 0.7 ppm uncertainty in CO₂ff.

CO₂ff mole fraction derived from the grass samples varies from 0.4 to 3.9 ppm in the August samples, and -0.2 to 17.0 ppm in the October samples. A negative CO₂ff value is non-physical, but -0.2 ppm is within one sigma of zero. The highest CO₂ff values were observed in areas that were most consistently downwind of the plant, and locations closer to the plant typically had higher CO₂ff values (Fig. 6). In August, the wind direction was somewhat variable, dominantly bringing the plume to the east or south of the plant, but sites to the northwest were also occasionally downwind, resulting in small CO₂ff values at all these locations. In October, the winds were consistently from the west, resulting in larger enhancements to the east of the Kapuni plant than in the August samples, and no CO₂ff detected in the sample to the northwest.

4 Comparison of observation and model CO₂ff

4.1 Kite and surface flask samples

The model predicts CO₂ff in the Helikite and surface flask samples of 0 to 19.1 ppm. The model results for the kite samples are generally lower than the observed CO₂ff (Fig. 7), except for a few samples where observed CO₂ff was quite small. Other work shows that small errors in the simulated wind direction can result in large errors in the modeled CO₂ff mole fraction for individual samples (Dresser and Huizer, 2011). Thus the model may frequently miss the location of the plume over short time periods of a few minutes when the wind direction is fluctuating rapidly. We deliberately sampled in the center of the plume in the area of highest mole fraction, and the likelihood of modeling this specific point accurately is low given the error inherent in these types of models.

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The assumption that the time-averaging interval represents an equilibrium state of the atmosphere is built into the model; however, these conditions are most likely not met in our simulations. As mentioned earlier, WindTrax is known to perform poorly at time resolutions of less than about 10 min (Flesch et al., 2004). Our results reflect the bias in our sampling method as well as the model error associated with non-equilibrium conditions over very short time-averaging periods. The agreement is much better for the surface flasks, likely because of the longer averaging period of 15 min (Fig. 8).

4.2 Grass samples

The modeled CO₂ff values for the grass samples are shown in Fig. 6 and range from 0.4 to 4.9 ppm in the August samples and 0.7 to 17.4 ppm in the October samples. The modeled predictions, like the observations, have the highest CO₂ff values in the dominant wind direction, and samples taken closer to the source have higher modeled CO₂ff (Fig. 8). However, it can be seen that the model significantly underestimates CO₂ff in a number of the October samples collected to the southeast of the Kapuni plant. In August, the samples were collected from sites surrounding the Kapuni plant in all directions, and the wind direction was more variable, whereas in the October case, the wind direction was consistently from the west (Fig. 6). Discrepancies at the edge of the plume in the October suggest the model is not sufficiently dispersive in the horizontal.

The model simulations assumed moderately unstable atmospheric conditions. We tested the model with neutral and slightly unstable conditions but found that under these conditions, the model was even less dispersive in the horizontal (results not shown). This was most apparent in the October samples, where the slightly unstable model simulation predicted larger CO₂ff in the samples taken directly west of the plant, but very low CO₂ff in the samples taken to the north and south along the same transect shown in Fig. 1 and Fig. 6b. We also tested our choice of effective stack height for the emissions (45 m), but found poorer agreement between model and observations.

5 Uncertainty in emissions estimated from comparison of observations and model

We further quantify the comparison between the model and observations for the surface flasks and grass samples and evaluate the model-observation mismatch by determining the ratio $\text{CO}_2\text{ff}_{\text{model}} : \text{CO}_2\text{ff}_{\text{obs}}$ ($R_{\text{model:obs}}$) for each individual grass sample, and then calculate the mean $R_{\text{model:obs}}$. We also report the one-sigma scatter of the individual $R_{\text{model:obs}}$ results. As the model does a very poor job of simulating the Helikite observed CO_2ff , we exclude these samples from this analysis.

Using all 21 measurements, including the four surface flasks collected on 26 October 2012, eight grass samples from August 2012, and nine grass samples from October 2012, we find good overall agreement between the model and observations ($r^2 = 0.8$, Fig. 8). The mean $R_{\text{model:obs}} = 0.8 \pm 0.5$. That is, on average, the modeled CO_2ff is 20 % lower than the observed CO_2ff , but with significant scatter amongst the individual measurements. Using the August and October grass samples alone, we find $R_{\text{model:obs}}$ of 0.8 ± 0.6 . Examining just the August dataset ($n = 8$), we find a less biased but more uncertain agreement between observation and model, with mean $R_{\text{model:obs}}$ of 1.0 ± 0.7 . The larger scatter on this dataset is mainly because the CO_2ff values are quite small for this dataset. Looking at the October measurements alone, we find a slightly larger underestimate in the model, with $R_{\text{model:obs}} = 0.7 \pm 0.3$. In all cases, the model remains within one-sigma of a 1 : 1 match with observations.

To infer the uncertainty in emissions from our study, we tested the model response across a wide range of emission rates, and found that it is, as expected, linear. Thus, if model transport were correct, we would infer from this that the reported emission rate was too low by 30 % in our worst case for the October grass samples. However, for this experiment, we assume that the reported emissions from the Kapuni plant are correct, and therefore, any differences between the modeled and observed CO_2ff mole fractions must be due to uncertainties in our methods and modeling. Thus we estimate that the uncertainty in emissions from our grass sample pilot study is 30 % or better.

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6 Discussion and recommendations

Large CO₂ff mole fractions were observed in the “snapshot” Helikite samples collected over a few minutes, but the WindTrax model was unable to accurately predict the high observed CO₂ff mole fractions. Conversely, the model was quite skillful in predicting the observed CO₂ff mole fractions in the long-term averaged grass samples and in 15 min averaged surface flasks. The model performed best in capturing the broad spatial pattern of emissions around the Kapuni plant as shown in the August sampling pattern. The model was less skillful at capturing the somewhat finer-scale pattern of the October grass samples, which were predominantly sampled in the same sector. This result is consistent with findings from other studies (e.g. Dresser and Huizer, 2011) that show that small errors in model transport of point source emissions can result in the emission plume being incorrectly located. Averaging the model results over time can reduce the impact of these errors. This conclusion is likely broadly applicable to local scale plume dispersion models such as WindTrax, as well as to regional scale Lagrangian models. The model skill will likely also be improved by more detailed meteorological measurements, including estimates of boundary layer turbulence and atmospheric stability.

We found the long-term averaged grass sampling better suited to the model skill than the snapshot Helikite flask samples. Grass sampling is also far cheaper and easier than flask sampling, particularly from an elevated platform such as the Helikite. Grass sampling can be performed quickly without any special equipment, and laboratory ¹⁴C preparation and measurement of this type of organic material is routine. The particular environment at our Kapuni site is conducive to the grass sampling method, with rapid grass growth and regular grazing to consistently remove old growth before flowering. Biases in the $\Delta^{14}\text{C}$ of grass or other plant material due to the details of plant CO₂ assimilation through time may make this method challenging in other locations. In future work, we will examine alternative integrated sampling techniques such as NaOH absorption that would allow more control over the effective sampling period. This type

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of sampler could still be relatively easily deployed in the field, allows collection of large amounts of CO₂, and laboratory methods are well-established.

Uncertainties in observed CO₂ff for the grass samples come from the ¹⁴C measurement uncertainty, uncertainties in the CO₂ assimilation period, and from the choice of background. Large gains in ¹⁴C measurement uncertainty are unlikely in the near future, but the impact of measurement uncertainties could be reduced by measuring multiple aliquots of each sample, or preferably by collecting and measuring more samples to obtain a greater data resolution for the model – observation comparison. As already discussed, uncertainties in the CO₂ assimilation period could be reduced by using an alternative integrated sampling technique. There is also potential for bias in observed CO₂ff from the choice of background. We used a single background measurement for each dataset, and any bias in that background will result in a consistent bias in $R_{\text{model:obs}}$ calculated for each sample. Making several background measurements would reduce background uncertainty and bias.

The Kapuni plant emissions are quite small (two orders of magnitude) relative to many fossil fuel power plants around the world. The larger emissions from larger sources will result in larger observed CO₂ff mole fractions, and hence relatively smaller measurement uncertainties. However, many large power plants will have stack emission heights of 100 m or more, so that surface or near-surface measurements will need to be made further downwind to observe the plume. At these larger distances from the source, the plume will be more dispersed and hence observed CO₂ff mole fractions will likely be of similar magnitude to those we observe. Uncertainties from the sampling strategy and from transport modeling will also remain. More complex terrain would complicate the modeling component, as will multiple emission sources in close proximity.

In this pilot study, we found that atmospheric ¹⁴C measurements of ~ 1 week integrated samples could be used to estimate CO₂ff emissions from a point source to 30 % or better. Improvements outlined here could substantially improve the method and reduce uncertainties in the near future.

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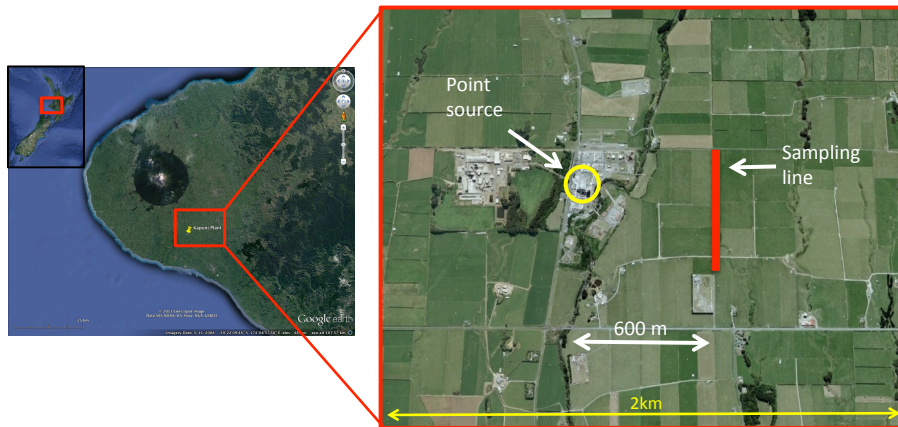


Fig. 1. Map showing location of Kapuni processing plant and kite sampling locations.

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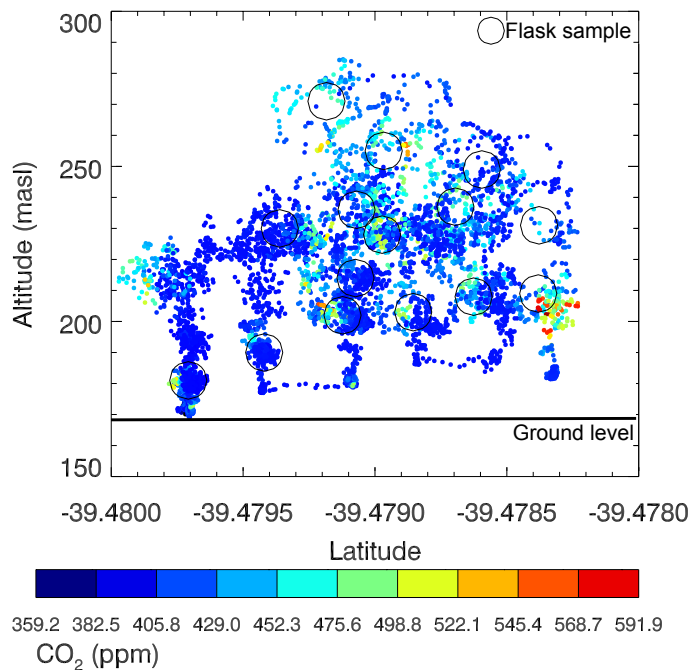


Fig. 2. Measured CO₂ mole fraction across transect from south to north. Large black circles indicate the flask sampling locations.

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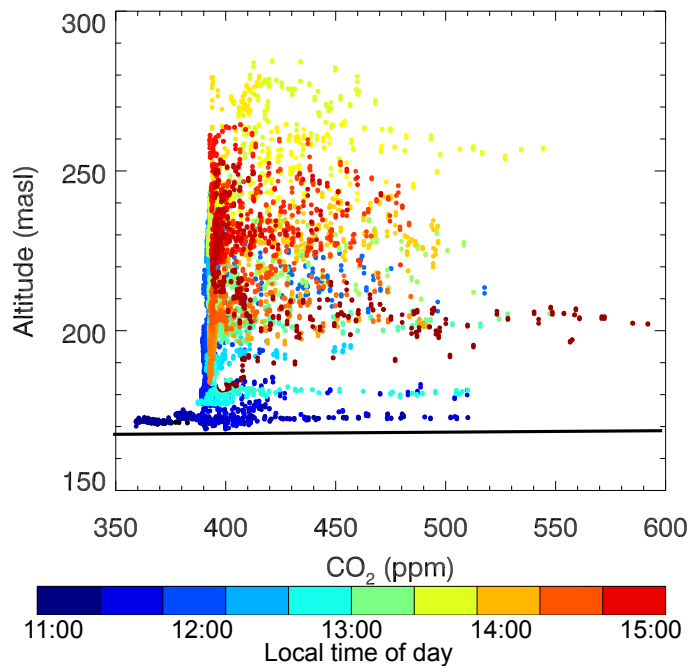


Fig. 3. Measured CO₂ mole fraction as a function of altitude. Colours indicate the time of day.

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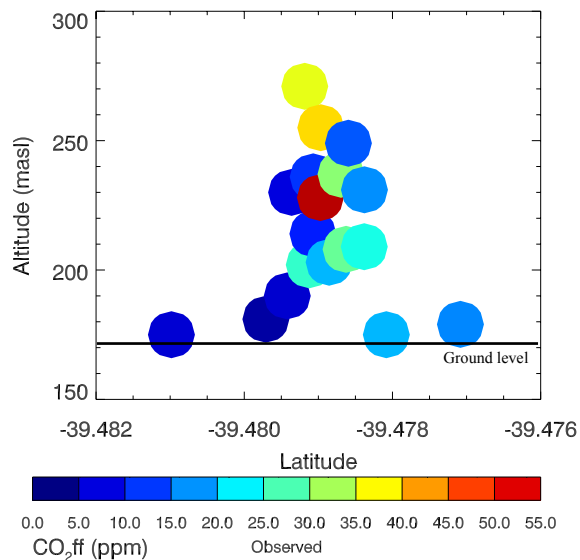


Fig. 4. CO₂ff calculated from flask samples from the Helikite and surface flasks on 26 October 2013.

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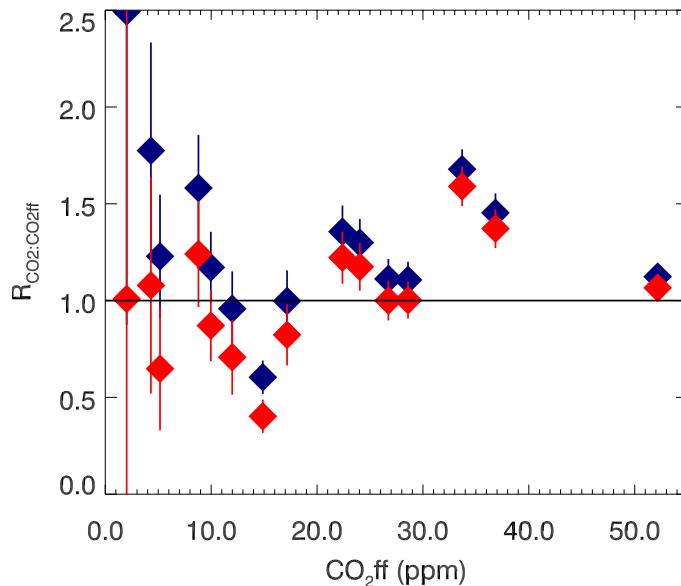


Fig. 5. $R_{\text{CO}_2:\text{CO}_2\text{ff}}$ in each flask sample. Blue points use the assigned CO₂ background values, red points apply a 3 ppm bias to the CO₂ background values in calculating $R_{\text{CO}_2:\text{CO}_2\text{ff}}$.

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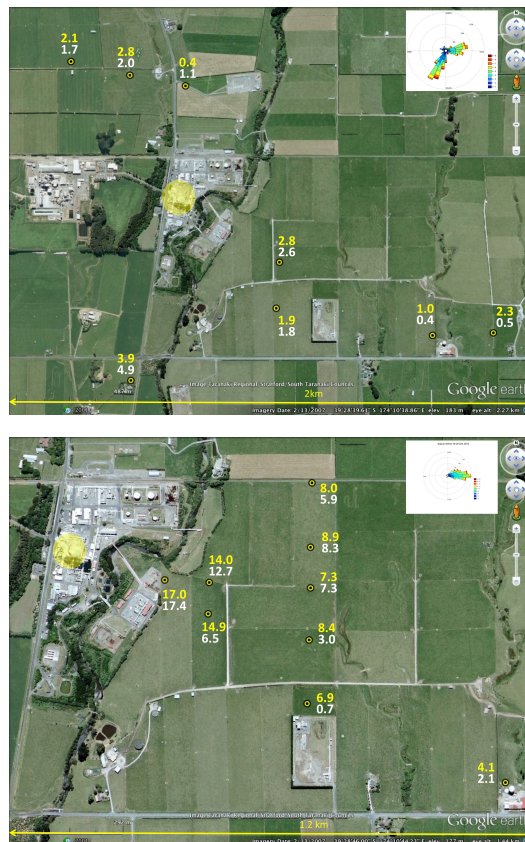


Fig. 6. CO₂ff in grass samples collected on 14 August 2012 (top) and 24 October 2012 (bottom). The observed CO₂ff derived from $\Delta^{14}\text{C}$ is shown in yellow, and the modeled CO₂ff prediction is shown in white. Markers indicate the exact sampling location. A wind rose showing the direction the wind patterns over previous one week period is inset (bars indicate the direction the wind is traveling to).

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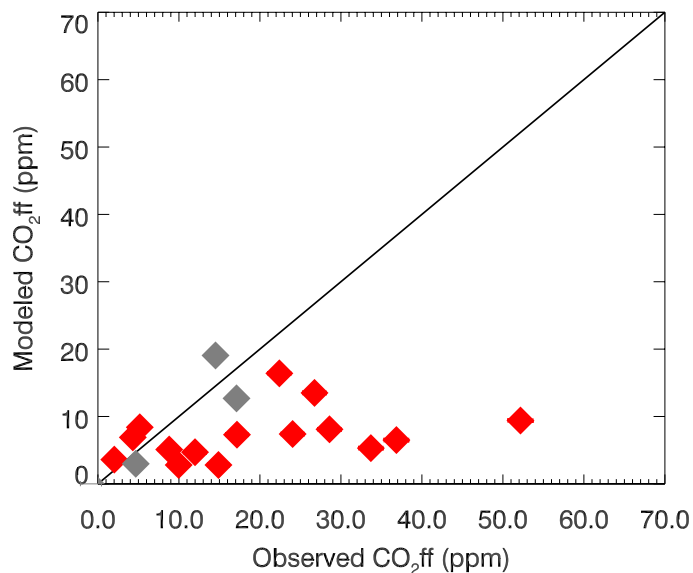


Fig. 7. Observed CO₂ff vs. modeled CO₂ff for the kite (red) and surface (grey) flask samples. Error bars are omitted for clarity.

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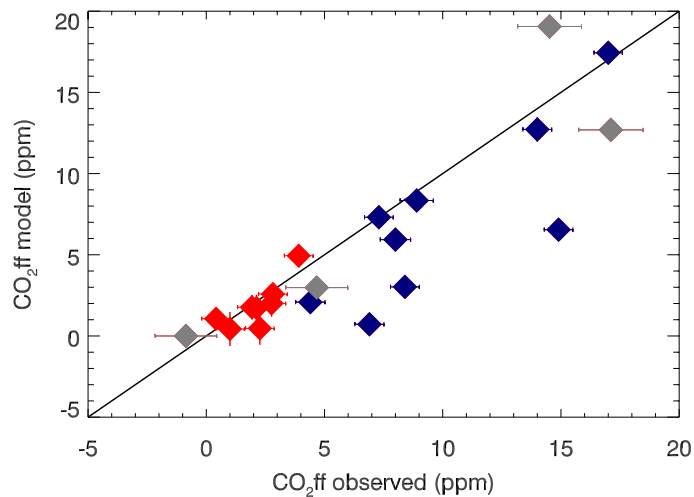


Fig. 8. Comparison of observed and modeled CO₂ff from the August (red) and October (blue) grass samples, and 26 October surface flasks (grey). The 1 : 1 line is shown in black.

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