

## ***Interactive comment on “Atmospheric measurement of point source fossil fuel CO<sub>2</sub> emissions” by J. C. Turnbull et al.***

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Thank you to both reviewers for their thoughtful comments and suggestions. We have responded directly to most of the comments in the revised manuscript.

In addition to the reviewer comments, we have also changed the title to use the term “fossil CO<sub>2</sub>” rather than “fossil fuel CO<sub>2</sub>”, since in this particular instance, the emissions are not strictly fossil fuel, although they are fossil-derived.

Comments from Zoe Loh (referee):

P29074, line 22ff. “The meteorological conditions during the grass sampling periods may more correctly match neutral to slightly unstable conditions, but we found that

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under these conditions, the model underestimates the observed plume dispersion.” The reader is left wondering observed in what sense? This is discussed further in Section 4.2, and for clarity, I suggest adding, “See section 4.2.” at the conclusion of the paragraph.

Done.

P29077, line 12ff. “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 CO<sub>2</sub>ff detected in the northwest.” Figure 6b does not show any data to the northwest of the site. If there were measurements made, as implied by this sentence, it would be good to indicate these on the map.

This point was inadvertently omitted from the map, and has been added.

Comments from Felix Vogel (referee):

General comments (minor): Firstly, the method to derive CO<sub>2</sub>ff used here, i.e. calculating CO<sub>2</sub>ff from D<sup>14</sup>C observations using equation (1) is a common and established technique (e.g. Levin 2003 (GRL, doi:10.1029/2003GL018477). However, Vogel et al. 2013 (Radiocarbon, doi:10.2458/azu\_js\_rc.55.16347) found that it is advisable to use d<sup>14</sup>C whenever possible, especially when the local fossil fuel CO<sub>2</sub> offset is large and might be predominantly from sources depleted in d<sup>13</sup>C. For example, adding 50ppm CO<sub>2</sub>ff from burning an isotopically “heavy” fuel (e.g. pittsburgh coal, d<sup>13</sup>C = -25permil) will produce a different δ<sup>14</sup>C value compared to 50ppm from burning an isotopically “light” source (e.g. natural gas, often d<sup>13</sup>C < -40permil), as the d<sup>13</sup>C of the CO<sub>2</sub> in the samples will be significantly different, which is used to calculate D<sup>14</sup>C. As CO<sub>2</sub> from natural gas can be very isotopically depleted could have a noticeable effect? Do you have an estimate of d<sup>13</sup>C<sub>source</sub> in your samples to estimate if this might significant here?

In our case, the d<sup>13</sup>C of emitted CO<sub>2</sub> is -13.8‰ so the effect is minimal. We have

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added a paragraph to explain this: "A further very small bias is induced by the  $\delta^{13}\text{C}$  normalization in the calculation of  $\Delta^{14}\text{C}$ , since the  $\delta^{13}\text{C}$  of  $\text{CO}_2^{\text{ff}}$  is different from that of the atmosphere (Vogel et al., 2013). In our case, this is of minimal importance, since the  $\text{CO}_2^{\text{ff}}$  from Kapuni is  $-13.8\text{‰}$  (measured in our laboratory using  $\text{CO}_2$  supplied by the Vector Kapuni plant), quite close to that of the atmosphere. This implies an overestimate of  $\text{CO}_2^{\text{ff}}$  of 1 - 2 %, less than 0.1 ppm for most of our measurements. We ignore this bias, as  $\delta^{13}\text{C}$  was not measured on these samples, and in fact, the atmospheric  $\delta^{13}\text{C}$  value cannot be easily determined from the grass samples since isotopic fractionation occurs during assimilation of  $\text{CO}_2$  into the plant. Note that although  $^{14}\text{C}$  fractionation also occurs during assimilation, this is corrected for mathematically in the  $\Delta^{14}\text{C}$  notation."

Secondly, the main goals of this study are very well outlined at the end of the introduction (section 1). This study tackles these questions and discusses them, but especially the question of cost and complexity of measurements and how the uncertainty of the top-down flux estimates can be reduced most efficiently could be discussed more clearly (e.g. a more quantitative for the costs) in section 6.

We have substantially revised the text of section 6 to clarify.

Thirdly, the use of plants as natural integrative samplers is technique which is increasingly used, but has numerous complications. Those shortcomings are discussed in this study, but to fully understand their potential influence it is crucial to have more information about the "grass" sampling here. Which species of grass was sampled and what part of the plant? E.g. whole leaves or just the 20cm of recent regrowth? Have leaves of different grass plants been pooled to get a more representative average?

We have added this information to the text: The grass species was not specifically identified for these samples, but the dominant species in South Taranaki is a ryegrass, *Lolium perenne* (Roberts and Thomson, 1984). We collected samples of the ~20 cm regrowth, and radiocarbon measurement was performed on part of an individual

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grass leaf from each sample. We also noted in section 6 that homogenizing multiple leaves could improve the method. Overall, the execution and results of this study is of high quality and it includes a sound and careful analysis of the observational and modelling data. Its topic is highly relevant in the framework of developing monitoring tools for anthropogenic Greenhouse Gas emissions. It will surely be of interest to the readers of ACP and I thus fully recommend the publication, after addressing the minor additions/clarifications.

Specific comments:

P29062 – line 26: As this is an approximation please consider changing "decreases  $\text{D}^{14}\text{CO}_2$  by 2.6permil" to "decreases  $\text{D}^{14}\text{CO}_2$  by about 2.6permil"

Changed.

P29064 – line 2: Please consider adding a reference to Levin et al. 2003 (GRL, doi:10.1029/2003GL018477), who previously used the Radon-Tracer Method to derive two long-term  $\text{CO}_2^{\text{ff}}$  flux records for two sites.

Added.

P29066 – line 27: How was the measurement precision of 0.1 ppm determined? Is this an instrument specific value or a general estimate from the characteristic of the Picarro G1301 instrument series?

We added the following text: The measurement precision for  $\text{CO}_2$  is better than 0.1 ppm, determined from the spread of repeat measurements of an air standard sampled using an experimental setup similar to that used for this experiment.

P29069 – P29030: Please add the information about which type of grass was sampled and especially which part of the plant. (See general comments

Done. See response above.

P29073 – line 10 Please add information on how the bottom-up flux estimates were

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derived and why you assume a 3% diurnal variation of the emissions.

This information was provided by the site manager at the Kapuni plant. They have not provided any detailed information on how this was derived, and we understand that such a level of detail is sensitive information that the company does not wish to provide. Thus far, we have maintained a good relationship with Vector, the Kapuni plant operator, and do not wish to jeopardize this by publishing information against their wishes. We do not believe that omitting this detail materially impacts the conclusions of the paper. We have revised the text to explain that Vector provided the 3% variation estimate.

P29076 – line 14 Please change  $R(\text{CO}_2/\text{CO}_2\text{ff})$  to  $R(\text{dCO}_2/\text{CO}_2\text{ff})$  to reflect that this ratio only comprises the local offset  $\text{CO}_2$  ( $\text{dCO}_2$ ) and not  $\text{CO}_2$  overall. (Applies also to Figure 5) All the reviewer is strictly correct, we have not made this change as we feel it makes the subscripts more difficult to read, and the text clearly states what is meant. P29078 – line 26 How much worse was the model-observation mismatch when the effective stack height was used

We added text to describe this: We also tested our choice of effective stack height for the emissions (45 m), but found little change in the modeled results, with a significant change in the modeled result for only one of the sampling locations. There was no change overall in the coefficient of determination ( $r^2$ ) between model and observations.

P29079 – line 28 Please elaborate how you derive the 30% uncertainty and if this precision is true for all situation or if this is limited to e.g. afternoon values. Given that other point sources have a larger variability than 3% daily sometimes even reoccurring diurnal cycles (e.g. gas power plants, flaring sites in O&G industry) it is crucial to be clear if the 30% would apply there as well.

Given the small amount of data in this pilot study, we think it is premature to go into too much detail of the uncertainty analysis. Thus we added this sentence: Thus we estimate, from our worst case model-observation mismatch that the uncertainty in emis-

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sions from our grass sample pilot study is 30 % or better.

P29081 – line 19 It might be worthwhile to add that most fossil fuel power plants have an effective stack height well above 100m - typically: 324m-781m (see e.g. Pregger and Friedrich 2009, Environmental Pollution, doi:10.1016/j.envpol.2008.09.027). As you mentioned monitoring this type of site will have to be done further downwind, which will make a well-calibrated transport model and good meteorological data even more important.

Done.

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Interactive comment on Atmos. Chem. Phys. Discuss., 13, 29059, 2013.

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