We would like to thank all four anonymous Referees for taking the time to read our manuscript and for their helpful comments and suggestions. These have been addressed individually. The reviewer comments are typeset in regular font, the replies in *italic*, while the proposed changes in the text are in **bold**.

Anonymous Referee #2

Specific comments:

1) Page 824, lines 4-9: The authors assume for the inorganic soil nitrogen pool, which may serve as substrate for the microbial N_2O formation, a $\delta^{15}N$ value of 5‰ and refer to one reference from the literature (Makarov et al., 2010). However, from the literature there is ample evidence available that soil nitrate and ammonium $\delta^{15}N$ values are highly variable in time and space and thus, cannot be simplified ascribed with one $\delta^{15}N$ value of 5‰. E.g. Durka et al. (1994, Nature 373: 765-767) found for nitrate from forest soils a range of $\delta^{15}N$ values from -6 to +6‰, Wrage et al. (2004, Rapid Commun. Mass Spectrom. 18: 1201-1207) found even a wider range for nitrate $\delta^{15}N$ values from grassland soils spanning from about -20 to +5‰. Thus, I urgently recommend a more careful consideration of the potential variability of $\delta^{15}N$ values in the soil inorganic nitrogen pool when calculating net isotope effects.

The authors agree that the assumption and use of a single $\delta^{15}N$ value for the inorganic soil nitrogen pool is a simplification, a fact that is already reflected on page 824 lines 5 – 8: "As the focus of the present study was on method development for ambient air monitoring and not on soil science, no supplementary soil parameters were determined."

To be more precise the following text changes were added (page 824 lines 8 et seqq.):
… were determined. $\delta^{15}N$ of nitrate and ammonium in soils may vary considerably, depending on the nitrogen source (e.g. soil nitrogen, atmospheric deposition, fertilizer, manure) and fractionation during nitrogen transformation processes (Kendall and Doctor, 2011). In the present study for inorganic soil nitrogen a $\delta^{15}N$ content of 0 ‰ was assumed, which is in the range of data observed in a number of field studies (Wrage et al., 2004; Durka et al., 1994).

Additionally, $\Delta\delta^{15}N^{bulk}_s$ values are corrected throughout the text:

*Page 824 lines 9 et seqq.: **This results in a net isotope effect ($\Delta\delta^{15}N^{bulk}_s$) between 5 and 26 ‰, which is …***

*Legend Fig. 6 (page 838): … **values between 5 and 42 ‰. …For $\delta^{15}N$ (substrate) 0 ‰ were assumed before fertilizer addition (before 22 September), afterwards …***

Additionally Figure 6 is updated.

References:

Durka, W., Schulze, E. D., Gebauer, G., and Voerkelius, S.: Effects of forest decline on uptake and leaching of deposited nitrate determined from ^{15}N and ^{18}O measurements, Nature, 372, 765-767, doi: 10.1038/372765a0 1994.

Kendall, C., and Doctor, D. H.: Stable Isotope Applications in Hydrological Studies, in: Isotope Geochemistry, edited by: Holland, H. D., and Turekian, K. K., Elsevier Academic Press, Amsterdam, 182-226, 2011.

Wrage, N., Lauf, J., del Prado, A., Pinto, M., Pietrzak, S., Yamulki, S., Oenema, O., and Gebauer, G.: Distinguishing sources of N_2O in European grasslands by stable isotope analysis, Rapid Commun. Mass Spectrom., 18, 1201-1207, doi: 10.1016/j.soilbio.2003.09.009, 2004.

2) Page 824, lines 11-16: Microbial denitrification and nitrification are widely considered as processes involved in soil N_2O emission, though nitrification has already been shown to be probably of very minor importance under natural conditions (see Tilsner et al. (2003) Biogeochemistry 63: 249-267 and Wrage et al. (2004) Rapid Commun. Mass Spectrom. 18: 1201-1207). Of probably much greater importance for soil N_2O emissions than nitrification is a microbial process that came just since recently in a major focus, namely nitrifier denitrificantion (see e.g. Wrage et al. (2001) Soil Biol. Biochem. 33: 1723-1732 and Kool et al. (2011) Soil Biol. Biochem. 43: 174-178). I recommend considering the latter process in the manuscript.

The authors agree that nitrifier denitrification should be considered in the discussion on N_2O source processes. Therefore, the following changes were added on page 824 lines 10 et seqq.:

This results in a net isotope effect ($\Delta\delta^{15}N^{bulk}_s$) between 5 and 26 ‰. According to pure culture studies these values are characteristic for N_2O produced by heterotrophic denitrification or nitrifier denitrification by ammonium oxidizing bacteria (Sutka et al., 2006; Sutka et al., 2003, 2004; Toyoda et al., 2005; Yoshida, 1988). Recent field studies confirm the importance of both processes for N_2O production in soils (Kool et al., 2011; Wrage et al., 2001). In contrast, N_2O produced…

Page 825, lines 7 et seqq.:

… are indicative for N_2O production by heterotrophic or nitrifier denitrification without or with only minor N_2O to N_2 reduction (Sutka et al., 2006; Sutka et al., 2003, 2004; Toyoda et al., 2005; Yoshida, 1988).

Page 826, lines 1 et seqq.:

Before fertilizer application, $\Delta\delta^{15}N^{bulk}_s$ indicates heterotrophic or nitrifier denitrification as the main N_2O production pathway. … Denitrification remained the main …

Page 838: **Fig. 6. … indicate heterotrophic or nitrifier denitrification …**

References:

Kool, D. M., Dolfing, J., Wrage, N., and Van Groenigen, J. W.: Nitrifier denitrification as a distinct and significant source of nitrous oxide from soil, Soil Biol. Biochem., 43, 174-178, doi: 10.1016/j.soilbio.2010.09.030, 2011.

Sutka, R. L., Ostrom, N. E., Ostrom, P. H., Gandhi, H., and Breznak, J. A.: Nitrogen isotopomer site preference of N_2O produced by Nitrosomonas europaea and Methylococcus capsulatus bath, Rapid Commun. Mass Spectrom., 17, 738-745, doi: 10.1002/rcm.968, 2003.

Sutka, R. L., Ostrom, N. E., Ostrom, P. H., Gandhi, H., and Breznak, J. A.: Erratum: Nitrogen isotopomer site preference of N_2O produced by Nitrosomonas europaea and Methylococcus capsulatus Bath (Rapid Communications in Mass Spectrometry (2003) 17(738-745)), Rapid Commun. Mass Spectrom., 18, 1411-1412, doi: 10.1002/rcm.1482, 2004.

Wrage, N., Velthof, G. L., Van Beusichem, M. L., and Oenema, O.: Role of nitrifier denitrification in the production of nitrous oxide, Soil Biol. Biochem., 33, 1723-1732, doi: 10.1016/s0038-0717(01)00096-7, 2001.

3) Page 825, lines 9-13: Please note that N_2O consumption in soils is not only driven by soil nitrate availability, but also by soil water content (Goldberg & Gebauer (2009) Global Change Biology 15: 850-860) and soil temperature regime (Goldberg et al. (2010) Biogeochemistry 97: 21-30). These aspects should be discussed.

The authors agree that N_2O consumption in soils aside the soil nitrate availability is driven by a number of other factors including the soil water content and the soil temperature. As the emphasis of the present study is on the development of a novel analytical technique and its characterisation regarding long term precision, accuracy and field applicability a detailed discussion of soil microbial transformation processes is beyond the scope of this manuscript. However, extended field measurements including detailed discussions of the obtained dataset will be part of future campaigns.

Anonymous Referee #3

1.) I would add an off-axis ICOS reference (specifically, Los Gatos instrument) to the introduction as those instruments are relevant in the context of the discussion of Mid-IR nitrous oxide sensors that are capable of doing isotopic measurements. Additionally, I would recommend comparing the performance of those sensors (and perhaps others) to the results derived with this instrument in the discussion section 3 (a mention of typical per-mil specs). The LGR instruments are capable of extremely low per-mil specs-likely best in the industry, and I believe they now have a commercial instrument that is capable of real-time isotopomer analysis of nitrous oxide for at least ambient air samples. It too could likely be interfaced with a preconcentration unit and achieve similar or better performance to that presented here.

The authors agree that cavity ring-down spectroscopy (CRDS) and off-axis integrated cavity output spectroscopy (OA-ICOS) are promising techniques for the analysis of trace gases and their relative isotope ratio differences. Therefore the following text changes were implemented in the introduction (page 816 lines 7 et seqq.):

A significant improvement was obtained in recent years by the implementation of quantum cascade laser absorption spectroscopy (QCLAS) to reach a precision of 0.5 ‰ for $\delta^{15}N^{\alpha}$ and $\delta^{15}N^{\beta}$ at N_2O mixing ratios of 90 ppm (Wächter et al., 2008). Other important techniques for isotope ratio measurements include cavity ring-down spectroscopy (CRDS) (Crosson, 2008) and off-axis integrated cavity output spectroscopy (OA-ICOS) (Baer et al., 2002). These methods have been widely used in the near infrared spectral region. Recently, commercial CRDS and OA-ICOS instruments with mid-IR QC lasers have been announced, taking advantage of the fact that the absorption of N_2O is more than 4 orders of magnitude stronger in the MIR as compared to the NIR.

References:

Baer, D. S., Paul, J. B., Gupta, M., and O'Keefe, A.: Sensitive absorption measurements in the near-infrared region using off-axis integrated-cavity-output spectroscopy, Appl. Phys. B, 75, 261-265, doi: 10.1007/s00340-002-0971-z, 2002.

Crosson, E. R.: A cavity ring-down analyzer for measuring atmospheric levels of methane, carbon dioxide, and water vapor, Appl. Phys. B, 92, 403-408, doi: 10.1007/s00340-008-3135-y, 2008.

Moreover, citation of manufacturer specifications not documented by publications is not scientific practice. Therefore no comparison of performance criteria was added to the Results and Discussion section 3. The Referee rightly suggests that the preconcentration unit may also be combined with other analytical techniques, but may not necessarily lead to an enhanced performance. Therefore, the conclusion of Referee #3 that a spectrometer based on OA-ICOS technology in combination with a preconcentration unit would achieve a similar or better precision than the presented instrumentation is speculative and has to be confirmed experimentally.

2.) In Section 2.2.2 it would be useful to quantify the improvement in the new spectrometer compared to the previous embodiment, perhaps as equivalent absorption sensitivity per cm or otherwise for both systems.

The authors agree that it would be useful to specify the improvement of the new spectrometer and added the following wording to section 2.2.2 (page 819 lines 4 et seqq.):

For six minutes spectral averaging a precision below 0.1 ‰ is obtained, which is almost one order of magnitude lower than previously published (Wächter et al., 2008). The maximum precision at ….

3.) The equivalent absorption sensitivity should be mentioned independently if not in the above when the spectrometer is the limiting factor- for example, in the 1permil/hz1/2 spec is this the spectrometer precision or the other, e.g. sampling limited value.

Text added as suggested on page 819 line 6 et seqq.:

The minimum equivalent absorbance of 4.1 x 10^{-6} was calculated based on the absorption spectrum and Allan variance plot.

4.) What is the precision of the 8kPa pressure measurement, and is the cell stabilized and if so to what precision?

The reviewer question is indeed very relevant, because the adjustment of pressure (and temperature) in the cell and the precision of pressure and temperature measurements are critical for the overall performance of the analyser. Thus, the following wording was added to page 819 lines 13 et seqq.:

… to a cell pressure of 8 kPa (± 0.02 kPa) monitored by means of a capacitance manometer (722A, MKS Instruments, USA). Finally, the …

Page 818 lines 23 et seqq.:

Gas temperature was stabilized to 0.05 K and additionally monitored by a calibrated 10 kΩ thermistor (TCS-610, Wavelength Electronics Inc., USA).

5.) In Section 2.4, there is a mention of a laser intensity anomaly leading to 2% "bad" data that is a bit unclear to me, even after having read it several times. There is no value of this discussion unless the problem is more thoroughly described and the connection to mixing ratio corrections made clear. Overall, I think it is not germane to the paper and could probably just be omitted. If it is kept, the connection between the "moreover" clause to the prior information regarding the isotope mixing ratios is what needs work.

This is a misunderstanding; there is no causality between the "concentration dependence of the isotope deltas" and the "changes in the laser intensity". To clarify this issue, the respective sentences were rephrased (page 821 lines 14 et seqq.):

Besides, sudden changes in the laser intensity significantly influenced individual measurements, which were discarded.

Anonymous Referee #4

1) 'liquid nitrogen-free', 'HayeSep D trap'; operating a field setup without liquid nitrogen is truly an advantage, but defining what is used (instead of what is not) would be more helpful in text (p816l12) and abstract. For instance, 'sorption-based' instead of 'liquid nitrogen-free'. In addition, please describe 'HayeSep D', with the product and manufacturer details in parenthesis. For instance, a 'porous polymer sorption trap (HayeSep D, ...)'.

The authors agree to integrate technical details on the applied adsorbent (HayeSep D) on page 818 line 7:

… on a porous polymer adsorption trap (HayeSep D 100-120 mesh, Hayes Separations Inc., USA) ….

However, the authors believe that the term "liquid nitrogen free" describes a relevant and characteristic attribute of our device and should be kept. As mentioned by Referee #4, the use of liquid nitrogen is a severe handicap for the field applicability of a technique. Furthermore liquid nitrogen is routinely applied for (sorption-based) N_2O preconcentration prior to isotopic analysis by IRMS.

2) 'real-time'; The 'real-time' aspect of the approach, as mentioned in title and text (e.g., abstract, p816l10, p825l15), may be misleading when using an alternating sample collection and sample analysis stage. The approach predetermines discontinuous sampling and may give the impression it results in true time-series of the mixing ratios of N_2O isotopomers, whereas Fig. 2 shows the intermittency of the automated schedule. Also, similar laser spectroscopy instruments are used for measurements at much shorter integration times that more closely relate to the time scales of the processes involved in exchange near the surface. In summary, I would argue that 'real-time' should be reserved for a measurement setup that would not need pre-concentration. 'In-situ' would be more appropriate terminology.

The authors agree that the meaning of "real-time" is different in various context. However, in atmospheric chemistry a "real-time analytical technique" is defined as both acquiring and analysing samples on time-scales (typically between 0.1 s and 1 h) that capture most atmospheric variability (Farmer and Jimenez, Real-time Atmospheric Chemistry Field Instrumentation, Anal. Chem., 2010, 82 (19), pp 7879–7884 doi: 10.1021/ac1010603). In this respect "real-time" is applied correctly in the manuscript and has not to be replaced by "in-situ". Furthermore, it may be questioned whether an extractive method can be considered as "in situ".

3) A discussion is missing on how the presented setup is expected to perform in summer when a different temperature regime influences sampling & analysis, and N_2O exchange processes are expected to be different. As the trap temperature is raised to 10 degrees, this would require cooling on a hot day? Information of the environmental conditions during the experiment (temperature) would be helpful. This may also lead to a positive argument, as the system was able to detect significant diel cycles in a presumably cool part of the season.

The authors agree that more pronounced changes in N_2O mixing ratios and isotope ratio differences can be expected at elevated soil temperatures during summer. However, the temperature of the adsorption trap is independent of the ambient weather conditions as it is mounted on the base-plate of the refrigeration unit located in the vacuum chamber (Mohn et al. Atmos. Meas. Tech., 3, 609–618, 2010). No changes were implemented in the text.

4) It would be useful to know if the problematic laser driver was replaced with a unit of the same make and model, or not (p821l15).

The authors agree that this information might be useful for the reader and added the following wording on page 821 lines 16 et seqq.:

… was recently replaced by a different unit (PWS4323, Tektronix Inc., USA).

5) Details of the fertilizer experiment are given in the Results & Discussion section on p822l15 and the caption of Fig. 3, but not in the Methods section.

The authors agree and added the following wording to the "Materials and Methods" section (page 817 lines 5 et seqq.):

… of the sampling site. Measurements were executed from 8 to 31 September on a grassland plot (5 m x 20 m) which was fertilized on 22 September (220 kg N ha^{-1} NH$_4$NO$_3$, 400 kg C ha^{-1} sucrose). Air was continuously sampled at a flow rate ….

Additionally, the respective information was deleted from the "Results and Discussion" section.

6) The automation schedule is presented 'as is' without further discussion on how this could be changed or improved upon, or relaxed to increase number of samples. Could the std I-1 be measured in shorter intervals such as used around 200 min and after 400 min. And what would be the resulting performance if samples and standards are integrated over shorter intervals? The data abundance of a QCLAS would easily allow such an analysis, for example by averaging fractions of the data in the scheduled stages shown in Fig 2. In addition, from Fig 2 it seems that longer time periods are used for the measurement of std-I-1 than for measurement of preconcentrated air (e.g. in the first 190 min). Is that correct? If so, why? If this is determined by the trapping time, please discuss if this can be reduced too, for instance by higher flow rates or otherwise.

The authors agree that the invented approach of combining high precision laser spectroscopy with preconcentration has the potential to offer data at even higher temporal resolution than indicated in the present manuscript. As correctly mentioned by Referee #4, it could be useful for the reader to learn more about factors limiting temporal resolution. Therefore the following wording was inserted in the "Materials and Methods" section (page 818 lines 6 et seqq.):

During standard operation, 10 l of ambient air are preconcentrated on a porous polymer adsorption trap (HayeSep D 100-120 mesh, Hayes Separations Inc., USA) at a flow rate of 500 sccm (standard cubic centimetre per minute) within 20 minutes. Desorption is accomplished by 10 sccm of synthetic air, within approximately 5 minutes, …

As correctly mentioned by Referee #4, Figure 2 displays different timing for analysis of standard 1 and sample gas, which is not correct. Therefore, Figure 2 was updated. To demonstrate the potential of the applied approach regarding temporal resolution the following paragraph was added to the "Results and Discussion" section (page 823 lines 2 et seqq.):

As more sensitive laser spectrometers become available, the time requirement for the adsorption step, which limits the temporal resolution of the complete analytical approach, might be significantly reduced. Another option to enhance the temporal resolving power is the less frequent determination of calibration factors for $\delta^{15}N^{\alpha}$, $\delta^{15}N^{\beta}$ and N$_2$O mixing ratios. This could be compensated by the preparation and use of standard gases which more closely correspond to ambient composition. Thus timescales for N$_2$O preconcentration and site-specific isotopic analysis could be reduced to around 15 minutes.

7) The Keeling plot approach is only briefly introduced. As a two end-member mixing model (following Keeling, 1958/1961) it relies on a number of assumptions. I wonder if the assumption of a stable background signal for N_2O is violated over the course of the day, for instance due to differences in conditions for day-time and night-time. Are the processes involved in production and exchange of N_2O and any isotopic signals (bulk, SP) continuous processes and is there a stable background signal? Please add convincing arguments why the 'Keeling-plot' approach can be used for 24 hour integration of N_2O data. Without consideration or discussion it may give the reader the impression that the used approach is sound, even if it is only applied to demonstrate the performance of the setup in relation to the natural and (fertilizer) treatment induced variability. With the above in mind, please review lines such as "After fertilizer application the isotopic source signatures are better constrained because of a larger diurnal change in N_2O mixing ratios".

Referee #4 correctly states that the application of "two-end mixing models" to identify source signatures is based on the assumption that background composition and source processes are (sufficiently) stable for the considered period. To better point out the underlying assumptions the following sentences were reformulated (page 823 lines 20 et seqq.)

This approach implies the assumptions that the background air N_2O composition and the soil microbial N_2O production pathways with their isotopic signatures are basically constant for one diurnal cycle. Although these parameters were not monitored in depth, the low scatter in the Keeling plots (i.e. Fig. 5) indicates that the model is at least adequate to demonstrate the performance of our instrumentation in capturing natural and fertilizer induced changes in N_2O mixing ratios. The appropriateness of the above mentioned assumptions is supported also by the moderate uncertainties in the linear regression parameters (Fig. 6).

Additionally the following text changes were inserted:

Page 824 lines 1 et seqq.:

… calculate daily N_2O source signatures ($\delta^{15}N^{bulk}_s$, SP_s), assuming steady background N_2O mixing ratios and isotopic composition.

Page 825 lines 1 et seqq.:

After fertilizer application larger diurnal changes in N_2O mixing ratios were observed (Fig. 6). These were used to allocate 24 hour isotopic source signatures, assuming stable N_2O production processes and background conditions.

Minor comments:

8) p820l21: A definition is given for $\delta^{15}N^{bulk}$ as the weighted average of two site-specific abundances (p815l3). Were the IRMS reference values for $\delta^{15}N^{bulk}$ also computed from the measured site-specific values or determined separately?

Added text on page 820 lines 21 et seqq.:

The IRMS reference values for $\delta^{15}N^{bulk}$ was determined by mass analysis of molecular ion (N_2O^+) whereas site-specific $\delta^{15}N^{\alpha}$ (central N) was determined by mass analysis of fragment ion (NO^+). The $\delta^{15}N^{\beta}$ was computed from $\delta^{15}N^{bulk}$ and $\delta^{15}N^{\alpha}$. Details are described in Toyoda and Yoshida (1999).

9) Please clarify acronyms used in figures in the figure captions and use acronyms consistently (CH or Switzerland, versus or vs.).

Changed:

Page 815 line 2: ...$^{15}N^{14}N^{16}O$ versus $^{14}N^{14}N^{16}O$.

Page 817 line 8: … pump (KNF Neuberger, Switzerland) …

Page 824 line 23: … share of N_2O reduction versus N_2O production. The N_2O versus ($N_2O + N_2$) ratio …

Page 837: … are plotted versus the inverse ….

Page 838: Fig. 6. SPs versus $\Delta\delta^{15}N^{bulk}{}_S$ …

10) Fig 4. Axis label 'Nr. of bins'. Is this 'Number per bin'?

Changed to "Nr. of counts"

11) p819l8: (..., Varian, ???) Located where?

Page 819 line 8: … pump (TriScroll 300, Varian, USA), …

12) Title mentions 'site selective', the text 'site-specific'. Please choose.

The term "site-specific" is commonly used in position dependant N_2O isotopic analysis to distinguish the relative isotope ratio differences $\delta^{15}N^{\alpha}$ and $\delta^{15}N^{\beta}$. In contrast "site selective" in the title is referred to the applied analytical technique. As both terms are appropriate in the respective context no changes were applied.