Response to anonymous referee #1 on "Evaluation of four years continuous d13C(CO2) data using a running Keeling approach"

We want to thank this anonymous reviewer for very helpful suggestions and comments, which have helped to improve the manuscript. We have revised the manuscript and outline the changes in the following.

General:

The manuscript deals with a four year combined record of $\delta_{13}C(CO_2)$ and CO_2 from Heidelberg in Germany. An of running Keeling plot approach has been applied in order to estimate the source signatures from the data.

The approach including their set criteria were tested using a STILT model dataset representing the Heidelberg conditions as good as possible. The agreement between the known source signature in these modelled dataset and those retrieved from it using their running Keeling approach is surprisingly well. The application of their approach to the four years observed dataset yields a clear seasonality of the retrieved source signature between quite well defined limits using a 100 hours smoothing filter. Then they discussed the shortcomings of the method to disentangle the different unknowns, namely the fossil fuel share and its isotope composition as well as the isotope signature of biosphere source. They conclude that it is only possible to retrieve robust results under quite strict conditions, i.e. (i) a monotonous CO₂ increase of at least five ppm over a five hours interval and (ii) an uncertainty of below two permil for the source signature. This restricts their derived source signature dataset by 85%, which is very substantial, which is somewhat a disadvantage.

Furthermore, they nicely document that the biosphere source signal can only reliably be estimated during summer. The fossil fuel source signature is in contrast only reliable during winter, when only $\delta_{13}C(CO_2)$ and CO_2 measurements are available. I really enjoyed reading this manuscript and I suggest accepting it with only minor revisions.

Detailed comments:

Abstract: L 4: ...opening the door to the quantification of CO₂ shares...or opening the door to quantify CO₂ shares...

We have added "the", such that it reads: "...opening the door to the quantification of...".

L8: Disentangling this seasonal source signature into shares of source components is, however,

We have changed this in the revised manuscript.

L13: ..., such as D14C(CO2) or oxygen/carbon dioxide concentration ratios.

As oxygen/carbon dioxide concentration ratios have not been used quantitatively to distinguish between fossil fuel and biospheric CO₂, we have decided to not include this sentence here in the abstract. For consistency, we also remove ¹⁴C(CO₂) in the abstract. However, we mention both tracer methods in the conclusion of the revised manuscript instead.

Main text

P2, L6-7: style, two times insight intoreformulate one

We have changed the second one to "This may be used to study biospheric responses...".

P2, L32-33: eq. 2 and 3 are equivalent, therefore the about equal has to be changed to an equal sign in eq. 3.

We use an equal sign in the revised manuscript.

P3, L10ff and L23ff is referring to the same topic, namely what kind of regression analyses should be used. These two parts should be combined. I personally would move the second part up.

L10ff refers to the difference between Keeling plot approach and Miller-Tans plot approach and I. 23ff refers to the fitting algorithm. We agree that these two topics should be discussed together and move the second part up, as suggested by the reviewer.

P3, L 20f: This statement is two strict and has not been mentioned like this by Miller and Tans (2003). Otherwise, the comparison between regression filtered and STILT filtered source estimates would not be as good since most of the time simultaneous occurring sinks and sources are present.

Miller and Tans (2003) state that "counter-intuitive results can occur any time fluxes of opposing sign are combined and then sampled in the atmosphere" and that "the precision [...] depends on choosing our measurement environment to match closely the assumptions in our models". We agree that the statement "the determination of source mix is not per se possible" is too strict and instead write that biases may be introduced when fluxes of opposing sign occur simultaneously.

P3, L25: What is WTLS? Is it the same as geometric mean regression (GMR) as discussed in Zobitz?

WTLS (weighted total least square fit) is similar to a ODR (orthogonal distance regression) used by Zobitz et al. (2006). It has been developed by Krystek and Anton (2007) as stable algorithm for line fitting and takes into account the uncertainty in x and y direction. We give the citation and add a comment in the revised manuscript.

P4, L1: occurring

We have changed this in the revised manuscript.

P4, L4: this approach leads to a strong auto-correlation of the source signature values.

We have changed this in the revised manuscript to "this approach leads to a strong auto-correlation of neighboring source signature values."

P4, L5: maybe reformulate to something like: We choose five hours as a compromise between maximal number of data points and source mix constancy.

We have reformulated this sentence to "We choose five hours as a compromise between number of data points and thus, of robust regression, and source mix constancy."

P4, L21: ...as a decrease would be due ...(delete of)

We have deleted "of".

P4, L19ff: Why do you not apply a simple r2 criteria? Your criteria yield a significant reduction of data and corresponds to r2 larger than 0.9. What is the benefit of using your criteria of source signal uncertainty? R2 would also be independent on the regression method applied, the retrieved slopes and intercepts not. Maybe the errors are again independent, I have not checked it.

As the reviewer points out, R^2 is the same for different regression models. The reason is that R^2 is independent of the uncertainty of $1/CO_2$ and $\delta^{13}C$. However, the standard deviation of the offset (and of the slope) in the WTLS-fit takes into account the errors in x and y (see Eqs. 24 c,d in Krystek and Anton, 2007). We therefore prefer using the standard deviation of the offset instead of R^2 .

In preliminary work, which we do not show in the manuscript, we have also tried using a $R^2>0.9$ criteria to filter the data and have found no significant differences to using the standard deviation of the offset. Both criteria seem to be similarly valid in the studied catchment area.

Section 2.3:

(structure) For the reader it would better to improve the visibility of the actual criteria in use: maybe with (i) ...(ii)

We have adapted this numbering at the end of section 2.3 in the revised manuscript to summarize the filter criteria.

P5, L11: ...are 0 - 2‰ more enriched than the "filtered" source signatures (blue) as expected from our criteria.

We feel that the insertion "as expected from our criteria" is not necessary here, as this is explained in the following sentence.

P5, L16: ...Keeling method and the used filter criteria on the model...

We have changed this in the revised manuscript.

P5, L26: about instead of ca.?

We now use "about" in the revised manuscript.

P6, L12f: this finding is in excellent agreement with a previous source seasonality estimate by Sturm et al, which should be mentioned: Sturm, P., M. Leuenberger, F.L. Valentino, B. Lehmann, and B. Ihly, Measurements of CO2, its stable isotopes, O2/N2, and Rn-222 at Bern, Switzerland, Atmospheric Chemistry and Physics, 6, 1991-2004, 2006.

We have added this reference by Sturm et al., 2006 in the revised manuscript together with Schmidt, 1999.

P6, L27 delete sub-title 4.2.1

We have deleted the subtitle 4.2.1. Note that upon suggestion of reviewer #2, we have applied a new and more classical structure to the manuscript.

P7, L17: maybe it is better to use whether instead of if

We use "whether" in the revised manuscript.

P7, L24: ...the mean measured isotope signature.

Ok.

P7, L25: delete significantly

We have deleted significantly in the revised manuscript.

P8, L29 and 33: Why are the values different (1.5 ‰ and 1‰)?

They should actually be the same and be 1.0 ‰. We have changed this in the revised manuscript.

P9, L2: Assuming constant isotopic end members over the course of one year, we would be able....

We have made this stylistic change in the revised manuscript.

P9, L6:to the change in the fraction of respiration...

We have added "the" in this sentence.

P9, L6: is it correct to say that in principle photosynthesis would also lead to an isotopic change but since you are analysing only positive CO2 gradients, i.e. CO2 release, you restricted it to respiration only. You might state this explicitly.

Yes, this is correct. We make a respective comment in the revised manuscript (Sect. 2.3).

P9, L14: ...into the fuel CO2 share.

We added "share" at the end of this sentence.

P9, L17: ...there is a need of either ...at the sources.

We have deleted this subsubsection on request of reviewer #2, and have embedded it into the conclusions. There we now use "there is a need of" instead of "must be", as recommended.

P9, L15ff (4.2.5): Nothing is said about the possibility to use oxygen measurement. A clear distinction between biospheric and fossil fuel sources can be calculated based on the different oxidation ratios for these two sources. Furthermore, calibrated CO/CO2 measurements are helpful as well as already documented in various studies.

In this study, we want to focus on using δ^{13} C and CO₂ only as tracer. However, it is true that O₂/N₂ measurements provide an additional promising tracer to separate between fossil fuel, biogenic and oceanic sources (e.g. Keeling, 1988; Bender et al., 2005; Steinbach et al., 2011). To our knowledge, using O₂/N₂ as tracer for fossil fuels on a regional scale has not been comprehensively studied so far. On the other hand, studies using CO/CO₂ at regional scale are various (e.g. Levin and Karstens, 2007; Vogel et al., 2010; Vardag et al., 2015b). We have added a short comment in the conclusion, but we do not ponder upon the different tracers, as this is not the scope of the manuscript.

P9, L27: ..aiming at an improved quantitative ...

We have made this stylistic change in the revised manuscript.

P9, L29: ...and CO2 records for a potential partitioning of source contributions.

We have changed this in the revised manuscript.

P9, L29f: this last sentence is not clear, please reformulate or delete it.

We have deleted this sentence in the revised manuscript.

P10, L26: ditto as P8, L29 and L33.

We change these numbers that both read 1.0 ‰ in the revised manuscript.

Appendix A: P11, L3: ...air parcel originated from.

We have added "from" in the revised manuscript.

P11, eq. A1: still not clear to me why one has to use absolute concentration values. It leads to different delta values.

Indeed using the absolute values leads to different numbers. However, as Miller and Tans (2003) point out and as we elaborate in this manuscript (see Fig. 1c), as soon as negative fluxes occur, the resulting source signature does not lie within the range of the source signature end members anymore. Respective results are, thus, not interpretable as gross-flux weighted mean source signature anymore. As we are interested in determining the gross-flux weighted mean source signature, we take absolute values for the calculation of the reference mean source signature. In this way, we can check if the computed source signature equals the gross-flux weighted mean of all sources; with that is an interpretable and intuitive measure.

P18, Fig1c: The lengths of the red and green arrows is not the same since one has to balance CO_2 and not $1/CO_2$. However, it might be not visible

Upon impulse of this reviewer, we have checked and can confirm that the difference is not visible for typical CO_2 (and $1/CO_2$) ranges.

P18, Caption: ...or wind direction change (transportation)

We have changed this in the revised manuscript.

P18; Caption, line 3: what do you mean with correct isotope signature, it is still a mixture and it has not been split up yet.

Here, we mean the flux-weighted mean isotopic source signature (following eq. A1 in the manuscript). We have added a comment in the figure caption of the revised manuscript.

P20, It would be worthwhile to have the CO2 changes along with these graphs (at least for b and c).

We add the CO₂ changes to Fig. 3 in the revised manuscript.

P21: high values in 2011? Correct or artefact due to calibration issues?

Even though 2011 was the very first year of our measurements, we do not have any hints (e.g. target gas measurements or other), which would explain any artefact due to calibration issues. Therefore, we suggest that this is a real effect. P21: It would be nice to add the modelled curve for the year 2012.

We have now added the modelled curve for the year 2012 in Figure 4.

P22: Why don't you use the radiocarbon that you have available and base your fossil fuel on inventory estimates?

Good point: We have actually considered including this record initially. However, we have decided to leave ${}^{14}CO_2$ out because of three main reasons:

1) We felt that the main statement of the manuscript, which concerns the usefulness and pitfalls when evaluating and interpreting continuous δ^{13} C-CO₂ measurements, would be weakened by including an additional tracer. 2) Many monitoring stations do not have ¹⁴C measurements available. Therefore, our study is more representative if not including the ¹⁴C-CO₂ measurements, but using (generally available) emission inventory data instead.

3) We only have integrated samples of ${}^{14}C(CO_2)$ available, which cannot be compared to continuous $\delta^{13}C$ -CO₂ measurements directly due to the integration effect (described in Vardag et al., 2015b).

P23: are the lower and upper 5% important? Have you used this filtering?

They are not used in the manuscript. We have removed these in the revised manuscript.

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Response to anonymous referee #2 on "Evaluation of four years continuous d13C(CO2) data using a running Keeling approach"

We want to thank this anonymous reviewer for very helpful suggestions and comments. We have revised the manuscript respectively and outline our replies and changes in the following.

This manuscript of Vardag et al. presents an analytical approach to evaluate the CO2 source signature $\delta^{13}C_s$, using continuous, high resolution time-series of CO2 and $\delta^{13}C$, recorded with an FTIR. The analysis is based on the Keeling-plot method, where a time-window of 5 hours is continuously moved across the whole data set, resulting in a continuous source signature estimate over the observation period of fouryears. The manuscript is generally well written, uses an outstanding datarecord and validates the proposed method using pseudo data from the STILT model. However, the major findings, like the strong limitation of the Keeling-plot method for urban catchment areas with multiple and variable sources as well as the seasonal variation of the source signatures are known since many years and discussed in a vast number of publications, some of which are also referenced by the authors. Although, it is useful (but not novel) to see the difficulties of estimating the year-round CO2 fossil fuel or biosphere share in urban atmosphere using the CO2 and δ 13C data only, the reader is left with vague alternatives and a method, which is empirically tuned to a specific spatial and temporal setting, rejecting about 85% of the estimated values. This manuscript would strongly gain scientific value by including further tracers such as 14CO2, 18CO2, CO, and 222Rn, discussing the advantages and pitfalls of such a combined approach, and deducing measurement strategies for future monitoring activities. As the authors have the above mentioned data (see e.g. Vogel et al. Tellus, 65, 2013) and a detailed model investigation (Vardag et al, ACP, 15, 2015), I strongly recommend using these in a concerted fashion to facilitate a better and clearer understanding of the limiting factors, requirements and identification of best practice for an efficient and unbiased monitoring of CO2 source signatures. Without such major revision, the manuscript does not fulfill the high standards required for publication in Biogeosciences.

A lot of instruments measuring atmospheric $\delta^{13}C(CO_2)$ continuously have been installed recently with the objective of better understanding the measured CO₂ signal (e.g. Torn et al., 2011; Tuszon et al., 2011; Griffith et al., 2012; Griffis, 2013; Sturm et al., 2013; Vardag et al., 2015b). The expectation when using these continuously measuring instruments was to disentangle different CO₂ source contributions at high temporal resolution and with that, to obtain a complete picture of the source mixes and their variations at different measurement sites.

Many studies have shown qualitatively how a CO_2 and $\delta^{13}C$ record could be used (e.g. Zimnoch et al., 2010; Tuszon et al., 2011; van Asperen et al., 2014; Moore and Jacobson, 2015; Newman et al., 2016), paving the way towards a more comprehensive understanding of the CO_2 record in different settings.

However, to our knowledge, no study has yet calculated the mean CO₂ source signature at high temporal resolution (hourly) over a period of more than a year in an urban setting. Moreover, this is the first comprehensive evaluation showing that the retrieved source signature is not biased. This bias-check using synthetic data is vital, especially for CO₂, because the prerequisites of the Keeling plot method need to be fulfilled in order to obtain correct results.

Our paper aims at showing 1) how the source signature can be obtained from a continuous δ^{13} C and CO₂ record 2) what can be learned from a continuous isotopic source signature record alone and 3) where additional information is needed. To our knowledge, these aspects have not been discussed elsewhere, but we would highly appreciate hints on which work we might have overlooked.

Concerning the technical part, we share the reviewer's disappointment about the need to reject 85% of the data. However, this seems to be an intrinsic problem for an urban setting with multiple sources and sinks: Obviously, in many situations the prerequisites of the Keeling plot method are not fulfilled at our site. Thus, rejecting 85% of the data seems inevitable if biases in the source signature shall be minimized. We understand that we failed in making this point clear and have elaborated this important finding in more detail in the revised manuscript.

Further, the actual percentage of rejected data points depends on the biases, which are tolerated by the data user. But it depends also and especially on the setting (wind direction change, number of sources in the catchment area, photosynthetic flux, etc.). Therefore, we are not able to provide a universal recipe how to calculate the source signature that would be applicable at every given setting. We rather demonstrate how one can check the obtained mean source signature and which parameters indicate potential biases in the mean source signature.

Concerning the interpretation of the mean source signature, the results of this paper might seem sobering to some readers, as we failed to provide

here a straight-forward way to estimate the fossil fuel component using only $\delta^{13}C(CO_2)$ and CO_2 . However, we feel that it is important and timely to clearly state what can be learned and what cannot be learned from combined $\delta^{13}C(CO_2)$ and CO_2 measurements alone. This manuscript may, therefore, also guide the decision whether or not it is worth to equip a measurement station with CO_2 and $\delta^{13}C$ instruments.

As the reviewer states, the limitations of $\delta^{13}C(CO_2)$ -based approaches are often mentioned in publications. However, the consequences of these limitations are generally not discussed thoroughly, and results are presented without stressing the many assumptions, which are needed to obtain a quantitative result. We do not want to follow the approach to "fix" the problem by using more tracers plus additional assumptions as this was already done in different studies. E.g., Vardag et al. (2015b) compared different tracers (CO₂, $\delta^{13}C(CO_2)$, CO and ¹⁴C) and tracer combinations to estimate the fossil fuel share, as well as possible calibration strategies to obtain the stable isotope end members and with that the fossil fuel share using ¹⁴C. They have discussed advantages and pitfalls of combined approaches and have deduced specific measurement strategies for future monitoring activities.

In the present manuscript, we follow a more puristic approach by using only $\delta^{13}C(CO_2)$ and CO_2 measurements as firstly, many measurement stations do not have additional tracers available and secondly to highlight the additional assumptions required for a quantitative year-round determination of CO_2 source signatures.

Furthermore, we have considered including ¹⁸O-CO₂ in this study, as suggested by the reviewer. However, we are very certain that the ¹⁸O-CO₂ record will not provide additional insight into the isotopic signature of the fossil fuel sources or the plant respiration signal, at least not without implementing additional water isotope measurements and a sophisticated carbon-water model, as ¹⁸O-CO₂ is strongly coupled to the ¹⁸O-H₂O signal (see Vardag et al., 2015a). Even though the usage of the ¹⁸O-CO₂ record is in general a very interesting field of research, it by far exceeds the scope of this paper.

Moreover, it has been shown that ²²²Rn can be used to distinguish between concentration changes due to changes of the planetary boundary layer height and concentration changes due to emissions (Levin et al., 1999). This is especially valuable when deriving emissions from concentration changes (Schmidt et al., 2001). However, the source signature itself is independent of the absolute CO₂ signal. It only depends on the relative fossil fuel and biospheric CO₂ shares. Thus, the calculated source signature is independent of atmospheric mixing conditions. Therefore, we feel that it is not helpful to use ²²²Rn in this study.

Finally, we want to ascertain that we clearly see (and discuss in the manuscript) the shortfalls of using $\delta^{13}C(CO_2)$ and CO_2 only, as is correctly pointed out by the reviewer. However, demonstrating these shortfalls and at the same time showing the usefulness of collocated continuous CO_2 and $\delta^{13}C(CO_2)$ records, is exactly what we attempt to show in this paper and what we stress in the revised manuscript.

General comments:

A more appropriate title should be given. A "running Keeling approach" is awkward. First, the terminology broadly accepted by the community is the "Keeling plot approach (or method)". Second, the mathematical operation applied in the described approach is a moving average or moving time window. In addition, the method does not differ (except the trace gas species and window size) from the method published by Röckmann et al., so I strongly recommend to not increase the number of nomenclatures unnecessarily and stick with the name of "moving Keeling plot method" as proposed by Röckmann et al.

We agree that it may be helpful to follow the nomenclature of Röckmann et al.; we thus changed "running Keeling approach" to "moving Keeling plot method" in the title and throughout the entire manuscript, as suggested by the reviewer.

If the authors write four-years in the title then they should also give the signatures for all these years and not only limit to one particular year. Otherwise, give a reason why this year was selected as representative case and give estimates how the findings for 2012 can be extended to other years.

The mean source signature was computed for four years (see Fig. 4 of the manuscript). However, we do the analysis of the end members δ_{bio} and δ_{F} only for the year 2012 for two reasons. Firstly, in order to demonstrate the wealth of information from $\delta^{13}C(CO_2)$ and CO_2 only, we feel that it suffices to analyze only one year. Secondly, as described in the manuscript, the fuel contributions of the emission inventory (EDGAR) are only available for 2010 and have already been extrapolated to the year 2012. Therefore, for the years 2011-2015, we would have to use the same source mix as for

the year 2012, providing no additional insight. We add a respective comment to the revised manuscript (Sect. 3.3).

The abstract should also reflect the major drawbacks of the method: 85% of the data are rejected, because they do not fulfil the filtering criteria, mainly nighttime periods are considered, and the selected criteria are empirical and specific to a particular urban area. Furthermore, an additional smoothing (100 h window) is applied to the estimated values.

The reason why we reject 85% of the data is intrinsic as a Keeling plot can only be performed in situations, which fulfill the basic assumptions of the Keeling plot. We have added a respective comment in the abstract and explain this in more detail in the manuscript, as we seem to have failed to make this point clear in the original version of the manuscript.

The smoothing is applied in order to expose the synoptic and seasonal trends in the figures.

The manuscript would greatly benefit from a more conventional structure, such as Introduction, Methods, Results and Discussion. Several sub-sub-sections are not necessary and hinder the text flow, e.g. by adding many cross-references. More specifically, I recommend merging the subsections 3.1 and 3.2 into section 3 as paragraphs. Similarly, sub-subsections 4.2.1 - 4.2.5 can be included in the main text using simple paragraph-spacing.

We have adopted a more conventional structure such that chapter 2 was named "Methods", chapter 3 "Results and Discussion" and chapter 4 "Summary and Conclusions". Also we have removed all subsubsections and structure the revised manuscript by subsections only.

The averaging window was selected to be 5 hours, but the motivation is weak. In principle, the FTIR is able to produce 9 minute averaged values, so why not include the resulting 33 data points into the Keeling-plot intercept determination? The higher temporal resolution should lead to a more robust fit, and a better insight into the dynamics of source signature variations, which could eventually be used as a more objective filtering instead of the empirical criteria. Just consider Figure 1 with 10 fold better resolution. Arguing with the model resolution of 1 hour is not appropriate in this context. Similarly, the argument of being a period in which the source-mix does not change significantly is ambiguous because the large amount of rejected source signature estimates. For the reader it would be very useful to learn about the optimal temporal resolution but the respective limitation of the model and the instrument does, unfortunately, not allow to draw the corresponding conclusions.

This is a very good point. The FTIR is even able to produce 3-minute data points. Nevertheless, we have decided to use a 5 hour moving window for Keeling plot determination using hourly CO₂ and $\delta^{13}C(CO_2)$ data, which we discuss and explain in the following.

As the reviewer states correctly, our motivation for taking hourly data points comes from the model, which is available only at hourly resolution. An important output of our study is that we can assure that we are determining the source signature correctly. This can only be done by comparing it with the known source signature, which is provided by the model. We find this check not only appropriate, but also rather essential (and novel). Therefore, we disagree with the reviewer and in contrary understand that arguing with the model resolution of 1 hour is indeed appropriate.

As the reviewer points out, for the determination of the mean source signature using measured data, it may be advantageous to use 3-minutely instead of hourly values. In this case, changes of the source signature within an hour can also contribute to the scattering of the fit, improving or deteriorating the fit, but potentially providing additional information. However, we have no means (as the model resolution is not high enough)

However, we have no means (as the model resolution is not high enough) to check whether we get correct results when taking three-minutely values.

For curiosity and upon impulse of reviewer #2, we have nonetheless checked if the Keeling plot gives different results when using 3-minutely measurements instead of hourly averaged measurements. We have therefore calculated the source signature for the entire year 2012 in a 5 hour moving window using 3 minutely data (100 data points) and using hourly data (5 data points), but applying the same filter criteria (standard deviation of the offset <2 ‰, CO₂ increase >5ppm). We actually find a (small) differences between the source signatures at similar: The mean difference between the Keeling plot intercept using 3 minutely data (both in an 5 hour moving window) is 0.2 + 1.3 % (non smoothed). It is not possible to answer where the difference comes from and if the results still give the gross-flux weighted mean source signature, as it cannot be compared to any reference (provided by the model). Therefore, we are obliged to use hourly instead of three-minutely values for computation of the Keeling plot.

A second point raised by reviewer #2 concerns the length of the moving window. We have experimented using smaller (1h, 3h, 4h) and larger (6h, 7h, 8h) averaging windows and compared how much of the data is rejected by the filter criteria for which window size. For the one hour window size, we filtered data with CO_2 increase less than 1 ppm over one hour and standard deviation of the offset > 2 ‰, and for five hours, we

rejected data with CO₂ increase less than 5 ppm and standard deviation > 2 ‰ and respectively for the other window sizes. We found that for a window size of 5 hours, the coverage is maximal (ca. 15%) showing that five hours is the compromise between a period in which we encounter a significant increase of CO₂ (at fixed uncertainties of the CO₂ and $\delta^{13}C(CO_2)$ data), but also a period in which the source mix remains more or less constant and CO₂ is still increasing. For comparison, when using a window size of only one hour, the coverage is only ca. 5%. We have now added a comment in the revised manuscript (Sect. 2.2) to provide the reader with a more objective criteria for choosing the correct window size.

How representative are the STILT model data for urban areas? A city with its complex network of buildings and street canyons generates turbulent flows at scales that are certainly beyond the resolution of STILT. Also, what is the model sensitivity at various sampling heights within an urban area?

It is not of utmost importance that the STILT model is absolutely correct. We use the STILT CO₂ and $\delta^{13}C(CO_2)$ data set to determine the isotopic source signature and compare it to the modelled reference source signature. For this consistency check, it is important that the source mix is realistic, but it does not need to be exactly correct.

The modelled planetary boundary layer height introduces a large biases into the modelled concentration. However, as already mentioned above, the mean source signature is independent of the absolute concentrations, but only depends on the CO₂ shares. Therefore, as a rough indicator of the different variability of the source mix in the model and the measurements, we have compared the interquartile ranges of the mean source signatures around the smoothed mean source signature. It is 1.2 ‰ for model data and 1.8 ‰ for measured data (see Sect. 3.2), indicating a similar, but slightly lower (30%) variability in the model than in the measurements. We have added a respective comment in the revised manuscript.

The sampling height used in the model equals the actual measurement sampling height. As we are only interested in evaluating the data from this sampling height, we do not feel that it is necessary to elaborate the sensitivity for other sampling heights.

The filter criteria used in the manuscript are mainly fulfilled for nighttime, so it would be good to know the uncertainty of the transport model for nocturnal data. Advection and vertical mixing can significantly influence the urban CO2 signal, leading to vertical gradients. Therefore, wind speed

and direction data are most likely needed to adequately interpret the observed CO2 values. Thus, a discussion about the representativeness and sensitivity of the sampling site to wind speed and direction as well as its location and height would be highly recommended.

The STILT model has a transport error of about 40% during the daytime and up to 100% at night (Gerbig et al., 2008). This is mainly due to the uncertainty of the planetary boundary layer height affecting all absolute concentrations. However, the absolute value of the concentration does not influence the mean source signature. Only the share of the different components change the mean source signature. Therefore, the STILT model can be used to test the moving Keeling plot method, despite large vertical transport errors.

As the reviewer states correctly, the measured signal at the measurement station is strongly influenced by the footprint of the measurement site, which itself is influenced by advection, vertical mixing, wind speed, wind direction etc.. It is not the scope of this manuscript to make a detailed footprint analysis. We focus here only on the ability to derive the source signatures of fossil fuel emitters and the biosphere irrespective of what footprint we are looking at. We therefore do not discuss the measurement site and meteorological parameters in detail in the revised manuscript, but provide a reference for the Heidelberg measurement site and the catchment area (Vogel et al. (2010)).

The isotopic source signature of the biosphere is found to be more depleted than previously published value, but the analysis in the present work is mainly based on nighttime data, where photosynthesis is negligible distinguishing respiration dominates. Furthermore, and between respiration, coal burning and gasoline is difficult, because they have similar δ^{13} C. The authors should discuss this potential bias on their δ bio estimates. For such situations, the oxygen isotope ratio (δ 18O) could be used to distinguish between biogenic and anthropogenic CO2 as the evaporative enrichment of H218O in plants and soils imparts a unique signature. At the observed regional scale, it should be possible to provide the necessary model input.

We are not sure, which published value the reviewer is referring to. To our knowledge the literature values are distributed around -25 % (+/-2 %) (see e.g. Mook, 2001; Ballantyne et al., 2011 and others). As there seems to be hardly any discrimination during respiration (Lin et al., 1997), the nighttime respiration values should not differ significantly from daytime respiration values; therefore, the assumed biospheric isotopic signature is

our best estimate. The potential bias of the biospheric source signature end member is discussed in former Sect. 4.2.3 (now: Sect. 3.4) and is illustratively demonstrated in Fig. 5a where we take into account two different possible uncertainties to demonstrate the effect of the biospheric end member.

The reviewer correctly points out that distinguishing between respiration and coal burning is difficult, since they have a similar $\delta^{13}C(CO_2)$ value. That of gasoline is slightly more depleted, but still rather close, which makes a clear distinction of these sectors difficult. However, a distinction between the mean fossil fuel source and mean respiration source is still possible, as natural gas contribution leads to a more depleted mean fossil fuel signature.

We do not find it useful to include the oxygen isotope ratio to distinguish between biogenic and anthropogenic CO₂. As stated above, the reason is that the H₂¹⁸O signal (and consequently also CO¹⁸O signal) is highly variable, not well-known and different for soils and plants. Further, additional effects as e.g. soil invasion flux needs to be taken into account before using δ^{18} O quantitatively (see Vardag et al., 2015a). All these influences on the ¹⁸O-CO₂ signal need to be modelled with a coupled carbon-water model, which is fed by high-resolution meteorological data (e.g. precipitation, temperature etc.) and isotopic H₂O data. Such a model and such measurements would be very interesting to have, but are not available in Heidelberg and at many other stations.

In the same context, even the pseudo data shown in Fig. 2a indicate a systematic bias for the summer period between the filtered and unfiltered cases. This discrepancy should be discussed in terms of influence in determining source signatures.

The reviewer correctly remarks that the pseudo data is more depleted after filtering, as daytime data is more likely to be filtered out (see also Sect. 3.1). In the Conclusion we clearly state that the long-term source signature is only representative of the nighttime. As this point is very important, we now explicitly state in the conclusions of the revised manuscript that, obviously, as a consequence, also the isotopic end members of biospheric and fossil CO_2 can only be estimated in periods where the mean source signature can be computed, excluding especially daytime periods.

The source signature value (-32.5‰) found in this work is significantly different from the value (-25‰) published by the same authors for the same year (Vardag et al, 2015a). A discussion about this discrepancy is required.

The reviewer probably refers to Vardag et al. (2015b), where the mean biospheric value is -25 ‰. This is in correspondence to the present study, where the mean biospheric value is -25 ‰ as well, but the mean fossil fuel signature is -32.5 ‰. In Vardag et al. (2015a), the different fossil fuel sources are further separated into traffic, residential heating, energy production etc., but again the isotopic values in no way conflict the isotopic signatures used or found in the present publication.

Specific comments:

Abstract, L5: "without introducing biases" is a very strong statement and probably not applicable. "reducing biases" would be more appropriate.

In the revised manuscript we have deleted "without introducing biases" in that sentence and use "minimal biases" in the next (new) sentence.

Abstract, L6: state which model.

We explicitly name the model here.

Abstract, L7: are these bias values for the model data? If so, state this explicitly.

These are given for the model, as we are not able to quantify the bias for real data. We added this in the abstract.

Abstract, L13: This statement should be much more quantitative, which implies significant additional information and possibly research in the main section of the paper.

As elaborated in the first passage of this reply, we have aimed to demonstrate how much information can be retrieved by using $\delta^{13}C(CO_2)$ and CO_2 only. Other papers have dealt with a combination of different tracers (e.g. Vardag et al., 2015b), but this is not the scope of this paper. Even though some readers might find this result devastating, we think that it is important and novel to state the advantages and shortcomings in all explicitness.

Pg2, L1: use plural for optical techniques, since there are various approaches available on the market.

We have changed this to plural in the revised manuscript.

Pg2, L2: thereby

Ok.

Pg2, L21: "bias-free", see remark above

We have changed this to "retrieval with minimal biases".

Pg2, L27: the "classical" is not necessary, because up to date there is only this method.

We have removed classical.

Pg3, L4: this sentence is awkward, I recommend reformulating it.

We have reformulated this in the revised manuscript.

Pg3, Eq3: revise the formula, the CO2bg has a positive sign.

We have checked the formula and Eq. 3 seems to be appropriate as it is, but Eq. 4, must have a minus in front of CO_{2bg} . We correct this in the revised manuscript.

Pg3, L14: "the Keeling plot" instead of "a Keeling plot".

We have changed this in the revised manuscript.

Pg3, L28: why not to use measured data to test the different fit models? There should be no reason for synthetic data to deliver different results when applying different forms of the linear fitting routines. The situation can though be different when using real data.

As we added a statistical noise to the synthetic data (representing measurement uncertainty), the comparison of the linear fitting routines should not differ when using synthetic data or measured data. We therefore feel that it is not necessary to repeat this analysis with measured data.

Pg3, L29: for the very same criteria statement another reference is used (Sect 2.2 instead Sect. 2.3., see Pg3, L14)

Section 2.3 is the one, which we want to refer to in both cases. We have corrected this in the revised manuscript.

Pg3, L30: specify, how the weights are determined?

In the WTLS-fit, the uncertainties in x and y direction are both used to calculate the weights. In the revised manuscript we provide a citation to the WTLS-fit (Krystek and Anton, 2007) explaining also the weights (Eq. 11 in Krystek and Anton, 2007).

Pg3, L31: revise the section name (see comment above regarding title)

We have changed this in the entire manuscript.

Pg3, L33: "running" Keeling approach, again see above and delete this sentence.

Ok.

Pg4, L19: The threshold criterion of 2‰ error has no objective motivation. Try to give its meaning in the context of some quantity like a confidence interval or in terms of source allocation error.

The criteria have been motivated theoretically (see Fig. 1 and Sect. 2.3), but, as the reviewer points out correctly, the absolute values of these filter criteria have been established empirically (Sect. 2.3).

However, we check the effectiveness of the filter criteria by using the synthetic data set. This model comparison (difference between the model reference source signature and the Keeling plot based source signature of synthetic data) provides the basis for choosing the filter criteria and the interquartile range of the difference provides a measure of the precision of the estimate.

Nevertheless, for other measurement stations, other filter criteria would apply, depending on how heterogeneous the sources in the catchment area are and how fast the footprint changes. Therefore, it is not possible to provide a universal recipe for other measurement stations, but we only demonstrate how to choose the filter criteria based on the model comparison. We have added a comment about the generalization of these filter criteria in the revised manuscript (Sect. 2.3).

Pg4, L21: check wording "as a decrease of would be"

We have changed this in the revised manuscript.

PG4, L28: how does this compare with a situation of 6 hour period and 4 or 6 ppm increase criteria? Is there a way to generalize these filter criteria?

We choose a 5 hour moving window, as a compromise between a period in which we encounter a significant increase of CO₂ (at fixed uncertainties of the CO₂ and $\delta^{13}C(CO_2)$ data), but also a period in which the source mix remains constant and the CO₂ is still increasing. When using a window size of 5 hours, the coverage is maximal (ca. 15%) showing that 5 hours is preferential over other window sizes. For 6 and 4 hours moving windows, the coverage is slightly smaller than for 5 hours, but the source signature is not significantly different from using a 5 hour average.

Again, we are aware that our filter criteria were chosen empirically (after consulting the differences to the modelled source signature). This means, we have chosen our filter criteria such that the Keeling plot method prerequisites are fulfilled for our observational setting. This is necessary in order to obtain correct results.

Ideally, it would be nice to generalize the filter criteria and provide a universal recipe how to filter the source signature for every possible setting. However, as pointed out before, each measurement site is unique, has different absolute CO_2 variations, different emission patterns and footprint changes; therefore, we are unfortunately (but unavoidably) unable to generalize the filter.

What we can do and what we discuss in the manuscript (last paragraph in Sect. 3.1) is how a loosening of the filter criteria (higher or lower CO_2 increase) affects the data coverage and the biases introduced. We chose meaningful and descriptive scenarios so that the reader gets a feeling for the importance of the filter criteria.

Pg5. L7: give a reference for the STILT model.

We have added the reference (Lin et al., 2003) for the STILT model.

Pg5. L24: what was the decision criterion for smoothing the source signatures with 100 hours window size? Evaluating the smoothing effect on pseudo data and assuming its validity on real data can be prone to errors.

We have chosen the window size of n=100 hours (ca. 4 days), so that the synoptical and seasonal variations of the mean source signature can be

seen independent from diurnal variation. We have commented on this in the revised manuscript (Sect. 3.1).

As the simulated and real mean source signature nearly show the same variability, uncertainty and coverage, the smoothing effect of both data sets should not be biasing.

Pg6, L11. Remove "Heidelberg" before "CO2".

Ok.

Pg6, L16. The explanation of outliers is weak and hard to understand. What do you mean by "statistical"? The filtering criteria were selected to be rather strict, so what else determines the uncertainty of the method?

The pseudo-data experiment showed that even though we apply rather strict filter criteria, there are some outliers, which lead to an interquartile range of 1.2 ‰ (see Sect. 3.2). The interquartile range of all measured data points (around the smoothed curve) is 1.8 ‰ and with that only slightly higher than what we obtained from the pseudo-data, showing that the outliers in the source signature are not unusual for our applied filter criteria. We have reformulated the sentence.

Pg6, L18: are the values for inter-quartile ranges are for the smoothed data?

No, they are for the hourly non-smoothed data. We clearly point this out in the revised manuscript.

Pg7, L18 replace "we ask here, if we can" with "the question is whether it is possible to"

Ok.

Pg9, L1. this section has nothing to do with accuracy evaluation, being more a qualitative description of various scenarios. Revision is recommended. See also suggestion above regarding text-flow.

We agree that the term accuracy might not be well chosen as we discuss the resulting absolute values of the isotopic signatures rather than the quality of the data. We have therefore removed this title and instead discuss the content of this paragraph in Sect. 3.4 of the revised manuscript. Note that we also have shortened this section, and instead discuss the implications of this section in the conclusions.

Pg9, L15. This section is basically a repetition of what was already mentioned previously.

We deleted this paragraph in the revised manuscript and fed the information to the "Summary and Conclusion" chapter instead, where it is more appropriate to summarize the findings.

Pg10, L12: replace "real measured data set in Heidelberg" with "real data set measured in Heidelberg".

We have changed this in the revised manuscript.

Fig.3 add the measured δ 13CS to the figures.

Instead of adding the measured $\delta^{13}C_s$ in Fig. 3, we have decided to add the modelled $\delta^{13}C_s$ in Fig.4, so that both can be compared. This was suggested by Reviewer #1.

Fig.5 it is somehow strange that if one considers the periods between January-April and October-December, where the measured δ 13CS and assumed (or estimated) δ 13CF show little deviation for both scenarios, the δ 13Cbio exhibits extreme fluctuations (Fig.5b). Furthermore, the fact that the agreement is good between model and observed δ 13CS data would imply that the summer period should look similar for the δ 13Cbio as well. In other words, what would the situation look like, when fixing both end members δ 13Cbio and δ 13CF, and estimating δ 13CS?

The fluctuation of the estimated biospheric isotopic end member is high in winter as the biospheric CO₂ share is low and the source signature $\delta^{13}C_S$ is close to the assumed fossil fuel end member in winter. The biospheric end member is therefore not well constrained by $\delta^{13}C_S$, leading to a large uncertainty of the biospheric end member.

Furthermore, in Fig. 5, we use only the measured (not modelled) $\delta^{13}C_{S.}$ Thus, we are sorry, but do not understand the second part of the reviewers comment.

Appendix A, L7:

Röckmann et al. found that fossil-fuel related emissions may be overestimated in EDGAR and using this inventory data leads to source signatures that are too enriched. Would this also apply to the CO2 data presented in this work?

If the fossil fuel share were overestimated also for CO_2 , the mean source signature would be influenced by a too large share by fossil fuels and a too small share of the biosphere. Therefore, in order to obtain the same measured mean source signature, the resulting source signature of fossil fuels (and of the biosphere) would be too enriched. However, since we do not have any reliable information on an overestimation of the fossil fuel CO_2 share in EDGAR, and as the fossil

sources of CO_2 and CH_4 are very different, we do not incorporate this in the revised manuscript.

Appendix A, L17-18: To what extent are the remote measurements made at Mace Head representative as background values for quantifying the regional atmospheric impact of urban CO2 emissions in Heidelberg?

The STILT model uses TM3 boundary conditions to retrieve the CO₂ concentration at the model domain boundary. TM3 is fed by measurements at different clean air sites, including Mace Head. The European model domain boundary is geographically very close to Mace Head. Therefore, the STILT domain value is closely follows the measurements performed at Mace Head for CO₂, which we were able to confirm for two exemplary years (not shown). In this manuscript, we use the correlation of CO₂ and δ^{13} C in Mace Head to achieve a boundary δ^{13} C value, which seems reasonable regarding the good agreement in CO₂. This boundary value is necessary to compute the modelled total δ^{13} C.

However, for the moving Keeling plot approach presented in this study, we do not require an explicit background value (see Sect. 2.2) and therefore the choice of the boundary δ^{13} C hardly influences the resulting source signature.

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Evaluation of four years continuous $\delta^{13}C(CO_2)$ data using a moving Keeling plot method running Keeling approach

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Abstract. DAs different carbon dioxide (CO₂) emitters can be distinguished by theirhave different carbon isotope ratios. Therefore, measurements of atmospheric $\delta^{13}C(CO_2)$ and CO₂ concentration contain information on the CO₂ source mix in the catchment area of an atmospheric measurement site. ThisOften, this information may be is illustratively presented as mean isotopic source signature. Recently an increasing number of continuous measurements of $\delta^{13}C(CO_2)$ and CO₂ have become

- 5 available, opening the door to the quantification of CO₂ shares from different sources at high temporal resolution. Here, we present a method to compute the CO₂ source signature (δ_S) continuously , without introducing biases and evaluate our result using model data from the Stochastic Time-Inverted Langrangian Transport model. Only when we restrict the analysis to situations, which fulfill the basic assumptions of the Keeling plot method, our approach provides correct results with minimal biases in δ_S . On average, this bias is We find that biases in δ_S are smaller than 0.2 % with an inter-quartile rangeuncertainties
- 10 of about 1.2 % for hourly model data. As a consequence of applying the required strict filter criteria, 85 % of the data points mainly daytime values – need to be discarded. Applying the method to a four year data set of CO₂ and $\delta^{13}C(CO_2)$ measured in Heidelberg, Germany, yields a distinct seasonal cycle of δ_S . Disentangling this seasonal source signature into shares of its source components is, however, only possible if the isotopic end members of these sources, i.e., the biosphere, δ_{bio} , and the fuel mix, δ_F , are known. From the mean source signature record in 2012, δ_{bio} could be reliably estimated only for summer to (-25.0
- 15 \pm 1.0) % and δ_F only for winter to (-32.5 \pm 2.5) %. As the isotopic end members δ_{bio} and δ_F were shown to change over the season, no year-round estimation of the fossil fuel or biosphere share is possible from the measured mean source signature record without additional information from emission inventories or other tracer measurements, such as $\Delta^{14}C(CO_2)$.

1 Introduction

A profound understanding of the carbon cycle requires closing the atmospheric CO_2 budget at regional and global scale. For 20 this purpose it is necessary to distinguish between CO_2 contributions from oceanic, biospheric and anthropogenic sources and sinks. Monitoring these CO_2 contributions separately is desirable for improving process understanding, investigating climatic feedbacks on the carbon cycle and also to verify emission reductions and designing CO_2 mitigation strategies (Marland et al., 2003; Gurney et al., 2009; Ballantyne et al., 2010). A possibility to distinguish between different CO_2 sources and sinks utilizes concurrent ${}^{12}CO_2$ and ${}^{13}CO_2$ observations in the atmosphere. The carbon isotope ratio can be used to identify and

25 even quantify different CO₂ emitters if every emitter has its specific known δ^{13} CO₂ signature. For example, the CO₂ fluxes

from land and ocean can be distinguished using the ratio of stable carbon isotopologue ${}^{13}\text{CO}_2/{}^{12}\text{CO}_2$ in addition to CO₂ concentration measurements (Mook et al., 1983; Ciais et al., 1995; Alden et al., 2010). In other studies, measurements of ${}^{13}\text{CO}_2$ have been used to distinguish between different fuel types (Pataki, 2003; Lopez et al. 2013; Newman et al., 2015) or to evaluatedetect ecosystem behavior (Torn et al., 2011), giving only a few examples of the many published in the literature.

- In the last decade, new optical instrumentation havehas been developed, simplifying continuous isotopologue measurements. This led to an increasing deployment of these instruments, thereby increasing the temporal and spatial resolution of ${}^{13}C(CO_2)$ and CO₂ data (Bowling et al., 2003; Tuzson et al., 2008; McManus et al., 2010; Griffith et al., 2012; Vogel et al., 2013; Vardag et al., 2015a, Eyer et al., 2016). These data records may lead to an improved understanding of regional CO₂ fluxes, allowing estimates of mean $\delta^{13}C$ source signatures at high temporal resolution. Estimating mean source signatures from concurrent
- 10 $\delta^{13}C(CO_2)$ and CO_2 records over time provides e.g. insight into temporal changes in the signatures of two different CO_2 sources such as fossil fuels and the biosphere, if their relative share to the CO_2 offset is known. This may be used to studye.g. give insight into biospheric responses to climatic variations like drought, heat, floods, vapor pressure deficit etc. (Ballantyne et al., 2010; Ballantyne et al., 2011; Bastos et al., 2016). Likewise, the mean source signature can be used to separate between different source CO_2 contributions, if the isotopic end members of these sources are known at all times (Pataki, 2003; Torn et al., 2011; Lopez et al. 2013; Moore and Jacobson, 2015; Newman et al., 2015).
 - Many studies have successfully used the Keeling- or Miller-Tans- plot methodapproach (Keeling, 1958; 1961; Miller and Tans, 2003) to determine source signatures in specific settings (e.g. Pataki, 2003; Ogée et al., 2004; Lai et al., 2004; Knohl et al., 2005; Karlsson et al., 2007; Ballantyne et al., 2010). However, the situations in which Keeling and Miller-Tans plots yield correct results need to be selected carefully (Miller and Tans, 2003). Only if all possible pitfalls are precluded, the Keel-
- 20 ing intercept (or the Miller-Tans slope) can be interpreted as gross flux-weighted mean isotopic signature of all CO_2 sources and sinks in the catchment area of the measurement site. Especially in polluted areas with variable source/sink distribution, estimation of isotopic signature using a Keeling- or Miller-Tans-plot requires a solid procedure, e.g. accounting for wind direction changes or simultaneously occurring CO_2 sinks and sources. In this study, we discuss the possible pitfalls of CO_2 source signature determination from a continuous data set using the Keeling plot methodapproach and follow a specific modification
- of this method for automatic retrieval of and bias-free mean source signature with minimal biasesdetermination. We test this method with model-simulated CO₂ mole fraction and δ^{13} C(CO₂) data. Using a modeled data set where all source signatures are known, enables us to testcheck if the calculated source signature is correct, which is vital when evaluating measured data with an automated routine. Having found a method to determine the isotopic signature of the mean source signature correctly from measured CO₂ and δ^{13} C(CO₂) data, we discuss, which information can be reliably extracted from these results.

2 MethodsDetermination of source signature

2.1 Classical-Keeling and Miller-Tans plot methodapproach

Keeling (1958, 1961) showed that the mean isotopic signature of a source mix can be calculated by re-arranging the mass balance of total CO_2

$$5 \quad CO_{2tot} = CO_{2bg} + CO_{2S} \tag{1}$$

and of δ^{13} C of total CO₂, i.e. δ_{tot} :

$$\delta_{tot} \cdot CO_{2tot} = \delta_{bq} \cdot CO_{2bq} + \delta_S \cdot CO_{2S} \tag{2}$$

to:

$$\delta_{tot} = \underline{\approx} CO_{2bq} / CO_{2tot} \cdot (\delta_{bq} - \delta_S) + \delta_S \tag{3}$$

10 where CO_{2bg} and δ_{bg} are the concentration and $\delta^{13}C(CO_2)$ of the background component and CO_{2S} and δ_S are the concentration and $\delta^{13}C(CO_2)$ of the mean source, respectively. PIn a graphical evaluation when plotting δ_{tot} versus 1/CO_{2tot}, this yields a y-intercept of δ_S as the δ -intercept of the regression of all measurement points (cf. Fig.1a).

Miller and Tans (2003) have suggested an alternative approach to determine the mean isotopic signature by re-arranging Eqs. 1 and 2 such that δ_S is the regression slope when plotting $CO_{2tot} \cdot \delta_{tot}$ versus CO_{2tot} :

15
$$CO_{2tot} \cdot \delta_{tot} = \delta_S \cdot CO_{2tot} - + CO_{2bg}(\delta_{bg} - \delta_S)$$
 (4)

They argue that this approach might be advantageous since the isotopic signature does not need to be determined from extrapolation to $1/CO_2=0$, which could introduce large errors in the δ_S estimate. Zobitz et al. (2006) have compared the Keeling and the Miller-Tans plot methodapproach (Eqs. 3 and 4) and found no significant differences between both approaches when applied to typical ambient CO₂ variations. We were able to reproduce this result with our model-simulated data set (cf. Sect. 3.1).

- 20 Differences between both approaches were (0.00 ± 0.04) ‰ when applying certain criteria (standard deviation of intercept < 2 ‰, CO₂ range within 5 hours >5 ppm), which will be motivated in Sect. 2.3. Also the choice of fitting algorithm has been discussed in the literature. Pataki (2003), Miller and Tans (2003) and Zobitz et al. (2006) compared different fitting algorithms for the regression and came to different recommendations. Orthogonal distance regression (ODR) and weighted total least squares fits (WTLS) (model 2 fits) take into account errors on x and y, whereas ordinary least squares (OLS) minimization (model 1
- 25 fit) only takes into account y-errors. Zobitz et al. (2006) have found differences between both fitting algorithms especially at small CO₂ ranges. We have also applied a model 1 (OLS) and model 2 (WTLS) fit to our simulated data and have not found any significant differences ((0.00 ± 0.01) ‰) between them when applying certain criteria (error of intercept < 2 ‰, CO₂ range within 5 hours >5 ppm, see Sect. 2.32.2). In our study, we use a WTLS-fit (Krystek and Anton, 2007) as stable algorithm for fitting a straight line to a data set with uncertainty in x and y direction in a Keeling plot methodapproach. a Keeling plot for
- 30 calculation of the mean source signature, but using a Miller-Tans plot seems just as good. Note that the isotopic signature of the

mean source δ_S can be determined from linear regression without requiring a background CO₂ and $\delta^{13}C(CO_2)$ value. However, the Keeling and Miller-Tans plot methodsapproaches are only valid if the background and the isotopic signature of the source mix δ_S are constant during the period investigated (Keeling, 1958; Miller and Tans, 2003). Further, the approaches are only valid when sources and sinks do not occur simultaneously. Miller and Tans (2003) gave an example, which showed that

- 5 as soon as sources and sinks of different isotopic signature/fractionation occur simultaneously, the determination of isotopic signature of the source/sink mix may introduce biasesis not *per se* possible. In these cases, the results cannot be interpreted as mean flux-weighted source signature anymore. This has very unfortunate consequences, since in principle we are interested in determining the isotopic signature of the source mix of a region during all times, i.e. also during the day when photosynthesis cannot be neglected.
- 10 Pataki (2003), Miller and Tans (2003) and Zobitz et al. (2006) compared different fitting algorithms for the regression and came to different recommendations. Orthogonal distance regression (ODR) and weighted total least squares fits (WTLS) (model 2 fits) take into account errors on x and y, whereas ordinary least squares (OLS) minimization (model 1 fit) only takes into account y-errors. Zobitz et al. (2006) have found differences between both fitting algorithms especially at small CO₂ ranges. We have also applied a model 1 (OLS) and model 2 (WTLS) fit to our simulated data and have not found any significant
- 15 differences ((0.00 ± 0.01) ‰) between them when applying certain criteria (error of intercept < 2 ‰, CO₂ range within 5 hours
 >5 ppm, see Sect. 2.2).In this study, however, we use a WTLS-fit (Krystek and Anton, 2007) for the determination of the intercept and its uncertainty.

2.2 Moving Keeling plot methodRunning Keeling approach

For a continuous long-term data set, we suggest an automatic routine to determine the mean isotopic signature of the source mix.

- 20 We call this approach the "running" Keeling approach. It is similar to the moving Keeling plot for CH₄ currently suggested by Röckmann et al. (2016). In our case of CO₂, we also have to take into account the possibility of simultaneously occurring sinks and sources, which is not important in the case of CH₄. Our moving Keeling plot methodrunning Keeling approach is a specific case of the classical Keeling plot methodapproach (Eq. 3) (Keeling, 1961) as it uses only five hourly-averaged measurement points of CO₂ and $\delta^{13}C(CO_2)$ fitting a regression line through these five data points (cf. Fig. 1a, illustrated only for three data
- 25 points for clarity of inspection). We choose five5 hours as a compromise betweenof maximum number of data points and thus, of robust regression and of source mix constancy. This compromise also manifests itself in such a manner that a window size of five hours leads to maximum coverage.in a minimizing period, in which the source mix does not change significantly. No background value is included in the regression. The moving Keeling plot methodrunning Keeling approach works such that, e.g. for the determination of the mean source signature at 3 pm, we use the hourly CO₂ and $\delta^{13}C(CO_2)$ measurements from 1
- 30 pm to 5 pm and fit a regression line. Next, for the determination of the source signature at 4 pm, we use the CO₂ and $\delta^{13}C(CO_2)$ measurements from 2 pm to 6 pm and so on. Note that this approach leads to a strong auto-correlation of neighboring source signature values.

2.3 Filter criteria of the moving Keeling plot methodrunning Keeling approach

In order to prevent pitfalls in the regression-based determination of mean isotopic signature, we set a few criteria for the movingrunning Keeling plots to "filter" out situations, in which a Keeling plot cannot be performed. These filter criteria are also similar in type to the ones introduced by Röckmann et al. (2016). We here explain why these filter criteria are needed

- 5 for CO_2 and how they are set. A prerequisite for the Keeling plot is that the source mix as well as the background need to stay constant during the investigated period (see Fig. 1a). Varying source mixes may occur when e.g. the wind direction and therewith the footprint of the measurement site change, or if the emission patterns themselves change over time. This may lead to strong biases of the regression-based mean isotopic source signature (illustrated in Fig. 1b). We eliminate these cases by inspecting the error of the determined intercept δ_S . If the source mix or the background significantly change within five hours,
- 10 the data points will not fall on a straight line and the error of the intercept will increase. We here set an error of 2 $\%_0$ (in a WTLS fit) as threshold between an acceptable and a "bad" fit, after having inspected many Keeling plots individually. Also, we demand a monotonous increase of CO₂ within 5 hours, as a decrease of would be due to either a sink of CO₂ or a breakdown of the boundary layer inversion potentially associated with a change of catchment area of the measurement, both biasing the resulting mean source signature.
- As mentioned before, the determination of a mean isotopic signature is not *per se* possible during the day when CO_2 sinks and sources are likely to occur simultaneously (Miller and Tans, 2003). This can be explained in the Keeling plot by the vector addition of CO_2 source and sink mixing lines with different isotopic signatures, resulting in a vector with an intercept different from the expected one, leading to an isotopic signature, which can even lie outside the expected range of the isotopic source end members (see Fig. 1c). This potential bias is stronger, the smaller the net CO_2 signal is. Therefore, e.g. for evaluation
- of the Heidelberg data, we demand an increase in CO_2 during the five5 hour period of at least 5 ppm to exclude periods where the photosynthetic sink is similarly strong as total CO_2 sources. This normally leads to an exclusion of daytime periods, when the boundary layer inversion typically breaks up and the photosynthetic sink is most pronounced. Therefore, we are mainly rejecting periods, in which isotopic discrimination during photosynthesis dominates the mean isotopic source signature. During winter, it may happen that the inversion does not break up due to the cold surface temperatures, but in this season,
- 25 photosynthetic activity is typically much smaller than fossil fuel emissions and therefore biases of the regression-based mean source signature are only small.

In the next section, we show that with these filter criteria, , i.e. (i) error of the Keeling plot intercept < 2 %, (ii) monotonous increase during five hours and (iii) increase of > 5ppm during five hours, which we chose empirically, we are able to successfully rejectremove those source signatures, where the underlying assumptions for the Keeling plot methodapproach are not met. In

30 Sect. 3.1, we will also briefly discuss how sensitive the result is to the choice of filter criteria. Note that the filter criteria may differ for different measurement sites depending on the source heterogeneity and footprint of the catchment areas. Therefore, respective filter criteria need to be designed individually for each measurement station.

Results and Discussion 3

5

3.1 Evaluation of the moving Keeling plot method Test of the running Keeling approach with modeled data

We apply the moving Keeling plot methodrunning Keeling approach to a modeled CO₂ and $\delta^{13}C(CO_2)$ data set. As also pointed out by Röckmann et al. (2016) in their CH_4 study, this has the advantage that we can test and evaluate our filter criteria as we know exactly the individual isotopic source signatures that created the modeled data set and thus, the contribution-weighted mean isotopic source signature at every point in time. Details on the STILT model (Lin et al., 2003) and on the computation of the modelled CO₂ and δ^{13} C(CO₂) record as well as of the resulting mean source signature, δ^{STILT}_{S} , are given in Appendix A.

Filter criteria of modeled source signature

We apply the same filter criteria to the calculated mean source signature of the STILT modelled data set δ_{S}^{STILT} , as to the regression-based mean source signature (Sect. 2.3). The "unfiltered" source signatures (black in Fig. 2a) are 0-2% more 10 enriched than the "filtered" source signatures (blue). This offset is mainly caused by the daytime source signatures, which are on average more enriched than nighttime source signatures (Fig. 2b), but more likely to be filtered out based on the criteria of Sect. 2.3.

Evaluation of running Keeling approach

- 15 We havecan now evaluated the moving Keeling plot methodrunning Keeling approach and the used filter criteria based on the model data and tested if they allow a bias-free retrieval of the mean source signature. In Fig. 3a, we compare the regressionbased source signatures to the filtered reference source signature of Fig. 2a, which we have extracted from the model. We do not only compare the mean difference of the mean source signature, but the hourly differences of the mean source signature as well as the smoothed difference. This enables us to clearly state how well we are able to determine the hourly mean source 20
- signature and its long-term trend.

Fig. 3a displays the filtered seasonal changes of the source signature exemplary for the year 2012. The moving Keeling plot methodrunning Keeling approach is able to extract the seasonal variability of the mean isotopic signature correctly. The median difference (and inter-quartile range) between smoothed regression-based (red) and smoothed modeled (blue) approach (both smoothed with 50% percentile filter with window size of 100 hours, no smoothing 50 points in front of large data gaps) is 0.0

- ± 0.4 %. A smoothing window size of 100 hours (ca. 4 days) was chosen, so that synoptical and seasonal variations of δ_S can 25 be seen while diurnal variations are supressed. On a shorter diurnal time scale, we also compare individual hourly results for the source signature (stars in Fig. 3b, c). The inter-quartile range of the filtered hourly difference between both the reference δ_{S}^{STILT} and the movingrunning Keeling plot signature is aboutea. 1.2 % throughout the year, but the median difference is small (0.2 %). The source signature of the model reference and movingrunning Keeling plot source signature show the same
- 30 temporal pattern both, in summer and in winter. Further, we find that if we do not apply all of the criteria described in Sect. 2.2 (unfiltered data in Fig. 3b, c), we see larger differences between regression-based source signature (from the movingrunning Keeling plot) and the STILT reference values.

Note, however, that with the criteria established in Sect. 2.3, we have to rejected about 85% of all estimated source signatures. This seems to be an intrinsic problem for an urban setting with any different sources and sinks. Obviously, in many situations the prerequisites of the Keeling plot method are not fulfilled and if not filtered out, these data would introduce biases in the retrieved mean source signature. Depending on the application, it may be worthwhile to loosen the filter criteria to increase the

- data coverage. For example, if one sets no criteria for the minimal CO_2 range, but only for the error of the offsetslope (< 2%), 5 about 60% of all data remain for the estimated source signature, but the median difference between model- and Keeling-based results increases to 0.3 % and the interquartile range increases to 2.4% (hourly data), which is about twice of what we found before. Withdrawing all filter criteria, but using only night time values, leads to a coverage of about 35% (night time) and an interquartile range of 3.5%. The filter criteria, which we use here (Sect. 2.3) are, thus, rather strict, but we are confident to precisely extract the correct source signature from the $\delta^{13}C(CO_2)$ and CO_2 record at highest temporal resolution.
- 10

Application of the running Keeling approach

3.2 The measured source signature record in Heidelberg

We now apply this approach to real measured Heidelberg data. We use the Heidelberg CO₂ and $\delta^{13}C(CO_2)$ record on hourly time resolution (Fig. B1) to compute the isotopic source signature via regression (Fig. 4). The quality of the Heidelberg CO_2 and $\delta^{13}C(CO_2)$ record is assessed in the Appendix B. The measurement site and its surrounding catchment area is described 15 by Vogel et al. (2010). We observe a distinct seasonal cycle of the mean isotopic source signature in Heidelberg. Smoothed minimum values of about -32 % are reached in winter. Maximum values of about -26 % occur in summer. This annual pattern is reproduced every year and is similar to annual patterns observed by e.g. Schmidt (1999) for Schauinsland, Germany or by Sturm et al. (2006) for Bern, Switzerland. Additionally, the first year shows a more enriched summer maximum source signature. A number of data points (less than 0.5%) lie outside the range of realistic end members between -20 and -45 % 20 of any source in the catchment area (see Table A1). These outliers are not unusual in an urban setting, asean be explained statistically by the uncertainty of the running Keeling approach. From the model analysis, we expect the inter-quartile range of the modelled δ_S for the Heidelberg catchment area isto be about 1.2 % for hourly (non-smoothed) data, which is only variability in the model may be due to a lower variability in the coarse resolution emission inventory used in STILT (0.1°x 25

0.1°).

Our four-year record of the mean source signature in Heidelberg (see Fig. 4) provides a first insight into the source characteristics at the measurement station. It reaches its minimum in winter when we expect residential heating (mainly isotopically depleted natural gas, see Tab. A1) to contribute significantly to the source mix. The source signature reaches its maximum

in summer when more enriched biospheric fluxes are expected to dominate the CO₂ signal. This observed seasonal cycle in 30 Heidelberg (Fig. 4) is very similar to the filtered modelled source signature (Fig. 3a) in amplitude as well as in phase.

3.3 Information content derived from δ_S Extracting information on the isotopic end members δ_{bio} and δ_F from δ_S

We now want to elaborate what quantitative information can be drawn from the mean source signature record in Heidelberg about its components. Details on the Heidelberg measurement site and catchment area can be found in Vogel et al., 2010. Formulation of question For an urban continental measurement site such as Heidelberg, we have to assume that there are at

5 least two main source types of CO₂ in the catchment area: Fuel CO₂ and CO₂ from the biosphere. In this simplest case, we essentially have one equation for δ_S , (Eq. 6) with three unknown variables (δ_{bio} , δ_F and the fuel (or biosphere) share f_F); and only if two of these variables are known, the third variable can be quantified from the measurements:

$$\delta_S = \frac{CO_{2F}}{\Delta CO_2} \cdot \delta_F + \frac{\Delta CO_2 - CO_{2F}}{\Delta CO_2} \cdot \delta_{bio} \tag{5}$$

$$= f_F \cdot \delta_F + (1 - f_F) \cdot \delta_{bio} \tag{6}$$

Which of the variables is the one to be estimated depends, of course, on the research question. If the fossil fuel share and end members are well known from inventories, one could be especially interested in determining the isotopic end member δ_{bio} in order to study biospheric processes and their feedback to climatic parameters (Ciais et al., 2005; Ballantyne et al., 2010; Salmon et al., 2011). Contrary, one may be interested in determining the relative share of fossil fuel CO₂ in the catchment area (with known δ_{bio} and δ_F) to monitor emission changes independently from emission inventories. In our discussion, we focus on the determination of the fossil fuel share, but the arguments for most parts are analog for other research questions.

As noted, a quantification of the relative shares of fossil fuel and the biospheric CO₂ at continental stations is only possible if information on the isotopic end members of both source categories are available. For example, Vardag et al. (2015b) used the isotopic signatures of δ_{bio} (assumed to be known within a fixed uncertainty) and δ_F (obtained by calibration with $\Delta^{14}C(CO_2)$) to calculate the fossil fuel CO₂ contribution from the (continuously) measured CO₂ and $\delta^{13}C(CO_2)$ signal. However, knowing

- 20 the isotopic signatures δ_{bio} and δ_F over the entire course of the year, requires an extensive number of measurements at the relevant sources throughout the year and further assumptions how to scale up theseextrapolate the source signature of the point measurements to a mean source signature of all relevant sources. Therefore, the question, which we adress here, is whether it is possible towe ask here, if we can obtain information on these end members from our measured source signature record, despite the fact that we have three unknown variables and only one equation. In the following, we discuss this question exemplary for
- 25 the year 2012, for which we have modeled data, inventory information and the mean measured isotope signature. We restrict the discussion to a single year as we focus on discussing, which information can principally be obtained from a year-round mean source signature record.

One source approximation

We have noted that In general, in order to obtain information from δ_S on δ_{bio} (δ_F), we require information on the fuel CO₂ 30 share and δ_F (on the fuel CO₂ share and δ_{bio}). However, in cases where the relative share of the biosphere (fossil fuels) is negligible, the isotopic signature of δ_F (δ_{bio}) would equal the mean measured isotopic signature. In these cases, the number of unknown variables would be reduced to one, as the fossil fuel (biospheric) share is $\approx 100\%$ and δ_{bio} (δ_F) does not contribute significantly to the mean source signature. In a typical catchment area, the relative share of fossil fuels and of the biosphere will not be negligible throughout the year, but in winter, fossil fuel CO_2 will dominate while in summer the biospheric CO_2 will dominate the CO_2 offset compared to the background. E.g. from the STILT model results for Heidelberg (Sect. 3.1 and Appendix A), we perceive that on cold winter days in Heidelberg, the fossil fuel share can be about 90 to 95% of the total CO_2

5 offset. In summer, it reaches a minimum of at about 20%. We may, thus, be able to obtain information about the isotopic end members of δ_F in winter (δ_{bio} in summer), when the mean source signature is dominated by the fossil fuel (biospheric) share.

3.4 Evaluation of δ_S in Heidelberg

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To calculate the resulting isotopic end members of δ_i from the measured source signature in Heidelberg (and with that to solve Eq. 6), we require the fossil fuel CO₂ share, which we take here from STILT and the bottom-up emission inventory EDGAR. However, as we only require the share and not the absolute concentration, we are largely independent from potentially large model transport errors. We thus, assume an absolute uncertainty of 10 % of the fossil fuel share (and of the biospheric share respectively).

To determine δ_F in addition to the fuel CO₂ share, we require a value for δ_{bio} . Here we use a typical mean value of the isotopic end member of δ_{bio} = -25.0 % and assume a seasonal cycle as determined for Europe by Ballantyne et al. (2011) (see

- Fig. 2 and 3 in Ballantyne et al. (2011)) displayed in Fig. 5a as solid green line. We show δ_{bio} with two possible uncertainties of 0.5 and 2.0 %. As expected, the uncertainty of the unknown δ_F is only acceptably small when the relative share of the biosphere becomes negligible, which is the case in winter (Fig. 5a). The isotopic end member of δ_F in winter is about (-31.0 ± 2.5) % in January to March 2012 and decreases to (-32.5 ± 2.5) % in November to December 2012. Further, Fig. 5a shows that the best estimate of the resulting isotopic signature δ_F is more depleted in summer than in winter. This curvature is opposite
- 20 tofrom what we would expect from EDGAR (2010) transported by STILT (see assumed δ_F in Fig. 5b). Only when assuming an uncertainty of the biospheric end member of $\pm 2 \%_0$ or more, the uncertainty range of the estimated δ_F allows more enriched δ_F signature in summer than in winter. This suggests that the isotopic source signature of the biosphere in summer is most probably more depleted (by about 2 %₀) than the previously assumed δ_{bio} value based on Ballantyne et al. (2011).

To estimate δ_{bio} (Fig. 5b), we require (besides the fossil fuel share) the isotopic source signature δ_F . Here we use δ_F

- 25 calculated with the STILT model on the basis of EDGAR emissions and source signatures according to Tab. A1. Its annual mean value is -31.0 % and it shows a seasonal cycle with more enriched signatures in summer than in winter. We show the results for δ_{bio} for two possible δ_F uncertainties of 1.0 and 3.0 % (see Fig. 5b). The best-estimate of the isotopic end member of δ_{bio} in summer is about -25.0 ± 1.0 % in June to August 2012. This reinforces the presumption that δ_{bio} is more depleted than the assumed δ_{bio} value based on Ballantyne et al. (2011) during summer.
- The uncertainty of the isotopic end members in Fig. 5a and b has three components: (1) The uncertainty of the fossil fuel CO₂ share estimated from STILT, which we assume to be about 10% (absolute) in our case, (2) the uncertainty of the other known isotopic end member (0.5 and 2 % for δ_{bio} or 1.0 and 3.0 % for δ_F) and (3) the uncertainty of the measured mean source signature itself (ca. 0.40.5 %, see Sect. 3.1 for interquartile range of difference between smoothed regression-based and smoothed modelled source signature). Note, that an uncertainty of 10% of the fossil fuel share is at the low end of uncertainties.

However, an uncertainty of 20% of the fossil fuel share would increase the uncertainty in the unknown isotopic end members by only 0.2 - 0.4 % for δ_{bio} in summer and δ_F in winter, respectively.

The derived uncertainty of δ_F in winter is about 2.5 % in winter and that of δ_{bio} in summer is about 1.01.5 % in summer. An uncertainty of ± 2.5 % for δ_F is rather large if we want to use this observation-based top-down result for further quantitative

- 5 source apportionment. Vardag et al. (2015b) showed that a misassignment of 2.5 $\%_{o}$ in δ_{F} leads to a bias in the continuous fuel CO₂ estimate of about 15% for an urban measurement site like Heidelberg. The observation-based biospheric end member δ_{bio} has an uncertainty of only about 1.01.5 $\%_{o}$ in June to August 2012, which is a very well constraint value for this period. We cannot assume that the isotopic end members δ_{bio} and δ_{F} remain constant over the course of the year: δ_{bio} typically shows a seasonal cycle possibly due to seasonal changes in the fraction of respiration from C3/C4 plants as well as due to influences of
- 10 meteorological conditions on biospheric respiration. Likewise, δ_F typically shows more enriched values in summer, when the contribution of residential heating (and therewith of depleted natural gas) is much smaller than in winter. Therefore, also no year-round estimation of fuel CO₂ share is possible from CO₂ and δ^{13} C(CO₂) only.

Evaluation of accuracy

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If both isotopic end members stayed constant over the course of one year, we would now be able to actually estimate the fossil fuel CO₂ share (and its uncertainty) continuously throughout the year without requiring any additional information, such

- as inventories or Δ^{14} C(CO₂) for calculation of δ_F from the mean source signature. However, from bottom-up information, we would neither expect the isotopic value of the biosphere nor that of the fossil fuel mix to remain constant throughout the year. In contrary, we would expect the biosphere to show a distinct seasonal pattern e.g. due to the change in fraction of respiration from C3/C4 plants over the course of the year or influences of climatic conditions on biospheric respiration (e.g. Still et al.,
- 20 2003; Ciais et al., 2005). A seasonal cycle of δ_F is also expected with more enriched values in summer, when the contribution of residential heating (and therewith of depleted natural gas) is much smaller than in winter. Therefore, if we have varying isotopic end members of δ_F and δ_{bio} , we cannot estimate the fossil fuel share correctly for the entire year. But, if the amplitude of these changes is small, the biases in fossil fuel CO₂ will be small as well. Vardag et al. (2015b) have shown that from a limited number of $^{14}C(CO_2)$ grab samples distributed over the year, the true annual mean value of δ_F can be obtained. Here
- 25 we show that from the mean δ^{13} C source signature only a reliable winter value is obtained, potentially introducing summer biases (as well as annual averaged biases) into the fuel CO₂ share.

Possible strategy to obtain δ_F and δ_{bio}

To determine δ_{bio} , one can take the summer value of δ_{bio} from the source signature record following Sect. ??. As no reliable determination of δ_{bio} is possible during the rest of the year based only on atmospheric observations, there is a need ofmust be either very good bottom-up literature values for the catchment area of interest or frequent measurement campaigns at the sources must be performed. However, the disadvantage of using a bottom-up approach is that usually only information from few specific sites are available, which need then to be upscaled correctly such that they are representative of the entire catchment area. For a determination of δ_F in the entire year, one can use $\Delta^{14}C(CO_2)$ measurements (following Vardag et al. (2015b)) or rely on the bottom-up inventory information. To obtain correct source signatures of the different fossil fuel categories, measurements close to these sources are required to support or refute the inventory-model based estimates. These measurements again need to be upscaled correctly.

4 Summary and Conclusions

Many measurement stations are currently being equipped with new optical instruments, which measure $\delta^{13}C(CO_2)$ aiming

- 5 at an improveda more quantitative understanding of the carbon fluxes in their catchment area. If this additional $\delta^{13}C(CO_2)$ data stream is not directly digested in regional model calculations, the mean isotopic source signature is often computed from the $\delta^{13}C(CO_2)$ and CO₂ records for a potential partitioning of source contributionsfor the analysis of the source composition. Essentially, this source signature provides the same degree of information as the measured $\delta^{13}C$ and CO₂ records themselves, but is a more intuitive and therefore common form for further interpretations. AWe re-emphasize here that a bias-free deter-
- 10 mination of source signature, however, requires carefully selecting the data for situations, in which determination of source signature with a Keeling plot method can provide reliable results. This excludes (1) periods, when sinks and sources occur simultaneously, (2) when the source mix changes or (3) when the signal-to-noise ratio is too low (Keeling, 1958; 1961; Miller and Tans, 2003).

We therefore developed filter criteria and show that the routine and accurate determination of $\delta^{13}C(CO_2)$ source signature

- 15 is possible, if the introduced filter criteria are applied. As suggested by Röckmann et al. (2016), we use a modeled data set for validation of the approach. We find that for a station like Heidelberg the bias introduced by our analysis is only (0.2 ± 1.2) % for hourly data. The uncertainty decreases in the long-term to (0.0 ± 0.4) %. We are, therefore, able to estimate the source signature correctly, but. However, 85% of the data are rejected by the filter criteria. Further, as the filter criteria are such that the source signatures are more likely to be filtered out during the day than during the night, the long-term source signature
- 20 is not representative of real daily averages, but only of periods, where the data was not filtered out (mainly nighttime). As a consequence, also the isotopic end members δ_{bio} and δ_F , can only be estimated for these periods. This problem does not occur for CH₄, which has only weak daytime sinks.

By applying the moving Keeling plot methodrunning Keeling procedure to a real measured data set measured in Heidelberg, we wereare able to determine the source signature over the course of four years. We find a distinct seasonal cycle of the mean source signature with values of about $-26 \%_0$ in summer and about $-32 \%_0$ in winter. This general behavior was expected due to the larger relative contribution of more depleted fossil fuel CO₂ in winter. For a unique interpretation of the mean source signature, possible sources in the catchment area need to be identified. As soon as there isare more than one source, the source signature is a function of the isotopic end members of all sources, as well as of their relative shares. Therefore, to study the seasonal and diurnal changes of fossil fuel shares at a continental station, information on the isotopic end members of the fossil

30 fuel mix as well as of the biosphere are required on the same time resolution. Unfortunately, the isotopic end members are often not known with high accuracy. The uncertainty of the isotopic end members often impedes or even prevents a unique straightforward determination of the source contribution in the catchment area (e.g. Pataki, 2003; Torn et al., 2011, Lopez et al. 2013; Röckmann et al., 2016) and calls for elaborated statistical models based on Bayesian statistics. This important fact is sometimes mentioned, but the consequences for quantitative evaluations are rarely emphasized, preserving the high expectations associated with isotope measurements.

We showed that for the urban site Heidelberg, we can use the observation-based mean source signature record to estimate the isotopic end member δ_F in winter and the isotopic end member δ_{bio} in summer within the uncertainties of $\pm 2.5 \%$ and

- 5 $\pm 1.01.5$ %, respectively. Here we assumed, when assuming an uncertainty of ± 10 % for the fossil fuel and the biospheric CO₂ share and an uncertainty of the other isotopic end member δ_F of ± 3.0 %, and δ_{bio} of ± 2.0 %. However, in the winter season we cannot obtain any reliable information on δ_{bio} and in summer we cannot study δ_F . For a year-round determination of fossil fuel share, δ_{bio} and δ_F are required throughout the year. If the isotopic end members would not change within seasons, it would be possible to determine these constant isotopic signature from our obtained estimates. However, this is not a valid assumption.
- 10 As no reliable determination of δ_{bio} and δ_F is possible during the entire year based only on atmospheric observations, there is a need of either very good bottom-up information for the catchment area of interest or frequent measurement campaigns close to the sources. However, the disadvantage of using such a bottom-up approach is that usually only information from few specific sites are available, which need then to be upscaled correctly such that they are representative of the entire catchment area. For a determination of δ_F during the entire year, one can possibly utilize $\Delta^{14}C(CO_2)$, CO/CO₂ measurements (following
- 15 Vardag et al. (2015b)) or O₂/N₂ measurements (e.g. Sturm et al. 2006; Steinbach et al., 2011), all of which exhibit their own deficiencies, which are discussed elsewhere (e.g. Ciais et al., 2015); Vardag et al., 2015b.

Finally, we could show, that even though it is not possible to determine the isotopic end members throughout the year, it is possible to refute certain literature values. E.g. a respiration signature of -23 % in August and September 2012 as reported by Ballantyne et al. (2011) is most likely too enriched as this would lead to more depleted δ_F values in summer than in winter. This, which is in contrast to what we would expect based on emission inventories.

Appendix A: The STILT model

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We use the Stochastic Time Inverted Lagrangian Transport (STILT) model (Lin et al., 2003) to evaluate our moving Keeling plot methodrunning Keeling approach. The STILT model computes the CO₂ mole fraction by time-inverting meteorological fields and tracing particles emitted at the measurement location back in time to identify where the air parcel originated from. This so-called footprint area is then multiplied by the surface emissions in the footprint to obtain the CO₂ concentration at the site in question. Photosynthesis and respiration CO₂ fluxes are taken from the vegetation photosynthesis and respiration model (VPRM, Mahadevan et al., 2008). Anthropogenic emissions are taken from EDGARv4.3 emission inventory (EC-JRC/PBL, 2015) for the base year 2010 and further extrapolated to the year 2012 using the BP statistical review of World Energy 2014 (available at: http://www.bp.com/en/global/corporate/about-bp/energy-economics/statistical-review-of-

30 world-energy.html). Additionally, we use seasonal, weekly and daily time factors for different emission categories (Denier van der Gon et al., 2011). Since the EDGAR inventory is separated into different fuel types, we obtain a CO₂ record for each fuel type as well as for respiration and photosynthesis. This allows us, to construct a corresponding $\delta^{13}C(CO_2)$ record by multiplying the isotopic signature of every emission group i to its respective CO₂ mole fraction $\delta^{13}C(CO_2)_i \cdot CO_{2,i}$ (see Tab.

A1), adding these to a far-field boundary value of $\delta^{13}C(CO_2) \cdot CO_2$ and dividing it by the total CO₂ at the model site. The CO₂ far-field boundary value for STILT is the concentration at the European domain border (16°W to 36°E and from 32°N to 74°N) at the position where the backwards traced particles leave the domain. The concentration at the domain border is taken from analyzed CO₂ fields generated with TM3 (Heimann and Körner, 2003) based on optimized fluxes (Rödenbeck, 2005).

- 5 The isotopic boundary value is then constructed artificially by fitting the linear regression between CO₂ and $\delta^{13}C(CO_2)$ in Mace Head (year 2011 from World Data Center for Greenhouse Gases, (Dlugokencky et al., 2015)) and applying the function of the regression to the boundary CO₂ values in the model. Since, in reality, we also have measurement uncertainties of CO₂ and $\delta^{13}C(CO_2)$ we also include a random measurement uncertainty of 0.05 ppm and 0.05 ‰, respectively to the modeled data sets. The CO₂ and $\delta^{13}C(CO_2)$ records are used to calculate the regression-based mean source signature following the moving
- 10 Keeling plot methodrunning Keeling approach (Sect. 2.2).

A1 Computation of mean modeled source signature

For the reference modeled mean source signature we use a "moving""running" background. In particular, we chose the minimum CO₂ value within 5 hours centered around the measurement point as the background value and all contributions from fuel CO₂ (c_{*F*,*i*}), respiration (c_{*resp*}) and from photosynthesis (c_{*photo*}) are computed as offsets relative to the background (c_{*bg*}). This
is then comparable to the regression-based moving Keeling plot methodrunning Keeling approach as the lowest and highest CO₂ values within five hours span the Keeling plot. We are then able to define and compute the reference modeled mean source signature as:

$$\delta_S^{STILT} = \frac{\sum_i \delta_{F,i} |c_{F,i}| + \delta_{resp} |c_{resp}| + \delta_{photo} |c_{photo}|}{\sum_i |c_{F,i}| + |c_{resp}| + |c_{photo}|} \tag{A1}$$

Note that we use absolute values of all contributions since photosynthetic contributions (c_{photo}) are generally negative while source contributions (c_{resp} and $c_{F,i}$) are generally positive, but both should lead to a negative source signature in a Keeling plot. The calculated source signature δ_S^{STILT} (from Eq. A1) can be seen in Fig. 2a (blue). If we would not take into account the different signs of respiration and photosynthesis, we would construct isotopic signatures, which are counter-intuitive and not interpretable as mean source signature (Miller and Tans, 2003) as the denominator could converge against zero. When calculating the isotopic source following Eq. A1, we can interpret δ_S^{STILT} as gross flux weighted mean isotopic signature of sources and sinks.

Appendix B: CO₂ and δ^{13} C(CO₂) measurements in Heidelberg

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A necessary prerequisite of determining the mean source signature correctly at a measurement site is a good quality of CO₂ and $\delta^{13}C(CO_2)$ measurements. Therefore, we briefly describe here the instrumental set-up in Heidelberg, assess the precision of the CO₂ and $\delta^{13}C(CO_2)$ measurements and finally present our four years' ambient air record of CO₂ and $\delta^{13}C(CO_2)$ in Heidelberg.

B1 Instrumental set-up and intermediate measurement precision

Since April 2011, atmospheric trace gas mole fractions are measured with an *in-situ* Fourier Transform-Infrared (FTIR) spectrometer at three-minute time resolution at the Institut für Umweltphysik in Heidelberg (Germany, 49°25'N, 8°41'E, 116 m a.s.1 +30 m a.g.l.) (see Fig. B1 for CO₂ and δ^{13} C(CO₂)). A description of the measurement principle can be found in Esler

5 et al. (2000) and Griffith et al. (2010, 2012). Hammer et al. (2013) describe the Heidelberg-specific instrumental set-up in detail and Vardag et al. (2015a) describe modifications to this set-up and the calibration strategy for the stable isotopologue measurements.

The intermediate measurement precision of the FTIR is about 0.05 ppm for CO₂ and 0.04 % for $\delta^{13}C(CO_2)$ (both 9 minute averages) as determined from the variation of daily target gas measurements (Vardag et al., 2014; Vardag et al., 2015a).

10 In this work, we only use hourly CO_2 and $\delta^{13}C(CO_2)$ values, since simulation runs often have an hourly resolution and thus, observations and simulations can directly be compared. However, from Allan standard deviation tests, we know that the intermediate measurement precision of hourly measurements is only slightly better than for nine-minutely measurements (Vardag et al., 2015a).

B2 Four years of concurrent CO₂ and δ^{13} C(CO₂) measurements in Heidelberg

- 15 The CO₂ concentration in Heidelberg varies over the course of the year and has its maximum in winter and its minimum in summer (Fig. B1). This pattern is mainly driven by larger fossil fuel emissions in winter than in summer. Especially, emissions from residential heating are higher in the cold season. Furthermore, biospheric uptake of CO₂ is lower in winter than in summer. The minimum of the isotopic $\delta^{13}C(CO_2)$ value coincides with the maximum in CO₂ concentration and vice versa. The features are anti-correlated since almost all CO₂ sources in the catchment area of Heidelberg are more $\delta^{13}C$ -depleted than
- the background concentration and therefore a CO₂ increase always leads to a depletion of δ¹³C(CO₂) in atmospheric CO₂. Also, the biospheric CO₂ sink, dominating in summer, discriminates against δ¹³C(CO₂), leaving the atmosphere enriched in ¹³C(CO₂), while CO₂ decreases. On top of the seasonal cycle, CO₂ in Heidelberg (Fig. B1) slightly increases over the course of four years by about 2 ppm year⁻¹. At the same time δ¹³C(CO₂) decreases by about 0.04 ‰ year⁻¹. These rates are similar to the CO₂ increase and δ¹³C(CO₂) decrease rates in Mauna Loa, Hawaii, USA (Dlugokencky et al., 2015; White et al., 2015)
 and therefore reflect the global increase of CO₂ from ¹³C-depleted sources moderated by air-sea gas exchange. It is not visible
- to the eye, how the degree of depletion in $\delta^{13}C(CO_2)$ varies over the course of the year (see Fig. B1). To analyze this behavior, the mean source signature must be computed (see Sect. 2.2 and Fig. 4).

Author contributions. S. Vardag developed the moving Keeling plot methodrunning Keeling approach in exchange with I. Levin. S.Vardag verified this approach using pseudo data from the STILT model and applied the approach to measured data. The measured data was partly

30 taken by S. Hammer (until Sept. 2011) and mainly by S. Vardag (Sept. 2011 to June 2015). The final discussion and manuscript writing profited from input from all three authors.

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Figure 1. Regression-based determination of source signature using a Keeling plot. For clarity of illustration, we only draw three data points instead of five, which we use for our computation. a) Constant source mix during the time of source signature determination leads to the correct flux-weighted mean isotopic signature (following Eq. A1), δ_S . b) Change of source mix during the period of determination of a Keeling plot due to either a temporal change of emission characteristics or a wind direction change (transportation) leads to a biased result. These situations can be usually identified by a large error of the intercept, δ_S (we choose an error >2 ‰ to reject these results) c) Sources and sinks with different isotopic signatures or sink fractionation occur at the same time and lead to a wrong apparent source signature. Strong biases are prevented by choosing a minimum net CO₂ concentration range of 5 ppm and demanding a monotonous increase of CO₂ during the five hours (see text for more details). Note that the background value is displayed for illustration, but it is not used in the moving Keeling plot methodrunning Keeling approach.



Figure 2. Source signature as calculated with the STILT model following equation A1. a) Unfiltered in black and filtered (for monotonous increase and minimal range) in blue. Only about 15% of all data points fulfill our strict criteria. However, they are distributed approximately evenly throughout the year. b) Diurnal cycle of modeled mean source signature due to diurnally varying mean source mix. Gray areas denote times when source signature is usually filtered out.



Figure 3. Comparison between modeled reference source signature (blue) and the movingrunning Keeling plot intercept (red), which is regression-based using the modeled CO₂ and δ^{13} C(CO₂) records. a) Long term comparison for the year 2012. The smoothed lines of window size 100 are also shown in the respective colors. b) Summer excerpt and c) winter excerpt (grey areas in a) of both reference and regression-based source signature. The crosses denote unfiltered data and bold stars denote filtered data. The green lines in panel b) and c) give the measured CO₂ concentration during the summer and winter periods.



Figure 4. MovingRunning Keeling plot method-approach-based source signature in Heidelberg from 2011 until mid of 2015. The black line is the smoothed measured sourcerunning Keeling signature and the blue line gives the smoothed modelled source signature (both 50%-percentile filter with window size=100 hours). Half a window size before the beginning of a large data gap the data is not further smoothed to prevent smoothing artifacts.



Figure 5. a) A fixed isotopic end member of the biosphere (green, \pm uncertainty of 0.5 % (light green area) and 2 % (crosshatched green)) together with the measured source signature (black) results in δ_F (red, \pm its uncertainty). b) A fixed isotopic end member of the fuel mix (red, \pm uncertainty of 1.0 % (salmon pink) and 2.0 % (crosshatched gray-pink)) together with the measured source signature (black) results in δ_{bio} (green, \pm its uncertainty). In both cases, also the fuel CO₂ share (or biospheric CO₂ share) is required. We here use the share calculated with STILT on the basis of EDGAR v4.3 and assume an absolute uncertainty of 10%.



Figure B1. Continuous Heidelberg hourly FTIR record of (a) CO₂ and (b) δ^{13} C(CO₂) from April 2011- June 2015. Data gaps occur when the instrument was away during a measurement campaign or when instrumental problems occurred. The lower (and upper) 5% envelope is drawn for CO₂ and δ^{13} C(CO₂) in dark green and light blue, respectively.

Emission source	Used $\delta_{F,i}$ or δ_{bio} [%]	Range of literature values $\delta_{F,i}$ or δ_{bio} [‰]	Reference				
				Fuel types			
				Coal		-23 to -27	Mook, 2000
- Hard Coal	-25						
- Brown coal	-27						
Peat	-28	-22 to -29	Mook, 2000; Schumacher et al., 2011				
Oil	-29	-19 to -35	Andres et al., 1994; Mook, 2000; Schumacher et al.				
			2011				
Gas							
-Natural gas	-46	-20 to -100	Andres et al., 1994				
-Derived gas	-28	-26 to -29	Bush et al., 2007				
Solid waste	-28	-20 to -30	typical range of C3 and C4 plant mixes (Mook, 2000)				

typical range of C3 and C4 plant mixes (Mook, 2000)

typical range of C3 and C4 plant mixes (Mook, 2000)

typical range of C3 and C4 plant mixes Mook, 2000

typical range of C3 and C4 plant mixes (Mook, 2000)

Widory et al., 2012; Levin et al., 1993

Lloyd and Farquhar, 1994; Mook, 2000

-20 to -30

0 to -16

Solid biomass

Bio liquid

Biosphere

Respiration

Photosynthesis

Biogas

-27

-29

-11

-23

-25

Table A1. δ^{13} C(CO ₂) source signature of fuel types and biosphere as used in the model and the range of literature values. Note, that for a
specified region, the range of possible isotopic signature can often be narrowed down, if the origin and/or production process of the fuel type
is known.