We thank the reviewers for their encouragements and for their comments that helped improve this manuscript. Our actions and response are detailed below.

S. Hall

This is a very interesting and important study.

Thank you.

I agree that Fe redox cycling could be part of the explanation for your finding of systematically low RQ in acidic soils. It might be useful to include a brief discussion of the magnitudes of Fe reduction and oxidation that would be necessary to explain the observed deviations in RQ from predicted values, and whether these are realistic in light of observed patterns of Fe reduction/ oxidation in terrestrial soils.

Added

There have been some recent published estimates of soil Fe(II) concentrations and net rates of reduction/oxidation in terrestrial soils that could provide important context for your work.

These papers are now cited.

R. Keeling

I quibble with the statement on line 27 of page 12052 that "this is the first report of directly observing this discrepancy (i.e. Co2 flux versus respiration), based on O2 measurements." Figure 4.4 of Severinghaus (1995) provides a very graphic demonstration of this effect using O2 measurements, where the effect is also explained in terms of complications of CO2 chemistry in soil water. In some ways, the Severinghaus approach is even more compelling as an iconic demonstration because it shows that CO2, rather than O2 is the impacted species based on the much stronger temporal trend for CO2.

Corrected to "first quantification of this effect using O2 for intact soil profiles" as suggested. Please note that Severinghaus'es PhD thesis (1995) was already cited in the original text.

Anonymous Referee #3

Overall, I found this paper highly informative and potentially very important. The measurements and their interpretation appear technically solid,

Thanks

and I recommend the paper for publication.

If significant amounts of soil CO2 respiration have indeed been missing from soil chamber and eddy covariance measurements, this would alter the picture of ecosystem carbon balance at many sites worldwide. This is also my biggest concern with the manuscript. The authors need to describe better the potential significance of these findings and also comment on a way forward.

Added, including final suggested caution at the end of the paper.

Is the oxygen measurement technique they discuss easy (and cheap) enough for others to adopt?

We added a discussion of this, and a citation for a manuscript in preparation that will give details on the methods and will allow others to adopt this approach.

It seems that the ARQ numbers they calculate are too variable for others to adopt an average value, though (and there are significant differences across ecosystems).

True. This is why we suggest measuring the ARQ.

A few comments: (page, line)

12041, 17: insert ‘hydrological’ before ‘system’ for clarity.

Corrected to "soil solution"

eq. 1: The whole point of the paper is in a sense that eq. 1 is not correct. i.e. that R(z) does not directly translate into surface fluxes of CO2. Perhaps the derivation could be prefaced by saying that we start with incorrect formulation and modify it appropriately.

Corrected R to P which stands for production, and defined in the text as the net rate of CO_2 production which integrates the effects of respiration and of CO_2 storage/release
12052, 15: Shouldn't the _13C of soil carbonate minerals be around 0 per mil? In either case, providing a reference would be useful.
Corrected (to "producing soil CO_2 in equilibrium with carbonate minerals…")
My other concern with the paper is that the use of English could be improved. I will leave copy-editing to the authors (especially Davidson, who is a native speaker). The paper is understandable, but there are small errors throughout.
(some examples:p12040 line 1, comma after respiration is not necessary; 12042 line 13, 'Roots respired CO2'; 12055, line 21 'This explanations', etc.)
These examples were corrected, and the manuscript went through additional editing cycles.

Anonymous Referee #1
GENERAL COMMENTS: It is a well written manuscript
Thanks

about how to get a correct quantification of the respired CO_2 combining O_2 and CO_2 measurements in different soil types (Mediterranean, Temperate and Alpine forest).
The paper concludes that in calcareous soils not all the respired CO_2 is immediately emitted from the soil to the atmosphere during some seasons because part of this CO_2 is temporally storage into the soil (mainly dissolving into soil water or reacting with carbonates), this is not new.
While the idea that some of the soil CO_2 will be dissolved into soil water or react with carbonates is of course not new (and we cite relevant papers), as far as we know, this is the first time it is shown directly in soil profiles. Moreover, here we have actually quantified by direct measurements the fraction of respired CO_2 which reacted with the soil solution, and found it to be surprisingly large - over 70% of the respired CO_2 in some cases. This finding is new, and not known yet to most of the biogeosciences community which is measuring CO_2 efflux while reporting "soil respiration".

Thus, the paper recommends to divide the measured CO_2 efflux by the ARQ to estimate the correct respired CO_2 on weekly and seasonal timescales. This recommendation is new but the paper do not convince me why is so important to know the respired CO_2 instead of the CO_2 flux from the soil to the atmosphere.

This of course depends on the focus of a particular study. For example, if the aim is to assess and develop predictive tools to assess the biological response to change, e.g. to upscale point measurements, on particular dates, for the entire year and entire region, this is usually done by fitting the efflux data to some temperature and soil moisture functions - assuming that the efflux is controlled only by the biological response of respiration. Based on the data we show here, it seems important in some cases to correct the efflux to non-biological processes. We agree with the reviewer that this point should be more clearly explained in the introduction, and have now done so.
what is more, it is not clear when do we have to do this, for all seasons?
Based on the evidence provided here, yes, and we suggest this as a routine measurement.
From my point of view, if finally the paper is considered publishable, here are two major comments that should be consider prior to publication: - To argue the importance to estimate the respired CO_2 instead of the CO_2 emitted to the atmosphere. The time-scale can be an argument, however this argue only appear in conclusions and should be mention in the introduction, giving some examples.
The argument was added to the discussion
-Methodology is a mess. A table including the main characteristics of the sites (including a short name for each site instead of numbers) together with type and days of measurements is indispensable to follow the paper.

We are not sure this is necessary, and the other reviewers seem to find this section fine. Also, we do use general names for group of sites like "Mediterranean calcareous sites" when referring to them in the discussion.

SPECIFIC COMMENTS:

Introduction: Pg 3 Ln 5-7: Did you do this calculation about the amount of C into the soil? Could you give us any reference?

We made now clear that we made the calculation.

Pg 3 Ln 8: "few is vague, please, give values.
Corrected
Pg 3 Ln 9: I do not understand the meaning of "significant" here.
Corrected
Pg 3 Ln 10-11: in Mediterranean ecosystem with low rain, the CO2 stored into gas phase in fissures and cavities can be very important, even more than those dissolve into water.
We did write that when large cavities increase, gas phase storage could be important.
Pg 3 Ln 14:I would reference here the equation 1 (to the right) instead the inclusion of equation 2 (the process is already included in eq. 1)
Not sure what is the reviewer argument. Clearly the calcium carbonate dissolution is not included in equation 1.
Pg 22 Ln 4: I would delete "for instance"
Corrected (assuming the reviewer meant Pg 5, Ln 10)
Eq. 5: It is not clear to me how to get eq. 5 from eq. 4. Could you give us more information?
Added
Pg 6 Ln 2: " It can be showed numerically that eq. 7 is valid also under other respiration profiles", the sentence is not clear to me.
Corrected
Pg 6 Ln 3: Please, define OR.
Defined.
Methodology: I would include in the beginning of this section a summary (part of the first paragraph of results could be moved here) about the measured plan.
Corrcted
Section 2.1: Could you please argue the reason to choose these sites?
Given in section 2.1
Section 2.3: Could you please explain the reason you did soil incubation only for the alpine site?
The reason was that we were surprised to find low RQ in these non-calcareous soils, and wanted to make sure that this is not due to root respiration.
Section 2.4: The two first sentences are also in section 2.1. I would use the section 2.1 only for explaining the sites and then I would include a section 2.2 about gas analysis, to avoid to repeat information.
Corrected
Discussion: Pg 14 Ln 2-4: This is wrong. If advection is dominating the gas exchange it will not depend on the vertical gradient of the gas, thus, equation 7 cannot be apply.
Equation 7 does not include any vertical gradient, and it can be applied to describe eddy diffusion flux.
Pg 14 Ln 9-12: Please, revise this sentence.
Corrected
Tables and Figures: Please, avoid in the figure and table captions, some comments that should be include in the result section (such us the caption of Figure 4).
Corrected

Please, be consistent and use the same template for all figures
Table 1: In methodology you explain you measured twice. Are these values the average?
We added now that this is an average value for replicates
Could you include the standard deviation?
The error in ARQ was added.
TECHNICAL CORRECTIONS:
Pg 17 Ln 24: Amazonian instead of Amzonian.
Pg 27 Ln 10: percent instead of precent
Pg 27 Ln 10: order instead of oreder
Pg 10 Ln 17: calculated instead of calculated.
All the technical corrections were made.

Anonymous Referee #4

The authors present profiles of CO_2 and O_2 and use them to calculate apparent respiratory quotients (ARQs) for soils from three Mediterranean and three forest sites. They posit, based on the elemental composition of plants and soils, that RQs should be in the range 0.9 ± 0.1, and they subsequently observe much lower ARQs in field soils. The authors conclude this is due to CO_2 dissolution from the calcareous soil sites, because carbonates produce non-biological CO_2 fluxes. They suggest that in the non-calcareous forest soil site the low ARQs may be due to oxidation of previously-reduced minerals.
In contrast to previous reviewers, I do not think the importance of carbonate-derived DIC fluxes needs to be further justified by the authors. A case for the importance of DIC fluxes has been established in several recent papers, most recently by et al. (2013).
The referee forgot to add in the name of the author they cited above. Maybe this was Ma et al. (2013, now cited in our paper)? However, this paper only discussed the reason for "negative" fluxes. In any case, it is still not well accepted in the Biogeosciences community to add a DIC correction for soil respiration from calcareous soils.
The authors did not mention the basic linkage between redox potential and RQ, which would provide useful context to help the reader understand the metabolic processes responsible for the range in soil RQ. As soil oxygen and redox potential decrease, RQ can approach infinity because CO_2 is produced by anaerobic respiration and no oxygen is consumed.
Added to the introduction as requested.
In observing RQs << 1, the authors found RQs that are lower than expected for anaerobic respiration. The two major possible explanations for RQs <<1 are therefore, 1) Dissolution of CO_2 from carbonates. Because soil water can store and release much more CO_2 than O_2, this would tend to lower RQ, and 2) Respiration of substrates that are more reduced than sucrose (e.g. other sugars, lipids, lignin, and phenolics).
The RQ of lipids, lignin etc., was in the discussion, and now also added to the introduction.
I was initially enthused for this paper, because the RQ of soil respiration has not received a lot of attention,
We agree.
and technique development to identify CO2 fluxes from bicarbonate dissolution would make a welcome contribution to the field.
We also agree to this, which contradicts the later claim of the review that everything in this field is known, and there is no need for new techniques.
Unfortunately, however, I believe this study is based on a flawed premise, which is that the RQ of soil respiration should reflect the stoichiometric ratios of C to O found in organic matter.

On average and on sufficiently long temporal scale, or in steady state, the RQ of decomposing soil organic matter must reflect the stoichiometric ratios of C to O found in organic matter. This is added now to the introduction,

A more thorough review of the literature for root and soil studies would have revealed that RQ is highly dynamic and often much less than 0.9,

Actually, it can be much less than 0.9 only when lipids are used. Moreover, in the studies tabulated in Luo (2006), which the reviewer cited below, the roots RQ is above 0.8 as we claimed (for 22 values out of 23, with only one exception resulting from ozone treatment).

depending on respiration substrates and plant stress. The elemental composition of plant and soil organic matter should deviate from RQ because 1) organic matter reflects long term metabolism rather than instantaneous conditions, and 2) not all respiration contributes to formation of organic matter. Plant physiologists distinguish between "growth respiration" and "maintenance respiration", and in perennial plant systems most root respiration is "maintenance respiration",

The issue of growth versus maintenance respiration is irrelevant here. Lower then 0.8 can only result from using lipids as substrates.

i.e. used for nutrient uptake, turgor maintenance, cellular repair, etc. These fluxes contribute to soil respiration without producing new tissue. Because plants carry out these processes even under non-optimal growth conditions the substrates can be expected to vary dynamically with soil environment and photosynthetic conditions. The form of N that is available for plant uptake appears to be another significant factor (Luo, 2006).

True, but this will only make RQ>1. We added this point.

The authors own incubations of forest soils also produced RQs < 0.7.

It seems to me that the authors need to propose a way to assess the RQ of biologically-produced CO_2, before they can use CO_2/O_2 ratios as a means to correct for carbonate contributions. It seems that the RQ of biologically-produced CO_2 can vary too much to make the assumption that it is 0.9 ± 0.1. For instance, Luo and Zhou (2006) provide a nice synthesis of root respiration RQs from a number of studies, and show a range of 0.39 (this low RQ was from an ozone-stress study) to as much as 1.5 (for sunflower roots). This range for root respiration far exceeds the range for soil respiration proposed by Angert et al, and suggests that their estimates of carbonate contributions could be either far over- or under-estimated.

This is only for roots respiration, which is only part of the total soil respiration, and under artificial lab conditions, but we agree that the roots component must be determined, as now clearly stated it in the paper. Also note that the diffusion experiments were done with sterilized roots-free soil.

Can the RQ of biological CO_2 production be determined first, through incubations, in order to subsequently apply the partitioning technique? The authors own incubations show that RQs change very quickly with hours into an incubation. By quickly incubating fresh soils, however, such estimations may be robust. For root respiration, Lipp and Anderson (2003) found that incubating detached roots did not alter RQ relative to attached roots. Therefore, including roots in soil incubations may produce an estimate—albeit with limitations, because of disturbance—of biologically-produced soil respiration. In this reviewer's opinion, an incubation-derived RQ would be a more reliable estimate of the biological RQ than the generic assumption of 0.9 ± 0.1, because it would be specific to the substrates found in each soil, the plant functional types in each ecosystem, and the specific environmental conditions encountered at the time of sampling.

Incubation of detached roots is a great idea to get this component. We added this suggestion to the text. However, note that the values that Lipp and Anderson (2003) (cited by the reviewer) found were in the ranged we assumed (0.8-0.95).

I feel using CO_2/O_2 ratios as a method for distinguishing biological CO_2 fluxes from carbonate-derived fluxes is not sufficiently vetted by the experiments described in this paper. In addition to resolving the question of what biologically-respired RQ is,

See replies above.

the authors should apply other, independent methods to validate their estimates of carbonate-related CO_2 fluxes, such as ^{13}C partitioning (Stevenson and Verburg, 2006).

As we have already discussed in the text, 13C can give us some indication about reactions with rock carbonates taking place, but this reactions can exist with zero net flux, and still show a 13C signal, since the stable isotopes are controlled by the gross fluxes.

In addition, there are a number of editorial problems with the manuscript, as described below:

1) The manuscript lacked specific research questions, goals, or hypotheses.

Added

2) Over the last several years a rich literature has developed on distinguishing biological fluxes from carbonate-related fluxes, using modeling approaches (Ma et al., 2013; Wang et al., 2014) and 13C (Stevenson and Verburg, 2006), among other techniques. These references are important to discuss from the methodological standpoint, as they provide alternative approaches to address the same problem. Although the introduction was generally quite good, I thought this methodological context was missing.

We added these references to the introduction.

The limitation of the 13C approach is noted above.

Modeling is of course a great tool, but can't replace direct observation. As far as we are aware, the ARQ approach is the only way to directly distinguish biological fluxes from carbonate-related fluxes. Even with some uncertainty regarding the biological RQ, having direct measurements is far better than relying only on modeling.

3) The purpose of the different methods were not clearly linked to research questions. In particular, the purpose of the laboratory diffusion experiment and the soil incubations were not clearly explained.

For the lab diffusion experiments, we wrote:

"To study the effects of soil chemistry and gas diffusion separately from biological effects, we conducted a set of experiments with sterilized soils columns."

For the soil incubation experiment, we wrote:

" To study the effects of heterotrophic respiration, separately from the effects of root respiration and that of gas diffusion in the soil profile, we conducted incubation experiments."

Furthermore, the results were very brief, and seemed almost like an unfinished outline. They did not provide clear tie-in to research questions.

We made the tie-in at the discussion section.

Citations.

Lipp, C. C. and Andersen, C. P.: Role of carbohydrate supply in white and brown root respiration of ponderosa pine, New Phytol., 160(3), 523–531, doi:10.1046/j.1469-8137.2003.00914.x, 2003.

Luo, Y. and Zhou, X: Soil respiration and the environment, Elsevier Academic Press, Amsterdam; Boston., 2006.

Ma, J., Wang, Z.-Y., Stevenson, B. A., Zheng, X.-J. and Li, Y.: An inorganic CO2 diffusion and dissolution process explains negative CO2 fluxes in saline/alkaline soils, Sci. Rep., 3, doi:10.1038/srep02025, 2013.

Stevenson, B. A. and Verburg, P. S. J.: Effluxed CO2-13C from sterilized and unsterilized treatments of a calcareous soil, Soil Biol. Biochem., 38(7), 1727–1733, doi:10.1016/j.soilbio.2005.11.028, 2006.

Wang, W., Chen, X., Luo, G. and Li, L.: Modeling the contribution of abiotic exchange to CO2 flux in alkaline soils of arid areas, J. Arid Land, 6(1), 27–36, doi:10.1007/s40333-013-0187-6, 2014.