

Dear Dr. Zhongjun Jia,

We would like to thank you and the reviewers for the constructive and helpful comments for our manuscript. We have carefully considered them and revised our manuscript accordingly. All other comments were also carefully considered and incorporated. Grammatical mistakes have been corrected throughout by our native co-authors. In order to make the changes easily viewable, we marked the main revision with color in the revised manuscript. Detailed responses to each comment are listed below.

**Response to associate editor:**

**Questions 1:**

As for non-carbonate soil on the basis of CO<sub>2</sub> measurement. Please provide the detection limit. Moreover, it has to be specified about the amount of soil, the HCl added, and the volume of headspace". The readers will otherwise has no ideas of what the authors want to say. For example, if one injects 1 mL pure CO<sub>2</sub> into a 2 ml-bottle, the CO<sub>2</sub> concentration can reach 50%. However, if this 1-ml CO<sub>2</sub> is injected into a vast tank (1 million cubic meters), the concentration is virtually zero. Therefore, pls do provide the detailed information of your CO<sub>2</sub> measurement.

**Reply:**

We agreed with you that the pressure of the released CO<sub>2</sub> will change with the variation of headspace volume. Hence, different instrument has different detection limit. The detection limit of the instrument used in the present study was 0.1 mm of

released CO<sub>2</sub>. To reduce the above measurement error, we made a standard curve graph using standard matter calcium carbonate before soil carbonate measurement. We have added these information in the revised manuscript. See Page 9-10, Line 185-187.

### **Questions 2:**

The authors assume that sulfate content in surface soils might account for the negative correlation between soil pH and inorganic carbon concentration. Pls add few sentences for discussion.

### **Reply:**

It is a pity that we cannot provide more sound reason for the affect of sulfate on the relationship between soil pH and inorganic carbon concentrations. Nevertheless, its absence does not weaken the main findings and conclusions in this paper. Further studies are needed to deal with this matter.

### **Questions 3:**

Please add one or two sentences why HNO<sub>3</sub> is somehow justified for pBHC determination. The widely used protocol does not necessarily the correct one.

### **Reply:**

The nitrate anion is preferable because it tends to have fewer interactions with soil materials than other anions.

### **Questions 4:**

Figure 1 legend. Please specify whether the same/similar figure has been used in other papers, and mention it properly in figure legend to avoid confusion for readers.

**Reply:**

Yes, the similar figure was published in our previous paper (i.e., Wang et al, 2014). To avoid the confusion for readers, we have put this figure into the supporting information.

**Questions 5:**

Figure 1 legend. The authors apparently would like to use these 52 sites as indicator of a 3600-km long transect. How representative it is. The author may add few sentences to explain why the regions with green shading can be represented by these 52 sites. For example, in the remote western region, there is no sampling site but with green shading. Figure 1 legend. The authors state that from east to west, there is a gradient of increasing temperature and decreasing precipitation. This statement needs to be supported with solid evidence. Please make two column with color gradients showing the change of temperature and precipitation respectively.

**Reply:**

We have put this figure into supporting information and revised its legend in the revised manuscript. We also put a inset to showing the changes of mean annual temperature and precipitation from west to east along the transect in the revised paper.

**Questions 6:**

Figure 2 legend. It is still confusing. The authors state that “Effects of acid addition (16 mmol H<sup>+</sup> kg<sup>-1</sup> soil) (approximately the average cumulative amount of acid deposited over 10 years) on soil pH in the carbonate containing soils (squares) and the non-carbonate containing soils (circles)”. This statement has no point. What does soil pH in y-axis mean? Soil pH in y-axis is an absolute value. The authors added 16mmol acids per kilo soil, and very likely could have resulted in CHANGE of soil pH. Only through the inset, can one see the effect of acid addition on soil pH. But what information does your main figure 2 represent, except for the inset?

**Reply:**

Thank you very much. We have revised the figure legend in the revised manuscript as you suggested.

**Response to reviewer 1:**

**Question 1:**

The key problem in this study is how to separate carbonate containing soils from non-carbonate ones. I am very curious that there is no carbonate in alkaline soils (pH>7). In addition, I have noticed that there are some overlaps for soil collecting sites between this study and Yang et al. (2012), where they put out high-carbonate regions vs. low-carbonate soils. Maybe the authors can consider this kind of expression.

**Reply:**

Thanks very much for your suggestion. Yes, it is difficult to separate carbonate

containing soils and non-carbonate containing soils. In the Method Section, we have defined the non-carbonate soils as those from which we were unable to detect the CO<sub>2</sub> release upon addition of HCl (lower than the detection limit). See Page 10-11 Line 208-210.

**Question 2:**

Because soil pH is widely used in many studies, and can be used as an effective and direct parameters to assess soil acidification status, I would like to see the pattern of soil pH, and its relationship with soil pHBC, and other environmental parameters.

Reply:

According to reviewer's suggestion, the relationships of soil pH with soil and climatic variables (new Figure S5 and S6) were reported in the revised manuscript. The relationships between soil pH and soil pHBC were shown in several places in the version accepted for discussion (original Figure 3).

**Question 3:**

I think the new point in this study is the different patterns of soil pHBC in regions with different aridity index. So it is better to put it out in the abstract.

Reply:

Thank you very much for the suggestions. In the revised manuscript, we have added the information in the abstract section.

**Question 4:**

Line 98, I would like to see the response to the second question in the discussion

question. If possible, please show the data of acid deposition in the studied regions.

Reply:

The amount of acid deposition is unknown across northern China. Thus, we are unable to provide detailed data showing the patterns of acid depositions. We must admit that this lack of data is unfortunate. Nevertheless, its absence does not weaken the main findings and conclusions in this paper. Further studies are needed to deal with this matter.

**Question 5:**

Line 190, 201: AI is an important index in this study, please show how to calculate it in detail.

Reply:

Thank you very much for the suggestion. In the revised manuscript, we provided additional text to illustrate how to calculate aridity index (AI) in detail. See Page 10 Line 200-206.

**Question 6:**

line 280-281: please give the reference.

Reply:

We have added the reference as suggested.

**Question 7:**

Line 314-315: Please add some references for this statement.

Reply:

We have given more references for the statement in the revised manuscript.

**Question 8:**

L333-339: I would like to see the confirmation on clay mineralogy type in this study.

Reply:

We agree that this information would be very useful. Unfortunately, this information is not available. While our study is mainly focused on the relationship between pHBC and environmental variables, a detailed description of the clay mineralogy at each sampling point across the 3,600 km transect is beyond the scope of this paper.

**Question 8:**

L358, "...effects" is not exactly here. It is just a positive relationship.

Reply:

In the revised manuscript, these words have been revised according to your suggestions as following. "In our study, there was a significant positive relationship between soil pHBC and soil exchangeable Na concentration among the carbonate containing soils."

**Question 9:**

L366: Figure 4.

Reply:

We checked manuscript, and corrected it accordingly.

**Question 10:**

I cannot find climate information in Fig. S1. Please have a check on all Figures, so that they can be matched well.

Reply:

Sorry for these mistakes. In the revised manuscript, we have checked all Figures according to your suggestions.

**Question 11:**

L404-409: "the first" sounds not very exact, considering there are similar studies in the same regions, and soil pHBC can be an alternative parameters for assessing soil acidification except soil pH.

Reply:

In the revised manuscript, we deleted these words and rewrote this sentence.

**Question 12:**

Table 1, please give how to measure soil pH. Did the authors measure it using water suspension (e.g., a soil: water ratio of 1 : 2.5 )? If so, please give an annotation.

Reply:

Thanks very much for your suggestions. We have added the information in the revised manuscript according to your comments.

**Response to reviewer 2:**

**Question 1:**

Generally speaking the higher soil pH, the stronger soil pH buffering capacity. It is thus quite unusual that in carbonate-containing soil that there is a negative relationship between soil initial pH and soil pHBC. If this is true, soil initial pH would

not have significantly positive correlation with carbonate, i.e., SIC. Since the authors determined SIC content, it is thus interesting to see what kind of correlation exist between initial soil pH and SIC.

Reply:

A new figure (i.e. Figure S5) showing the relationships between initial soil pH and soil inorganic carbon concentration has been added in the revised manuscript. In line with your expectation, a negative relationship between soil pH and inorganic carbon concentration was found, as shown in our revised manuscript. Yes, this result was quite unusual, which may be associated with higher sulfate in topsoil of this region.

**Question 2:**

In addition, it seems highly unlikely that non-carbonate containing soil released no any CO<sub>2</sub> gas upon 2M HCl addition. Pls explain.

Reply:

Thanks very much for your suggestion. Yes, it is difficult to separate carbonate containing soils and non-carbonate containing soils. In the Method Section, we have defined the non-carbonate soils as those from which we were unable to detect the CO<sub>2</sub> release upon addition of HCl (lower than the detection limit). Page 10-11 Line 208-210.

**Question 3:**

Meanwhile, it is also likely that the protocol has some drawbacks for pHBC measurement. For example, how about pHBC measured by addition of H<sub>2</sub>SO<sub>4</sub>? The authors may briefly discuss the advantage and drawbacks of HNO<sub>3</sub>-based pHBC

measurements.

Reply:

Thanks very much for your comments. The reviewer is right that the pHBC can be measured by titrating soils with different kinds of acids, such as H<sub>2</sub>SO<sub>4</sub>, HCL, and HNO<sub>3</sub>. However, the most widely accepted one is the use of HNO<sub>3</sub> as adopted by many standard soil analysis and testing protocols ) (e.g., Bowman et al., 2008; Nelson and Su, 2010; Xu et al., 2012; Lu et al. et al., 2015), because the nitrate anion tends to have fewer interactions with soil materials than other anions.

**Question 4:**

Please provide data about the correlation between soil aridity and initial soil pH.

Reply:

A new picture (i.e. figure S6) showing the relationship between aridity index and soil pH was added in the revised manuscript as suggested by this reviewer.

**Question 5:**

In addition, please provide information about acidification process and rate of soils in northern China in the introduction section. The authors repeatedly stated that acidification rate and processes are important but they provide no solid evidence in support of these statements.

Reply:

Thanks very much for your valuable suggestions. In the revised manuscript, we have provided more information about soil acidification processes induced by nitrogen and sulfur depositions in northern China in the Introduction Section.

**Question 6:**

Page 13216 Lin 20-21. The authors present no data of rates, risks and impact of acidification.

Reply:

In the revised manuscript, we deleted these words according to the comment.

**Question 7:**

Page 13217 Line 1. Please delete some references as 7 might be too much for one statement. Or you can simply assign these reference to different topics you would like to emphasize

Reply:

According to the suggestion, we have deleted three of the references in the revised manuscript.

**Question 8:**

Page 13217 Line 21. The study in 1992 and 2000 are not recent studies.

Reply:

In the revised manuscript, we changed "recent studies" into "previous studies" according to the suggestion.

**Question 9:**

Page 13217 Line 11-18. I would like to see justification of why large-scale study is required.

Reply:

Thanks very much for your suggestions. A new section was added to show the

importance of large-scale patterns of soil pHBC. Page 5 Line 83-87.

**Question 10:**

Page 13217 Line 26. Please briefly explain the mechanisms of how high temperature, high evaporation and low precipitation can increase carbonate precipitation?

Reply:

Thanks very much for your suggestions. In the revised manuscript, we added a new section to show the mechanisms of how high temperature, high evaporation and low precipitation increase carbonate precipitation. Page 5 Line 76-81.

**Question 11:**

Page 13217 Line 29. I guess the authors may start this paragraph by saying there are three main pH buffering mechanisms in soils. And then explain it in detail.

Reply:

Thanks very much for your suggestions. In the revised manuscript, we have revised the manuscript according to the comment. Page 4-5 Line 65-68.

**Question 12:**

Page 13218 Line 5. What is the cause of soil acidification in northern China?

Nitrogen deposition or sulfur deposition, pls specify their relative contributions if flexible.

Reply:

We agree with you that this information is very important for predicting the acidification rates of this region. However, we did not find these data in the previous studies or via personal communication, and hence cannot provide the information in

the current paper. We hope that this would not influence the content and framework of the manuscript.

**Question 13:**

Page 13219 Line 9. Please cite appropriate reference for Chinese soil classification.

Reply:

Thanks very much for suggestions and an appropriate reference has been added in the revised manuscript.

**Question 14:**

Page 13219 Line 11. What does soil fertility mean?

Reply:

Here, "soil fertility" may be not appropriate and was deleted.

**Question 15:**

Page 13226 Line 10. Replace who demonstrated with demonstrating

Reply:

Replaced as suggested.

**Question 16:**

Page 13226 Line 19. Delete between our results and previous results.

Reply:

We have deleted these words in the revised manuscript.

**Question 17:**

Page 13226 Line 20. It seems more likely to be associated with the structure (i.e. type) of soil organic matter rather than quantities. If it is caused by the quantities, then

one would be able to see significant correlations.

Reply:

Thanks for your suggestions. We agree with you that it was associated with the structure (i.e. type) of soil organic matter rather than quantities. Hence, we deleted the "quantities and" in the revised manuscript.

**Question 18:**

Page 13228. The figure legend might be wrong. It is a mere correlation between longitude and initial soil pH, and pH change upon acid addition was shown in the inset?

Reply:

We think the confusion might be cleared up because we have changed that reference from Figure 2 to Figure 4.

**Question 19:**

Page 13229. It is quite perplexing that there is soil inorganic carbon in non-carbonate soils.

Reply:

You may mean page 13239. The transect was divided into carbonate containing soils and non-carbonate containing soils. Hence, there is no inorganic carbon in the non-carbonate containing soils, or the tiny amount of CO<sub>2</sub> released was not detected.

We have also revised the whole manuscript thoroughly to incorporate comments from the editor and the anonymous reviewers and to improve the overall quality of the manuscript. All changes are marked in color in the revised manuscript.

Once again, thank you very much for your comments and suggestions.

Kind regards,

Wentao Luo