

## ***Interactive comment on “Impact of different fertilizers on the carbonate weathering in a typical karst area, Southwest China: a field column experiment” by Chao Song et al.***

**Chao Song et al.**

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1- The English is not up to standard: you really need to make sure the paper is being read/corrected by a native English speaker (or somebody with substantial experience in publishing in English-speaking journals) who is familiar with your domain.

Changed in the manuscript: we have re-edited the language question by the Language Services of Elsevier.

2. While there is now a statistical analysis, it is not correct (in my opinion). You need a two way ANOVA as you have both a treatment (fertilizer) and a rock type (dolostone

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or limestone) effect. You cannot evaluate the treatment effect correctly if you do not account for the rock type effect and vice versa. This needs to be corrected.

Responses: Thanks for your pointing it out. Given that the primary objective of the statistical analysis is to test the accordance between limestone and dolostone, we plotted the linear correlation diagram of the dissolution rates for these two rocks to make this problem clearer and easy to understand. Changed in the manuscript: we added Fig. 4, a linear correlation diagram ( $R^2=0.9773$ ), instead, to illustrate no difference in the dissolution rates between limestone and limestone. See the details in the manuscript.

3.- The analysis and discussion of the results needs further improvement in presentation and in analysis. You did add some additional data but: - you mention that there are several studies that already studied the effect of fertilizers on carbonate weathering. Yet you do not quantitatively compare your results with those of these studies Responses: we had done some comparison our results with others in section 4.4. The conclusion is that it is difficult to compare between the results from the carbonate-rock-tablet test and the riverine hydro-chemical method.

4. In the comparison you make you use a weathering rate expressed in  $\text{g m}^{-2} \text{y}^{-1}$ . This raises several questions: -Grams of what ?  $\text{CaCO}_3$  or Ca ? Or rock ? - How do you convert the results of your tablet experiments to a rate per unit of surface area; as far as I can see this is nowhere explained in the text. Responses: In fact, we have mentioned it in Methods section.  $\text{Raw} = (W_i - W_f)/(S \cdot T)$  (3) where  $W_i$  is the initial weight of the carbonate rock tablets,  $W_f$  is their final weights,  $S$  is the surface area of carbonate rock tablets, and  $T$  is the length of the experimental period.  $W_i$  and  $W_f$  is grams of carbonate rocks (limestone or dolostone) that we used in this study.  $S$  is the surface area of rock tablets. Changed in the manuscript: in order to make it clearer, we added an information in Table 2:  $\text{Raw} = (W_i - W_f)/(S \cdot T)$ , where  $W_i$  is the initial weight of the carbonate rock tablets, and  $W_f$  is their final weight.  $S$  is the surface area of carbonate rock tablets (In this study, we used a same  $S=7 \text{ cm}^2$  for every tablets), and  $T$  is the experiment period.

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5.- The presentation needs also other improvements: Table 3 is a case in point. You should provide all weathering reactions that a reader needs to understand the calculations you make (e.g. about the amount of NH<sub>4</sub> released per mole of fertilizer). This needs to be done in consistent way: give the chemical formulation of every fertilizer, make sure that numbers are given to the remarks only. Responses: Some treatments are difficult to describe with a specific reaction, E.g.: for treatment 7, 8, 9, 11 etc. we used a simply reaction on inhibition of phosphate to calcite dissolution/precipitation ( $\text{Ca} + \text{PO}_4 \rightarrow \text{Ca-P}$ ) instead. Changed in the manuscript: we polished the Table 3. See it in the manuscript. We added notes in table 3: (1) Common ion effect: The  $\text{Ca}(1-x)\text{Mg}_x\text{CO}_3$  produces when the concentrations of  $\text{Ca}^{2+}$   $\text{Mg}^{2+}$  and/or  $\text{HCO}_3^-$  increases (for Treatment 7, 9 and 11):  $(1-x) \text{Ca}^{2+} + x\text{Mg}^{2+} + 2\text{HCO}_3^- \rightarrow \text{Ca}(1-x)\text{Mg}_x\text{CO}_3 + \text{CO}_2 + \text{H}_2\text{O}$  (2) Inhibition of phosphate to calcite dissolution/precipitation: calcium orthophosphate (Ca-P) precipitation produces on the surface of calcite after the addition of  $\text{PO}_4^{3-}$  in soil, resulting in inhibiting the dissolution/precipitation of calcite (for Treatment 7, 8 and 9):  $\text{Ca} + \text{PO}_4 \rightarrow \text{Ca-P}$  We added notes in table 4: wd=without data; The amount of added fertilizer (g) divided by its molecular mass (g/mol) was the molar amount of fertilizer (mole); The amounts of fertilizer-derived NH<sub>4</sub><sup>+</sup> is calculated by their own ionization or hydrolysis processes. The maximum of N products is estimated by their main reactions in table 3.

6- There are also substantial remarks in the report of reviewer 2 that you need to address. Please read them carefully and respond to all of them. - You will find more remarks in the manuscript file that is attached. Please read them carefully and respond to all of them. Responses: In fact, we had revised according to the reviewer 2 including remarks in PDF file. Here, we give a point to point response and revision description. Responses and revision descriptions on reviewer 2' comments in pdf manuscript

Abstract 1. Note in "fertilization": You should add a sentence after this, stating as to why fertilization may affect carbonate weathering (release of protons...) Changed in the manuscript: we added the clause to interpret. "since the addition of fertilizers tends

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to change the chemical characteristics of soil such as pH value".

2. Revision suggestions about English language in the rest part of Abstract section Changed in the manuscript: we changed it according to these suggestions

Introduction 3. The statement of the sentence " However, a disturbance to CO<sub>2</sub>. . . . . of N-fertilizer. Changed in the manuscript: It is changed into: However, fluvial alkalinity may also be produced by other processes including the reaction between carbonates and the protons derived (i) from the nitrification of N-fertilizer (Barnes and Raymond, 2009; Chao et al., 2011; Gandois et al., 2011; Hamilton et al., 2007; Oh and Raymond, 2006; Perrin et al., 2008; Pierson-wickmann et al., 2009; Semhi and Suchet, 2000; West and McBride, 2005), (ii) from the sulfuric acid (Lerman and Wu, 2006; Lerman et al., 2007; Li et al., 2008; Li et al., 2009), (iii) from organic acid secreted by microorganisms (Lian et al., 2008) as well as (iv) from acidic soil (Chao et al., 2014; Chao et al., 2017).

4. Note in "acidic soil": Can you be more specific about the process here ? What do you mean here ? Responses: The acidity or proton in acidic soil can lead to carbonate weathering. Changed in the manuscript: we changed the statement and added a new reference Chao, S., et al., Impact of animal manure addition on the weathering of agricultural lime in acidic soils: The agent of carbonate weathering. Journal of Groundwater Science and Engineering, 2017. 5(2): p. 202-212.

5. Note in "the deficit of CO<sub>2</sub> uptake due to N-fertilizer addition: This is a strange formulation, difficult to understand what you really mean: is this not 'estimated that N-fertilizers contributed up to Changed in the manuscript: we changed it into: Perrin et al. (2008) estimated that the contribution of N-fertilizer (usually in form of NH<sub>4</sub>NO<sub>3</sub>) represent up to 5.7-13.4% and 1.6-3.8% to carbonate dissolution for France and on a global scale, respectively.

6. Note in "Our results show that. . . . experiment": You cannot discuss your results before you presented them. Changed in the manuscript: we changed it into: yet it is

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a preferred option for the condition controlled contrast or stimulated experiment (Chao et al., 2017; Chao et al., 2014; Chao et al., 2011). 7. Revision suggestions about English language in the rest part of Introduction section Changed in the manuscript: we changed it according to these suggestions.

Materials and Methods 8. Note in “2013”(section 2.1): Also give the surface area of the agricultural area in the district so that the reader knows what the average application rate per unit of surface area is. Changed in the manuscript: we changed “0.8 Mt in 1980 to 1.0 Mt in 2013” into “from 150 kg/ha in 1980 to 190 kg/ha in 2013”.

9. Note in “the amount of added fertilizers” (section 2.3): How was the fertilizer applied ? Changed in the manuscript: we added the information to explain this point. The 6 kg soil was weighed (bulk density=1.3 g/cm<sup>3</sup>), mixed perfectly with above fertilizer, respectively, and filled in its own column

10. Note in “3-5%” ( section 2.4) “The percentages do not add up: if there is min 98% crystal dolomite you cannot have 3% calcite”. Changed in the manuscript: we changed it into: dolostone with 98-99% pure crystal dolomite, 1% pyrite and trace quantities organic matter.

11. Revision suggestions about English language in the rest part of Materials and Methods section Changed in the manuscript: we changed it according to these suggestions.

Results 12. Note in “carbonate” ( section 3) : So, you finally calculated carbonate loss: then this should be defined higher up. Changed in the manuscript: we note this point, we re-organized this section.

13. Note in “Acw, Rcw and Racw” (section 3): Is this distinction between rates and amounts meaningful. I do not think so as the experiments were carried out (as far as I understand) over a single, fixed time period. Responses: we noted this problem. Changed in the manuscript: Considering this point, we deleted some of them, and

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re-wrote this paragraph.

14. Note in “-0.0028g and -0.0007g for limestone and dolomite” (section 3): You mention in the methods section that you will discuss results in terms of carbonate loss: this is not what you do here. You need to be consistent. Changed in the manuscript: we deleted them.

15. Note in “of two different carbonate in. . . . . a negative value” (section 3): I do not understand this. Responses: it can be easily understood according to the formula of  $R_w$  and  $R_{aw}$ .  $R_w = (W_i - W_f) / W_i$   $R_{aw} = (W_i - W_f) / (S * T)$  where  $W_i$  is the initial weight of the carbonate rock tablets,  $W_f$  is their final weights,  $S$  is the surface area of carbonate weathering tablets, and  $T$  is the length of the experimental period. If the  $R_w$  and  $R_{aw}$  is positive, it shows carbonate dissolves; if negative, carbonate mineral produces.

16. Revision suggestions about English language in the rest part of Results section Changed in the manuscript: we changed it according to these suggestions.

Discussion 17. Note in “in this study, . . . . . are therefore valid and credible” (section 4): The fact that the columns were the same is logical: to what extent the results are ‘valid’ is determined your results, not your judgment. Responses: we noted this problem. Changed in the manuscript: Considering this point, we deleted them

18. Note in “which can originate from . . . . .acidic soil (Chao et al. 2014)” (section 4): This is a repetition of what has already been said in the text Responses: it is used for interpreting the different problem Changed in the manuscript: we changed it into another one to avoid repeating.

19. Note in “in habiting that the. . . . . fertilizer amendment” (section 4): unclear Changed in the manuscript: we deleted it.

20. Note in “The  $R_{cw}$  of limestone tablets. . . . Fig. 4” (section 4): This can be much clearer presented Note in “results” (section 4): I do not clearly see how you can have exactly 1 mole of  $NH_4$ : instead you should calculated the amount of fertilizer-derived

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NH4 per unit surface area of your columns. Changed in the manuscript: we added much information to make it clearer, including Figures and Tables.

21. Note in page 11(section 4): There also important differences between the treatments which you do not discuss. The weathering rate under treatment 3 is only half of that of treatment 10 (urea) Changed in the manuscript: we added much information to interpret it. We have noted that the  $R_w$  values in  $\text{NH}_4\text{HCO}_3$  and  $(\text{NH}_4)_2\text{CO}_3$  treatment are lower than even half of those in urea treatment in spite of adding the same amount of fertilizer-derived  $\text{NH}_4$  (about 1.07 mole). This is probably because the two fertilizers,  $\text{NH}_4\text{HCO}_3$  and  $(\text{NH}_4)_2\text{CO}_3$ , are easier to decompose and produce the  $\text{NH}_3$  and  $\text{CO}_2$  gases as following Eq. (20) and (21), resulting in the amount of fertilizer-derived  $\text{NH}_4$  of lower than 1.07 moles.  $\text{NH}_4\text{HCO}_3 \rightarrow \text{NH}_3 + \text{H}_2\text{O} + \text{CO}_2$  (20)  $(\text{NH}_4)_2\text{CO}_3 \rightarrow 2\text{NH}_3 + \text{H}_2\text{O} + \text{CO}_2$  (21)

22. Note in" the enhanced  $\text{HCO}_3^-$ “(section 4): Why do we jump to the regional scale here ? Changed in the manuscript: we deleted it.

22. Note in" phosphate“(section 4): Do you have any data supporting this hypothesis ? Responses: it is used for interpreting the different problem

23 Note in"  $\text{NaNO}_3$ “(section 4): You give the weathering reactions for all your other treatments, you should also present this one. Perhaps it is better to group all these reactions in a table. Changed in the manuscript: we added the reaction and listed a table including all the reactions.

24. Note in" This will result in doubled overestimation. .... carbonate weathering“(section 4): Unclear Responses: For  $\text{NH}_4\text{NO}_3$  fertilizer, the (Eq. (12)) show that the two moles of  $\text{Ca}^{2+}+\text{Mg}^{2+}$ ,  $\text{NO}_3^-$  and  $\text{HCO}_3^-$  will be produced when one mole  $\text{NH}_4\text{NO}_3$  react with 2 moles of carbonate, where only half of  $\text{NO}_3^-$  originate from nitrification described as Eq. (8). This will result in a double overestimation on the contribution of the nitrification to carbonate weathering and thus mislead the estimation of  $\text{CO}_2$  consumption therein. Responses to Referee 2 Comment 1 - The authors

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did not present very well the process/method of weathering which has been used in this experiment: (1) did the authors perform a leaching of the soil column? How are the fertilizers introduced in the soil column? Are spread mixed with soil or spread in solutions? The lack of explanation of the method used does not allow us to assess the results at their fair value. There is also a lack of discussion and comparison of numerical values obtained in other experiments and in natural and agricultural catchments. The carbonate weathering is only estimated based on the weight of each rock tablets. It is not checked by the geochemistry of both rock tablets and the potential weathering/soil solution. Indeed, it would have been interesting to have an estimation of the chemical weathering. Answer: The fertilizer was mixed with soil before filling in columns. Changed in the manuscript: We added a sentence to explain this. The soil was weighed, mixed perfectly with above fertilizer, respectively, and filled in its own column. Comment 2 – To speed up the carbonate weathering, the fertilizers were introduced by increasing their amount by 30 times (Why 30 times?). It is a bit problematic, because the authors changed the soil/fertilizers ratio compared to “natural/anthropogenic” ratio? What is this ratio in the local agricultural catchments? What are the specificities these local catchments compared to national Chinese catchments and worldwide catchments? Answer: Because the added amount of fertilizer can magnify and quicken the fertilization effect in the short-term according to another experiment from us, and can't affect the phenomenon we want to observe in this study. Another paper of ours (in preparation) about a series of different amount of fertilizer addition will discuss this issue. The added amounts of these 11 fertilizers were designed only by the average amount of N, P and K fertilizer in the local practical use. Changed in the manuscript: We have added the amount of N, P and K fertilizer in local practical use in this manuscript like this: (N fertilizer: 160 kg  $\text{N}\hat{\text{A}}\hat{\text{U}}$  ha-1; P fertilizer: 150 kg  $\text{P}_2\text{O}_5\hat{\text{A}}\hat{\text{U}}$  ha-1; K fertilizer: 50 kg  $\text{K}\hat{\text{A}}\hat{\text{U}}$  ha-1) Comment 3 – The variability of the experimental replicates should be shown (average and standard deviations), presented and discussed. This can be presented in Table 2. Answer: We did it. Comment 4 – In general, the authors used limestone and dolostone tablets.

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They did not discuss the results of dolostone tablets, only those from limestone tablets. In the discussion, the difference or similarity between dolostone and limestone is erased as the authors discuss about carbonates. More attention, or at least an explanation about the use of the general term of “carbonates” instead of the difference between dolostone and limestone should be given. Answer: The difference between limestone and dolostone is not noteworthy, so we use carbonate instead. Yes, we need to give some sentences to explain this. Changed in the manuscript: We added the statement “The result between limestone and dolostone weathering under different fertilization treatment were similar. We will explain the results with carbonates instead of individual dolostone and limestone.” in this manuscript to explain Comment 5: In several times in the manuscript (last sentence of the abstract, first paragraph of the results, and the last sentence of the conclusion) the authors used the expression “can aid carbonate weathering”: they should precise if the fertilizers enhance, increase, or decrease carbonate weathering. Changed in the manuscript: The statement that nitrogenous fertilizer can aid carbonate weathering should be replaced by ammonium fertilizer” in this manuscript is not precise. We deleted it. And we replaced the rest aids with the word “increase”. Comment 6: Introduction: - L.43 - The authors should add references showing the relationship between carbonate weathering and climate in addition to Liu et al. (2010, 2011); for example Kump et al., 2000). – Changed in the manuscript: We added it. Comment 7: L.47 - The authors should precise that the disturbance of CO<sub>2</sub> consumption disturbance may be overestimated at a local scale by taking into account Ca<sup>2+</sup> and Mg<sup>2+</sup> produced by a natural carbonate weathering and those produced indirectly by anthropogenic activities in the watershed. And what about this disturbance at a global scale? Answer: Here, we are just trying to introduce the potential disturbance at the regional/global scales by summarizing and classifying some references in the 1st paragraph. And the specific disturbances from fertilizer addition were further discussed in the 2nd paragraph. Comment 8: 2.2. Soil properties : - At which depth did the authors sample their soils? - Should precise pH(H<sub>2</sub>O) - Precise what OM means: organic matter I suppose. - Precise what ASI

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method means. - What is the soil typology? Answer: The pH had been listed in Table 1. Changed in the manuscript: The meanings of OM and ASI have been added. We changed the statement “The soil used in this column experiment was sampled from the B horizon (below 20 cm in depth) of yellow-brown soil in a cabbage-corn or capsicum-corn rotation plantation in Huaxi district.” to explain the soil samples and typology. Comment 9: 2.3. Soil column - What is the filter material? Answer: Yes, it is a misleading expression here. Changed in the manuscript: It has been changed into: A Polyethylene net (Ø 0.5 mm) was placed in the bottom of the columns to prevent soil loss. A filter sand layer with 2 cm thickness including gravel, coarse sand and fine sand was spread on the net. Comment 10: What kind of carbonate rocks did the authors use for their experiment? Are they reference rocks or rocks from karst area of HuaXi district? Answer: yes, it was collected from karst area of Huaxi district. Changed in the manuscript: We added this information in this manuscript. Comment 11: How did the authors deposit each fertilizer in the column? In liquid or solid form? At which temperature has the experiment been performed? - Did you leach the soil column with a solution? If yes, with which solution? Answer: The soil fertilizer was weighed and mixed with soil before filling in columns. Changed in the manuscript: We added a sentence to explain this. The soil was weighed, mixed perfectly with above fertilizer, respectively, and filled in its own column. Comment 12: - In figure 2: the authors draw 3 rock tablets, while the authors put only 2 rock tablets at the bottom of the column. Should change it. Changed in the manuscript: We have changed this. Comment 13: - Did the authors perform the same experiment without rock tablets if they leach their column in order to observe the leaching solution of the column? Answer: We didn't design that in this study. We didn't collect the soil solution. The leaching depended on the rainfall. Comment 14:- Did the authors put the 2 different rock tablets (calcite and dolomite) in the same column? Answer: Yes, we did. Comment 15: The authors should explain the reason of the fertilizer weight use in the experiment. Answer: Because the added amount of fertilizer can magnify and quicken the fertilization effect in the short-term according to another experiment from us, and can't affect the

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phenomenon we want to observe in this study. Another paper of ours (in preparation) about a series of different amount of fertilizer addition will discuss this issue. The added amounts of these 11 fertilizers were designed only by the average amount of N, P and K fertilizer in the local practical use. Changed in the manuscript: We have added the amount of N, P and K fertilizer in local practical use in this manuscript like this: N fertilizer: 160 kg N $\hat{u}$  ha-1; P fertilizer: 150 kg P<sub>2</sub>O<sub>5</sub> $\hat{u}$  ha-1; K fertilizer: 50 kg K $\hat{u}$  ha-1) Comment 16: 3. Results - L.164-165: Do not repeat Table 2 and Fig. 3. You may write: "The results are presented in Table 2 and in Figure 3. Changed in the manuscript: We have changed this. Comment 17: 4. Discussion - 4.1.: the first paragraph (L. 182-197) is quite general and it would be worthy to move it either in the introduction, or at least in the Materials and Methods section. Changed in the manuscript: We moved them to the introduction. Comment 18: 4.1. L.213-219: It is exactly the same text as in the introduction (L. 48-54) The authors may express their idea at least a little bit differently. Answer: Because they are for elaborating different problem, we think we should put one of them another way. Changed in the manuscript: We changed the statements in section 4.2. Comment 19: Information about soils and soil solutions are needed in order to understand their chemical evolution during the carbonate weathering. - Would it be possible to present the chemistry of each fertilizer used in this experiment? This can be added in supplementary information. Answer: yes, it is very important. Most of them have been discussed in section 4.2 and 4.3

Please also note the supplement to this comment:

<http://www.earth-surf-dynam-discuss.net/esurf-2016-50/esurf-2016-50-AC3-supplement.pdf>

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