Interactive comment on “Gas transfer velocities of CO$_2$ in subtropical monsoonal climate streams and small rivers” by Siyue Li et al.

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General comments The manuscript of Li et al. presents measured CO2 fluxes, transport coefficients based on CO2, and calculated pCO2 data of running waters in a subtropical monsoonal climate zone. These data are complemented by among others water chemistry parameters such as DOC, DTN, DTP, as well as hydrogeomorphology data (e.g. water depth, flow velocity). They provide data and insights about transport coefficients for a so far understudied region and highlight the spatial variability and subsequent uncertainty for regional upscale estimates. By investigating the key parameter for CO2 flux estimates - the transport coefficient - in an understudied region, Li et al. address a very relevant topic. Narrowing down the uncertainties of regional upscaling estimates of riverine CO2 fluxes is of wide interest, hence this study would
make a good contribution to the literature and the subject matter is thus of interest to Biogeosciences readers.

Response: We thank you for your overall positive comments, and accordingly revised the Ms.

However, in my opinion, the manuscript has some problems: (1) The terminology used in this manuscript is quite confusing to me. It seems to me that "streams“, "rivers“, "river networks“ are used interchangeably (without definition and consistency), which makes it hard to follow the red line of the story. The terminology needs to be clarified and unified.

Response: Based on the delineation of river systems by Alin et al., 2011 (JGR), small rivers and streams encompass rivers with channels < 100 m. We have clarified the term in the method.

(2) The sampling design is not very clear to me. All investigated running waters seem to be in the Three Gorges Reservoir (TGR) region, but in addition two larger streams (Daning and Qijiang) were sampled. In the results and discussion, these investigated running waters are combined, sometimes split, which makes it hard to follow (in the main text and tables). In my opinion, these three "regions“ need to be presented in a unified way (always separated or combined, possibly both in each table and figure), and presented more clearly in the text.

Response: We provided both separated and combined data in Tables and Figures, please refer to Figs 2 and 3, as well as Figs. S2 and S3. In addition, we also clearly stated in the “Method” part.

“Spatial differences (Daning, Qijiang and entire tributaries of TGR region) were tested using the nonparametric Mann Whitney U-test. Multivariate statistics, such as correlation and stepwise multiple linear regression, were performed for the models of k600 using potential physical parameters of wind speed, water depth, and current velocity
from separated data and combined data (Alin et al., 2011).”

(3) One of the main messages is the presentation of transport coefficients in a sub-tropical monsoonal climate zone, which is interesting, but I can imagine that there is a large difference in the wet and dry season. However, all the measurements were done in the wet season. I think this issue should be clearly acknowledged and discussed.

Response: We agreed your opinion and addressed this issue in an additional section 4.4. In this section, effects and uncertainty of sampling seasonality on errors of annual CO2 flux estimation were included.

“Sampling seasonality considerably regulated riverine pCO2 and gas transfer velocity and thus water-air interface CO2 evasion rate (Li et al., 2012; Ran et al., 2015). We sampled waters in the rainy season due to that it showed wider range of flow velocity and thus rainy season covered the k levels in the whole hydrological season. Rainy season generally had higher current velocity and thus higher gas transfer velocity (Ran et al., 2015), while aquatic pCO2 was variable with seasonality. We recently reported that riverine pCO2 in the wet season was 81% the level in the dry season (Li et al., 2018), and prior study on the Yellow River reported that k level in the wet season was 1.8-fold higher than in the dry season (Ran et al., 2015), while another study on the Wuding River demonstrated that k level in the wet season was 83%-130% of that in the dry season (Ran et al., 2017). Thus, we acknowledged a certain amount of errors on the annual flux estimation from one-time sampling campaign during the wet season in the TGR area, while this uncertainty could not be important because that the diluted pCO2 could alleviate the potentially increased k level in the wet season.”

(4) There are two technical issues: (i) The measurements with the floating chambers are poorly described. The only information Li et al. provide is that the floating chambers were “deployed”. If the flux measurements are done in an anchored or free floating manner is critical (see e.g. Lorke, A., Bodmer, P., Noss, C., Alshboul, Z., Koschorreck, M., Somlai-Haase, C., Bastviken, D., Flury, S., McGinnis, D. F., Maeck, A., Müller, D.,
and Premke, K.: Technical note: drifting versus anchored flux chambers for measuring greenhouse gas emissions from running waters, Biogeosciences, 12, 7013-7024, https://doi.org/10.5194/bg-12-7013-2015, 2015.). Hence, this issue needs to be addressed clearly. (ii) It seems that all the flux and pCO2 measurements were done distributed during the day. The fact that there is a diurnal cycle of CO2 was not considered (see e.g. Pascal Bodmer, Marlen Heinz, Martin Pusch, Gabriel Singer, Katrin Premke, Carbon dynamics and their link to dissolved organic matter quality across contrasting stream ecosystems, Science of The Total Environment, Volume 553, 2016, Pages 574-586, ISSN 0048-9697, https://doi.org/10.1016/j.scitotenv.2016.02.095.), and values directly compared. This issue should at least be discussed.

Response: A new section of “4.4. Uncertainty assessment of pCO2 and flux-derived k values” was added. We assessed systematic errors and random errors of measurements, drifting chamber and anchored chambers, sampling time. We carefully read the two article and the two citations were included. In addition, the following text was added in the Method section.

“Similar to other studies (Alin et al., 2011), sampling and flux measurements in the day would tend to underestimate CO2 evasion rate (Bodmer et al., 2016).”

(5) Developing models to estimate transport coefficients is meaningful, but the process of the model development is poorly described. Additionally, which data were used for the models, and which not is confusing to me (goes along with my comment (2) above).

Response: The issue was addressed as follows.

Water samples from a total of 115 sites were collected. Floating chambers with replicates were deployed in 101 sites (32 sampling sites in Daning, 37 sites in TGR river networks and 32 sites in Qijiang). The sampling period covered spring and summer season, our sampling points are reasonable considering a water area of 433 km2. For example, 16 sites were collected for Yangtze system to examine hydrological and geomorphological controls on pCO2 (Liu et al., 2017), and 17 sites for dynamic biogeo-
chemical controls on riverine pCO2 in the Yangtze basin (Liu et al., 2016). Similar to other studies, sampling and flux measurements in the day would tend to underestimate CO2 evasion rate (Bodmer et al., 2016).

Prior to statistical analysis, we excluded k600 data for samples with the air-water pCO2 gradient <110 µatm, since the error in the k600 calculations drastically enhances when ΔdCO2 approaches zero (Borges et al., 2004; Alin et al., 2011), and datasets with ΔdCO2 >110 µatm provide an error of <10% on k600 computation (please refer to the Fig. 1 in the bottom). Thus, we discarded the samples (36.7% of sampling points with flux measurements) with ΔdCO2 <110 µatm for k600 model development, while for the flux estimations from diffusive model and floating chambers, all samples were included.

Multivariate statistics, such as correlation and stepwise multiple linear regression, were performed for the models of k600 using potential physical parameters of wind speed, water depth, and current velocity as the independent variables from both separated data and combined data (Alin et al., 2011). k models were obtained by water depth using data from the TGR rivers, while by flow velocity in the Qijiang.

We also highlighted separated or combined data used in the Tables and Figures legends.

(6) From what I see in these data, there are several running waters undersaturated with respect to CO2 (Fig. S2 and Fig. 1), and hence a sink of CO2. This aspect is totally neglected and the investigated running waters are generalized as CO2 sources to the atmosphere. In my opinion, this aspect of influxes of CO2 is very valuable and should be properly discussed.

Response: We addressed this issue by revision in the parts of “Result” and “Discussion”. Firstly, we revised in the “Result” section as follows. “pCO2 varied between 50 and 4830 µatm with mean of 846 ± 819 µatm (Table 1). There were 28.7% of samples that had pCO2 levels lower than 410 µatm, while the studied rivers were overall super-
saturated with reference to atmospheric CO2 and act as a source for the atmospheric CO2.”

Secondly, the under-saturated pCO2 levels were further examined in the “Discussion” part.

“The calculated pCO2 levels were within the published range, but towards the lower-end of published concentrations compiled elsewhere (Cole and Caraco, 2001; Li et al., 2013). The total mean pCO2 (846 ± 819 µatm) in the TGR, Danning and Qijiang sampled was lower than one third of global river’s average (3220 µatm) (Cole and Caraco, 2001). The lower pCO2 than most of the world’s river systems, particularly the under-saturated values, demonstrated that heterotrophic respiration of terrestrially derived DOC was not significant. Compared with high alkalinity, the limited delivery DOC particularly in the Daning and Qijiang river systems (Figs. S2 and S3) also indicated that in-stream respiration was limited. These two river systems are characterized by karst terrain and underlain by carbonate rock, where photosynthetic uptake of dissolved CO2 and carbonate minerals dissolution considerably regulated aquatic pCO2 (Zhang et al., 2017).”

(7) As far as I see, there is some arbitrariness regarding data handling/processing. The cut-off at 110 µatm (line 198) for the air-water CO2 gradient for k600 calculations, as well as “When several extremely values are removed: : :” (line 303), needs to be described/demonstrated/justified much more clear.

Response: We provided more details on this concern. Prior to statistical analysis, we excluded k600 data for samples with the air-water pCO2 gradient <110 µatm, since the error in the k600 calculations drastically enhances when â¬¬spCO2 approaches zero (Borges et al., 2004; Alin et al., 2011), and datasets with â¬¬spCO2 <110 µatm provide an error of <10% on k600 computation” (see the Fig. 1 in the bottom)

Regarding ““When several extremely values are removed: : :” (L 303) for revised model, we supplied data including extremely data and excluding extremely data in Fig.
(8) CO2 fluxes were measured, while pCO2 and transport coefficients were calculated. This should be clearly stated throughout the manuscript to be transparent.

Response: We highlighted this in the section of “Method” (see section 2.4), and changed “measured k or observed k to flux-derived k or derived k or calculated k”.

(9) I am not a native English speaker, but I think that the manuscript should be revised for the English language. (see exemplarily in the specific comments and technical corrections below) I think this is a valuable study, but the combination of the points mentioned above make the manuscript hard to follow and the conclusions and main messages drawn in the current state of the manuscript too general. In a revised version, the study would get more shaped, more detailed and informative, and the conclusions and main messages can be specified and more related to the investigated region.

Response: We edited the English and revised the Ms based on comments and suggestions.

Specific comments Abstract: Line 20: Indicate how many river networks (see general comment (2))

Response: 60 rivers

Line 24: As far as I understood not when all data were included. Please be more specific here.

Response: corrected and provided details in “Method” section.

Lines 30 – 33: This is not really new. Maybe you can specify this statement for the investigated region?

Response: Addressed. The sentence was revised as follows.
“We concluded that simple parameterization of k as a function of morphological characteristics was site specific and hence highly variable in river systems of the upper Yangtze River. k models should be developed for stream studies to evaluate the contribution of these regions to atmospheric CO2.”

Introduction: Line 41: Bastviken et al., 2011 totally focuses on CH4. I suggest replacing this reference with a more suitable one.

Response: Bastviken et al., 2011 was replaced by “Raymond et al., 2013; Butman and Raymond, 2011”

Line 42: But you did not present "new accurate measurement techniques“ in your study, what are your reasons to mention this in the introduction?

Response: “new” as removed.

Lines 50 – 58: This equation is pretty standard knowledge and can just be described in words here. The equation can be moved to the methods.

Response: Yes, it is very standard knowledge, while the text would be more shape, and easily to follow with equations here.

Line 63: The standardized transport coefficient (k600) should be explained here.

Response: k600 (the standardized transfer coefficient at a temperature of 20 0C)

Line 80: You set the scene of seasonal precipitation, but in the study, you only measure in the wet season. This is contradictory. This issue should be discussed.

Response: We changed “concentrated seasonal precipitation” to “hydrological seasonality”

Lines 84-89: Kind of repetition and partially contradictory to the text in lines 43-49.

Response: The topic is different. The former focuses on flux determination, while the latter talked about k measurement method. We clarified the main text.
Lines 92-99: The relevance of the study (first time in this region, etc.), the objectives and how these objectives were approached should be written more clearly. At this point, the input parameters for the model development is totally unclear.

Response: We re-wrote this part as follows, we also provide details for k models.

To contribute to this debate, extensive investigation was firstly accomplished for determination of k in rivers and streams of the upper Yangtze using FC method. Models of k were further developed using hydraulic properties from flux measurements and TBL model.

Our recent study preliminarily investigated pCO2 and air – water CO2 areal flux as well as their controls from fluvial networks in the Three Gorges Reservoir (TGR) area (Li et al., 2018). The past study was based on two field works, and the diffusive models from other continents were used. In this study, we attempted to derive k levels and develop the gas transfer model in this area (mountainous streams and small rivers) for more accurate quantification of CO2 areal flux, and also to serve for the fluvial networks in the Yangtze River or others with similar hydrology and geomorphology. Moreover, we did detailed field campaigns in the two contrasting rivers Daning and Qijiang for models (Fig. 1). The study thus clearly stated distinct differences than the previous study (Li et al., 2018) by the new contributions of specific objectives and data supplements, as well as wider significance.

Our new contributions to the literature include (1) determination and controls of k levels for small rivers and streams in subtropical areas of China, and (2) new k models developed using hydraulic parameters in the subtropical mountainous river networks.

Materials and methods: Line 105: In my opinion, Figure S1 should go to the main text. There are no sampling points for Daning and Qijiang, which is confusing to me.

Response: We supplied the map in the main text as Fig. 1 (see Fig. 2 in the bottom).

Lines 105-109: Please add a reference for this statement.
Response: “Li et al., 2018” was cited here.

Lines 110-118: Please see my general comment (2): Please restructure this, make clear how many running waters were sampled where, the size of the sampled running waters (Strahler stream order is fine), and why in these three regions. Otherwise, it is hard to follow your storyline.

Response: We provided details in the section 2.2.

Water samples from a total of 115 sites were collected. Floating chambers with replicates were deployed in 101 sites (32 sampling sites in Daning, 37 sites in TGR river networks and 32 sites in Qijiang). The sampling period covered spring and summer season, our sampling points are reasonable considering a water area of 433 km2. For example, 16 sites were collected for Yangtze system to examine hydrological and geomorphological controls on pCO2 (Liu et al., 2017), and 17 sites for dynamic biogeochemical controls on riverine pCO2 in the Yangtze basin (Liu et al., 2016). Similar to other studies, sampling and flux measurements in the day would tend to underestimate CO2 evasion rate (Bodmer et al., 2016). In our sampling points, all measured fluxes were retained since the floating chambers yielded linearly increasing CO2 against time following manufacturer’ specification.

Prior to statistical analysis, we excluded k600 data for samples with the air-water pCO2 gradient <110 µatm, since the error in the k600 calculations drastically enhances when δŠpCO2 approaches zero (Borges et al., 2004; Alin et al., 2011), and datasets with δŠpCO2 >110 µatm provide an error of <10% on k600 computation. Thus, we discarded the samples (36.7% of sampling points with flux measurements) with δŠpCO2 <110 µatm for k600 model development, while for the flux estimations from diffusive model and floating chambers, all samples were included.

Line 141-142: What is "PP"?

Response: EGM-4 (Environmental Gas Monitor; PP SYSTEMS Corporation, USA)
Line 148: I don’t really understand what you mean by this sentence, please revise.
Response: Changed to “All the solvents and reagents used in experiments were of analytical - reagent grade”

Lines 155-156: This sentence is confusing to me, please revise.
Response: Changed “The relationship was yielded when z=1 (U10=1.208×U1). ” to “U10=1.208×U1 as we measured the wind speed at a height of 1 m (U1). ”

Line 158: Do you mean CO2SYS? If yes, please add the corresponding reference.

Line 167: What was the brand of the tubing?
Response: Changed to “CO2 impermeable rubber-polymer tubing”

Line 170: What is DC?
Response: “DC” was removed.

Line 173: Please see my general comment (4) (i)
Response: Uncertainty of chambers was discussed in the additional section 4.4. In our study, both drifting chamber and anchored chambers were used, which is dependent on in situ current velocity. The following text was added.

“In sampling sites with low and favorable flow conditions (Fig. S1), freely drifting chambers (DC) were executed, while sampling sites in rivers and streams with higher flow velocity were conducted with anchored chambers (AC) (Ran et al., 2017). AC would create overestimation of CO2 emissions in our studied region (Lorke et al., 2015).”

C11
The units are confusing to me. Why is there two times pressure and temperature? Please double check if the units match up in the end, to me they do not.

Response: We have carefully checked and revised.

Please be more specific: k was calculated by reorganizing Eq (1)

Response: Revised.

Sc to the power of 0.5? This seems weird. What do you mean here?

Response: Corrected.

Please justify the cut-off at 110 _atm. Maybe add a figure to the supplementary material.

Response: Revised. Please refer to general comment (7).

I read about water depth and current velocity the first time here. These measurements need to be described before.

Response: Measurements of water depth and current velocity were added in the part of “Methods”.

The pH is quite high. This in combination with influxes of CO2 requires at least a short discussion about chemical enhancement.

Response: We revised the text in the section of “Result” (see the first paragraph below), and added text (see the second paragraph below) in the Discussion section (4.1).

“pH varied from 7.47 to 8.76 with exceptions of two quite high values of 9.38 and 8.87 (mean: 8.39 ± 0.29 from total dataset). Much lower pH was observed in TGR rivers (8.21 ± 0.33) (Table 1; p<0.05; Fig. S2).”

“Higher pH levels were observed in Daning and Qijiang (p<0.05 by ANOVA), where more carbonate rock exists that are characterized by karst terrain. Our pH range was comparable to the recent study on the karst river in China (Zhang et al., 2017). Quite
high values (i.e., 9.38 and 8.87) were recorded in the investigated sites, where chemical enhancement would increase the influx of atmospheric CO2 to alkaline waters (Wanninkhof and Knox, 1996), while 1.7% of sampling sites that were strongly affected by chemical enhancement were not significant on a regional scale. This chemical enhancement of CO2 influx was also reported to be limited in high-pH rivers (Zhang et al., 2017).


Line 214: Please see my general comment (6)
Response: Addressed. Please refer to general comment (6)

Lines 218-222: This paragraph belongs to the discussion section.
Response: We moved this to Discussion (see 4.1)

Lines 223-227: This paragraph should be revised because it is not very clearly written. Please add the p-values to the text in case of significances.
Response: We re-wrote this part.

“The much higher concentrations of dissolved organic carbon (DOC) and dissolved nutrients (DTN and DTP) were observed in the TGR rivers (p<0.01 by ANOVA; Fig. S3). In comparison to Daning, Qijiang showed significantly higher concentrations of DOC and DTN (p<0.05), and much lower TDP concentration (p<0.05; Fig. S3).”

Lines 235-237: What is the meaning of this ratio? Please add a few words what the reader can get from this information.
Response: Removed.

Line 242: These models and how you developed them should be explained better (in the method section).
Response: We provided details in the section of “Method”.

Lines 246-248: I do not understand this sentence. What do you mean by "binned“?

Response: Changed to “combined”

Discussion: Lines 270-274: How does this paragraph support the discussion of your study?

Response: These texts could support the discussion on relationship between spatial change in k values and physical characteristics (i.e., current velocity, slope and the water depth) of three river systems.

Spatial differences of k values and their controls of physical characteristics of current velocity, slope and the water depth were discussed for the three rivers systems (please refer to section 4.2).

“This could substantiate the higher k600 levels and spatial changes in k600 values of our three river systems. For instance, similar to other turbulent rivers in China (Ran et al., 2015; Ran et al., 2017), high k600 values in the TGR, Daning and Qjiang rivers were due to mountainous terrain catchment, high current velocity (10 – 150 cm/s) (Fig. 4b), bottom roughness, and shallow water depth (10 - 150 cm) (Fig. 4a). It has been suggested that shallow water enhances bottom shear, and the resultant turbulence increases k values (Alin et al., 2011; Raymond et al., 2012). These physical controls are highly variable across environmental types (Figs. 4a and 4b), hence, k values are expected to vary widely (Fig. 3). The k600 values in the TGR rivers showed wider range (1-177 cm/h; Fig. 3; Table S1), spanning more than 2 orders of magnitude across the region, and it is consistent with the considerable variability in the physical processes on water turbulence across environmental settings. Similar broad range of k600 levels was also observed in the China's Yellow basin (ca. 0-123 cm/h) (Ran et al., 2015; Ran et al., 2017).

Contrary to our expectations, no significant relationship was observed between k600
and water depth, and current velocity using the entire data in the three (TGR, Danning and Qjiang) river systems (Fig. S4). There were not statistically significant relationships between k600 and wind speed using separated data or combined data, and it is consistent with earlier studies (Alin et al., 2011; Raymond et al., 2012). Flow velocity showed linear relation with k600, and the extremely high value of k600 was observed during the periods of higher flow velocity (Fig. S4a) using combined data. Similar trend was also observed between water depth and k600 values (Fig. S4b). The lack of strong correlation between k600 and physical factors are probably due to combined effect of both flow velocity and water depth, as well as large diversity of channel morphology, both across and within river networks in the entire catchment (60,000 km²). This is further collaborated by weak correlations between k600 and flow velocity in the TGR rivers (Fig. 4), where one or two samples were taken for a large scale examination. k600 as a function of water depth was obtained in the TGR rivers, but it explained only 30% of the variance in k600. However, model using data from Qijiang could explain 68% of the variance in k600 (Fig. 4b), and it was in line with general theory. Nonetheless, k600 from our flow velocity based model (Fig. 4b) was potentially largely overestimated with consideration of other measurements (Alin et al., 2015; Ran et al., 2015; Ran et al., 2017). When several extremely values were removed, k600 (cm/h) was parameterized as follows (k600 = 62.879FV + 6.8357, R² = 0.52, p=0.019, FV-flow velocity with a unit of m/s), and this revised model was in good agreement with the model in the river networks of the Yellow River (Ran et al., 2017), but much lower than the model developed in the Yangtze system (Liu et al., 2017) (Fig. 4c). This was reasonable because of k600 values in the Yangtze system were from large rivers with higher turbulence than Yellow and our studied rivers. Furthermore, the determined k600 using FCs was, on average, consistent with the revised model (Table 2). These differences in relationship between spatial changes in k600 values and physical characteristics further corroborated heterogeneity of channel geomorphology and hydraulic conditions across the investigated rivers.”

Lines 286-288: No significances: : : But still, you developed the models considering
all data? This is not at all clear to me. Did you split/separate the data set for the models? This is not clear in Table 2. Please see my general comment (2). I think these data/models are valuable, but at the moment they seem arbitrary and should be better explained. This would help to give them more weight.

Response: We now provided details of model developing in the “Method” (see the response to general comment (2), (5) and (7). We also clearly stated the separated or combined data for models in the captions of Tables and Figs.

Lines 286-309: I see a lot of results here, which are presented in the discussion for the first time. The part presenting pure results should be moved to the results section.

Response: Revised

Line 303: Please justify the removal of "extremely values". Maybe add a figure to the supplementary material. If there is no objective criteria and justification, I do not see why data should be removed.

Response: We provided details in the Method and also supplied figure with or without extremely values in the main text (Fig. 4).

Lines 327-333: Why discussing k values and not k600 values? I think this needs to be unified/consistent throughout the manuscript.

Response: We unified to k600 though k600 and k were widely discussed in previous studies.

Conclusion: Lines 358-360: Very general, but actually, the regions had to be separated/split, no?

Response: The words were removed.

Lines 368-369: I think you should focus the conclusion on the investigated region.

Response: “in the river systems of the upper Yangtze River” was added.
Tables: Table 3: b) Why not presenting k600 values here which can be directly compared with other studies?

Response: We unified to “k600”

Figures: Fig. S1: Was always everything sampled at each point? "Samples“ should be replaced by "sampling point“

Response: We moved it to the main text as Fig. 1, and “Samples” was changed to “Sampling point”.

Fig. S4: There is no reference to this figure in the main text.

Response: Fig. S4 was cited in the main text.

Technical corrections Line 22: Delete "were“ Line 44: add "by“ or "via“ before "floating chambers“ Line 59: Replace "precisely“ with "well“ Line 127: "consisted“ instead of "consists“ Line 139: "pH sonde“ "was“ instead of "is“ Line 225: "Daning“ instead of "Danning“

Response: All the typos were corrected.

We also provided tracked main text for you reviewing

Please also note the supplement to this comment:

Fig. 1. Theoretical error (±%) on the computation of the gas transfer velocity of CO$_2$ ($k_{600}$) as a function of the air–water gradient of CO$_2$ ($\Delta$pCO$_2$ in ppm), assuming a constant uncertainty on $\Delta$pCO$_2$ of ±3% (Borges et al., 2004).
Fig. 1. Map of sampling locations of major rivers and streams in the Three Gorges Reservoir region, China (Please see in the main text).

Fig. 2.