Soil

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Manuscript Title: Environmental behaviors of (*E*)-Pyriminobac-methyl in agricultural

soils

Article Type: Research paper

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Response to the first reviewer's comments

First of all, we would like to thank you for your valuable comments

and suggestions which help us to improve our manuscript. Below we

try to address all the points which you have indicated in your

assessment opinions.

General comment:

Comment: Pesticides, as chemical compounds widely and excessively used in the world,

pose a significant threat to soil and water ecosystems. The presented publication raises

the important issue of pesticides behavior in soil and their leaching potential. The

manuscript is generally well written and contains many research results, however some

issues that need to be improved. The introduction and discussion needs enhancement in

some paragraphs and the figures should be corrected as they are illegible. All

recommendations are listed in the below comments.

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<u>Response:</u> Thank you very much for your support of our manuscript. We further revised our manuscript according to your comments.

Specific comments:

Comment 1: Abstract:

Resents well-organized information reflecting the contents of the manuscript.

<u>Response 1:</u> This suggestion has been adopted. We have revised the abstract. Please see Lines 21-39 in the revised manuscript.

Comment 2: Keywords:

Should not be included in the title. Please reworded.

<u>Response 2:</u> This suggestion has been adopted. We have revised the keywords. Please see Line 40 in the revised manuscript.

Comment 3: Introduction:

1.34-46 What are the national standards/regulations for herbicide use in China and what are the detected exceding of their concentrations?

<u>Response 3:</u> This suggestion has been adopted. We have added the national standards for herbicide use in China and what are the detected exceding of their concentrations. Please see Lines 45-54 in the revised manuscript.

Comment 4: 1.68: Double parenthesis. Please correct

<u>Response 4:</u> This suggestion has been adopted. We have corrected. Please see Line 66 in the revised manuscript.

Comment 5: 1.69: Please explain the acronym 'PM'

<u>Response 5:</u> This suggestion has been adopted. 'PM' is the abbreviated form of 'Pyriminobac-methyl'. Please see Line 49 in the revised manuscript.

Comment 6: 1.75-83: What is the greater risk - leaching or uptake by plants? How half-life time of EPM affects the residence time of a compound in soil. Please outline the background for the research.

Response 6: This suggestion has been adopted. We deem that leaching of herbicide is more harmful than uptake by plants. **Please see Lines 86-99 in the revised manuscript**.

Comment 7: 1.109-115: Is the method used 'own' or standardized? The individual analytical steps indicate the determination of the available EPM fraction, not the total fraction (usually used with more aggressive / stronger solvents).

Response 7: This suggestion has been adopted. The method used 'own'. The details of the extraction method and HPLC-MS analytical method were reported previously (Jia et al., 2019a).

The recovery of EPM from paddy water investigated QuEChERS using five different solvents for extraction: methyl alcohol, acetonitrile, dichloromethane, acetone, and Ethyl acetate. The results showed that acetonitrile extraction recovery was the highest among the five solvents(Jia et al., 2019b). **Please see Line 214 in the revised**

manuscript.

Reference:

Jia, H. R., Zhang, Y., Li, W., and Li, B. T.: HPLC- tandem Mass Spectrometry Method for the Determination of Pyriminobac- methyl 10% WP, Agrochemicals, 58, 106-108, 2019a.

Jia, H. R., Zhang, Y., W, L., Li, B. T., Shi, X. G., and Tang, L. M.: Residue of pyriminobac-methyl in rice and environment, Chinese Journal of Pesticide Science, 2, 250-254, 2019b.

<u>Comment 8:</u> 1.125: Please provide the determination parameters of the chromatographic method, i.e. repeatability, reproducibility, recovery, measurement uncertainty, detection limit and limit of quantification.

Response 8: This suggestion has been adopted. The detail information of the determination parameters of the chromatographic method, i.e., repeatability, reproducibility, recovery, measurement uncertainty, detection limit and limit of quantification were shown in the supplementary material (Fig. S2-S4 and Table S2-S4).

Please see Fig. S2-S4 and Table S2-S4 in the revised supplementary material.

Comment 9: 1.126-134: what is the estimated environmental stability of EPM based on the literature data? This information is necessary for appropriate analysis of the presented data.

<u>Response 9:</u> This suggestion has been adopted. We have added the estimated environmental stability of EPM based on the literature data. Please see Lines 100-107 in the revised manuscript.

Comment 10: 1.218, 223, 230, 234: Illegible chart. Please correct

<u>Response 10:</u> This suggestion has been adopted. We have corrected the illegible charts. Please see Lines 250, 255, 262, 267 in the revised manuscript.

Comment 11: 1.261-266: How were outliers dealt with?

Response 11: This suggestion has been adopted. Aguinis et al. (2013) recommendations on how to define, identify, and handle outliers are based on two overarching principles. The first category consists of error outliers, or data points that lie at a distance from other data points because they are the result of inaccuracies. The second category represents interesting outliers, which are accurate data points that lie at a distance from other data points and may contain valuable or unexpected knowledge. The third category refers to influential outliers, which are accurate data points that lie at a distance from other data points, are not error or interesting outliers, and also affect substantive conclusions. The approaches to identifying and handling error and interesting outliers are similar across data-analytic techniques. However, the way influential outliers are identified and handled depends on the particular technique-for example, regression versus SEM. Thus, they first provide a discussion regarding error and interesting outliers and then offer a separate treatment of influential outliers within each of the specific contexts of regression, SEM, and multilevel modeling. As seen in Figure 1, they recommendation is that all empirical studies follow the same sequence of steps. We handled outliers as they recommend.

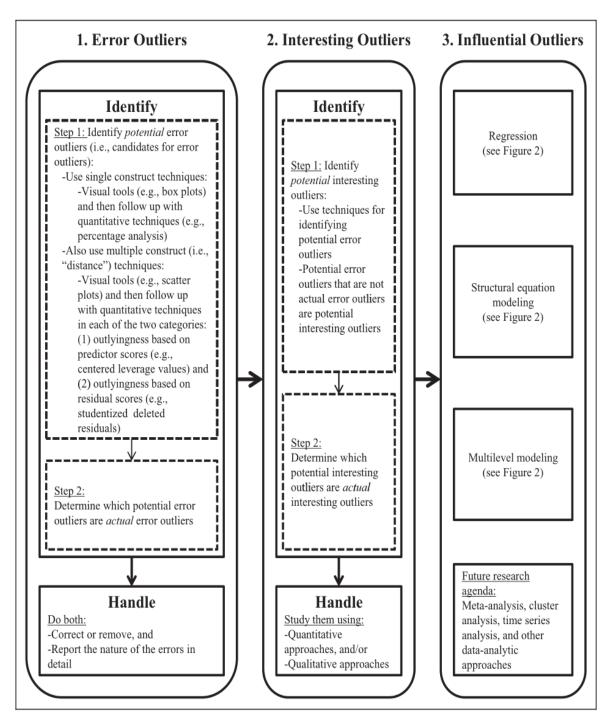


Fig. 1 Decision-making tree summarizing sequential steps in the process of understanding the possible presence of outliers (Aguinis et al., 2013).

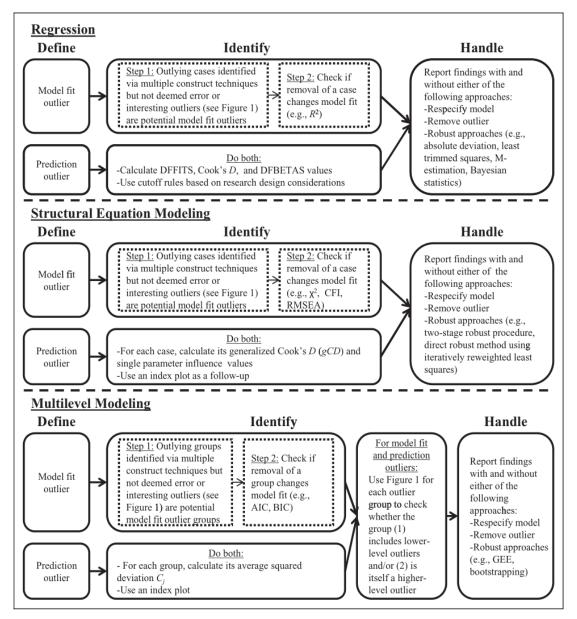


Fig. 2 Decision-making tree summarizing sequential steps in the process of defining, identifying, and handling influential outliers in the context of regression, structural equation modeling (SEM), and multilevel modeling (Aguinis et al., 2013).

Reference:

Aguinis, H., Gottfredson, R. K., and Joo, H.: Best-Practice Recommendations for Defining, Identifying, and Handling Outliers, Organizational Research Methods, 16, 270-301, 10.1177/1094428112470848, 2013.

Comment 12: Results and discussion:

Results are very good described but discussion should be strengthened especially in the

first subsection. 1.286-287: The logical statement. Please expand the discussion about

sorption affinity.

Response 12: This suggestion has been adopted. We have expanded the discussion

about sorption affinity. Please see Lines 317-332 in the revised manuscript.

Comment 13: 1.405-406: Repetition. This information is contained in the materials and

methods section.

Response 13: This suggestion has been adopted. We have deleted the duplicate

information.

Comment 14: Conclusions:

Conclusions are properly written and do not require corrections.

Response 14: Thank you very much!

Thanks again for your kindly comments.

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Response to the second reviewer's comments

First of all, we would like to thank you for your valuable comments

and suggestions which help us to improve our manuscript. Below we

try to address all the points which you have indicated in your

assessment opinions.

General comment:

Comment: This study provide results on herbicide EPM behaviour in paddy soils. I

think that these experimental data bay help understand this compound in risk

assessment.

Response: Thank you very much for your support of our manuscript. We further

revised our manuscript according to your comments.

Specific comments:

Comment 1: Suggestions:

For degradation study, did the author test the degradation products by MASS or other

detection means?

Response 1: This suggestion has been adopted. We apologize for not analyzing and

testing the degradation products. Thus, this experiment has been included in our work

this year. Thank you for your valuable suggestions to improve our research.

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Comment 2: It's recommended to provide the analytical method performance in validation, and typical chromatograms.

<u>Response 2:</u> This suggestion has been adopted. We supplemented typical chromatograms of the analytical method performance in the supplementary material (Fig. S2-S4). Please see Fig. S2-S4 in the revised supplementary material.

Thanks again for your kindly comments.

Response to the third reviewer's comments

First of all, we would like to thank you for your valuable comments and suggestions which help us to improve our manuscript. Below we try to address all the points which you have indicated in your assessment opinions.

General comment:

Comment: The manucript "Environmental behaviors under the title of (E)-Pyriminobac-methyl in agricultural soils" is relevant to the scope of the Journal, scientifically sound and valid. The Authors performed an immense work to study the adsorption—desorption, degradation, and leaching behaviors of **EPM** in physicochemically various soils, from five exemplar sites in China.

The data presented in the study is comprehensive, very detailed, discussed thoroughly an the conclusions supported by the mathematical models, which makes the paper a great source of data - also as an experimental approach in the pesticide studies.

The only suggestion I would have is to postpone part. 2.2 Extraction and final analyses a bit further in the Matrials and Methods part, as the potential reader may be confused by getting the detailed information about the extraction and final assessment of the pesticide before the methodological approach is revealed (description of the soil spiking, adsorption-desorption studies etc.). I believe that would make the work more transparent.

Differences in the sorptive behaviour of the soils are well explained (by various mineralogical composition of soils, especially clay minerals and organic matter contents, CEC value etc.). Results of this study demonstrate the high degradability of EPM, as well as its high adsorption affinity and low mobility in soils with abundant organic matter content and high cation exchange capacity.

The paper may serve as a a solid basis for predicting the environmental impacts of EPM and a great reference for the other researchers in this field, as there are still only a few studies on the EPM behaviour in the soil. Therefore, I support its publication.

<u>Response:</u> Thank you very much for your support of our manuscript. We further revised our manuscript according to your comments.

Specific comments:

<u>Comment 1:</u> The only suggestion I would have is to postpone part. 2.2 Extraction and final analyses a bit further in the Matrials and Methods part, as the potential reader may be confused by getting the detailed information about the extraction and final assessment of the pesticide before the methodological approach is revealed (description of the soil spiking, adsorption-desorption studies etc.). I believe that would make the work more transparent.

Response 1: This suggestion has been adopted. We have moved part 2.2. Extraction and final analyses after part 2.5. Leaching experiments. Thank you for your valuable suggestions to improve our research. **Please see Lines 208-236 in the revised**

manuscript.

Thanks again for your kindly comments.