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Biogeosciences Discussions

Interactive comment on "Technical Note: Enhanced reactivity of nitrogenous organohalogen formation from plant litter to bacteria" *by* J. J. Wang et al.

Anonymous Referee #2

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The paper "Enhanced reactivity of nitrogenous organohalogen formation from plant litter to bacteria," by Wang et al., presents a refreshing take on the natural formation of organohalogens, focusing on halogenation of bacterial cultures and monomers. The hypothesis is novel, the data are clearly presented and discussed, and the results are compelling. After reading the manuscript, I have a few lingering questions, which are enumerated below.

Comments on Methods:

The Methods section skimps on details. I would appreciate a very brief outline of the EPA method used to analyze the samples, as well as some details on how the plant litter extracts were made. Also, the Methods section does not describe the conditions for the bromination studies (although we can infer the KBr concentrations from the Figure 1 caption).

Why were these reactions performed at basic pH (8.0 +/- 0.2)? I imagine this must have to do with the added NaOCl, which is very basic. However, terrestrial soils are generally more acidic. It would be good for the authors at least to justify their selection of this high pH value and comment on its relevance to actual environmental systems.

What is the "Cl residual" mentioned in the Methods in line 24? Please define this term.

Comments on Results and Discussion:

Although the data are nice, the underlying motivation for the bromination studies remains unclear. We would expect bromide added to a NaOCl solution to become oxidized to hypobromite, a reactive brominating species, through the equilibrium NaOCl + Br- = NaOCl + Cl-. Why, then, is the formation of brominated C1/C2 compounds surprising or interesting? The authors should expand the discussion to explain the meaning and importance of the bromination studies.

In Figure 1b, in the middle graph, the concentrations of mono- and dibromoacetonitriles plummet at high [Br-]. The authors mention that this could be due to formation of other species, e.g., cyanogens halides. Why does this only apply for the nitrile compounds and not the chloro/bromoforms or hydrates? Was tribromoacetonitrile measured? Also, how repeatable were the results presented in the Figure 1b graphs across all the bacterial species examined?

In Figure 1a, there is a good correlation between bacterial [C] with dichloroacetonitrile and chloral hydrate formation, but not much of a correlation with chloroform formation. The authors present a cogent explanation for in lines 21-29 of the Results, stating that chloroform formation is highly variable even for the studies of the bacterial monomers. This trend emerges clearly from the data in Figure 2 and resonates with the results in

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Figure 1a. Could the authors speculate on the molecular basis for this variable chloroform formation? What about the molecular structure of chloroform and the potential mechanisms of its formation lead to this variability?

With regard to Figure 3, the discussion of these very interesting results should be expanded. In particular, I am curious about the high variability in dichloroacetonitrile formation amongst the different bacteria. Why does it skyrocket for the B7 bacterium, despite its similar molar C/N ratio to the other species?

The data in Figure 3 also made me eager to see the production of dichloroacetonitrile (as well as the other organohalogens) in extracts and bacterial cultures WITHOUT NaOCl added. To what extent do these compounds form under the natural oxidative conditions of soil organic matter decomposition?

As a point of curiosity, why did the authors choose these three particular organochlorines to analyze? The difference in formation of the N-containing organochlorine vs. the others becomes clear at the end of the article, with the discussion of the data in Figure 3, but what was the original rationale for the selection of these three compounds?

As a final note, I appreciate the title but don't think it encapsulates the main thrust of the paper, which is focused more generally on bacterial production of C1 and C2 organohalogens, not just the comparatively greater formation of dichloroacetonitrile by bacteria compared with plant litter extracts. In short, the title seems too narrow, only representing a part of this paper's contribution. Thus, it might be beneficial to formulate a broader title that better describes the overall findings of the study.

Minor editorial corrections:

In line 9 of the Introduction, "widespreadly found" would be better replaced by "are widespread."

The sentence in lines 18-20 of the Introduction is awkward and should be rewritten for clarity.

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