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Interactive comment on "Seasonal variations in concentration and composition of dissolved organic carbon in Tokyo Bay" *by* A. Kubo et al.

Anonymous Referee #2

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Referee Comment 2 Biogeosciences Discussion., 11, 10203-10228 Title: Seasonal variations in concentration and composition of dissolved organic carbon in Tokyo Bay Authors: A. Kubo, M. Yamamoto-Kawai, and J. Kanda

Manuscript Overview: This work assessed differences in broad pools of dissolved organic carbon (DOC) in Tokyo Bay and at two additional freshwater sites within the Arakawa River, which empties into the Bay. One main goal was to evaluate the significance of DOC degradation for the C budget in coastal waters and export to the open ocean. Another objective was to compare differences to previous work by Ogura (1975) to assess changes in degradation potential due to sewage treatment facility upgrades. To assess bioavailability, the bulk DOC pool was divided into bioavailable DOC (BDOC) and recalcitrant DOC (RDOC) after 150 day degradation experiments.

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RDOC was classified as the DOC remaining after 150 days, and BDOC the difference between T-final and T-zero DOC concentrations. The authors also attempted to assess DOC sources after using multiple regression analysis of RDOC, salinity, and chlorophyll a. Main findings include:

– Rapid degradation of the labile pool of DOC at freshwater sites and Tokyo Bay during the first 20 days of incubation experiments;

– RDOC accounted for a larger proportion of DOC than BDOC at all sites;

– Terrestrial RDOC dominated all study sites compared to phytoplankton RDOC;

– Tokyo Bay was a source of terrestrial RDOC to the open ocean, because BDOC was rapidly degraded prior to export;

– RDOC and BDOC concentrations have decreased at all sites since 1975 due to advances in sewage treatment and less overall input of DOC into the riverine ecosystem.

General Comments: In aquatic and marine environmental studies, dissolved organic matter (DOM) composition refers to the assessment of some aspect of DOM's chemical characteristics. For example, the contribution of carbohydrates, proteins, or lipids to total DOC concentrations, or assessing bulk DOC concentrations in different size fractions of DOC (i.e. Low and High molecular weight material). The bulk pool of DOC or DOM, however, has been classified into broad "pools of lability", which includes the labile, semi-labile, and refractory pools. It is in my opinion that this manuscript actually assessed differences in the lability of ambient DOC rather than DOC composition. Thus, the title and all associated references to composition within the text should be changed to reflect that the authors studied DOC lability.

Another major issue has to do with the methodology of apparently not filtering surface water before conducting the DOC degradation experiments and the DOC samples from these experiments. This suggests that, for the experiments, TOC was actually analyzed, which could enhance the decay of TOC in the experiments because parti-

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cles are less diagenetically altered and general more bioavailable than accumulated DOC. Thus, the BDOC and RDOC abundance and removal rate estimates would be corrupted.

Another problem is the way that RDOC is being defined and used throughout the text. The issue is that bottom water RDOC concentrations are significantly less than experimental RDOC concentrations after 150 days. Yes, this leads to export of "RDOC" from terrestrial sources to the ocean, but it would help if the authors better defined their lability timescales of RDOC as a whole. One could argue that, relative to bottom water concentrations, the exported "terrestrial RDOC" is actually semi-labile. Clarity would help with this confusion.

Lastly, the discussion sections of the paper need quite a bit of work as there is little discussion relative to other studies in other systems, including the significance of looking at DOM sources and comparison to different methodologies (e.g. isotopic vs. multiple regression using salinity and chla).

Specific Comments:

Title page: Change composition to lability, as no DOM compositional analysis was conducted.

Abstract Page 10204 line 1: Abstract topic sentence is long and should be shortened.

Page 10204 line 20: Remove words "DOC", and leave as "exported mostly RDOC"

Introduction Page 10205 line 2: Add "diverse mixture of carbon with varying timescales of lability", or something similar.

Page 10205 line 15: Change composition to lability (do so onward for this issue).

Page 10205 paragraph 2: Tell us why you've studied BDOC and RDOC and the significance.

Materials and Methods Page 10206: Freshwater and seawater DOC samples were

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G/FF filtered, but the degradation experiments appear to be conducted with unfiltered surface water. If this is the case, this is problematic because particles could be contributing to the bioavailable signal, thus impacting all the rate constant calculations and estimates of RDOC vs. BDOC. Please account for this.

Results and Discussion Page 10208 line 25: add the word concentrations after POC

Page 10209 line 1: At this point in the paper, all we have to go on for whether water is being contaminated by sewage is DOC concentration. It would be really helpful if some other water quality indicator could be included, such as N and P concentrations, etc.

Page 10210 Section 3.2 Tokyo Bay: The Tokyo Bay bottom water DOC and RDOC concentrations are lower than those of RDOC at the end of the 150 day experiments. How can both be called RDOC? The authors need to clarify these differences in lability timescales upfront.

RDOC Sources Page 10213 Lines 6-20: Some discussion of the % breakdown of RDOC sources and how it compares to other studies that use a similar or isotopic approach would be helpful. As it stands, this section is mainly more results than discussion.

What is significant about the bay exporting terrestrial RDOC to the ocean? Is this common? How rapidly is terrestrial DOM thought to be degraded in coastal systems? What impact does salinity have on terrestrial DOM degradation? Discussion of things like this would help round out the paper.

Figures and Tables Table 3. Define X.

Figure 3. POC concentrations are not properly labeled.

Biogeosciences Specific Questions 1. Does the paper address relevant scientific questions within the scope of BG? Yes.

2. Does the paper present novel concepts, ideas, tools, or data? No.

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3. Are substantial conclusions reached? No. Conclusions are reached, but the significance of them could be discussed in greater detail.

4. Are the scientific methods and assumptions valid and clearly outlined? There is an issue with the methodology of how the degradation experiments were set up. It appears that samples were not filtered, which means the authors assessed TOC degradation rather than DOC. This is problematic because particles would be included in TOC measurements, and can generally be more bioavailable than DOC. Additionally, these differences could affect RDOC and BDOC calculations and thus the source calculations.

5. Are the results sufficient to support the interpretations and conclusions? Somewhat, but it really depends on whether the ambient water was filtered for experiments.

6. Is the description of experiments and calculations sufficiently complete and precise to allow their reproduction by fellow scientists (traceability of results)? Not really, due to the issue stated above.

7. Do the authors give proper credit to related work and clearly indicate their own new/original contribution? Yes, could do more in some discussion areas.

8. Does the title clearly reflect the contents of the paper? No. The authors actually measured lability, not composition of DOC.

9. Does the abstract provide a concise and complete summary? Somewhat. The first sentence is rather long. Overall the abstract could be shorter and more concise.

10. Is the overall presentation well structured and clear? Yes.

11. Is the language fluent and precise? Yes, for the most part. There are some grammatical errors.

12. Are mathematical formulae, symbols, abbreviations, and units correctly defined and used? Yes.

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13. Should any parts of the paper (text, formulae, figures, tables) be clarified, reduced, combined, or eliminated? Figure label clarification.

14. Are the number and quality of references appropriate? Could use more discussion.

15. Is the amount and quality of supplementary material appropriate? Yes, but a reference to the text where the RDOC calculation of Bay water is would be helpful in the SI Table 1 header.

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