

## ***Interactive comment on “Review article: Potential application of surface methods for the monitoring of organic matter dynamics in marine systems” by Galja Pletikapić and Nadica Ivošević DeNardis***

**A. Podestà (Referee)**

alessandro.podesta@mi.infn.it

Received and published: 3 August 2016

**General comments** The manuscript of Pletikapic et al is dedicated to the assessment of the potential of two surface characterization techniques, electrochemical chronoamperometry and atomic force microscopy (AFM), for the monitoring and study of organic matter in the marine ecosystem, with particular attention to the Northern and Southern Adriatic Sea. The authors convincingly discuss how these techniques can be useful in providing a quantitative characterization of the micro- and nano- physical-chemical state of organic matter in the marine systems, to the advantage of establishing more reliable predictive indicators and protocols for important events such as the formation of extended mucilage volumes or the spillage of contaminants and pollutants into the

C1

water. Interestingly, the authors discuss experimental data collected using the two techniques in field-oriented studies: a long-term Croatian National Monitoring Programme of organic microparticle distribution, taken as an early warning sign for mucilage formation, and the investigation of the impact on the marine ecosystem of the accidental sinking of a ship in 2013 in the bay of Boka Kotorska, Montenegro, followed by the spilling of diesel fuel. Moreover, the authors discuss the peculiarities of the two techniques with respect to the possibility of using them for monitoring purposes. They demonstrate that the electrochemical approach meets the requirements for sensing and monitoring purposes, due to its ability to quickly and reliably characterize a large amount of raw sea-water samples, providing quantitative information; the second technique, AFM, while not possessing the same monitoring capability, can be a very powerful complement of the first one due to its ability to accurately visualize and characterize in size and shape the constituents (particles and aggregates) of the organic matter. Overall, the manuscript represents an interesting review of two powerful and complimentary techniques mastered by the authors for the quantitative investigation and monitoring of the marine ecosystem. The authors are convincing in assessing the relevance of the proposed combined approach for the study, understanding and preservation of the marine ecosystem. Some more details could be provided in order to make the manuscript more complete and informative.

**Specific comments** 1) According to what is written in Page 6, line 30, sample are imaged by AFM in dehydrated conditions, and this is found to be "the most adequate condition". A line of comment here would be useful, as the reader may not find obvious that such fragile samples (including vesicles) can be studied outside their native aqueous environment. Another question that may arise is to which extent dehydration preserves the native properties of the objects under study. This also marks an asymmetry with respect to the chronoamperometry investigation, where the measurement is carried on in water. 2) Page 8, the last sentence starting at line 20. A new (AFM-based ?) approach is mentioned (Shon et al, 2013...), but nothing is said about it. It is not clear what could be the advantage of this approach (it is not even clear which approach is

C2

this), with respect to the possibility of exploiting the full potential of AFM. This sentence should be expanded so to shortly present and discuss alternative and/or complementary (AFM-based) approaches, not only the one proposed by Shon et al, so to provide an overview of extra AFM capabilities and their potential to the study of the organic matter in marine systems. For example, one such approach could be the combination of topographic and mechanical characterization, which would widen the spectrum of information on the system under study, in particular on the structural properties of the network/aggregates of particles; another could be the combination of topographic and chemical/affinity mapping, by means of functionalized tips, etc... These approaches could be very effective also for the study of small vesicles. In summary, the authors describe mostly the topographic imaging capabilities of the AFM, but it would be very interesting to provide a short overview also of the (many) other interfacial characterization capabilities of the AFM technique. 3) The possibility of imaging the oil micro/nano droplet by AFM is intriguing. It would be useful if the authors could comment a bit more on which particular information can/could be extracted by a similar investigation. For instance, could AFM help characterizing biodegradation processes, i.e. the interaction of hydrocarbon-degrading bacteria and small oil droplets? And why and how would AFM be better than other conventional techniques (such as high-resolution optical microscopy etc.). 4) What is the role of inorganic particles in the processes relevant to the marine ecosystem? The attention of the authors is focused on the organic fraction only, and as far as I understand the e-chem method is sensitive to it, only. But what are we missing in the global picture, for instance in the two case-studies presented, by neglecting the inorganic component? A short comment on this would be useful in the manuscript, with some advices on how to address the study of the inorganic matter (whenever relevant). 5) The chronoamperometric method is based on the study of the current vs time curves. Qualitative examples are provided of different curve shapes corresponding to different organic matter composition/structure as well as to different interfacial phenomena. For online monitoring purposes, the qualitative interpretation of these curves is probably the most effective approach. However, I wonder whether

C3

there exist also models of the e-chem interface that can be used to interpret more quantitatively the chronoamperometric output (in terms i.e. of equivalent circuits etc.)? A short comment on this would make the picture more complete.

Technical corrections

1) Section 3.3 has been skipped. Check the section numbering. 2) Page 4, line 22. The acronym DME should be introduced before in the text. Same for the acronym SAP (surface active particles). 3) Page 8, line 3-5. Sentence not clear, please rephrase. 4) Page 5, line 15: delete the parenthesis before "as a measure...". 4b) Page 5, line 16: delete the extra parenthesis after "hydrophobicity". 5) Page 5, line 1: explain → explaining 6) Increase figures with maps as much as possible, as characters are small.

In general, re-read and check carefully the manuscript for typos and english.

---

Interactive comment on Nat. Hazards Earth Syst. Sci. Discuss., doi:10.5194/nhess-2016-178, 2016.

C4