

# ***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***

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We thank Anonymous Referee #2 for his comments. We have responded to his comments bellow and incorporated subsequent changes in the manuscript. The new version of the manuscript is uploaded as separate pdf file.

General comments:

1) The authors discuss the potentials of non-invasive surface method which should be suitable to study the organic carbon down to the nano/microscale both for studying the aggregation of organic aggregates (northern Adriatic sea study case) and in the oil spill in the coastal water (South Adriatic sea study case). Although the chronoamperometric

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and atomic force microscopy have wide potential for the study and monitoring of the dynamics of organic matter in marine systems the ms has a main weakness: it is not a complete review and it does not demonstrate soundly the applicability to the marine environment in the two case studies considered. I strongly suggest clarifying the aims of the ms: is it a review of the methods which deals with the applications in the marine environment of chronoamperometry and AFM or it wants to demonstrate the applicability considering two case studies? In the first case other studies should be considered (e.g.: Guo et al., 1998; Nishino et al., 2004; Villacorte et al., 2015); in the second case a more robust presentation of the results obtained in the case studies should be presented and further discussed. The organization of the chapters needs to be revised as it is not consequential, moreover when presenting the case studies the emphasis should be more on the kind of organic matter and dynamic process that was investigated in the different areas than on the location of the studies.

Answer: The aim of this review is to present the application of surface analytical methods, chronoamperometry and atomic force microscopy (AFM), for monitoring of organic matter dynamics and oil pollution in the marine environment. We demonstrate the added value of combined methodological approach which relies on fast and direct characterization of marine organic matter from micro to nano level. The chapters are organized to first describe the basics of corresponding methods and then to show their applications for the monitoring needs. In the first case, referring to the monitoring of organic matter dynamics in the seawater, our focus is on naturally occurring, non living and micrometre sized surface-active particles which are described as vesicle/micelle-like structures formed by self-assembly of organic matter, primarily of lipid, polysaccharide and proteinaceous components deriving from phytoplankton excreted and/or from their decomposed products (Žutić and Svetličić, 2000). Those particles possess affinity to accumulate at the estuarine mixing zones interface, or sea surface or halocline of the Adriatic Sea, and can be measured electrochemically on the single particle level based on their interfacial properties, structural organization and hydrophobic/hydrophilic character as stated in introduction. Application of electro-

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chemical method with mercury electrode as sensor for organic matter characterization in aquatic samples is being in use over four decades (Zvonarić et al., 1973; Žutić et al., 1977, 1984, Žutić and Legović, 1987). Both surface analytical methods become used for seawater samples characterization in the framework of the Project Jadran, where complementarities became evident on analysis of large number of seawater samples showing particular trend before natural macroaggregation event occurs (increased concentrations of GeP or surfactant activity determined electrochemically were in line with visualization of polymer gel network on nanometre scale, increased concentration of SAP in subsurface layer, Svetličić et al., 2005). In the second case, we focused on the application of surface analytical methods for monitoring of anthropogenic oil pollution, in particularly to track remaining dispersed oil droplets from micrometer to nanometer sized fraction which persisted after clean up procedure due to the accidental sinking of the ship and spilling of diesel fuel oil in the Boka Kotorska Bay (Montenegro). We adjusted aim and included references. Please note that the following reference is already included in the reference list: “Santschi, P. H., Balnois, E., Wilkinson, K. J., Zhang, J., and Buffle, J.: Fibrillar polysaccharides in marine macromolecular organic matter as imaged by atomic force microscopy and transmission electron microscopy, *Limnol. Oceanogr.*, 43, 896–908, doi: 10.4319/lo.1998.43.5.089, 1998.”

2) The authors state that the methods are “non-invasive” and “do not need any sample pretreatment” however they do not provide sufficient information on the time between the sampling and the measurements, were the samples preserved or not?, were the analyses performed on board of the vessel used for the surveys? could changes have occurred in the natural samples after collection, prior to the analytical measurements?

Answer: Accepted. Seawater samples of 500 mL were placed in glass bottles and kept in closed cooler box (at approx. 40C) to slow down bacterial activity or any aggregation/degradation processes. No sample fixation. Measurements were done within 24 h after sampling in the laboratory on the land.

3) In the presentation of the North Adriatic case study there are many references to

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the “Project Jadran” which is not available through publications or web site. I strongly suggest presenting the data in order to better sustain the case studies or to specify that are unpublished data.

Answer: We remove reference Croatian monitoring program (Project Jadran) from the References. A great part of the results from the Project Jadran, referring to the other parameters studied, were presented in detail in reference: Giani, M., Degobbis, D., and Rinaldi, A.: Mucilages in the Adriatic and Tyrrhenian seas, Sci. Total. Environ., 353,1-380, doi:10.1016/j.scitotenv.2005.09.006, 2005a.)

Specific comments:

1) The Title is not representative of work presented as the ms describe some application of methods to the monitoring of organic matter dynamics in marine systems.

Answer: We agree with the Referee to change the title, and now it reads: Review: Surface analytical methods for the monitoring of organic matter dynamics and oil pollution in marine systems

2) The term surface methods is misleading as one could expect that they are applicable only to surface water monitoring whereas the term refer specifically to the analytical method.

Answer: Surface methods term is replaced with surface analytical methods.

3) In the Abstract (P.1 L.14, P.3 L.23) “raw seawater samples” is used; do the author refer to natural seawater samples? In affirmative case they could omit the term “raw” which could be misleading.

Answer: Raw seawater sample is replaced with natural seawater sample.

4) In the Introduction (P.1 L. 22) “DOM is mainly produced by primary production” should be changed as the DOM can be produced by phytoplankton, macrophytes, marine plants through primary production

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Answer: OK.

5) In introduction (p. 2 L. 16-24) Studies of TEP distribution have been carried out also in Adriatic sea, the authors should consider these studies as their case studies refer specifically to the Adriatic sea: Radić T, Kraus R, Fuks D, Radić J, Pecar O. 2005. Transparent exopolymeric particles' distribution in the northern Adriatic and their relation to microphytoplankton biomass and composition. *Sci Total Environ.*353(1-3): 151-61. Schuster S., Herndl G. J. 1995. Formation and significance of transparent exopolymeric particles in the northern Adriatic Sea. *Mar Ecol Prog Ser* 124: 227-236.

Answer: References are included.

6) When the authors state that “giant aggregates (> 1m) observed by a scuba diver” they should be aware that as many studies are cited the observations were carried out by different scuba divers.

Answer: Corrected.

7) Check and correct the name of the authors of the references as there are errors. (P.2 L. 23).

Answer: Corrected, thank you.

8) In the section 2.1 Electrochemical methods: The meaning of the sentence is unclear: “atomically smooth” and “ fluid chemically inert with a large set of interfacial data in various aqueous electrolyte solutions” (P. 4 L. 1-3).

Answer: Mercury as liquid possesses atomically smooth surface. The glass capillary is filled with mercury. Depending on the properties of capillary, each 2 seconds, a new fresh mercury drop is formed at the end of the glass capillary, and dropping is reproducible. In order to quantitatively analyze amperometric signal of a particle in terms of organic particle diameter, particle surface area at the interface, number of molecules in the monolayer, surface charge of the particle, critical interfacial tensions of adhesion, and kinetic parameters of the adhesion process, it is necessary to know

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interfacial data at the mercury/aqueous electrolyte interface (such as: surface charge densities and interfacial tensions). Revised version is slightly changed.

9) Molecular adsorption, adhesion, spreading and particle collisions are processes I suggest to avoid the term “phenomena” (P.4 L.14-16).

Answer: Done.

10) “diesel oil (D2)” : specify the meaning as it is a type of diesel oil (P. 8 L. 28).

Answer: OK.

11) In the conclusions (P. 10 L. 13-14) “Possible application: : :. Include : : :and monitoring of organic pollution “. I would suggest to substitute “organic” with “oil” as the authors did not considered other organic pollutants.

Answer: Accepted.

12) In the references “kucuckcekmece” bay the first letter should be capital (P. 14 L.29).

Answer: Thank you, it is corrected.

13) The quality of the figures needs to be improved. The Map in figure 1b is not readable. In the Figure 2, most of the titles of the graphs are not readable.

Answer: Improved.

14) In the caption of Figure 4 “analysis of raw seawater” I suggest to delete “raw” or to use “natural”.

Answer: OK.

15) The reference to not available sources is not common practice in scientific journals. I suggest presenting and using the data to better sustain the applicability in the case studies presented.

Answer: Reference is removed.

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16) In the figure 5, I suggest separating the presentation of the methods used and from the part regarding their application to study the dynamics of organic matter.

Answer: Done.

Please also note the supplement to this comment:

<http://www.nat-hazards-earth-syst-sci-discuss.net/nhess-2016-178/nhess-2016-178-AC2-supplement.pdf>

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

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