Ocean Sci. Discuss.,
doi:10.5194/os-2017-10-RC1, 2017

Ocean Science Discussions

Interactive comment on "Determination of dissolved nitric oxide in coastal waters of the Yellow Sea off Qingdao" *by* Chun-Ying Liu et al.

Anonymous Referee #1

Received and published: 24 April 2017

This paper describes a new method for NO in water samples and reports studies of NO in coastal waters. This seems to be the first such report in coastal waters and one of the few in any marine environment.

Since NO is undoubtedly a difficult analyte to measure, and since there is little work on it, larger-than-usual uncertainties in results are tolerable; however, at some point very uncertain data lose usefulness.

Although this work appears to be carefully done and well described in many aspects, there are major ambiguities and concerns about this method, including major uncertainties as to how reported [NO] values relate to [NO] in situ. Both aspects need clarification in order to render the MS acceptable. Method – chemistry: (1) The equation (line 141-144) is incomplete and disagrees with that reported: It is unbalanced, since NO

has an odd number or electrons whereas the products do not. Also, (2) O2 is involved in the DAN->NAT reaction: Biol. Pharm. Bull 21(12) 1247-1250 (1998) states"... The reaction of NO and O2 with 2,3 diaminonaphthalene (DAN) produced a fluorescent triazole." but in this study the only O2 present is the variable amount in the sample. Less-soluble O2 is stripped out faster than is NO, so as NO reaches the DAN solution, the pO2 varies over time, potentially altering the (NO->NAT) yield. (3) The equation (line 232) is incorrect. (4) NO reacts with O2 in both gas phase and solution; rate = k[NO]^2[O2] (ks are known). No evaluation of the roles of these reactions potentially consuming NO is given in the time between sampling and analysis (30 minute stripping period).

Method optimization: Table 1's large variations in reaction efficiency clearly establish that near-optimal conditions need to be better defined. At 300 ml/min/45 min (13.5 L gas) the NAT yield is 21%, while at 400 ml/min/30 min (12 L gas), the yield is 69%. Thus, a 12.5% decrease in purge gas volume results in a 328% increase in DAN yield! This huge sensitivity demands better characterization of yield-controlling factors. Also, how can the efficiency also drop at longer times - is the DAN/NAT solution unstable?

Calculations: Figure 4 lacks critical points at [NO2-]=0. The bottom 3 curves are roughly the same, $\sim$850 units $\pm$7%. Is this a "method blank"? Is any blank subtracted? For lab and at-sea measurements, the equation relating fluorescence units to [NO] should be given, along with any blank term(s) used.

Environmental [NO] data:

(1) In prior marine NO work by others, the NO source has been assigned to microbial processes that were assumed to continue, perhaps at perturbed rates, even during the stripping step, minimizing any losses, or to nitrite photolysis occurring while samples were stripped. Compared to this work, time-dependent losses were previously minimized (most microbial samples were also suboxic or anoxic). Nonetheless, likely all reported data underestimate [NO] to some extent. In contrast, here the minimum time

seems to be (?) minutes in the dark, plus 15 minutes on average in the degasser. Thus comparing these data with literature values without qualification/explanation is unjustified.

(2) In irradiated/sunlit waters, light may also induce NO losses by forming NO-reactive radicals from CDOM. NO loss has been used to estimate rates of CDOM + hv -> radicals {Marine Chem., 30, 45–71 (1990); J. Geophys. Res. 96(C3), 4939–4945 (1991)} and Olasehinde et al. stated, “Thus, our findings indicate that the reaction of NO with photochemically generated free radicals might be a major pathway for NO loss in natural waters.” Given high [DOC] in these waters, likely also rich in CDOM (it IS the “Yellow Sea”), it seems likely that NO consumption occurred. Was onlu a small residual [NO] detected?

(3) What can be reliably said about the reported data’s implications for [NO] in-situ, if one ignores the absolute values of [NO] as uncertain and assumes only a roughly constant reaction efficiency? The patterns of Figures 5, 6 seem consistent with a positive light-dependence of the source/sink balance.

(Reviewer will be traveling and unable to comment from 9 May to 3 June 2017)

Interactive comment on Ocean Sci. Discuss., doi:10.5194/os-2017-10, 2017.