Author Comment with regard to:

"Attribution of Atmospheric Sulfur Dioxide over the English Channel to Dimethylsulfide and Changing Ship Emissions"

by M. Yang et al.

14 March, 2016

Many thanks for the thoughtful *comments and suggestions from Anonymous Referee #2*. We are very glad to hear that the referee found our contribution valuable. Below are our replies to the specific comments, which are in *italic*.

Anonymous Referee #2

This manuscript presents an important dataset that explores the contribution of shipping to atmospheric sulphur dioxide concentrations on the English Channel coast. I recommend that the authors consider revision in respect of the following points before publication.

1. The change in SECA regulations in January 2015 involved a 10-fold reduction in the maximum sulphur content of bunker fuel. However, the abstract (lines 14-16) states that a threefold reduction in SO2 emissions was observed, and that there was a high level of SECA compliance in 2015. The differing factors of 3 and 10 are not discussed: the reason becomes clear from Figure 10, which shows that many ships were already complying with the 2015 regulations in 2014. This point should be clearly made in order to avoid confusion (also in the Conclusion, p11, line 24).
Thanks for the comment. We have clarified this in the revision.

2. p2, lines 24-25: needs rephrasing, e.g. "These regulations aim to reduce sulphur emission tenfold in SECAs by reducing the maximum allowed sulphur content of fuel from 1% to 0.1% by mass." The later sentence on open ocean regulations should also make clear that the percentages apply to the sulphur content of bunker fuel. It could be worth mentioning here that the SECA regulations allow ships to use scrubber technology as an alternative to low-sulphur fuel: the mention of scrubbers on p8, line 26 is otherwise mysterious to the uninitiated.
Suggestions accepted. Thanks.

3. p5, line 20: in Figure 4, the sector with few mixing ratios over 0.5 ppb in 2015 is southwest, not southeast.
There were indeed few occurrences >0.5 ppb in 2015 for the southwest sector. Though here we were making the point that the distribution shifted towards lower SO2 mixing ratios in the southeast.

4. p5, line 29 – p6, line 1: Why not use the same months in both years for this averaging?
We thought it would be useful to show the SO2 diel averages from nearly a whole year (2015). Seasonal variations are illustrated in Fig. 8 and 9.

5. p7, line 9: Liss and Slater (1974) state that both the hydration and the subsequent oxidation of SO2 are rapid, but they gave no reference to the oxidation kinetics. It may well be that rapid hydration is enough to justify the assumption of near zero concentration of dissolved SO2. This point should be discussed more fully. Rate constants for the kinetics of sulphite oxidation can be found in Zhang and Millero (Geochim. Cosmochim. Acta, 57, 1705-1718, 1993).

Thanks for the comment. As summarized by Schwartz (1992), SO2 dissociates almost instantaneously to form HSO_3^- and then sulfite in seawater. The effective solubility of SO2 in seawater (pH ~8) due to this chemical enhancement is very large (dimensionless water:air solubility of about 5e8), which means that air-sea SO2 exchange should be gas phase controlled.

Oxidation to sulfate permanently removes sulfite from the ocean with a time scale of minutes to hours. This results in low sulfite concentration in the surface ocean (e.g. a few μM or less, Campanella et al 1995; Hayes et al 2006). Even a large dissolved SO2 concentration of 10 μM would only equate to an equilibrium atmospheric SO2 concentration of 2e-5 nmole/L of air (equivalent to 0.5 ppt, 2-3 orders of magnitude lower than typical atmospheric mixing ratio). From these calculations, we see that the air-sea concentration gradient in SO2 resides essentially all in the atmosphere.

6. p11, line 1: It is not clear what reductions are being discussed, in particular how does a reduction in 2014 arise?

Sorry for the confusion. "Reduction" here refers to the difference in the computed mean SO2 mixing ratio caused by excluding the very coastal ship plumes.

References:

Campanella, L., Cipriani, P., Martini, T.M., Sammartino, M.P., Tomassetti, M.: New enzyme sensor for sulfite analysis in sea and river water samples. Anal. Chim. Acta 305(1–3), 32–41, 1995.

Hayes, M., Taylor, G., Aster, Y.M., Scranton, M.J., Vertical distributions of thiosulfate and sulfite in the Cariaco Basin. Limnology and Oceanography 01/2006; 51(1):280-287. DOI: 10.4319/lo.2006.51.1.0280, 2006.

Schwartz, S.E.: Factors governing dry deposition of gases to surface water. In: Schwartz, S.E., Slinn, W.G.N. (eds.) Precipitation Scavenging and Atmosphere-Surface Exchange: Volume ii. Hemisphere Publishing Corp, Washington, 1992.