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Do emissions from ships have a significant impact on concentrations of nitrogen oxides in the marine boundary layer?

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Abstract. The potential impact of ship emissions on concentrations of nitrogen oxides and reactive nitrogen compounds in the marine boundary layer is assessed using a global chemical transport model. The model predicts significant enhancements of these compounds over large regions, especially over the northern midlatitude oceans. This result is consistent with a recently published study, though the impacts predicted here are more widespread and the peak enhancements are not as large. However, comparisons of model results with recent measurements over the central North Atlantic Ocean do not provide support for these model predictions. While one cannot completely overlook the possibility that emissions of nitrogen oxides from ships may be overestimated, our analysis suggests that there may be a gap in our understanding of the chemical evolution of ship plumes as they mix into the background atmosphere in the marine boundary layer. On a related note, it is also possible that the overestimate of the impacts of ships on nitrogen oxides in the marine boundary layer by global models is due to the lack of parameterized representations of plume dynamics and chemistry in these models.

Introduction

It is being increasingly recognized that emissions of trace gases, such as nitrogen oxides (NO_x) and sulfur oxides, from ships may significantly perturb the chemical composition of the marine boundary layer (MBL) [*Corbett and Fischbeck*, 1997; *Corbett et al.*, 1999; *Capaldo et al.*, 1999]. Recent model calculations by *Lawrence and Crutzen* [1999] (hereafter referred to as LC99) indicate that emissions from ships can lead to surface NO_x enhancements of over two orders of magnitude in open ocean regions where ship traffic is high. LC99 further estimate that significant surface NO_x enhancements (at least a factor of 2) occur over most of the North Pacific, North Atlantic, and Indian oceans, resulting in a significant enhancement of MBL ozone and hydroxyl radical concentrations in these regions.

In this study, we re-assess the impact of ship emissions on MBL NO_x using a global chemical transport model (GCTM). Our study is distinguished from the LC99 study in two important respects. Firstly, we use an updated inventory for NO_x emissions from ships which is based on ship positions reports [*Corbett and Fischbeck*, 1997; *Corbett et al.*, 1999]. This updated inventory likely provides a more realistic geographical distribution of emissions compared to the inventory used in the LC99 study. While the global magnitude of the ship NO_x emissions used in the LC99 study (3 Tg N yr^{-1}) is the same as in this study, ship emissions in the LC99 study are confined to the main shipping routes. Secondly, LC99 concluded that NO_x observations in the MBL are too sparse to assess the accuracy of the model-predicted impact of ship emissions on NO_x. In this study, we compare our model results with recent measurements of NO_x and reactive nitrogen (NO_y) in the MBL of the central North Atlantic ocean (which, as we shall show later, is the region where the modeled impact of ship emissions is largest). We will use these comparisons to assess whether the modeled impact of ship emissions is supported by measurements.

Model description

The GCTM used in this study is the 11-level Geophysical Fluid Dynamics Laboratory model, as configured to simulate the global distribution of NO_y compounds [*Levy et al.*, 1999]. The combined thickness of the bottom two model layers is approximately 1000 m (the centers of the bottom

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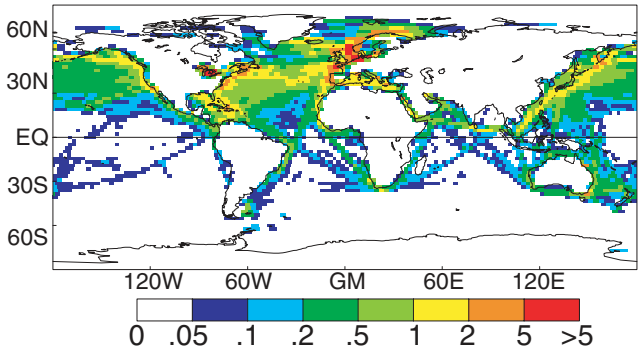

Plate 1. Annual-average emissions of NO_x from ships (10^{-12} kg N m^{-2} s^{-1}).

3 model levels are at standard heights of 80, 500, and 1500 m, respectively). The model explicitly simulates three NO_y species, namely NO_x, nitric acid, and peroxyacetyl nitrate. Interconversions between these species are calculated using prescribed rates as described in *Levy et al.* [1999]. While the NO_y chemical scheme used is highly parameterized, extensive comparisons with gas-phase and deposition measurements have shown that the model successfully simulates key features of the global NO_x and NO_y distributions [*Levy et al.*, 1999].

Two simulations, one excluding and one including ship emissions (hereafter referred to as the NOSHIP and SHIP simulation, respectively), have been performed to delineate the relative impact of these emissions on the NO_x distribution. Both simulations include NO_x emissions from land-based fossil fuel combustion (22.4 Tg N yr^{-1}), biomass burning (7.8 Tg N yr^{-1}), biogenic processes (5.0 Tg N yr^{-1}), lightning discharges (4.0 Tg N yr^{-1}), aircraft fossil fuel combustion (0.45 Tg N yr^{-1}), and stratospheric injection (0.64 Tg N yr^{-1}).

The SHIP run includes seasonally-varying emissions of NO_x from ships [*Corbett and Fischbeck*, 1997; *Corbett et al.*, 1999]. The annual, global magnitude of this source is 3 Tg N yr^{-1}. The global distribution of the annual-average NO_x emissions from ships used in this study is presented in Plate 1. A comparison of Plate 1 with Figure 1b of LC99 clearly shows the more widespread nature of the source used in this study.

A rough estimate of the potential significance of ship emissions can be obtained by considering the central North Atlantic ocean region, where annual-average ship emissions are 0.5-2.0 x 10^{-12} kg N m^{-2} s^{-1}. Assuming, a MBL depth of 1000 m and a NO_x lifetime of 1-2 days, a constant NO_x source of 10^{-12} kg N m^{-2} s^{-1} translates into a NO_x mixing ratio of 150-300 pptv.

Model results

Monthly-mean NO_x mixing ratios for January and July at the lowest model level from the SHIP simulation are shown in Plate 2. Also shown in Plate 2 are NO_x ratio fields relative to the NOSHIP simulation results. The total NO_x maps (top panels of Plate 2) show simulated surface NO_x mixing ratios in excess of 100 pptv over most of the North Atlantic and North Pacific north of 20N, and over the

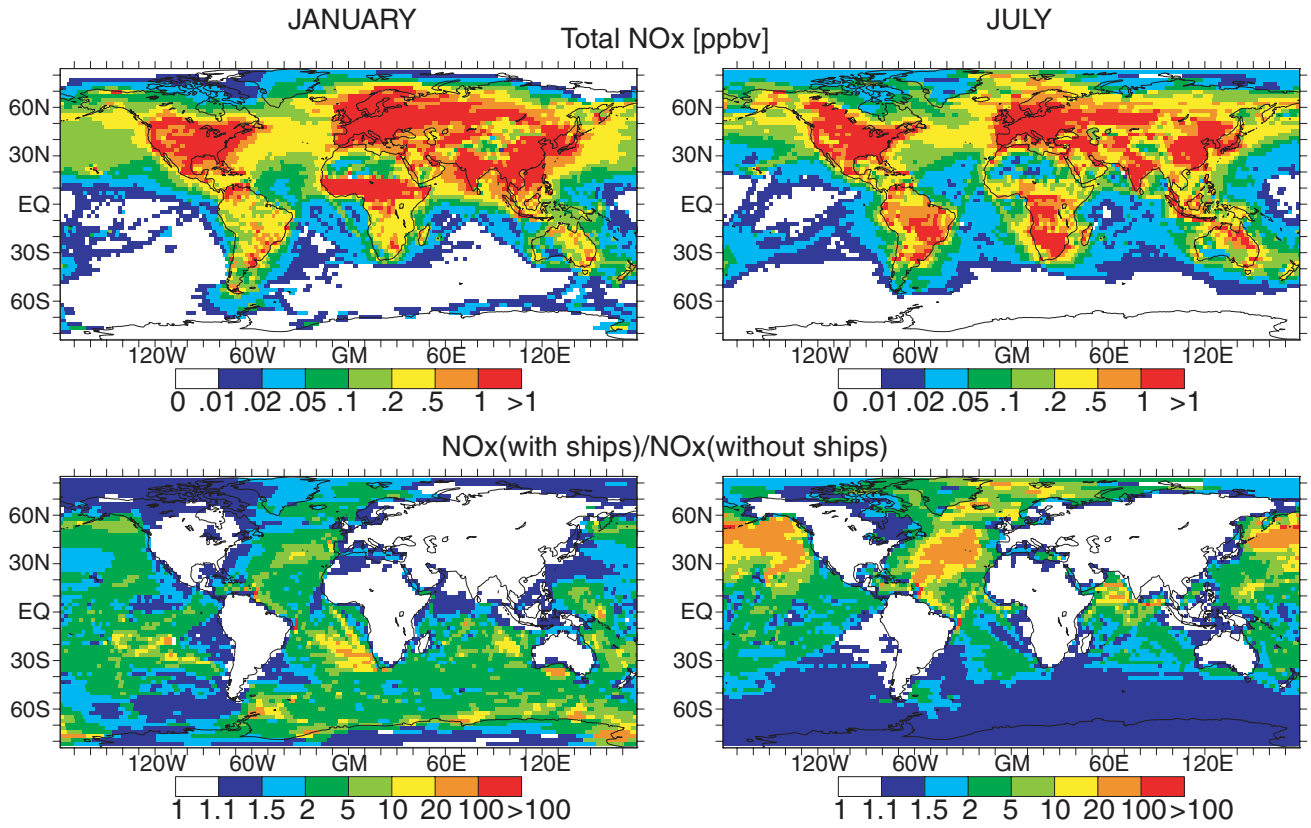

Plate 2. Simulated monthly-mean NO_x mixing ratios (ppbv) from the SHIP simulation (top) and the ratio of monthly-mean NO_x mixing ratios from the SHIP and NOSHIP simulation at the lowest model level during January and July.

Table 1. Comparisons of modeled NO_x and NO_y frequency distributions with measurements in the MBL over the central North Atlantic

Percentile	Azores				NARE 1997					
	OBS NO_y	NOSHIP NO_y	SHIP NO_y	SHIP NO_x	OBS NO_y	NOSHIP NO_y	SHIP NO_y	OBS NO_x[a]	NOSHIP NO_x	SHIP NO_x
5	45	6	92	35	163	23	176	b.d.l[b]	4	56
16.5	58	18	155	50	195	43	224	b.d.l[b]	9	78
50 (median)	73	43	283	100	262	87	358	12	20	149
83.5	84	100	421	191	339	199	584	26	46	270
95	109	140	792	346	477	349	830	38	81	374

[a]Calculated based on measured NO and O_3 assuming photostationary state.
[b]Below detection limit defined as 10 pptv NO_x for a 10 s average.

northern Indian ocean during January. In July, the surface NO_x levels over these regions are generally lower owing to the shorter lifetime of NO_x during summer. Nevertheless, surface NO_x mixing ratios in excess of 100 pptv are simulated over most of the extratropical North Atlantic ocean. During both January and July, simulated MBL NO_x mixing ratios are highest (in excess of 200 pptv) over parts of the North Atlantic and the western North Pacific.

Difference maps of NO_x (not shown here) roughly reflect the distribution of NO_x emissions from ships. Our model results indicate that emissions from ships of the magnitude prescribed here can contribute as much as 200-500 pptv of NO_x at the surface of the northern hemisphere midlatitude oceans. On a relative basis (bottom panels of Plate 2), the modeled impact of emissions from ships is particularly large over the central North Atlantic ocean and over the midlatitude North Pacific ocean during July. The combination of slower transport and shorter lifetime during summer results in a much weaker contribution from adjacent continental regions, leading to the relatively high contribution of the in-situ NO_x source from ships during this period.

A comparison of the results shown in Plate 2 with Figure 1d in LC99 shows that our results are generally consistent with the results of LC99, given the differences in the emission inventories in the two studies. While the peak relative enhancements in the LC99 study are larger, the influence of ship emissions is geographically more widespread in our model.

Comparisons with observations

Given the relatively large model-predicted impact of ship emissions on MBL NO_x in certain regions, an issue that must be considered is whether or not the model predictions are realistic. In this section, we attempt to address this issue by comparing our model results with recent measurements of NO_x and NO_y in the central North Atlantic MBL where the modeled impacts of ships are largest.

The first dataset we consider consists of NO_y measurements at a site in the Azores Islands (27.322W, 38.732N) from a field campaign during August 1993 [*Peterson et al.*, 1998]. Table 1 presents a comparison of the frequency distribution of NO_y mixing ratios from the model's MBL (bottom 2 levels) in the grid box containing the Azores Islands with the corresponding measured distributions for the data subset characteristic of the MBL (see *Peterson et al.* [1998] for a discussion of the data subset selection procedure). The MBL NO_y measurements used in Table 1 are believed to be minimally influenced by direct long-range transport [*Peterson et al.*, 1998]. In the model, which is climatological in nature, NO_y mixing ratios at the Azores during the second half of August are influenced by transport from Europe. In constructing the model NO_y statistics shown in Table 1, we have therefore used results only from the first 14 days in August in an effort to provide as representative a comparison as possible.

Table 1 shows that NO_y mixing ratios from the NOSHIP simulation are at most 30-40 pptv lower than the measurements. It is worth noting that the measurements include some that were influenced by orographic clouds which may have scavenged 10-45 pptv of nitric acid [*Peterson et al.*, 1998]. Adding ship emissions increases NO_y by a factor of 4-9 (except at the 5th percentile level which is increased by a factor of 15), resulting in NO_y mixing ratios that are significantly higher than the corresponding measurements. While concurrent measurements of NO_x are not available, the discrepancy in the model predictions is even more striking when one considers the modeled MBL NO_x mixing ratios from the SHIP simulation (see Table 1). The model-predicted median NO_x is higher than the median measured NO_y, and the 95th percentile modeled NO_x mixing ratio is a factor of 3 higher than the 95th percentile NO_y mixing ratio of the measurements.

Table 1 also shows comparisons of modeled NO_x and NO_y mixing ratios in the MBL (bottom 2 model levels) with aircraft-based measurements in the MBL (bottom 1 km) from the NARE field campaign during September 1997 [*Ryerson et al.*, 1999]. Periods of continental outflow were a particular focus of this field campaign. Since the focus of our study is on the impact of ship emissions, the comparisons with the measurements were limited to a latitude and longitude range of 37-50N and 35W-50W, respectively. These limits avoid the most intense continental outflow periods during the field campaign. For comparison, the model NO_x and NO_y statistics are based on the simulated 6-hourly mixing ratios in this region during September.

The comparisons with the NARE 1997 data also clearly show the overprediction of NO_x by the model when ship

emissions are considered. By contrast, the NOSHIP simulation predicts low values of NO_x which are generally consistent with, though somewhat higher than, the measurements. However, NO_y mixing ratios are underpredicted by 125 to 175 pptv in the NOSHIP simulation. While this discrepancy is rectified to some extent when ship emissions are considered, NO_y mixing ratios at the the upper end of the frequency distribution are significantly overpredicted in this case. Again, it is clear that adding ship emissions to the model leads to a significant overestimate of NO_x in the MBL over the central North Atlantic. This discrepancy increases if only model results in the lowest model level are considered since the median NO_x mixing ratios in the SHIP simulation are about 80 pptv higher in the lowest layer relative to the corresponding values in Table 1.

Discussion and conclusions

In this study, we have shown that the use of the best current estimates of NO_x emissions from ships in a GCTM leads to significant enhancements in the modeled MBL $NO_x$and NO_y mixing ratios over large parts of the ocean. This conclusion is broadly consistent with the results of LC99. However, recent measurements of NO_y in the MBL over the central North Atlantic provide only limited support for the predicted enhancements in NO_y. While the NO_y at the Azores are generally simulated to within $\pm$40 pptv without ship emissions, the consistent underprediction of NO_y in the NOSHIP simulation relative to the NARE 1997 data raises the possibility that about 150 pptv of NO_y in the central North Atlantic MBL may be due to ship emissions.

More significantly, the measurements do not support the large model-predicted enhancements of NO_x by ship emissions. It is important to emphasize that the focus of our study is on the impact on model-resolved spatial scales of a few hundred kilometers. While the reasons for the overprediction of NO_x are not obvious, one can speculate on various possibilities. It is possible that NO_x in ship plumes is oxidized relatively rapidly (i.e., at a rate significantly faster relative to the prescribed oxidation rate in summertime midlatitudes which corresponds to a NO_x lifetime of 0.75-1.0 days) on spatial scales not resolved by the model. It is worth noting that rapid NO_x oxidation rates have been calculated in some studies of power plant plumes, albeit in hydrocarbon-rich regimes [*Ryerson et al.*, 1998]. One also cannot discount the possibility that NO_x emissions from ships may in fact be overestimated, although the reported range in the magnitude of emissions is quite narrow (2.7-4.0 Tg N yr^{-1}) [*Corbett et al.*, 1999].

In light of the analysis presented here, the call by LC99 for the consideration of policies aimed at reducing ship emissions may be premature. However, the LC99 study and this study highlight the need for measurements to elucidate certain aspects of MBL photochemistry. Long-term measurements of NO_x, NO_y, and related species at locations such as the Azores, in concert with targeted field studies focused on understanding the chemical evolution of ship plumes as they mix into the background atmosphere, are needed. Such measurements will provide a better understanding of the impact of trace gas emissions from ships in particular, and of MBL NO_x and NO_y budgets in general. Our results also suggest that model predictions of the impact of ships on sulfur dioxide and sulfate in the MBL should be reassessed.

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