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Impact of Fuel Quality Regulation and Speed Reductions on Shipping Emissions: Implications for Climate and Air Quality

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Supporting Information

ABSTRACT: Atmospheric emissions of gas and particulate matter from a large ocean-going container vessel were sampled as it slowed and switched from high-sulfur to low-sulfur fuel as it transited into regulated coastal waters of California. Reduction in emission factors (EFs) of sulfur dioxide (SO_2), particulate matter, particulate sulfate and cloud condensation nuclei were substantial (≥90%). EFs for particulate organic matter decreased by 70%. Black carbon (BC) EFs were reduced by 41%. When the measured emission reductions, brought about by compliance with the California fuel quality regulation and participation in the vessel speed reduction (VSR) program, are placed in a broader context, warming from reductions in the indirect effect of SO_4 would dominate any radiative changes due to the emissions changes. Within regulated waters absolute emission reductions exceed 88% for almost all measured gas and particle phase species. The analysis presented provides direct estimations of the emissions reductions that can be realized by California fuel quality regulation and VSR program, in addition to providing new information relevant to potential health and climate impact of reduced fuel sulfur content, fuel quality and vessel speed reductions.

1. INTRODUCTION

Regulations on the atmospheric emissions from the transportation sector are motivated by the desire to reduce emissions of ozone (O_3)-forming chemicals, particulate matter (PM), acid rain- and PM-forming sulfur dioxide (SO_2), and other emissions harmful to human health and welfare. Regulation of fuel quality (sulfur, ash or aromatic hydrocarbon content) is one of several approaches that can be used to achieve reductions in these harmful emissions.[1] Commercial shipping has had limited fuel quality (or emissions) regulation until recently, even though the shipping industry emits (globally) 3 times more SO_2 than road traffic.[2] Commercial shipping, although fuel-efficient, mostly consumes low-quality residual fuel (or heavy fuel oil, HFO), which can have fuel sulfur content (S_F) exceeding 3 or 4% (by weight),[3] contain elevated concentrations of heavy metals[4] and emit significantly more PM (SO_4, particulate organic matter (POM) and black carbon (BC)) than more refined fuels.[5]

In recent years, the contribution of commercial shipping to air pollution has been recognized as significant (e.g., ref 6). In 2005 the International Maritime Organization (IMO) introduced a global cap to S_F of 4.5% (reducing to 3.5% in 2012 and 0.5% by

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2020),[7] motivated by PM reductions for air quality improvements that reductions in sulfur emissions are expected to achieve. Emission control areas (ECAs) have been established through the IMO in the North and Baltic seas to improve regional air quality. These ECAs require consumption of fuels with S_F < 1.0%.[8,9] In 2009 the US state of California introduced regulations that limit S_F consumed within 44.5 km of the Californian coast, which require the use of marine gas oil (MGO) or marine diesel oil (MDO) with a maximum S_F of 1.5% or 0.5%, respectively (by January 2012 S_F must be <0.1% [10]). In 2010 the IMO designated waters within 370 km of the United States and Canadian coast lines as an ECA requiring S_F <1% by August 2011, reducing to 0.1% in January 2015.[11] Expected benefits from the future global IMO regulations amount to ~41 200 avoided premature deaths annually (for 2012),[12] while up to 8000 avoided premature deaths per year are expected as a result of the future North American ECA regulation (for 2020).[13]

Consideration of the climate impacts of such regulatory changes has begun only recently. SO_4 emissions have a cooling effect on climate due to both light scattering by the particles (direct radiative effect) and from the cloud-forming and modifying ability of cloud condensation nuclei (CCN, indirect radiative effects). Eyring et al.[14] estimated the combined direct and indirect radiative forcing (RF) from shipping related SO_4 emissions to be $-0.44\ W\ m^{-2}$ (for 2005, globally averaged), with 90% of this from indirect effects. Concurrent emissions of other species (CO_2, O_3 precursors and BC), were estimated to have a net warming effect of $+0.07\ Wm^{2-}$. These forcings are global averages of the effect of both short-lived (e.g., PM) and long-lived (e.g., CO_2) forcing agents and have different spatial and temporal impacts.[15] Currently, there are no expectations that BC emissions will be reduced due to fuel sulfur regulations (CO_2 emissions may decrease slightly due to higher energy content of the more refined fuels), so IMO regulations are expected to decrease the net climate cooling from shipping emissions.[16]

The newly regulated coastal waters of California provide an opportunity to measure the influence of fuel quality regulation and speed reduction incentive programs on the magnitudes of emissions. These measurements will shed light on the potential air quality and climate effects of the impending regional and global fuel quality regulation, and possible vessel speed reduction (VSR) programs. In previous studies[5,17] we showed that correlations between some shipping emissions (e.g., SO_4, CCN) and S_F are observable in real-world operations. The variability around these correlations is largely due to intership variations in operating conditions, making a quantitative assessment of the potential impacts of fuel quality regulations challenging. The analysis of Winnes and Fridell[18] supports our assessment of previous data, suggesting that detailed characterization of emission factors from a single engine (or vessel) switching between high and low sulfur fuel is required (ideally on multiple vessels) to more accurately assess the impact of regulations on emissions. Here we provide emission factor comparisons from a container vessel where total exhaust emissions were measured as the vessel slowed and switched from high to low sulfur fuel near and within the California regulated waters during the 2010 CalNEX field campaign (http://www.esrl.noaa.gov/csd/calnex/).

2. FUEL SWITCH EXPERIMENT AND MEASUREMENT OF EMISSION FACTORS

Experiment Details. On the 21st of May, 2010, in collaboration with the Maersk Line shipping company, the NOAA *WP-3D* research aircraft[19] intercepted the *Margrethe Maersk* (*MM*) vessel on its way to the Port of Los Angeles, prior to the vessel starting the fuel switching procedure required by California state law (Figure 1a). The *MM* is a 371 m, 96 500 tonne container vessel running a 12 cylinder, 68.7 megawatt (MW) main diesel engine (3, 3.8 MW auxiliary engines). The *MM* was consuming HFO containing 3.15% sulfur and 0.05% ash (by weight) before a gradual blending of MGO containing 0.07% sulfur and <0.01% ash occurred over an 60 min period just outside California regulated waters.[20] On average, 60% of emissions were from the main engine, 10% from the auxiliary engines and 30% from boilers[20] (all engines switched fuels). The *MM* also participated in the Californian VSR incentive program,[23] changing speed across the fuel switch operation (22 knots prior and 12 knots after). These speed changes and differences in the relative fuel consumption between engines complicates the interpretation of results (discussed in more detail below). The emissions reductions reported here are due to both compliance with regulation (3.15% down to 1.5% S_F) as well as the choice of the vessel operator to use MGO with lower S_F than required by regulation (1.5% down to 0.07% S_F).

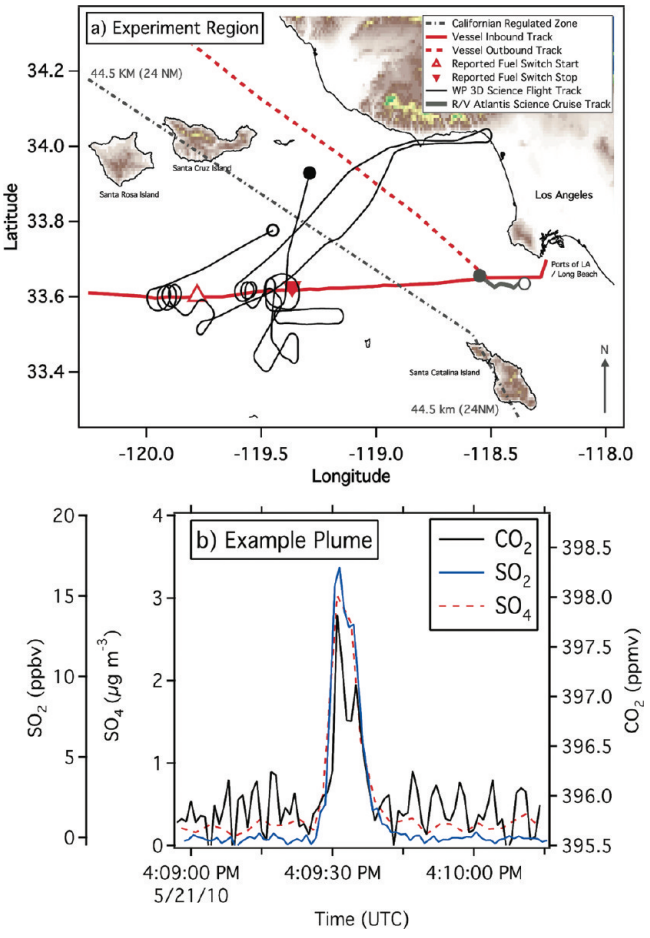

Figure 1. (a) Map showing section of California fuel sulfur regulation zone (dashed gray), course of the sampled *MM* for both inbound and outbound days (solid and dashed Red), the flight track of the NOAA *WP-3D* aircraft (black) and the track of the R/V *Atlantis* (solid gray). Red triangles mark the approximate location of the start and end of the fuel switch on the inbound journey (reported by Maersk). b) Example plume data for SO_2 (blue), SO_4 (red) and CO_2 (black).

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Table 1. Summary of Emission Factors Measured from the *MM* Outside and Within Regulated Waters

fuel or emission component	before fuel switch (outside regulated waters)		after fuel switch (within regulated waters)		units	% change
fuel sulfur (S_F − reported[a]	3.15		0.07		%	−98%
fuel sulfur (S_F) − calculated[b]	2.6 (±0.4)		0.21 (±0.03)		%	−92%
sulfur	25.6 (±4)		2.1 (±0.3)		g kg^{-1}	−92%
SO_2	49 (±7.5)		4.3 (±0.6)		g kg^{-1}	−91%
	measured	lack et al. (2009)[d]	measured	lack et al. (2009)[e]		
SO_4	2.94 (±1.0)	1.5 (±1.6)	0.08 (±0.03)	0.06 (±0.05)	g kg^{-1}	−97%
POM	0.58 (±0.2)	1.5 (±1.0)	0.17 (±0.06)	0.9 (±1.2)	g kg^{-1}	−71%
BC	0.22 (±0.09)	0.7 (±0.8)	0.13 (±0.05)	1.1 (±0.8)	g kg^{-1}	−41%
PM[c]	3.77 (±1.3)	3.0 (±1.7)	0.39 (±0.14)	1.8 (±1.4)	g kg^{-1}	−90%
N_{Tot}	1.0×10^{16} ($\pm 0.2 \times 10^{16}$)	1.4×10^{16} ($\pm 1.0 \times 10^{16}$)	1.4×10^{16} ($\pm 0.2 \times 10^{16}$)	1.0×10^{16} ($\pm 0.7 \times 10^{16}$	# kg^{-1}	+40%
CCN (SS = 0.3%)	4.0×10^{15} ($\pm 4 \times 10^{15}$)	2.4×10^{15} ($\pm 2.0 \times 10^{15}$)	0.1×10^{15} ($\pm 0.01 \times 10^{15}$)	0.2×10^{16} ($\pm 0.1 \times 10^{15}$)	# kg^{-1}	−97.5%
CCN/N_{Tot}	40 (±10)	34 (±27)	0.7 (±0.2)	7.4 (±6.0)	%	−98%
SO_4 / sulfur	4.1 (±0.7)	3.9 (±1.4)	1.2 (±0.2)	1.4 (±1.1)	%	−71%

[a] Provided by Maersk. [b] Calculated from $EF_S/10$ [26] [c] Sum of SO_4, POM and BC. Does not include SO_4-bound water or ash. [d] Average and standard deviation EFs from vessels using >0.5% S_F from Lack et al.[5] [e] Average and standard deviation EFs from vessels using <0.5% S_F from Lack et al.[5]

The *WP-3D* sampled the emissions plume of the *MM* before and during the fuel switching operation at approximately 100 m above sea level, 1−3 km downwind of the vessel (2−5 min). These times downwind are insufficient for significant atmospheric processing of SO_2, SO_4, BC, or POM.[5,17,21,22] Due to aircraft operational issues the flight was aborted before sampling of low S_F emissions could occur. Four days later (24th May, 2010) the NOAA-sponsored Woods Hole Oceanographic Institute research vessel R/V *Atlantis* sampled the *MM* emissions 2.5−7.5 min after emission while within the low-sulfur regulated zone (shown in figures as a triangle data point). The R/V *Atlantis* sample inlet was approximately 15 m ASL. A direct intercomparison between *WP-3D* and R/V *Atlantis* instrumentation was not possible during the campaign. The Supporting Information contains details of common calibrations used between instruments on both platforms. Due to these common calibrations we assume that measurements on both platforms are equally accurate to within the stated uncertainties. Calculation of emissions changes before and after the experiment therefore include these uncertainties.

Instrumentation. Measurements taken onboard the NOAA *WP-3D* research aircraft and the R/V *Atlantis* included concentrations of CO_2, SO_2, SO_4, POM, BC, particle number (N_{Tot}), and CCN as well as particle size distributions (note: NO_X data was not available for this analysis). Measurement techniques, uncertainties and references are provided in Supporting Information (Table S1). PM_1 mass is estimated as the sum of BC, SO_4, and POM mass. CCN are reported at a super saturation (SS) of 0.3%, a SS relevant for pristine stratocumulus and trade-wind cumulus clouds (e.g., ref 24). We determined emission factors (EF: amount emitted per kilogram of fuel burnt) by first determining the ratio between the integrated areas of the data of the plume intercepts for the species of interest and CO_2. An example plume encounter from the *WP-3D* is shown in Figure 1b. The average of CO_2 integrated areas from two independent measurement methods were used for *WP-3D* data. Maximum difference between the integrated areas of the two methods was 10% = CO_2 plume integration uncertainty. The measured emission ratios are converted to EFs according to Williams et al.[22] and Lack et al.[5] Instrument and CO_2 plume integration (10%) uncertainties are propagated through the calculation of the EF. Background pollutant levels and plume dilution/mixing are inherently accounted for via normalization of the emission to the measured CO_2 concentration. EFs are missing for some plume intercepts due to instrument filter or calibration periods. Engine load as a fraction of maximum load (f_{Load}) was estimated from the vessel speed (as load ∼ speed^3 [25]) recorded from the regular Automated Information System (AIS) radio broadcasts from the *MM*, where the maximum vessel speed is 25 knots.

3. RESULTS

Summary of Emissions. A summary of EFs and a comparison across the experiment is presented in Table 1. Detailed discussion is presented in the sections that follow. As the *MM* transitioned from high sulfur to low sulfur fuel and slowed, EFs for SO_2, SO_4, and CCN dropped by 91%, 97%, and 97.5%, respectively. PM, POM and BC EFs dropped by 90%, 71%, and 41% respectively. $EF_{N_{Tot}}$ change was variable and possibly increased after the fuel switch was complete. The various PM EFs for the *MM* prior to the fuel switch fall within the range of values observed in the comprehensive study by Lack et al.,[5] although the POM and BC prior to the fuel switch are about $^1/_3$ of the reported averages (Table 1). Measured PM EFs also compare well to other studies utilizing high S_F fuels (e.g., refs 4,18,26−29).

Sulfur Dioxide Emissions. Compliance with the fuel sulfur regulation provides direct and large reductions in EF_{SO_2} of 91% (Figure 2a). Some fuel sulfur is directly emitted as SO_3 (and quickly forms SO_4)[5,28] and so EF_{SO_4} and EF_{SO_2} are combined (accounting for stoichiometry) to determine an EF of total sulfur (EF_S). S_F as estimated from EF_S ($S_F \approx EF_S/10$ [26]) changed from 2.6% (HFO) to 0.2% (MGO) across the fuel switch. Maersk records indicate that S_F of the fuels dropped from 3.15% HFO to 0.07% MGO (98% drop). The source of this discrepancy is unknown, however several groups[18,30] have observed discrepancies (of up to 0.5%) between the S_F reported in the fuel analysis and that calculated from emission measurements. Nonetheless, it is

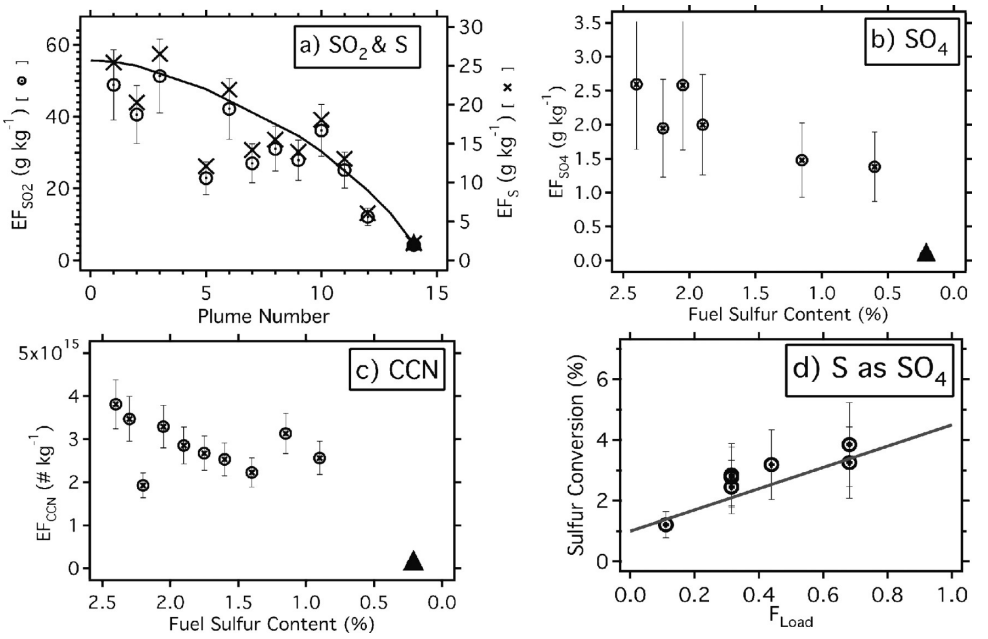

Figure 2. (a) EF_{SO_2} and EF_S, (b) EF_{SO_4}, (c) EF_{CCN} @ 0.3% SS during fuel switching operation, and (d) fraction of fuel sulfur converted to SO_4 versus engine load. Gray line is the trend of previous data from Petzold et al.[28] Note: Figure 2a uses a 3rd order polynomial fit $EF_S = -0.1 + -0.16x + 25.6x^2$.

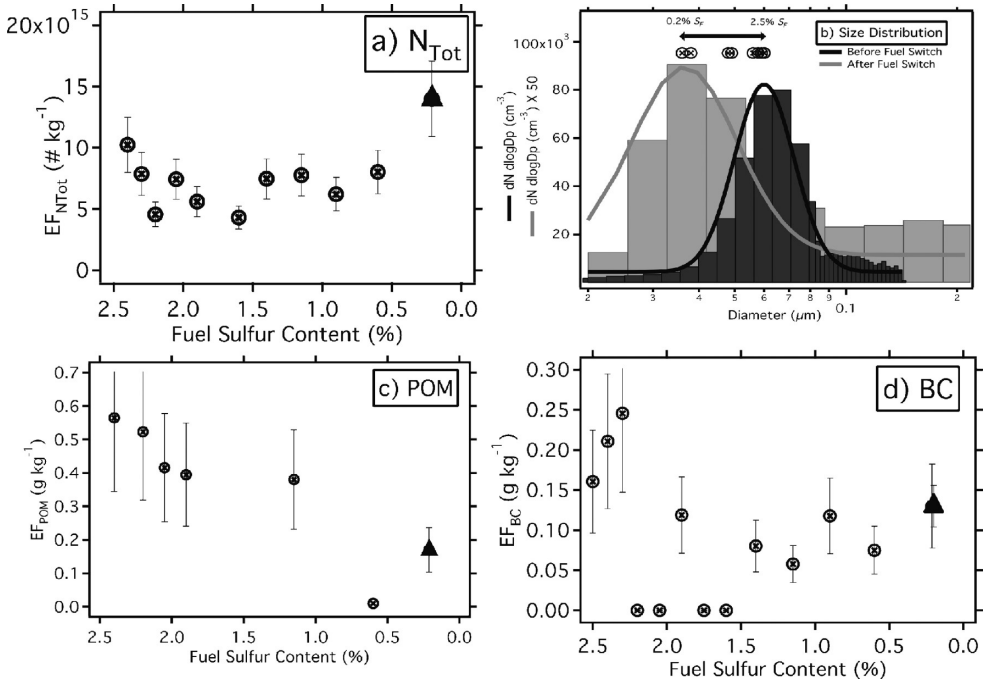

Figure 3. (a) $EF_{N_{Tot}}$ during experiment, (b) average size distributions (and log-normal fits) before and after the experiment, and median diameter (⊗) evolution (c) EF_{POM}, and (d) EF_{BC} during the experiment. For the lowest S_F EF_{BC} (R/V *Atlantis* intercept), three data points of almost identical magnitude are plotted (SP2 and two PAS instruments).

clear EF_{SO_2} is strongly correlated to S_F and we anticipate an equivalent reduction in secondary SO_4 produced from downwind oxidation of SO_2. We fit the general trend in EF_S vs plume encounter (black line, Figure 2a) and estimate an S_F for each plume encounter from this fit, which is used as the *x*-axes for Figures 2b,c and 3a,c,d.

Particulate Sulfate Emissions. EFs of directly emitted SO_4 decreased by 97% during the experiment (Figure 2b). The fraction of total sulfur emitted as SO_4[31] is 3.5% at high S_F ($f_{Load} = 0.7$) and 1.2% at low S_F ($f_{Load} = 0.1$) (Figure 2d). The observed variation in the SO_4 fraction with f_{Load} is in excellent agreement with the results of Petzold et al.[28] (gray line Figure 2d), although the f_{Load} effect does not account for the entire change observed. Therefore both S_F and f_{Load} contribute to the 97% reduction in EF_{SO_4}.

Cloud Condensation Nuclei, Particle Number Emissions and Particle Size. EF_{CCN} are strongly correlated with EF_{SO_4} and

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were reduced by almost 98% across the experiment (Figure 2c). The ratio between EF_{CCN} and $EF_{N_{Tot}}$ (f_{CCN}) gives an indicator of the efficacy of an emitted particle toward CCN formation and decreases from f_{CCN} = 0.4 to 0.007 (98% reduction). The ability of a given particle to act as a CCN (at a given %SS) depends on both the particle composition and size. Additionally, the ability of particles within a size distribution to act as CCN depends on the extent of internal vs external mixing. The composition effect on hygroscopicity can be approximately characterized assuming complete internal mixing, through calculation of the effective "Kappa" parameter (κ_{eff}) from the observations as follows:

$$\kappa_{eff} = \sum_i \left(\frac{V_i}{V_{tot}}\right)\kappa_i = \sum_i \left(\frac{m_i}{m_{tot}}\frac{\rho_{tot}}{\rho_i}\right)\kappa_i$$

$$= \sum_i \left(\frac{EF_i}{EF_{tot}}\frac{\rho_{tot}}{\rho_i}\right)\kappa_i \quad (1)$$

where V_x is volume, m_x is mass, ρ_x is density, and κ_i is the species-specific hygroscopicity of species i (or of the total).[32] We use ρ_i = 1.7, 1.3, and 1.8 g/cm^3 and κ_i = 0.9, 0.1, and 0.0 for SO_4 (from H_2SO_4), POM and BC, respectively.[33] Because the EFs for SO_4, POM, and BC all decrease with decreasing fuel sulfur, the calculated κ_{eff} does not change nearly as dramatically as either the observed EF_{CCN} or the f_{CCN}. In fact, κ_{eff} is stable around 0.68−0.73 for all encounters, with the exception of the R/V *Atlantis* encounter, when S_F was minimum, where κ_{eff} drops to 0.2. Thus it appears that the consistent decrease in EF_{CCN} and f_{CCN} with S_F is, in general, not being driven by changes to the particle composition despite the fact that the absolute EF_{SO_4} decreases continuously. Measured size distributions (Figure 3b) show that the median particle size decreased concurrent with the decrease in EF_{SO_4} (number-weighted particle diameter decreased from 60 to 36 nm). The calculated critical dry diameter for CCN activation of particles with the observed κ_{eff} at 0.3% SS is 60 nm,[32] which is consistent with the observation of f_{CCN} = 40% for the high S_F emissions. For a change in κ_{eff} to 0.2, the critical dry diameter at 0.3% SS would increase to about 90 nm. The combination of the decrease in particle size and the sudden drop in κ_{eff} leads to the very low f_{CCN} for the lowest S_F intercept. The measured reduction in EF_{CCN} during the experiment therefore results primarily from changes to the particle size distribution (which most likely result from changes in f_{Load}), but for the lowest S_F (and f_{Load}) both composition and size changes play a role. Similar to our results, for a test engine operating on HFO, Petzold et al.[28] observed a slight shift toward smaller particle sizes as f_{Load} was decreased (most notable at lower f_{Load}).

The $EF_{N_{Tot}}$ do not show a strong dependence on S_F (Figure 3a). Lack et al.[5] showed reductions in $EF_{N_{Tot}}$ between vessels burning high and low sulfur fuel, whereas Winnes and Fridell[18] report that the number of smaller particles may increase as S_F decreases. As shown in Lack et al.[5] these small particles quickly condense onto the larger particles, therefore although initial emissions of N_{Tot} may increase, the atmospheric lifetime is shorter than the larger particles. Petzold et al.[28] found that $EF_{N_{Tot}}$ increased by a factor of 1.65 as f_{Load} decreased from 85 to 50%. The variability across these studies suggest that N_{Tot} emissions are dependent on engine operating parameters including f_{Load} and S_F.

Particulate Organic Matter Emissions. Reductions in EF_{POM} (up to 71%) were observed across the experiment (Figure 3c). This reduction may be explained through two factors. First, the refining process for HFO concentrates aromatic and longer chain hydrocarbons, which have delayed burn times in some engines.[34] Thus, the higher POM emissions from high S_F likely result, in part, from the incomplete combustion of the aromatic and long chain hydrocarbons at high S_F. Second, there is larger consumption (and emission) of lubricating oils when HFO is used. However, short-term use of distillate fuels does not always require lubrication oil changes[35] and the *MM* did not alter the lube-oil regime for this fuel switch.[20] Petzold et al.[28] did not show any link between POM and f_{Load} for a single test-engine operating on HFO while Lack et al.[5] observed a clear correlation between POM and S_F. This suggests that the POM reductions observed in Figure 3c are likely due to organic composition changes within the fuel, which correlate to S_F.

Black Carbon Emissions. EFs of BC appeared to decline across the experiment, although measurement uncertainties indicate a range from 30 to 70% (average of 41%) (Figure 3d). Some measurements of BC were below instrument detection limits despite having measurable CO_2 enhancements (the reason for which is currently unknown). To our knowledge there are no published data that would suggest reductions in S_F should decrease EF_{BC}. However it has been observed that reductions in slow burning aromatic hydrocarbons within jet turbine fuels reduces BC emissions from these engines.[36] Ash, aromatic and long chain hydrocarbon compounds, which are concentrated in HFO, are decreased in refined MGO. We suggest that reduction in these components decreases the concentration of flame quenching nuclei, which decreases BC formation.

The results of Righi et al.[2] suggest that BC emissions are reduced for cleaner fuels (MGO, biodiesel) relative to HFO. However, recent studies by Agrawal et al.[37] (in-use vessel running HFO) and Petzold et al.[28] (medium speed diesel (MSD) engine running HFO) showed EF_{BC} increased 1.5−3 times respectively when f_{Load} changed from 0.7 to 0.1. While there is a net gain to vessel speed reduction (VSR) in terms of increased fuel efficiency (which acts to reduce *absolute* emissions of CO_2, SO_2, and PM, given a constant EF), an increase in the emission *factors* of BC may actually offset some of the fuel efficiency gains. If the results of Petzold et al.[28] and Agrawal et al.[37] are applicable to this experiment, the observed decrease in EF_{BC} (Figure 3d) is a lower limit in overall BC reductions due to the change in fuel quality. Alternatively, other results for show MSD engines burning low sulfur MGO suggest that EF_{BC} may increase.[38,39] Fuel efficiency gains to absolute BC emissions would then be enhanced by concurrent reductions in the EF_{BC}, and thus the influence of the fuel quality regulations alone on EF_{BC} would be smaller than shown in Figure 2d. Given that the observations in this study and those of Petzold et al.[28] and Agrawal et al.[37] were for engines or vessels burning HFO, it seems reasonable that the BC reductions observed here are linked to S_F rather than f_{Load}. Certainly more detailed investigation is necessary. Nonetheless, the overall effect of the fuel quality regulation and the VSR program appears to be a decrease in both EF_{BC} and absolute BC emissions. Any BC reduction due to improved fuel quality in ships will provide additional benefits for air quality although may have an uncertain impact of climate (see climate discussion below). Use of higher quality fuels by ships in the Arctic may result in less BC deposition to snow and ice (compared to the use of low quality fuels) resulting in positive climate benefits in that region.[40]

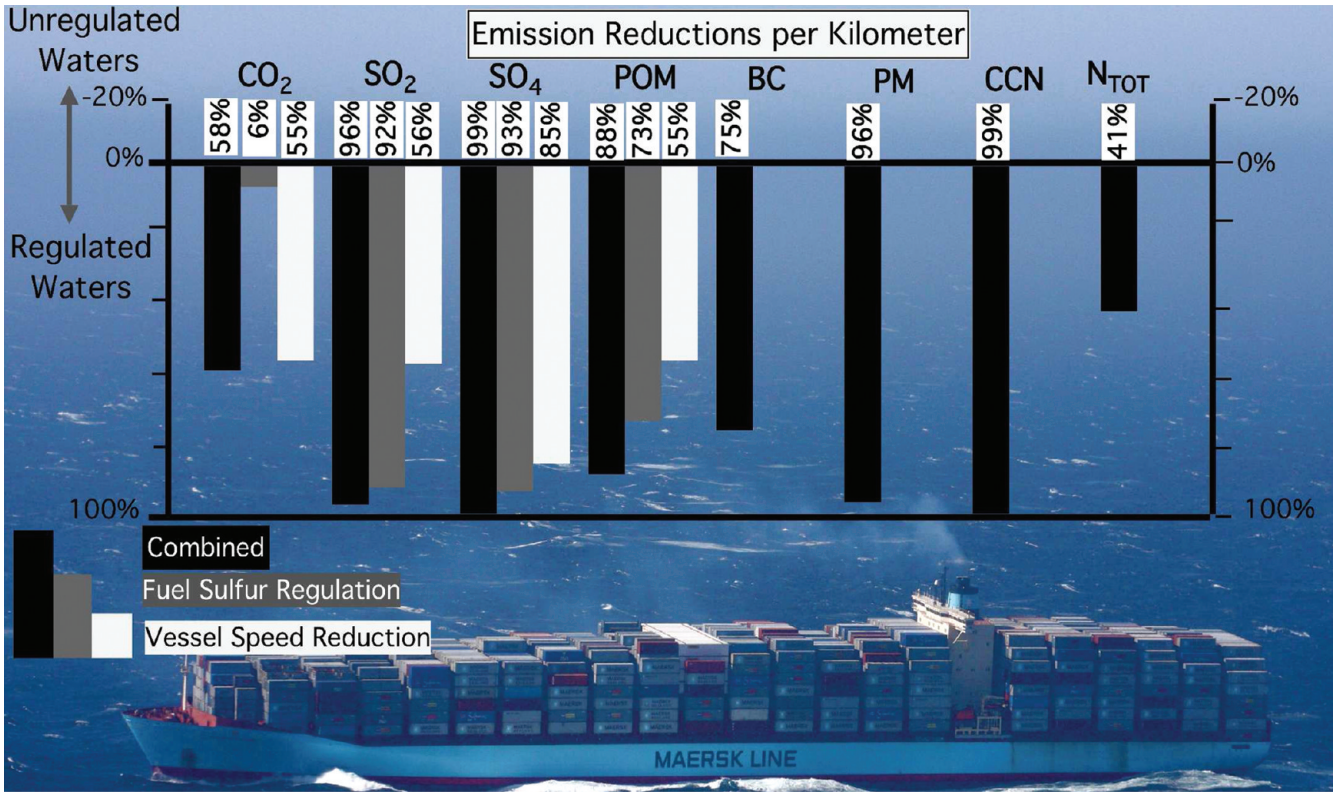

Figure 4. Emissions reductions (per km of travel) from the *MM* as a result of the State of California fuel sulfur regulation (gray), vessel speed reduction program (white) and combined (black).

4. DISCUSSION

Information Relevant to Impacts of Regional Regulation. On a per-kilometer (km) basis, emissions of most gas and particle pollutants from the *MM* dropped significantly once the *MM* entered the region where it is required to be in compliance with the California regulations. Figure 4 (and Supporting Information Table S2) summarizes the emissions for a km of travel outside and inside the regulated waters, calculated from the emission factors presented in Table 1. Estimates of fuel consumption by the *MM* at the speeds traveled inside and outside of the regulated waters were calculated using eq 2 and data obtained from Maersk:[20]

$$C_{\mathrm{Fuel}}(\mathrm{kghr}^{-1}) = F_{\mathrm{cons}} \times 1000 P_{\mathrm{MW}} \times f_{\mathrm{Load}} \quad (2)$$

where

$$F_{\mathrm{cons}}(\mathrm{kgkw}.hr^{-1}) = 0.0142 \times \left(\frac{1}{f_{\mathrm{Load}}}\right) + 0.195 \quad (3)$$

The engine manufacturer literature suggests that a new engine of the type installed on the *MM* has a fuel consumption rate (F_{Cons}) at maximum load of 0.17 kg $(\mathrm{kw.hr})^{-1}$ although 0.195 kg $(\mathrm{kw.hr})^{-1}$ is estimated to be an appropriate average value for in-use slow speed diesel engines.[41] F_{Cons} varies with engine load according to eq 3.[42] F_{Cons} for MGO is reduced by 6% due to the specific heat of MGO being 6% higher than HFO on this vessel.[20] P_{MW} is the maximum engine power in megawatts (68.7 MW). These data were converted to kilograms of fuel consumed per-kilometer (km) of travel, which were then converted to per-km emissions by multiplying C_{Fuel} with the measured EFs.

For all but CO_2, BC, and N_{Tot}, pollutant levels drop by 88% or more (58% for CO_2, 75% for BC and 41% for N_{Tot}) as a result of the vessel observing both the fuel quality regulation and VSR program (Figure 4). Note that most CO_2 reductions arise from the change in f_{Load}. Importantly, we can differentiate some of the emissions reductions by the effects of the fuel quality regulation or VSR program. To make this assessment, we have assumed that the observed EF reductions for SO_2 and POM are due entirely to the S_F change. At high f_{Load} SO_4 formation is 2.9 times higher than at low f_{Load} (Figure 2d and Petzold et al.[28]) and this load factor is removed from SO_4 emissions by multiplying the low-S_F, low-load EF_{SO_4} by 2.9. It is apparent that the emissions of BC, N_{Tot}, and CCN are complicated by S_F and f_{Load} and we do not separate by regulation for these species. Note that this analysis is specific to the *MM*, which was in compliance with the fuel quality regulation and was participating in the VSR program. We reiterate that these results are a snapshot for a single vessel with changing fuel type, fuel consumption distributions across main, auxiliary and boiler engines, and changing speed. Although these factors introduce uncertainly for detailed emissions analysis, the trends for the averaged vessel emissions are evident.

Information Relevant to Health Impacts. Reductions in the direct emissions of SO_4, BC, and POM per-km of travel of 99%, 75%, and 88%, respectively, will likely have influence on the ambient PM levels near the Californian coast where vessel traffic is significant, especially in the port regions. The reductions in EF_{BC} and EF_{POM} with improved fuel quality are significant variables that have not been considered in most assessments of the impact of shipping emissions on health. Assuming that reductions in PM emissions leads to reduced mortality, this new information would suggest that greater reductions in mortality

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would be found than reported in the North American ECA or global IMO regulation mortality assessments [11,12] (that do not include the BC and POM reductions). In addition, the finding that SO_4 emissions decrease with both S_F *and* engine load[28] shows that primary SO_4 emissions will be further decreased if VSR regulation is introduced. Reductions in SO_2 will also significantly reduce secondary SO_4 formation. Of further interest is the uncertainty surrounding $EF_{N_{Tot}}$ associated with reductions in S_F and speed changes. Multiple studies (including the current data) show opposing trends in $EF_{N_{Tot}}$ as vessel speed and S_F change, and should be investigated further.

Information Relevant to Climate Impacts. The indirect RF impacts of PM are difficult to assess and remain the least certain RF agent in global models. For shipping, it is estimated that emitted PM leads to a significant negative RF (i.e., cooling) that substantially exceeds the warming from the emitted CO_2.[2,14,16] The impact of fuel quality (predominantly reducing the S_F) would lead to a reduction in this cooling.[2,16] Eyring et al.[14] estimate (for 2005) that the globally averaged direct and indirect RF by shipping emissions of SO_4 and POM is -0.44 Wm^{2-} (net cooling), which is dominated by the indirect RF (-0.41 W m^{-2}). CO_2, O_3 (from NO_X emissions), decreased CH_4 (from NO_X) and BC from shipping together have a globally averaged positive RF of +0.03 Wm^{2-} (net warming). Righi et al.[2] estimate this indirect RF would decrease from -0.28 to -0.10 Wm^{2-} if low S_F fuels are introduced globally. For the data presented here, although absolute BC emissions decrease, the strong concurrent decrease in CCN emission (from both composition and size changes) could completely offset the cooling gained.[43] Given the observed, concurrent reductions in emissions of BC, POM, and CCN (75%, 88%, and 99%, respectively), we conclude that uncertainties in the magnitude of the RF balance from shipping are critically dependent on the composition of emitted PM, size distributions, and the ultimate fate of emitted non-CCN active particles in the atmosphere.

The direct RF impact of shipping emissions of PM, although small relative to the indirect effect, will also change due to fuel regulation. Over the past 15−20 years, fuel regulation in California for on-road vehicles and nonroad machines has focused on a variety of technological approaches, such as engine rebuilding or addition of emissions control systems.[44] The goal (and likely net result) of this regulation was (has been) to reduce primary emissions of BC[45] which, if it occurs in isolation, will lead to less warming. However, absorbing BC is usually coemitted with scattering (cooling) SO_4 and POM, which may also change upon implementation of a control measure.[46] The single scattering albedo (SSA) represents the balance between light scattered and absorbed by a particle and is one of the primary influences on whether a particle warms or cools the atmosphere. The SSA for the *MM* encounter (for high and low S_F) was estimated from the measured EF_{SO_4}, EF_{POM}, and EF_{BC} values using 532 nm mass extinction and mass absorption efficiencies (MEE and MAE) for the different species;

$$SSA_{532} \sim 1 - \left[\frac{MAE_{BC}EF_{BC}}{MEE_{SO4}EF_{SO4} + MEE_{POM}EF_{POM} + MEE_{BC}EF_{BC}}\right] \quad (4)$$

We use values for the MEE for SO_4 and POM from Malm et al.[47] (3 m^2/g and 4 m^2/g) and MEE/MAE values for BC from Bond and Bergstrom[48] (9 m^2/g and 7.5 m^2/g). The SSA for directly emitted PM from the *MM* decreased from 0.86 to 0.57 across the experiment. The estimated low-S_F SSA value compares favorably with the directly measured dry value of 0.64 (0.2% S_F, 532 nm). This is generally consistent with the observations of Lack et al.,[5] who found that the SSA decreased from 0.6 to 0.3, on average, as the S_F changed from 2.5 to 0.2%. Thus, not only will the absolute PM emissions from ships operating on low sulfur (instead of high sulfur) fuel be decreased, the particles that are emitted will be overall "darker" and can then have a stronger relative warming influence. It seems clear that the implementation of global fuel sulfur regulations will lead to a decrease in the cooling by ship PM emissions, both from changes in indirect and direct RF. We emphasize that the emission reductions observed with the *MM* introduce previously unaccounted emissions phenomena which may alter the specific RF balance from shipping described by recent model studies.[2,16]

Local, Regional And Global Policy Connections. The efficacy of Californian shipping fuel quality regulation and vessel speed reduction (VSR) program in reducing emission factors and absolute emissions (emissions per-km of travel with and without the regulation) of SO_2, SO_4, and (somewhat unexpectedly) POM and BC is evident from the results presented here. EFs of N_{Tot} (particle number) appear to increase due to the regulations, although it is likely that these are small particles that will quickly condense or coagulate with existing particles. On an absolute scale (per kilometer of travel), mass reductions of SO_2, SO_4, and PM are in excess of 96%; BC and POM reductions are 75% and 88% respectively. The regulations will significantly alter the direct climate cooling impacts of the emitted PM by reduction of the SO_4 formed just after emission and through secondary formation from SO_2 oxidation. In areas where low sulfur fuel is used, significant CCN reductions and particle size reductions will reduce the indirect cooling impacts from enhanced cloud formation, particularly in regions sensitive to inputs of CCN from shipping, such as at ∼30° N. This reduced cooling may be partially offset by a concurrent decrease in the climate warming impact of BC. Our observations suggest that air quality benefits from the fuel quality regulation and the VSR program are likely to be substantial, although these air-quality benefits are likely to occur concurrent with a reduction in anthropogenic cooling that results from shipping PM. If it is determined that air pollution (i.e., human health and welfare) goals can be met through near-coast regulation (i.e., ECAs), then the implementation of a more nuanced location-dependent global fuel quality regulation may be worthy of consideration. Lastly, possible reductions in BC emissions due to fuel quality changes might suggest a consideration of more refined fuels for future Arctic shipping.[40]

■ ASSOCIATED CONTENT

Supporting Information. Details on instruments uncertainty, literature and calibrations. This material is available free of charge via the Internet at http://pubs.acs.org.

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NOTE ADDED AFTER ASAP PUBLICATION

This paper published September 12, 2011 with an author name spelled incorrectly. Ibraheem Nuaaman's name appeared correct in the version of this paper published September 21, 2011.