

# Impact of Shipping Emission Regulations on Atmospheric Vanadium Along U.S. North Atlantic Coast and Over the Western North Atlantic Ocean

Francesca Gallo<sup>1,2</sup>, Armin Sorooshian<sup>3,4</sup>, Luke Ziemba<sup>1</sup>, Grace Betito<sup>3</sup>, Andrea F. Corral<sup>4</sup>, Ewan Crosbie<sup>1,2</sup>, Eva-Lou Edwards<sup>1,5</sup>, Miguel R. A. Hilario<sup>3\*</sup>, Simon Kirschler<sup>6,7</sup>, Claire Robinson<sup>1,2</sup>, Michael A. Shook<sup>1</sup>, Lee Thornhill<sup>1,2</sup>, Christiane Voigt<sup>6,7</sup>, Edward Winstead<sup>1,2</sup>, Kira Zeider<sup>4†</sup>, Richard Moore<sup>1</sup>

<sup>1</sup>NASA Langley Research Center, Hampton, VA, 23681, USA.

<sup>2</sup>Analytical Mechanics Associates, Inc., Hampton, VA, 23666, USA.

<sup>3</sup>Department of Hydrology and Atmospheric Sciences, University of Arizona, Tucson, AZ, 85721, USA.

<sup>4</sup>Department of Chemical and Environmental Engineering, University of Arizona, Tucson, AZ, 85721, USA.

<sup>5</sup>Oak Ridge Associated Universities, Oak Ridge, TN, 37831-0117, USA.

<sup>6</sup>Institute of Atmospheric Physics, German Aerospace Center, Oberpfaffenhofen, Germany.

<sup>7</sup>Institute of Atmospheric Physics, University of Mainz, Mainz, Germany.

\*Now at Space Science and Engineering Center, University of Wisconsin, Madison, WI, 53706, USA.

†Now at Office of Land & Emergency Management, EPA (through Oak Ridge Institute of Science and Education), Washington, D.C., 20004, USA.

Corresponding author: Francesca Gallo (francesca.gallo@nasa.gov), Richard Moore (richard.h.moore@nasa.gov)

## Key Points: 140 characters or less with no special characters or acronyms

- Shipping fuel regulations effectively reduced atmospheric vanadium concentrations along US eastern coast over 15 years of measurements
- Vanadium measurements alone outperform vanadium/nickel ratios for detecting ship emissions under low-sulfur fuel
- Vanadium from ship emissions over the western North Atlantic potentially catalyzes in-cloud and out-of-cloud oxidation reactions

**Abstract 250 words**

Ship emissions from high sulfur residual fuel oil (RFO) are a major source of air pollution in coastal and marine environments. Emissions include sulfur oxides as well as vanadium (V) and nickel (Ni) enriched fine particulate matter (PM<sub>2.5</sub>). Near coasts, the International Maritime Organization (IMO) has implemented Sulfur Emission Control Areas where ships have to operate on low sulfur marine fuel. In this study, we integrate 15 years of chemically speciated PM<sub>2.5</sub> data collected at IMPROVE sites along the U.S. east coast with in-cloud observations from the 2020-2022 NASA ACTIVATE flight campaign over the northwest Atlantic to assess the impact of maritime regulations on ambient vanadium concentrations. We find statistically significant reductions in coastal atmospheric vanadium (~ 80% - 89%) after IMO regulations implementation. Reductions in particulate nickel (67% - 79%) and sulfate (53% - 59%) levels are also observed. While the V/Ni ratio is traditionally used as tracer for RFO-operated marine engines, we show measurements in shipping lanes comparable to those in areas not affected by shipping emissions. This means that V/Ni is no longer a reliable marker for detecting plume exhaust from ships running on low-sulfur fuel, while vanadium alone represents a stronger tracer. Under a low-sulfur fuel regime, cloud water vanadium concentrations over the northwest Atlantic are an order of magnitude lower than in PM<sub>2.5</sub> at coastal sites. Vanadium concentrations above 75<sup>th</sup> percentile were observed in cloud droplets enriched in nss-sulfate and nitrate suggesting a potential role of ship-emitted vanadium in catalyzing in-cloud oxidation reactions.

**Plain Language Summary**

Maritime vessels operating on high-sulfur residual fuel oil have long been recognized as a significant source of atmospheric pollution in coastal regions. These emissions contain substantial quantities of sulfur oxides and fine particulate matter enriched with metallic elements, particularly vanadium and nickel, which pose environmental and public health concerns. To mitigate these impacts, the International Maritime Organization established Sulfur Emission Control Areas requiring vessels to transition to low-sulfur marine fuels in coastal waters. Our research examined the effectiveness of these regulatory measures by analyzing 1) a

comprehensive 15-year dataset of chemically speciated particulate matter collected at IMPROVE monitoring sites along the U.S. east coast, 2) in-cloud measurements obtained during NASA's ACTIVATE flight campaign conducted over the northwest Atlantic between 2020 and 2022. Statistical analysis demonstrates significant reductions in atmospheric pollutant concentrations following regulation implementation. Specifically, we observed decreases of approximately 80-89% in vanadium concentrations, 67-79% in nickel levels, and 53-59% in sulfate content. An important methodological finding emerged regarding ship plumes identification techniques. The traditional vanadium-to-nickel ratio, previously relied upon as an indicator of residual fuel oil combustion, is no longer a reliable marker in the current regulatory environment suggesting that vanadium concentration alone now serves as a more reliable tracer for detecting emissions from vessels operating on low-sulfur fuel. Additionally, our analysis indicates that cloud water vanadium concentrations over the northwest Atlantic are approximately an order of magnitude lower than particulate matter concentrations at coastal sites. These findings provide compelling evidence of the effectiveness of international maritime regulations in reducing atmospheric pollutant concentrations and provide valuable insights for future air quality monitoring methodologies in coastal environments.

## 1 Introduction

Ship emissions have long been recognized as a major source of particle and trace gas pollution in coastal areas and along shipping routes (Eyring et al., 2010). Marine vessel engines typically operate on high-sulfur residual fuel oil (RFO), a low-grade diesel fuel obtained from petroleum distillation, which has high sulfur content and is rich in heavy metals. As a consequence, RFO combustion contributes to increases in fine particulate matter ( $PM_{2.5}$ ) and other combustion related pollutants including sulfur oxides ( $SO_x$ ), nitrogen oxides ( $NO_x$ ), carbon monoxide (CO), carbon dioxide ( $CO_2$ ), and volatile organic compounds (VOC) (Anastasopoulos et al., 2021; Corbin et al., 2018; Golbazi & Archer, 2023). While the dominant aerosol component from shipping is sulfate ( $SO_4^{2-}$ ) from  $SO_2$  oxidation (Moldanová et al., 2009), trace metals have also been observed in ship-emitted  $PM_{2.5}$  after RFO combustion; vanadium (V) and nickel (Ni) are the most abundant metal components (Abou-Ghanem et al., 2023; Moldanová et al., 2009).

Consequently, the ratio between these two metals has been widely used as a tracer for PM emitted from RFO combustion (Agrawal et al., 2009; Cheng et al., 2022; Kotchenruther, 2015; Viana et al., 2009).

Approximately 70% of seagoing ship emissions occur within 400 km of coastal regions (Corbett et al., 2007; Eyring et al., 2010), where persistent marine low-lying clouds are thought to be highly sensitive to changes in aerosol properties. In recent years, an increased number of studies have assessed the perturbations caused by shipping activities on atmospheric aerosol and cloud properties. It is known that aerosol particles from burning RFO present as a typical bimodal distribution consisting of a sulfuric acid-dominated nucleation mode ( $D_p \sim 20$  nm), and a larger Aiken mode ( $D_p \sim 50$  nm) consisting of mostly solid, fractal soot (Agrawal et al., 2008; Petzold et al., 2008; Corbin et al., 2018). However, it has been observed that ship engine load conditions play a role in shaping the distribution of particles in the nucleation mode. Namely, Petzold et al. (2008) found that enhanced sulfuric acid concentrations linked to high engine loads promote particle coagulation and gas phase deposition on pre-existing nucleation mode particles, therefore growing nucleation mode particles towards larger sizes. Further studies have reported on the influence of ship exhaust on cloud condensation nuclei (CCN), underscoring a correlation between elevated concentration of sulfates, relatively high particle hygroscopicities, and a significant increase in the fraction of particles activated to CCN (Coggon et al., 2012; Hobbs et al., 2000; Manshausen et al., 2022; Noone et al., 2000; L. F. E. D. Santos et al., 2024). Langley et al. (2010) found that organic particles in ship plumes can act as condensation sites for sulfur species leading to an increase in CCN activity at low supersaturations typical of marine stratocumulus. Perturbations in cloud microphysics including enhanced cloud droplet number concentrations, reduced cloud drop effective radius, and increased liquid water content (LWC) by suppressing drizzle formation, have been observed concurrently with elevated below-cloud sulfate levels from ship exhaust (Diamond, 2023; Ferek et al., 2000; Hudson et al., 2000; Noone et al., 2000; Radke et al., 1989). As a consequence, sulfate has been recognized as the key component of ship track formation, which can affect cloud brightness and radiative forcing (Coakley et al., 1987; Manshausen et al., 2022; Yuan et al., 2022).

Equally important are the chemical changes occurring inside the cloud droplets. Gas phase  $\text{SO}_2$  can be taken up by cloud droplets and undergo aqueous phase oxidation, resulting in cloud water acidification and production of more oxygenated species that remain in the aerosol phase upon drop evaporation (Benedict et al., 2012; Coggon et al., 2012; Wang et al., 2014). It is thought that vanadium might play an important role in the uptake of sulfate in cloud droplets by acting as catalyst in the aqueous phase oxidation of  $\text{SO}_2$ . The catalytic role of vanadium in the oxidation of DMS and sulfur(IV) oxides in organosulfur has been previously reported in laboratory experiments (Brandt & van Eldik, 1995; Sahle-Demessie & Devulapelli, 2008). Subsequent field studies conducted along the California coast (Gaston et al., 2010) and over coastal areas of the western U.S. have highlighted the potential of vanadium in catalyzing methanesulfonate formation (Sorooshian et al., 2015). However, the extent to which vanadium from ship emissions influences cloud properties is still uncertain and difficult to quantify, in part due to limited direct measurements of in-cloud vanadium concentrations.

Over the past decades, the International Maritime Organization (IMO) has implemented regulations that mandate the utilization of low sulfur fuels. In 2005, IMO established Sulphur Emission Control Areas (SECAs) including the Baltic Sea, the North Sea, the English Channel and coastal waters of the US, Canada, and U.S. Caribbean Sea to reduce  $\text{SO}_x$  emissions by imposing fuel sulfur content (FSC) limits. The implementation of SECAs in the North American Emission Control Area occurred in two phases: 1) August 2012 (heretofore referred to as IMO 2012) requiring ocean-going vessels within the control areas to operate on fuel with sulfur content no higher than 1.0%; 2) January 2015 (heretofore referred as IMO 2015), further reducing the fuel sulfur content for vessels in the control areas to at or below 0.1%. The sulfur reduction can be achieved by using low sulfur distillate fuel, which contains negligible amounts of metal or ash. Alternatively, marine vessels can still operate on RFO using exhaust-cleaning devices (i.e. scrubbers) designed for sequestering  $\text{SO}_2$  (Lehtoranta et al., 2019). Large reductions in  $\text{SO}_2$  emissions have been observed in port and coastal cities following the implementations of the above-discussed regulations (Anastasopoulos et al., 2021; Zetterdahl et al., 2016). Furthermore, although none of these regulations explicitly address the reduction of PM and metal emissions, decreases in  $\text{PM}_{2.5}$  and vanadium along the coasts of the US, Canada, and Europe have also

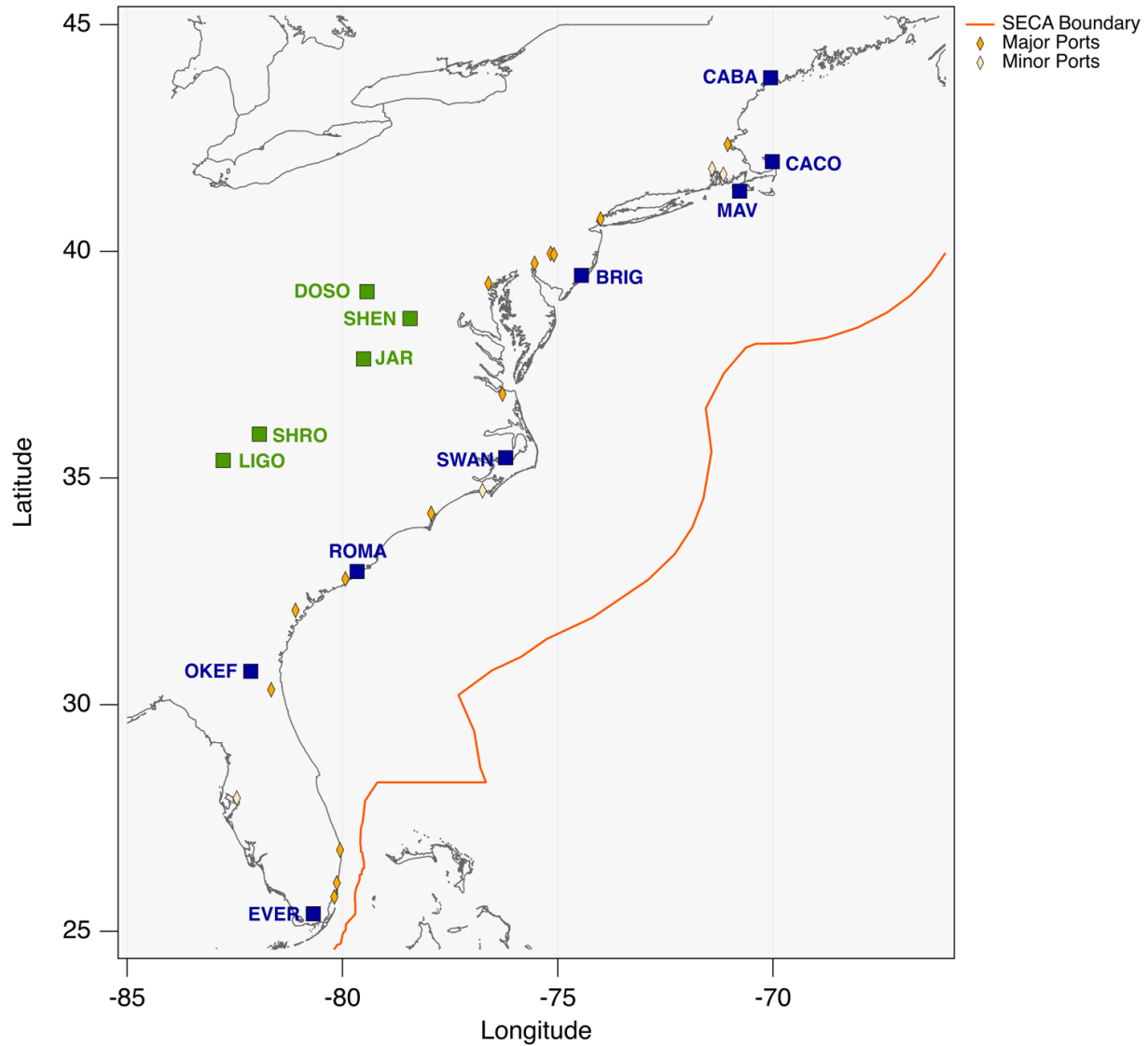
146 been reported after the implementation of SECAs (Cheng et al., 2022; Kotchenruther, 2015;  
147 Spada et al., 2018). Simultaneously, tests conducted on marine engines showed that the  
148 utilization of low-sulfur fuels resulted in the emission of smaller, hydrophobic particles that  
149 have a larger critical activation diameter (Santos et al., 2023). It is important to note that while  
150 the utilization of exhaust scrubbers with RFO combustion is reliable in decreasing ship exhaust  
151 SO<sub>2</sub>, particulate matter and metal emissions are only partially reduced (Lehtoranta et al., 2019;  
152 Passig et al., 2021). These works have provided invaluable insights into the impact of shipping  
153 emission regulations on atmospheric perturbations. However, most of them only show data  
154 collected up to 3 years after the implementation of IMO 2015, and thus are not representative  
155 of the longer-term effect of FSC limit regulations. Nevertheless, direct measurements of cloud  
156 water sulfate and vanadium away from land remain scarce, limiting our understanding of the  
157 current influence of ship emissions on cloud droplet composition and their impacts on climate-  
158 relevant processes.

159 In this study, we leverage 15 years of chemically speciated PM<sub>2.5</sub> data (including SO<sub>4</sub>,  
160 PM<sub>2.5</sub>, vanadium, and nickel) collected at Interagency Monitoring of Protected Visual  
161 Environments (IMPROVE) sites on the U.S. east coast, and we integrate them with in-cloud  
162 observations from the airborne NASA Aerosol Cloud meteorology Interactions oVer the western  
163 ATlantic Experiment (ACTIVATE) field campaign conducted over the northwest Atlantic ocean  
164 between 2020 and 2022, to: 1) examine the impact of marine vessel emissions along the U.S.  
165 North Atlantic coast and evaluate the potential effect of FSC limits on vanadium concentrations  
166 (Sect. 3.1), and 2) assess spatial distribution and seasonal variations of both airborne and cloud  
167 water vanadium within SECA after the implementation of the IMO 2015 (Sect. 3.2 and 3.3).  
168 With this work we aim to achieve a quantitative understanding of the influence of ship  
169 emissions on atmospheric vanadium concentrations and to provide a starting point for more  
170 studies to examine vanadium's process-level activity in the study region such as in catalyzing  
171 aqueous phase oxidation reactions.

## 2 Materials and Methods

### 2.1 IMPROVE stations

Chemically speciated measurements of  $\text{PM}_{2.5}$  are conducted routinely every third day at stations associated with the Interagency Monitoring of Protected Visual Environments (IMPROVE). Information about the IMPROVE network can be found at <http://vista.cira.colostate.edu/improve/>. In this study we analyze fine particulate concentrations of vanadium (V), sulfate ( $\text{SO}_4$ ), and nickel (Ni), and  $\text{PM}_{2.5}$  data collected at 8 IMPROVE sites located along the U.S. North Atlantic coast between 1 January 2008 and 31 December 2022. The sites selected are located in the vicinity of commercial ports and at elevation  $< \sim 50$  meters above sea level and are therefore expected to be potentially impacted by marine vessel emissions. Furthermore, we used V and Ni mass concentration data from five inland sites, which are likely to be unaffected by ship emissions (located at a distance  $> \sim 250$  km from commercial ports and at elevations  $> \sim 300$  meters) to assess the impact of low-sulfur fuel emissions regulations. A list of the IMPROVE sites selected for this study, including their geographic coordinates, elevation, and approximate distance from U.S. commercial ports is shown in Table 1 and represented in Figure 1. The data were divided in three distinct periods to target the effect of the implementation of FSC limits: 1) pre-regulations – data collected over a 4.5-years period between 1 January 2008 and 31 July 2012 prior to implementation of FSC, 2) IMO 2012 – data collected in the 2.5-years period between 1 August 2012 and 31 December 2014 to assess the effect of the initial phase of SECAs ( $\text{FSC} < 1.0\%$ ), 3) IMO 2015 - data collected in the 8-years period between 1 January 2015 and 31 December 2022 after the implementation of the second FSC limit ( $\text{FSC} < 0.1\%$ ). A non-parametric Wilcoxon-Mann-Whitney test (Kotchenruther, 2015) at the 99% confidence interval ( $p < 0.01$ ) was performed to determine whether the implementation of the low-sulfur regulations generated statistically significant reductions in the levels of fine particulate vanadium, nickel, and sulfate, and  $\text{PM}_{2.5}$  over the three periods of time analyzed.



**Figure 1.** Map of coastal and inland IMPROVE sites (blue and green squares, respectively), major and minor U.S. commercial ports, and the Sulfur Emission Control Area (SECA) boundary.



**Table 1.** Location of the IMPROVE sites used in this study, including site abbreviations, geographic coordinates, elevation, and distance from eastern U.S. commercial ports. Distances are calculated as straight-line-distance.

	Site name	Abbreviation	Coordinates	Elevation	Approximate distance from major (and minor) U.S. commercial ports
Coastal Sites	Casco Bay (ME)	CABA	43.83 N, 70.06 W	27 m	180 km from Port of Boston
	Cape Cod (MA)	CACO	41.97 N, 70.02 W	49 m	95 km from Port of Boston (115 km from Ports of Providence and Fall River)
	Martha's Vineyard (MA)	MAV	41.33 N, 70.78 W	3 m	115 km from Port of Boston (50 km from Ports of Fall River, and 75 km from Port of Providence)
	Brigantine NWR (NJ)	BRIG	39.47 N, 74.45 W	5 m	70 km from Ports of South Jersey, 80 km from Port of Philadelphia, 140 km from Port of New York and New Jersey, and ~190 km from Port of Baltimore (100 km from Port of Wilmington (DE))
	Swanquarter (NC)	SWAN	35.45 N, 76.21 W	-4 m	150 km from Port of Norfolk, and 200 km from Port of Wilmington (NC) (100 km from Port of Morehead City)
	Cape Romain NWR (SC)	ROMA	32.94 N, 79.66 W	5 m	30 km from Port of Charleston, 170 km from Port of Savannah, and 200 km from Port of Wilmington (NC)
	Okefenokee NWR (GE)	OKEF	30.74 N, 82.13 W	48 m	(30 km from the coast), 60 km from Port of Jacksonville, and 180 km from Port of Savannah
	Everglades (FL)	EVER	25.39 N, 80.68 W	1 m	60 km from Port of Miami (50 km from Port of Everglades)
Inland Sites	Dolly Sods Wilderness (WV)	DOSO	39.11 N, -79.43 W	1182 m	250 km from Port of Baltimore
	Shenandoah (VA)	SHEN	38.52 N, 78.43 W	1079 m	200 km from Port of Baltimore, and 270 km from Port of Norfolk
	James River Face (VA)	JAR	37.62 N, 79.51 W	290 m	300 km from Ports of Baltimore, and Norfolk
	Linville Gorge (NC)	LIGO	35.97 N, 81.93 W	969 m	400 km from Port of Charleston and 500 km from Port of Norfolk
	Shining Rock (NC)	SHRO	35.39 N, 82.77 W	1617 m	400 km from Port of Charleston and Savannah

### 2.1.2 Supporting datasets form IMPROVE study

In order to identify any potential confounding effect of changes of shipping activities on the impact of the regulations, we evaluate annual trends in ship traffic by assessing Department of Transportation (DOT) data of waterborne container traffic from the principal ports located on the U.S. east and south/gulf coasts (United States. Army. Corps of Engineers & Institute for Water Resources (U.S.), 2018). For each port, we analyzed port throughput as TEU (twenty-foot equivalent unit) which is the standard measure for container movements and ships. For simplicity, we define as major ports those with mean annual total loaded TEU higher than 100,000 over the period between the years 2008 and 2022. Similarly, we used U.S. Environmental Protection Agency (EPA) sulfur dioxide 2023 emissions reductions data from the Clean Air Markets Program Data (CAMPD) to assess annual sulfur dioxide concentrations over the US.

## 2.2 NASA ACTIVATE field campaign

The NASA Aerosol Cloud meTeorology Interactions oVer the western ATlantic Experiment (ACTIVATE) airborne field campaign was designed to study interactions between aerosol, clouds, and meteorology over the western North Atlantic Ocean. Between 2020 and 2022, two NASA aircraft (HU-25 Falcon and King Air) conducted 162 joint flights over the western North Atlantic regions, providing unique in situ and remote sensing observations of aerosol and cloud properties under different meteorological and seasonal regimes. A detailed description of ACTIVATE is given by Sorooshian et al. (2023). This study focuses on cloud water samples collected by the HU-25 Falcon during the six deployments of ACTIVATE. In situ measurements of aerosol properties were also used in Sect. 3.4 to investigate below-cloud air masses.

### 2.2.1 Cloud water analysis

Cloud water samples were collected via an axial cyclone cloud water collector (AC3) (> 60% collection efficiency for cloud droplets with diameter > 20  $\mu\text{m}$ ) (Crosbie et al., 2018) on the HU-25 Falcon. The AC3 centrifugally extracted cloud water from the airstream and directed it into the aircraft through a Teflon sampling line where samples were stored in 15 mL high-

density polyethylene centrifuge tubes. A shutter was used to close the AC3 inlet to reduce contamination from aerosol impaction when the HU-25 Falcon was out of cloud. A total of 535 samples were collected and the following analyses were conducted after the flights:

- ion chromatography (IC) for speciation and quantification of aqueous mass concentrations of several organic and inorganic anions including methanesulfonate (MSA), nitrate ( $\text{NO}_3^-$ ), and sulfate ( $\text{SO}_4^{2-}$ ), as well as cations including sodium ( $\text{Na}^+$ ), and calcium ( $\text{Ca}^{2+}$ );
- inductively coupled plasma mass spectroscopy (ICP-MS), for detecting several aqueous mass concentrations of trace metals including vanadium;
- pH analysis.

Samples contained variable volumes of cloud water due to different in cloud transit times, cloud LWC, and other AC3 performance factors as discussed in Crosbie et al. (2018, 2022), which constrained the type of analysis conducted for each sample.

To account for differences in LWC among clouds and enable a comparison between ACTIVATE and IMPROVE observations, we converted cloud-water-derived aqueous mass concentrations to air equivalent units ( $\mu\text{g m}^{-3}$ ). Briefly, we multiplied aqueous concentrations from IC and ICP-MS by the mean cloud LWC during the period of sample collection when LWC was greater than a threshold of  $0.02 \text{ g m}^{-3}$  (i.e., in cloud conditions) and divided by the density of water. LWC was calculated from droplet size distributions measured by a fast cloud droplet probe (FCDP, SPEC Inc.), and a two-dimensional stereo optical array probe (2D-S; SPEC Inc.), which sampled a combined droplet size range of 3 to  $1465 \mu\text{m}$  diameter.

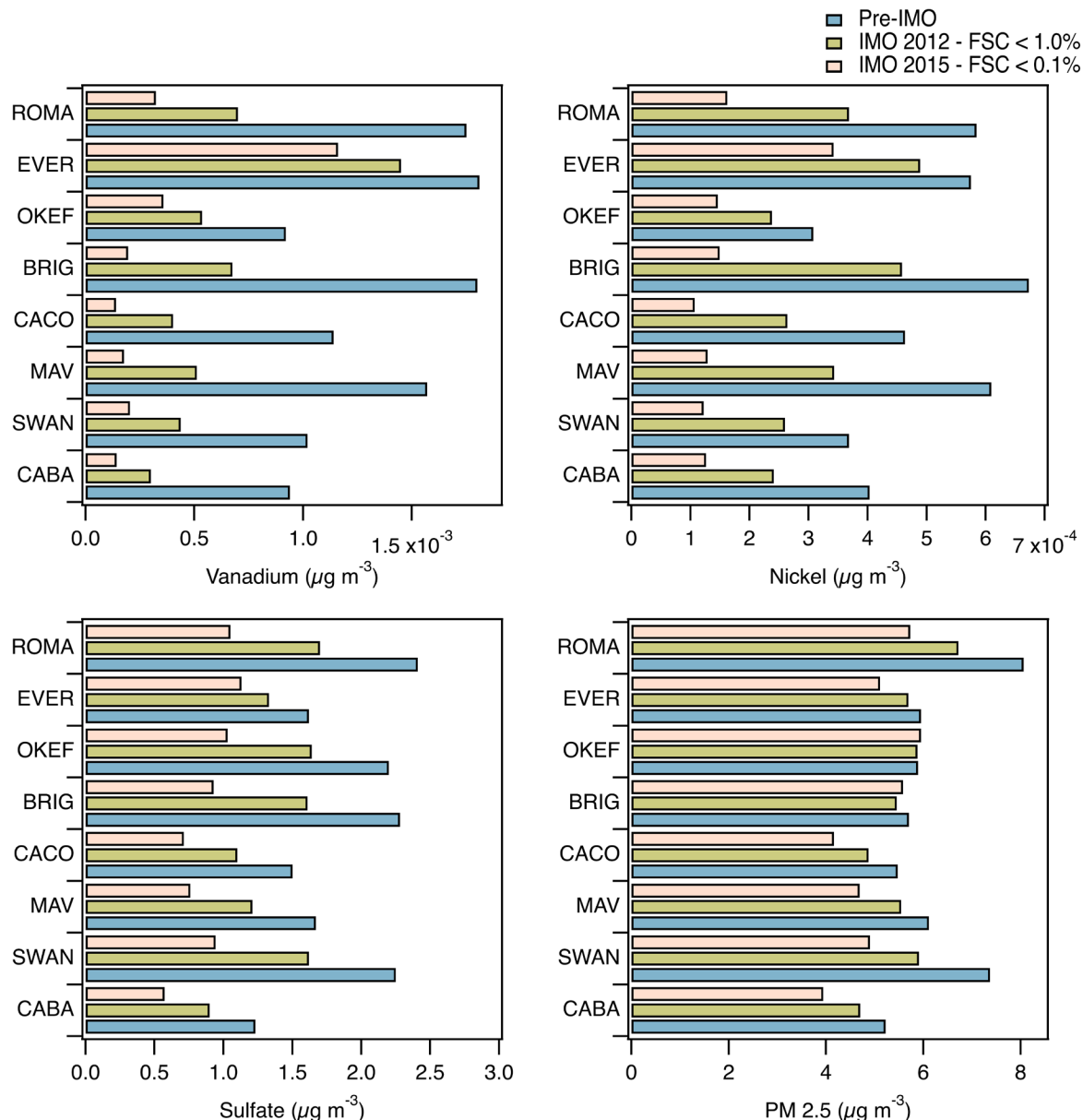
### 3 Results

#### 3.1 Effect of low-sulfur marine fuel regulation on the U.S. eastern North Atlantic coast

##### 3.1.1 RFO emissions influence at IMPROVE sites

Over the years, several studies have reported elevated particulate concentrations of vanadium and nickel in coastal cities, attributing them to emissions from ship activities. Figure 2 shows chemically speciated measurements of  $\text{PM}_{2.5}$  at eight IMPROVE sites located along the U.S. North Atlantic coast pre- and post-low-sulfur marine fuel regulations. IMPROVE sites in the plots are displayed in order of distance from the closest major commercial port, with ROMA

being the site located closest to a U.S. major port (~30 km) and CABA the farthest (~180 km). In a previous study, Agrawal et al. (2009) found the concentration of fine particulate V and Ni at monitoring stations throughout southern California to decrease with increasing distance from ports before the implementation of sulfur marine fuel regulations. Here, we found a similar trend for pre-regulation particulate vanadium and nickel concentrations with the highest mean concentrations (up to  $\sim 1.81 \times 10^{-3} \mu\text{g m}^{-3}$  and  $\sim 6.73 \times 10^{-4} \mu\text{g m}^{-3}$  for V and Ni, respectively) observed at three IMPROVE sites (ROMA, EVER, and BRIG) located  $< \sim 80$  km from major commercial ports, and the lowest (as low as  $9.39 \times 10^{-4} \mu\text{g m}^{-3}$  and  $\sim 3.68 \times 10^{-4} \mu\text{g m}^{-3}$  for V and Ni, respectively) at SWAN and CABA, which are situated  $> \sim 150$  km from the closest major commercial port. The lower mean V concentration observed at OKEF ( $9.20 \times 10^{-4} \mu\text{g m}^{-3}$  and  $\sim 3.08 \times 10^{-4} \mu\text{g m}^{-3}$  for V and Ni, respectively) compared to ROMA and EVER (similar distance and downwind from the major ports Charleston and Miami, respectively (Kracker, 2003)) might be related to a higher distance of the site to the coastline (~30 km), therefore supporting the hypothesis of stronger ship emission influences on coastal sites than in inland cities. Interestingly, we found mean V and Ni concentrations ( $1.81 \times 10^{-3} \mu\text{g m}^{-3}$  and  $\sim 6.09 \times 10^{-4} \mu\text{g m}^{-3}$  for V and Ni, respectively) at MAV (~115 km from a major commercial port) to be comparable to the ones observed at ROMA, EVER, and BRIG. This result is likely related to the presence of two minor ports located at ~50 km from the site and underscores the pervasive influence of ship emissions on atmospheric V and Ni concentration. The trend between fine particulate sulfate concentrations and distance from major commercial ports is less pronounced than in the case of V and Ni, and no clear trend is observed in the case of  $\text{PM}_{2.5}$ . Indeed, while atmospheric concentrations of V in coastal areas are predominantly due to exhaust emissions from shipping, atmospheric sulfate and  $\text{PM}_{2.5}$  originate from a wider array of sources, including industrial activities and coal-related operations, thus making the relative contribution from ship emissions comparatively limited.

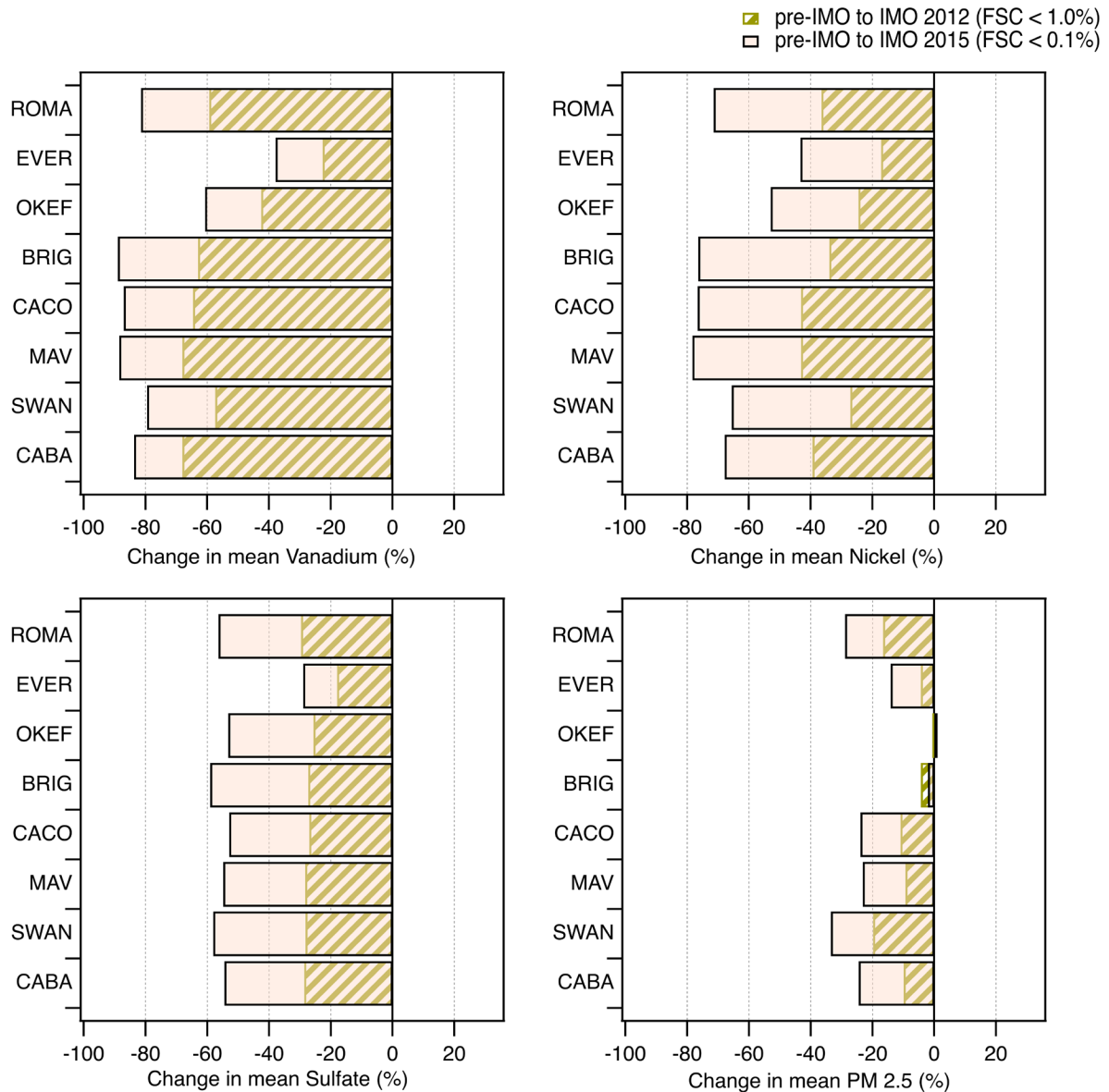


**Figure 2.** Mean concentrations of fine particulate vanadium, nickel, and sulfate, and PM<sub>2.5</sub> at IMPROVE sites pre-regulation (blue), and after the implementation of IMO 2012 (green) and IMO 2015 (pink). Sites are displayed in order of distance from the closest major commercial port, with ROMA being the site located closest to a U.S. major port (~30 km) and CABA the farthest (~180 km).

### 3.1.2 Effect of low-sulfur marine fuel regulations on ship emissions

Following the implementation of IMO 2012 and IMO 2015, large statistically significant reductions in the concentration of fine particulate vanadium, nickel, and sulfate were observed at all the IMPROVE sites presented in this study (Fig. 3), while changes in PM<sub>2.5</sub> concentrations were lower and statistically significant only at five locations. Of the four ship-related pollutants

analyzed here, vanadium showed the largest decreases in mean concentration with reductions > 80% and up to 89% between the 4.5-year period pre-regulation and the 8-year period after the implementation of IMO 2015, at most of the sites with the exception of EVER and OKEF, where concentrations of V were only 36% and 61% lower in the 8-year period after IMO 2015 implementation compared to the pre-regulation time. A similar trend was observed for fine particulate nickel that showed decreases between 67% and 79% from the years pre-regulation to the years after IMO 2015 implementation at all the sites except for EVER and OKEF (reduction of 41% and 53%, respectively). Assuming that most marine vessels operate on RFO outside SECAs, the small decreases in vanadium and nickel observed at EVER and OKEF might be related to the narrowing of the SECA zone along the southern eastern coast of Florida and the consequent arrival of shipping exhaust from outside SECAs. Supporting our hypothesis, a previous study has shown that PM<sub>2.5</sub> from shipping emissions can be transported 960 km from the source (Lv et al., 2018). Furthermore, the relatively low decrease at OKEF is consistent with the low V and Ni levels noted above and with the monitoring site being less impacted by shipping emissions due to its location 1) farther inland compared to the other sites, and 2) approximately 65 km from the Seminole coal power plant. It is important to note that analysis of waterborne container traffic at the major ports located on the U.S. east coast indicated an overall increase in annual shipping traffic between 2008 and 2022, therefore ruling out any potential confounding effect of changes of shipping activities on the impact of the regulations (Fig. S1).



**Figure 3.** Changes in concentration of fine particulate vanadium, nickel, and sulfate, and PM<sub>2.5</sub> at IMPROVE sites between the 5-year period pre-regulation and the 2.5-year period after the implementation of IMO 2012 (green lines), and the 5-year period pre-regulation and the 8-year period after the implementation of IMO 2015 (pink). Sites are displayed in order of distance from the closest major commercial port, with ROMA being the site located closest to a U.S. major port (~30 km) and CABA the farthest (~180 km).

Reductions in particulate sulfate between the pre-regulation period and the IMO 2015 period were similar at all the sites (53% - 59%) with the exception of EVER (30%). The decreasing rates of sulfate are lower than in the case of vanadium. Examining the regulation implementation periods more closely, we observed that for nickel and sulfate larger decreases

occurred between IMO 2012 and IMO 2015 implementation periods than between the pre-regulation and the IMO 2012 implementation periods, while vanadium followed the opposite trend. Previous studies have found a linear reduction ratio between concentration of fine particulate vanadium and sulfur, while decreases in PM nickel concentrations were less clear (Zhang et al., 2019; Zhao et al., 2021). These results suggest the occurrence of nickel and sulfate contributions from sources other than shipping, which are not affected by the IMO regulations and underscore the importance of vanadium alone as a tracer for ship emissions. Our hypothesis is consistent with SO<sub>2</sub> emissions trend data from the Clean Air Markets Program Data (CAMPD) that show a larger decrease in mean SO<sub>2</sub> emissions between the periods 2012-2014 versus 2015-2022 (62%) than the periods 2008-2011 versus 2012-2014 (44%). This is most likely attributable to a shift from coal to gas plants for electricity generation (Fig S2).

Changes in PM<sub>2.5</sub> levels between the pre-regulation and the IMO 2015 implementation periods were < 34% and no statistically significant reduction was observed at EVER, OKEF, and BRIG. Previous studies conducted on-board ships and laboratory tests on marine engine emissions have reported reductions in PM mass due to fuel change (Lehtoranta et al., 2019; Zetterdahl et al., 2016). The low changes in PM<sub>2.5</sub> might be related to background PM<sub>2.5</sub>. For example, Viana et al. (2009) found that in Europe, although the PM<sub>2.5</sub> increase due to ship emissions is small, the relative contribution is large because of low PM<sub>2.5</sub> background levels, while the opposite trend was observed in China. The lack of a statistically significant decrease in PM<sub>2.5</sub> observed in this study might be due to elevated PM<sub>2.5</sub> background levels due to plentiful sources of PM<sub>2.5</sub> in the study region, which make the impact of regulations less noticeable (Anastasopoulos et al., 2021; Jang et al., 2023).

### 3.1.3 Fuel regulations impact on vanadium/nickel ratios

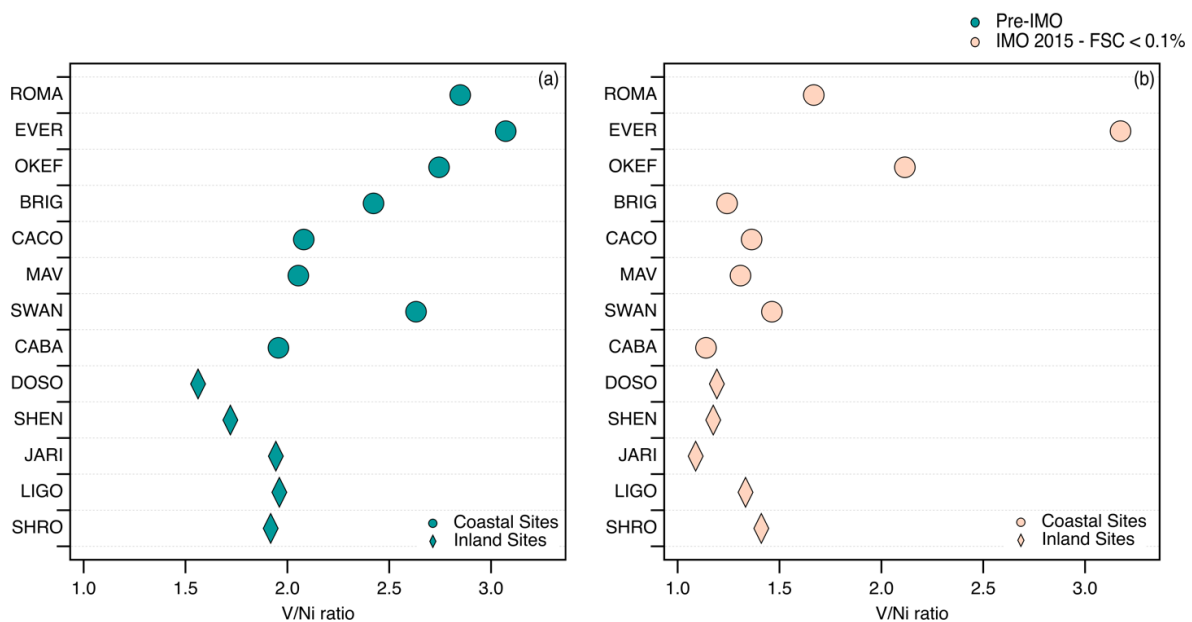
Vanadium and nickel are among the metals most associated with global-scale pollution from industrial and transportation processes (Moreno et al., 2010). In marine vessel emissions from RFO, the concentrations of V and Ni can vary depending on ship type and engine load. However, the ratio between these two metals (V/Ni) exhibits characteristic values making it a widely used tracer for ship emissions in studies aimed at quantifying the contribution of shipping activities on air quality (Abou-Ghanem et al., 2023; Agrawal et al., 2009; Corbin et al.,



2018; Jang et al., 2023; Viana et al., 2009). For example, Agrawal et al. (2008) and Popovicheva et al. (2012) found V/Ni values between 2.1 and 4.5 in particle samples collected onboard ocean-going cargo ships. In another study conducted in an Italian port city, Mazzei et al. (2008) observed fairly constant V/Ni ratios of 3.2 and 3 for different size fractions ( $<1\ \mu\text{m}$ ,  $<2.5\ \mu\text{m}$ , and  $<10\ \mu\text{m}$ ) by applying Positive Matrix Factorization (PMF). Similarly, Viana et al. (2009) and Pandolfi et al. (2011) reported V/Ni ratios of 4 and 3, respectively, for commercial shipping emissions in ambient  $\text{PM}_{2.5}$  and  $\text{PM}_{10}$  in Mediterranean locations in Spain, while Zhao et al. (2013) found values between 3.4 and 3.6 over China's largest port. However, Viana et al. (2009) reported high V/Ni ratio variability with values ranging between 2.2 and 6.7, which were dependent on ship type, with container ships having a distinctive V/Ni = 2.6, while no direct correlation was found between V/Ni and size of the ship. Slightly higher V/Ni values of 5.2 were observed in laboratory tests for  $\text{PM}_{2.5}$  emitted by marine engines operating on RFO, without dependence on engine load (Corbin et al., 2018). In the same study, the authors also reported V/Ni values 4- to 25-fold higher for soot particles and an increase for low load engines, suggesting an enrichment in vanadium related to its lower nucleation temperature.

Figure 4 shows median V/Ni values for the 5-year period pre-regulation and the 8-year period after the implementation of IMO 2015. To better evaluate the impact of ship emissions on coastal regions, we examined V/Ni values at five more distant sites located  $> 250\ \text{km}$  from the coast. Consistent with the previous studies discussed above, we found that median V/Ni values for the coastal sites were between 2.1 and 3.1 during the pre-regulation period, while for the inland site values were lower ( $< 1.9$ ). Similar to the inland V/Ni observed here, Pandolfi et al. (2011) observed V/Ni ranging between 0.9 to 1.9 in coastal areas influenced by Ni-enriched emissions from stainless steel plants. We find the ratio values decreasing with increased distance from the ports, with the IMPROVE sites located farthest from a major commercial port showing V/Ni values only slightly higher than those observed at inland locations. The only exception was SWAN with a mean V/Ni value of 2.4, likely due to the influence of minor commercial ports located at distance of  $\sim 80\ \text{km}$  from the site. Consistent with our results, Kotchenruther (2015, 2017) reported V/Ni linear best fit slopes between 2.1 and 2.8 for IMPROVE sites on the U.S. west coast over the years 2006 to 2009 and between 2.2

and 4.5 at 22 IMPROVE sites located along U.S. coasts during a 31 month period before the implementation of IMO 2012. After the implementation of IMO 2015, we observed median V/Ni values to drop below 2 at most of the coastal sites and being similar to those observed inland. However, median V/Ni values at EVER and OKEF sites were still above 2, consistent with the hypothesis of a potential influence from ships operating on RFO combustion outside the SECA zone along the southeastern coast of Florida. Our observations indicate that while V/Ni is a robust tracer for detecting plume exhaust from RFO combustion, it is unsuitable for the identification of emissions from ships operating on low-sulfur fuel. (Anastasopoulos et al., 2021; Jang et al., 2023).

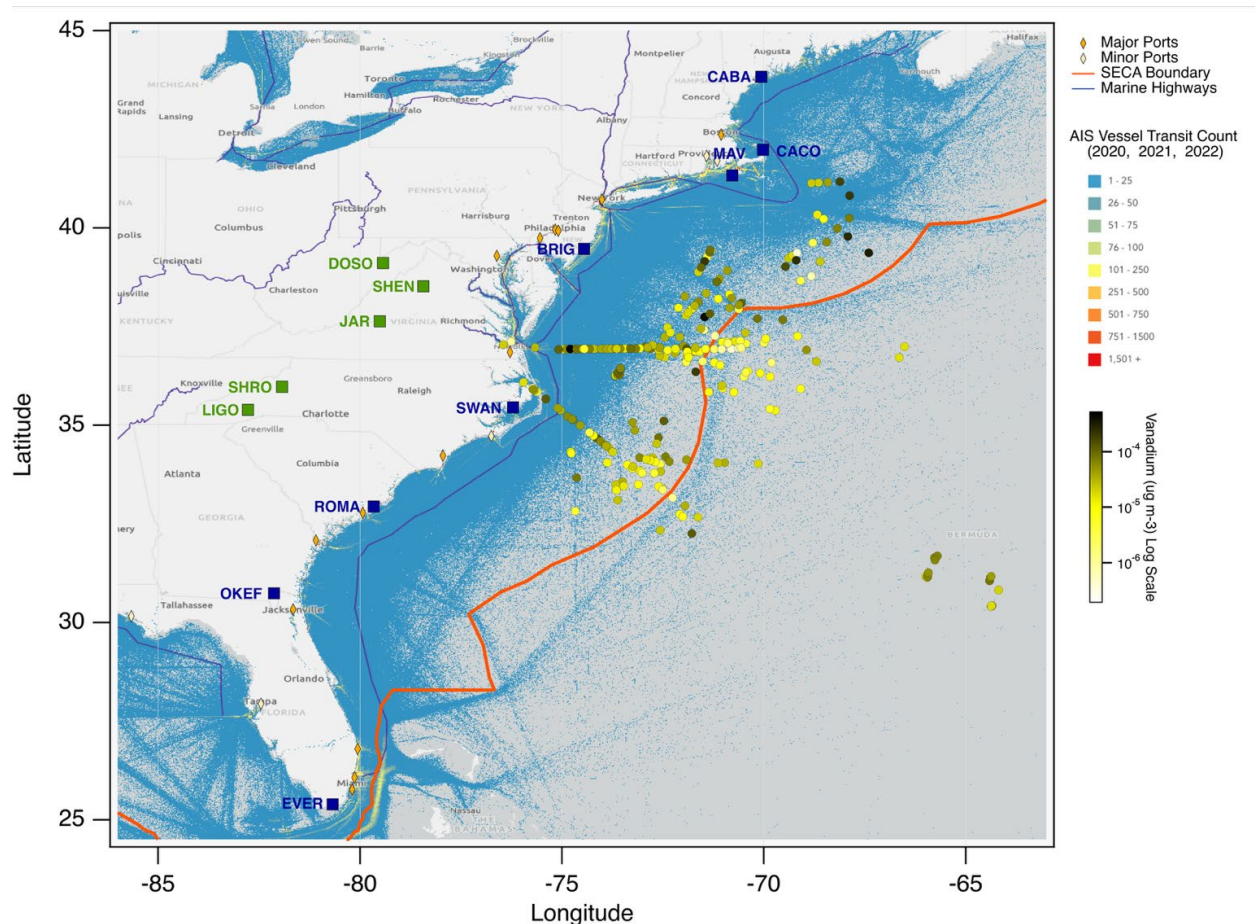


**Figure 4.** Median V/Ni ratios at coastal (circle) and inland (diamond) IMPROVE sites pre-regulation (blue) and after the implementation of IMO 2015 (pink). Coastal sites are displayed in order of distance from the closest major commercial port, with ROMA being the site located closest to a U.S. major port (~30 km) and CABA the farthest (~180 km).

### 3.2 Atmospheric and in-cloud vanadium concentrations under low-sulfur fuel regulations regime

Over the past years, several studies have reported on the concentrations of atmospheric fine particulate vanadium in port and at coastal sites, and on ships after the implementation of low-sulfur fuel regulations. Observations of in-cloud vanadium are scarce and limited to measurements out of the California coast before the FSC limits were implemented (Coggon et

al., 2012; Wang et al., 2014). Leveraging 3 years of ACTIVATE's datasets we show the spatial distribution of cloud water vanadium concentrations over the western North Atlantic Ocean (Fig. 5). Measurements were made without targeting specific ship plumes, so samples reflect the area in and around major U.S. east coast shipping routes. Here, no significant correlations between in-cloud vanadium and latitude or longitude were found. However, the presence of vanadium in all the samples analyzed and slightly higher values closer to the coast where vessel transit counts are enhanced are collectively suggestive of the influence of ship emissions on regional cloud water. Given the catalytic role of vanadium in oxidation reactions, these results suggest that vanadium-containing ship exhaust may play a substantial role in cloud-oxidation processes over the western North Atlantic, which in turn can affect cloud microphysics and radiative properties.

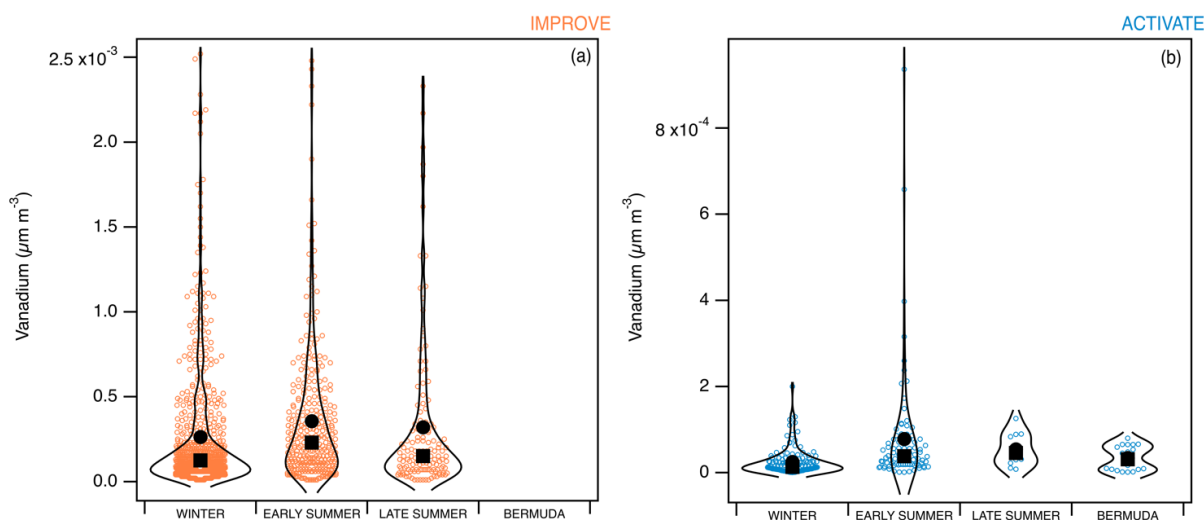


**Figure 5.** Map of spatial distribution of air equivalent mass concentrations of vanadium in cloud water over the western North Atlantic Ocean during ACTIVATE (yellow dots), major and minor U.S. east coast ports (diamonds), SECA boundary (red line), and marine highways (blue lines).

Vessel transit counts for the years 2020, 2021, and 2022 from the Automatic Identification System (AIS) Marine Cadastre (<https://marinecadastre.gov/data/>) are summarized at a 100-meter by 100-meter geographic area with a single transit counted each time a vessel track passes through, starts, or stops within a 100-meter grid.

Figure 6 shows seasonal variations in atmospheric fine particulate and in-cloud vanadium concentrations for coastal IMPROVE sites and over the western North Atlantic Ocean during ACTIVATE. Although not directly comparable, particulate concentrations of vanadium at the IMPROVE sites are approximately one order of magnitude higher than air-equivalent cloud-water concentrations observed during ACTIVATE (Fig. 6). Indeed, although particles emitted by ships have an important role in cloud formation, it is likely that not all of them are activated or scavenged within clouds during atmospheric convection (Durkee et al., 2000), due to either their size being below the critical activation diameter or to less hygroscopic composition. Supporting this hypothesis, vanadium-containing ship exhaust particles were reported in the free troposphere at altitude up to 13 km (Abou-Ghanem et al., 2023). In another study, Corbin et al. (2018) observed that during fuel combustion, vanadium can become incorporated into insoluble soot particles which have low hygroscopicity, hence potentially leading to lower in-cloud vanadium concentrations compared to those in ambient particulate matter. Also, lower levels in cloud water can simply be due in part to more dilution farther away from the ship exhaust sources near the ocean surface. However, it is worth noting that concentrations of vanadium in atmospheric PM<sub>2.5</sub> at IMPROVE sites and in cloud water samples followed similar seasonal variation trends with higher values in the summer and lower values in the winter (Fig. 6), likely due to a shallower and stronger marine boundary layer over the western North Atlantic region in the summertime (Gallo et al., 2023). In the case of ACTIVATE, no clear differences between early and late summer are observable. Analogous seasonal patterns in atmospheric vanadium concentrations have been previously observed at IMPROVE sites along the U.S. west coast and at coastal cities in Asia (Kotchenruther, 2017; Yu et al., 2021). In these studies, authors have found a peak in vanadium concentrations in spring and early summer associated with a stronger stability of the boundary layer in summer compared to the winter, leading to higher concentration of ship exhaust in the lowest atmospheric layer. Here, the substantial differences between mean and median values along with the datapoint

distributions within the violin plots for IMPROVE datasets suggest that while vanadium is ubiquitous over the eastern U.S. coastline, high-vanadium events likely attributable to ship plumes strongly affect V concentrations. Supporting this hypothesis, no significant differences between mean and median for the inland IMPROVE sites over the same period of time were found, suggesting that despite the implementation of low-sulfur regulations, ship emissions are still responsible for atmospheric vanadium concentrations at coastal sites (Fig. S1 and Fig. S3).



**Figure 6.** Violin plots, mean (circle), and median (square) of (a) atmospheric concentrations of V at coastal IMPROVE sites in winter (January to March 2020, 2021, and 2022), early summer (May and June 2020, 2021, and 2022), and late summer (August and September 2020); and (b) air equivalent mass concentrations of in-cloud V over the western North Atlantic Ocean during ACTIVATE (winter – research flights conducted in January to March 2020, 2021, and 2022; early summer – research flights conducted in May and June 2021 and 2022; late summer - research flights conducted in August and September 2020; Bermuda - research flights conducted over Bermuda in June 2022).

In the case of ACTIVATE, we find a higher number of samples with enhanced vanadium levels in the early summer, while similar mean and median values in the winter and late summer indicate similar amounts of vanadium in cloud water. Vanadium is known to catalyze the oxidation of  $\text{SO}_2$  to produce sulfate and sulfuric acid (Ault et al., 2010), and in the summer this process might occur even more rapidly due to increased photochemical activity (Becagli et al., 2012). As a consequence, higher amounts of vanadium-containing sulfur particles might be available to partition in cloud droplets leading to the higher in cloud vanadium concentrations

observed during ACTIVATE over the ocean. This finding is consistent with our observations of stronger correlations between in-cloud water non-sea-salt sulfate ( $\text{nssSO}_4^{2-}$ ) and vanadium in the early summer than in the winter (the linear regression  $R^2$  values are 0.8 for summer, 0.57 for winter, and 0.63 for late summer) (Fig. 7). Importantly, we found that in the early summer, mass concentrations of vanadium above the 75<sup>th</sup> percentile occur in cloud droplets enriched either in  $\text{nssSO}_4^{2-}$  and  $\text{NO}_3^-$  likely from anthropogenic sources (Fig. 7), or in MSA at lower altitudes ( $< 800$  m) (Fig. 8). These results underscore the critical catalytic role of vanadium in aqueous phase reactions over the western North Atlantic Ocean and highlight the importance that ship emissions, even if operating on low-sulfur fuel, have on marine cloud properties.

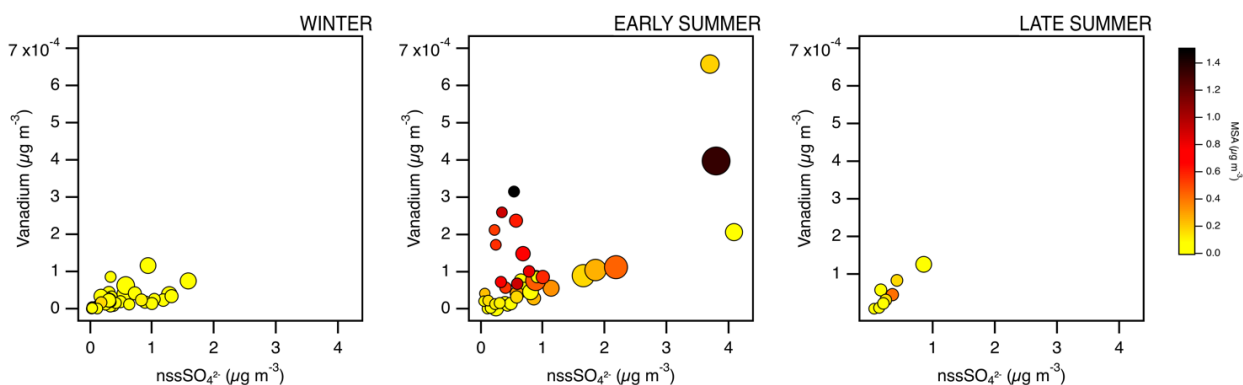


Figure 7. Scatterplots of air equivalent mass concentrations of in-cloud vanadium vs  $\text{nssSO}_4^{2-}$  over the western North Atlantic Ocean during ACTIVATE. Markers are colored as a function of air equivalent mass concentrations of MSA, while marker sizes are proportional to the air equivalent mass concentrations of nitrate.

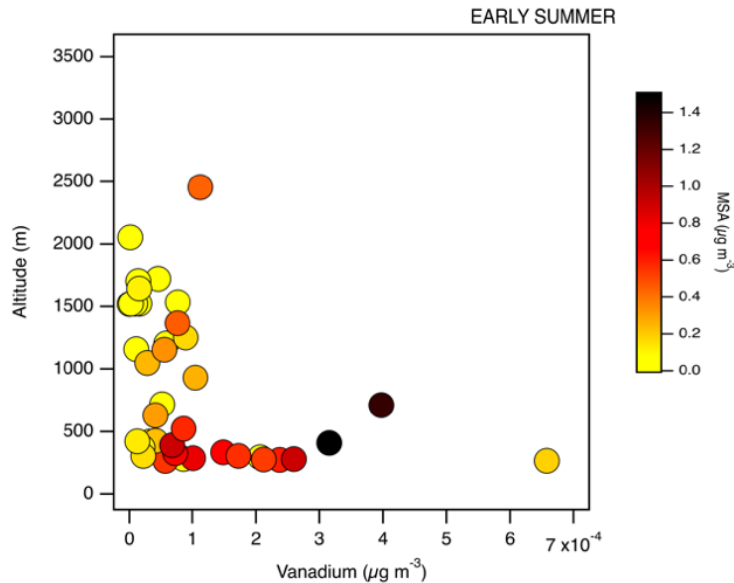


Figure 8. Vertical distribution of air equivalent mass concentrations of in-cloud vanadium over the western North Atlantic Ocean during early summer. Markers are colored as a function of MSA air equivalent mass concentration.

## 5 Conclusions

In this study, we assess the impact of shipping emission regulations on atmospheric particulate and cloud water concentrations of vanadium over the western North Atlantic Ocean. We analyze 15 years of chemically speciated measurements of  $\text{PM}_{2.5}$  collected at IMPROVE sites along the eastern coast of the U.S. and we provided substantial evidence that the implementation of regulations imposing sulfur content limits on marine vessel fuels is an effective strategy for reducing atmospheric vanadium concentrations in coastal regions. Particulate sulfate and nickel levels also decline in alignment with the timeline of the enforcement of these regulations. However, we observe that the decreasing trends for sulfate and nickel were less pronounced than for vanadium due to contributions from sources other than shipping. Furthermore, we evaluate the reliability of the ratio between vanadium and nickel as a tracer for detecting ship exhaust and assess the contribution of ship emissions to air pollution in source apportionment studies. For pre-regulation periods, we find distinctive V/Ni values consistent with previous literature focused on RFO combustions, while after the implementations of low-sulfur fuel regulations, V/Ni values at most of the coastal locations were comparable to those observed for inland areas.. Our findings show that under a low-sulfur

fuel regime, vanadium alone is a stronger tracer for ship emissions and V/Ni should only be used for marine engines operating on RFO.

The concentrations of cloud water vanadium over the western North Atlantic Ocean observed during the ACTIVATE field campaign between 2020 and 2022 were approximately an order of magnitude lower than in atmospheric particles. Higher levels of vanadium in the summer were found at both IMPROVE sites and during ACTIVATE likely related to different meteorological conditions and sulfur concentrations in the atmosphere. Furthermore, we found that in early summer vanadium above the 75<sup>th</sup> percentile correlated well with cloud water enriched in  $\text{nssSO}_4^{2-}$  and  $\text{NO}_3$  or in MSA at lower altitudes highlighting the potential importance of vanadium from ship emissions in catalyzing in-cloud and out-of-cloud oxidation reactions.

## Acknowledgments

ACTIVATE is a NASA Earth Venture Suborbital-3 (EVS-3) investigation funded by NASA's Earth Science Division and managed through the Earth System Science Pathfinder Program Office. University of Arizona investigators were supported by NASA grant no. 80NSSC19K0442. Christiane Voigt and Simon Kirschler were funded by the Deutsche Forschungsgemeinschaft (SPP-1294 HALO under project no. 522359172) and by the European Union's Horizon Europe program through the project A4CLIMATE (grant no. 101192301).

## Open Research

The Aerosol Cloud meteorology Interactions over the western Atlantic Experiment data are archived at the NASA Atmospheric Science Data Center (ASDC; <https://doi.org/10.5067/SUBORBITAL/ACTIVATE/DATA001>). Automatic Identification System (AIS) Vessel Transit Counts data are archived at Marine Cadastre on an initiative of the Bureau of Ocean Energy Management and NOAA (<https://hub.marinecadastre.gov/pages/vesseltraffic>).

## References

Abou-Ghanem, M., Murphy, D. M., Schill, G. P., Lawler, M. J., & Froyd, K. D. (2023). *Measurement report: Vanadium-containing ship exhaust particles detected in and above the*



- 539 *marine boundary layer in the remote atmosphere* [Preprint]. Aerosols/Field  
540 Measurements/Troposphere/Chemistry (chemical composition and reactions).  
541 <https://doi.org/10.5194/egusphere-2023-2176>
- 542 Agrawal, H., Eden, R., Zhang, X., Fine, P. M., Katzenstein, A., Miller, J. W., Ospital, J., Teffera,  
543 S., & Cocker, D. R. (2009). Primary Particulate Matter from Ocean-Going Engines in the  
544 Southern California Air Basin. *Environmental Science & Technology*, 43(14), 5398–5402.  
545 <https://doi.org/10.1021/es8035016>
- 546 Agrawal, H., Malloy, Q. G. J., Welch, W. A., Wayne Miller, J., & Cocker, D. R. (2008). In-use  
547 gaseous and particulate matter emissions from a modern ocean going container vessel.  
548 *Atmospheric Environment*, 42(21), 5504–5510. <https://doi.org/10.1016/j.atmosenv.2008.02.053>
- 549 Anastasopoulos, A. T., Sofowote, U. M., Hopke, P. K., Rouleau, M., Shin, T., Dheri, A., Peng, H.,  
550 Kulka, R., Gibson, M. D., Farah, P.-M., & Sundar, N. (2021). Air quality in Canadian port cities  
551 after regulation of low-sulphur marine fuel in the North American Emissions Control Area.  
552 *Science of The Total Environment*, 791, 147949. <https://doi.org/10.1016/j.scitotenv.2021.147949>
- 553 Ault, A. P., Gaston, C. J., Wang, Y., Dominguez, G., Thiemens, M. H., & Prather, K. A. (2010).  
554 Characterization of the Single Particle Mixing State of Individual Ship Plume Events Measured  
555 at the Port of Los Angeles. *Environmental Science & Technology*, 44(6), 1954–1961.  
556 <https://doi.org/10.1021/es902985h>
- 557 Becagli, S., Sferlazzo, D. M., Pace, G., Di Sarra, A., Bommarito, C., Calzolari, G., Ghedini, C.,  
558 Lucarelli, F., Meloni, D., Monteleone, F., Severi, M., Traversi, R., & Udisti, R. (2012). Evidence  
559 for heavy fuel oil combustion aerosols from chemical analyses at the island of Lampedusa: A  
560 possible large role of ships emissions in the Mediterranean. *Atmospheric Chemistry and Physics*,  
561 12(7), 3479–3492. <https://doi.org/10.5194/acp-12-3479-2012>
- 562 Benedict, K. B., Lee, T., & Collett, J. L. (2012). Cloud water composition over the southeastern  
563 Pacific Ocean during the VOCALS regional experiment. *Atmospheric Environment*, 46, 104–  
564 114. <https://doi.org/10.1016/j.atmosenv.2011.10.029>
- 565 Brandt, C., & van Eldik, R. (1995). Transition Metal-Catalyzed Oxidation of Sulfur(IV) Oxides.  
566 Atmospheric-Relevant Processes and Mechanisms. *Chemical Reviews*, 95(1), 119–190.  
567 <https://doi.org/10.1021/cr00033a006>
- 568 Cheng, K., Chang, Y., Kuang, Y., Ling, Q., Zou, Z., & Huang, R.-J. (2022). Multiple-Year  
569 Changes (2014–2018) in Particulate Vanadium Linked to Shipping Regulations in the World’s  
570 Largest Port Region. *ACS Earth and Space Chemistry*, 6(2), 415–420.  
571 <https://doi.org/10.1021/acsearthspacechem.1c00402>
- 572 Clean Air Markets Program Data. view-2023-capd-emissions-data, Office of Atmospheric  
573 Protection, Clean Air and Power Division United States Environmental Protection Agency  
574 (EPA). (n.d.). *CAMPD* [Dataset]. <https://doi.org/Available from EPA’s Air Markets Program>  
575 Data web site: <https://campd.epa.gov/>.

- Coakley, J. A., Bernstein, R. L., & Durkee, P. A. (1987). Effect of Ship-Stack Effluents on Cloud Reflectivity. *Science*, 237(4818), 1020–1022. <https://doi.org/10.1126/science.237.4818.1020>
- Coggon, M. M., Sorooshian, A., Wang, Z., Metcalf, A. R., Frossard, A. A., Lin, J. J., Craven, J. S., Nenes, A., Jonsson, H. H., Russell, L. M., Flagan, R. C., & Seinfeld, J. H. (2012). Ship impacts on the marine atmosphere: Insights into the contribution of shipping emissions to the properties of marine aerosol and clouds. *Atmospheric Chemistry and Physics*, 12(18), 8439–8458. <https://doi.org/10.5194/acp-12-8439-2012>
- Corbett, J. J., Winebrake, J. J., Green, E. H., Kasibhatla, P., Eyring, V., & Lauer, A. (2007). Mortality from Ship Emissions: A Global Assessment. *Environmental Science & Technology*, 41(24), 8512–8518. <https://doi.org/10.1021/es071686z>
- Corbin, J. C., Mensah, A. A., Pieber, S. M., Orasche, J., Michalke, B., Zanatta, M., Czech, H., Massabò, D., Buatier De Mongeot, F., Mennucci, C., El Haddad, I., Kumar, N. K., Stengel, B., Huang, Y., Zimmermann, R., Prévôt, A. S. H., & Gysel, M. (2018). Trace Metals in Soot and PM<sub>2.5</sub> from Heavy-Fuel-Oil Combustion in a Marine Engine. *Environmental Science & Technology*, 52(11), 6714–6722. <https://doi.org/10.1021/acs.est.8b01764>
- Crosbie, E., Brown, M. D., Shook, M., Ziemba, L., Moore, R. H., Shingler, T., Winstead, E., Thornhill, K. L., Robinson, C., MacDonald, A. B., Dadashazar, H., Sorooshian, A., Beyersdorf, A., Eugene, A., Collett Jr., J., Straub, D., & Anderson, B. (2018). Development and characterization of a high-efficiency, aircraft-based axial cyclone cloud water collector. *Atmospheric Measurement Techniques*, 11(9), 5025–5048. <https://doi.org/10.5194/amt-11-5025-2018>
- Crosbie, E., Ziemba, L. D., Shook, M. A., Robinson, C. E., Winstead, E. L., Thornhill, K. L., Braun, R. A., MacDonald, A. B., Stahl, C., Sorooshian, A., Van Den Heever, S. C., DiGangi, J. P., Diskin, G. S., Woods, S., Bañaga, P., Brown, M. D., Gallo, F., Hilario, M. R. A., Jordan, C. E., ... Wiggins, E. B. (2022). Measurement report: Closure analysis of aerosol–cloud composition in tropical maritime warm convection. *Atmospheric Chemistry and Physics*, 22(20), 13269–13302. <https://doi.org/10.5194/acp-22-13269-2022>
- Diamond, M. S. (2023). Detection of large-scale cloud microphysical changes within a major shipping corridor after implementation of the International Maritime Organization 2020 fuel sulfur regulations. *Atmospheric Chemistry and Physics*, 23(14), 8259–8269. <https://doi.org/10.5194/acp-23-8259-2023>
- Durkee, P. A., Chartier, R. E., Brown, A., Trehubenko, E. J., Rogerson, S. D., Skupniewicz, C., Nielsen, K. E., Platnick, S., & King, M. D. (2000). Composite Ship Track Characteristics. *Journal of the Atmospheric Sciences*, 57(16), 2542–2553. [https://doi.org/10.1175/1520-0469\(2000\)057<2542:CSTC>2.0.CO;2](https://doi.org/10.1175/1520-0469(2000)057<2542:CSTC>2.0.CO;2)
- Eyring, V., Isaksen, I. S. A., Berntsen, T., Collins, W. J., Corbett, J. J., Endresen, O., Grainger, R. G., Moldanova, J., Schlager, H., & Stevenson, D. S. (2010). Transport impacts on atmosphere and climate: Shipping. *Atmospheric Environment*, 44(37), 4735–4771. <https://doi.org/10.1016/j.atmosenv.2009.04.059>

- Ferek, R. J., Garrett, T., Hobbs, P. V., Strader, S., Johnson, D., Taylor, J. P., Nielsen, K., Ackerman, A. S., Kogan, Y., Liu, Q., Albrecht, B. A., & Babb, D. (2000). Drizzle Suppression in Ship Tracks. *Journal of the Atmospheric Sciences*, 57(16), 2707–2728. [https://doi.org/10.1175/1520-0469\(2000\)057<2707:DSIST>2.0.CO;2](https://doi.org/10.1175/1520-0469(2000)057<2707:DSIST>2.0.CO;2)
- Gallo, F., Sanchez, K. J., Anderson, B. E., Bennett, R., Brown, M. D., Crosbie, E. C., Hostetler, C., Jordan, C., Yang Martin, M., Robinson, C. E., Russell, L. M., Shingler, T. J., Shook, M. A., Thornhill, K. L., Wiggins, E. B., Winstead, E. L., Wisthaler, A., Ziemba, L. D., & Moore, R. H. (2023). Measurement report: Aerosol vertical profiles over the western North Atlantic Ocean during the North Atlantic Aerosols and Marine Ecosystems Study (NAAMES). *Atmospheric Chemistry and Physics*, 23(2), 1465–1490. <https://doi.org/10.5194/acp-23-1465-2023>
- Gaston, C. J., Pratt, K. A., Qin, X., & Prather, K. A. (2010). Real-Time Detection and Mixing State of Methanesulfonate in Single Particles at an Inland Urban Location during a Phytoplankton Bloom. *Environmental Science & Technology*, 44(5), 1566–1572. <https://doi.org/10.1021/es902069d>
- Golbazi, M., & Archer, C. (2023). Impacts of maritime shipping on air pollution along the US East Coast. *Atmospheric Chemistry and Physics*, 23(23), 15057–15075. <https://doi.org/10.5194/acp-23-15057-2023>
- Hobbs, P. V., Garrett, T. J., Ferek, R. J., Strader, S. R., Hegg, D. A., Frick, G. M., Hoppel, W. A., Gasparovic, R. F., Russell, L. M., Johnson, D. W., O'Dowd, C., Durkee, P. A., Nielsen, K. E., & Innis, G. (2000). Emissions from Ships with respect to Their Effects on Clouds. *Journal of the Atmospheric Sciences*, 57(16), 2570–2590. [https://doi.org/10.1175/1520-0469\(2000\)057<2570:EFSWRT>2.0.CO;2](https://doi.org/10.1175/1520-0469(2000)057<2570:EFSWRT>2.0.CO;2)
- Hudson, J. G., Garrett, T. J., Hobbs, P. V., Strader, S. R., Xie, Y., & Yum, S. S. (2000). Cloud Condensation Nuclei and Ship Tracks. *J. Atmos. Sci.*, 57, 2696–2706. [https://journals.ametsoc.org/view/journals/atsc/57/16/1520-0469\\_2000\\_057\\_2696\\_ccnast\\_2.0.co\\_2.xml?tab\\_body=pdf](https://journals.ametsoc.org/view/journals/atsc/57/16/1520-0469_2000_057_2696_ccnast_2.0.co_2.xml?tab_body=pdf)
- Jang, E., Choi, S., Yoo, E., Hyun, S., & An, J. (2023). Impact of shipping emissions regulation on urban aerosol composition changes revealed by receptor and numerical modelling. *Npj Climate and Atmospheric Science*, 6(1), 52. <https://doi.org/10.1038/s41612-023-00364-9>
- Kotchenruther, R. A. (2015). The effects of marine vessel fuel sulfur regulations on ambient PM<sub>2.5</sub> along the west coast of the U.S. *Atmospheric Environment*, 103, 121–128. <https://doi.org/10.1016/j.atmosenv.2014.12.040>
- Kotchenruther, R. A. (2017). The effects of marine vessel fuel sulfur regulations on ambient PM<sub>2.5</sub> at coastal and near coastal monitoring sites in the U.S. *Atmospheric Environment*, 151, 52–61. <https://doi.org/10.1016/j.atmosenv.2016.12.012>
- Kracker, L. M. (2003). *Literature Review for a Resource Characterization of Cape Romain National Wildlife Refuge*. NOAA Tech. Mem. NOS-NCCOS-CCEHBR-0008.

- Langley, L., Leaitch, W. R., Lohmann, U., Shantz, N. C., & Worsnop, D. R. (2010). Contributions from DMS and ship emissions to CCN observed over the summertime North Pacific. *Atmospheric Chemistry and Physics*, 10(3), 1287–1314. <https://doi.org/10.5194/acp-10-1287-2010>
- Lehtoranta, K., Aakko-Saksa, P., Murtonen, T., Vesala, H., Ntziachristos, L., Rönkkö, T., Karjalainen, P., Kuittinen, N., & Timonen, H. (2019). Particulate Mass and Nonvolatile Particle Number Emissions from Marine Engines Using Low-Sulfur Fuels, Natural Gas, or Scrubbers. *Environmental Science & Technology*, 53(6), 3315–3322. <https://doi.org/10.1021/acs.est.8b05555>
- Lv, Z., Liu, H., Ying, Q., Fu, M., Meng, Z., Wang, Y., Wei, W., Gong, H., & He, K. (2018). Impacts of shipping emissions on PM<sub>2.5</sub> pollution in China. *Atmospheric Chemistry and Physics*, 18(21), 15811–15824. <https://doi.org/10.5194/acp-18-15811-2018>
- Manshausen, P., Watson-Parris, D., Christensen, M. W., Jalkanen, J.-P., & Stier, P. (2022). Invisible ship tracks show large cloud sensitivity to aerosol. *Nature*, 610(7930), 101–106. <https://doi.org/10.1038/s41586-022-05122-0>
- Mazzei, F., D’Alessandro, A., Lucarelli, F., Nava, S., Prati, P., Valli, G., & Vecchi, R. (2008). Characterization of particulate matter sources in an urban environment. *Science of The Total Environment*, 401(1–3), 81–89. <https://doi.org/10.1016/j.scitotenv.2008.03.008>
- Moldanová, J., Fridell, E., Popovicheva, O., Demirdjian, B., Tishkova, V., Faccinnetto, A., & Focsa, C. (2009). Characterisation of particulate matter and gaseous emissions from a large ship diesel engine. *Atmospheric Environment*, 43(16), 2632–2641. <https://doi.org/10.1016/j.atmosenv.2009.02.008>
- Moreno, T., Querol, X., Alastuey, A., De La Rosa, J., Sánchez De La Campa, A. M., Minguillón, M., Pandolfi, M., González-Castanedo, Y., Monfort, E., & Gibbons, W. (2010). Variations in vanadium, nickel and lanthanoid element concentrations in urban air. *Science of The Total Environment*, 408(20), 4569–4579. <https://doi.org/10.1016/j.scitotenv.2010.06.016>
- Noone, K. J., Öström, E., Ferek, R. J., Garrett, T., Hobbs, P. V., Johnson, D. W., Taylor, J. P., Russell, L. M., Flagan, R. C., Seinfeld, J. H., O’Dowd, C. D., Smith, M. H., Durkee, P. A., Nielsen, K., Hudson, J. G., Pockalny, R. A., Bock, L. D., Grieken, R. E. V., Gasparovic, R. F., & Brooks, I. (2000). A Case Study of Ships Forming and Not Forming Tracks in Moderately Polluted Clouds. *Journal of the Atmospheric Sciences*, 57(16), 2729–2747. [https://doi.org/10.1175/1520-0469\(2000\)057<2729:ACSOSF>2.0.CO;2](https://doi.org/10.1175/1520-0469(2000)057<2729:ACSOSF>2.0.CO;2)
- Pandolfi, M., Gonzalez-Castanedo, Y., Alastuey, A., De La Rosa, J. D., Mantilla, E., De La Campa, A. S., Querol, X., Pey, J., Amato, F., & Moreno, T. (2011). Source apportionment of PM<sub>10</sub> and PM<sub>2.5</sub> at multiple sites in the strait of Gibraltar by PMF: Impact of shipping emissions. *Environmental Science and Pollution Research*, 18(2), 260–269. <https://doi.org/10.1007/s11356-010-0373-4>
- Passig, J., Schade, J., Irsig, R., Li, L., Li, X., Zhou, Z., Adam, T., & Zimmermann, R. (2021). Detection of ship plumes from residual fuel operation in emission control areas using single-

- particle mass spectrometry. *Atmospheric Measurement Techniques*, 14(6), 4171–4185.  
<https://doi.org/10.5194/amt-14-4171-2021>
- Petzold, A., Hasselbach, J., Lauer, P., Baumann, R., Franke, K., Gurk, C., Schlager, H., & Weingartner, E. (2008). Experimental studies on particle emissions from cruising ship, their characteristic properties, transformation and atmospheric lifetime in the marine boundary layer. *Atmospheric Chemistry and Physics*, 8(9), 2387–2403. <https://doi.org/10.5194/acp-8-2387-2008>
- Popovicheva, O., Kireeva, E., Persiantseva, N., Timofeev, M., Bladt, H., Ivleva, N. P., Niessner, R., & Moldanová, J. (2012). Microscopic characterization of individual particles from multicomponent ship exhaust. *Journal of Environmental Monitoring*, 14(12), 3101.  
<https://doi.org/10.1039/c2em30338h>
- Radke, L. F., Coakley, J. A., & King, M. D. (1989). Direct and Remote Sensing Observations of the Effects of Ships on Clouds. *Science*, 246(4934), 1146–1149.  
<https://doi.org/10.1126/science.246.4934.1146>
- Sahle-Demessie, E., & Devulapelli, V. G. (2008). Vapor phase oxidation of dimethyl sulfide with ozone over V2O5/TiO2 catalyst. *Applied Catalysis B: Environmental*, 84(3–4), 408–419.  
<https://doi.org/10.1016/j.apcatb.2008.04.025>
- Santos, L. F. E. d., Salo, K., Kong, X., Noda, J., Kristensen, T. B., Ohigashi, T., & Thomson, E. S. (2023). Changes in CCN activity of ship exhaust particles induced by fuel sulfur content reduction and wet scrubbing. *Environ. Sci.: Atmos.*, 3(1), 182–195.  
<https://doi.org/10.1039/D2EA00081D>
- Santos, L. F. E. D., Salo, K., Kong, X., Hartmann, M., Sjöblom, J., & Thomson, E. S. (2024). Marine Fuel Regulations and Engine Emissions: Impacts on Physicochemical Properties, Cloud Activity and Emission Factors. *Journal of Geophysical Research: Atmospheres*, 129(5), e2023JD040389. <https://doi.org/10.1029/2023JD040389>
- Sorooshian, A., Alexandrov, M. D., Bell, A. D., Bennett, R., Betito, G., Burton, S. P., Buzanowicz, M. E., Cairns, B., Chemyakin, E. V., Chen, G., Choi, Y., Collister, B. L., Cook, A. L., Corral, A. F., Crosbie, E. C., Van Dienenhoven, B., DiGangi, J. P., Diskin, G. S., Dmitrovic, S., ... Zuidema, P. (2023). Spatially coordinated airborne data and complementary products for aerosol, gas, cloud, and meteorological studies: The NASA ACTIVATE dataset. *Earth System Science Data*, 15(8), 3419–3472. <https://doi.org/10.5194/essd-15-3419-2023>
- Sorooshian, A., Crosbie, E., Maudlin, L. C., Youn, J., Wang, Z., Shingler, T., Ortega, A. M., Hersey, S., & Woods, R. K. (2015). Surface and airborne measurements of organosulfur and methanesulfonate over the western United States and coastal areas. *Journal of Geophysical Research: Atmospheres*, 120(16), 8535–8548. <https://doi.org/10.1002/2015JD023822>
- Spada, N. J., Cheng, X., White, W. H., & Hyslop, N. P. (2018). Decreasing Vanadium Footprint of Bunker Fuel Emissions. *Environmental Science & Technology*, acs.est.8b02942.  
<https://doi.org/10.1021/acs.est.8b02942>

- United States. Army. Corps of Engineers & Institute for Water Resources (U.S.). (2018).  
*Waterborne Tonnage for Principal U.S. Ports and all 50 States and U.S. Territories, The U. S. ports and states data* [Pdf]. US Army Corps of Engineers, Institute for Water Resources.  
<https://usace.contentdm.oclc.org/digital/collection/p16021coll2/id/1492>
- Viana, M., Amato, F., Alastuey, A., Querol, X., Moreno, T., García Dos Santos, S., Herce, M. D., & Fernández-Patier, R. (2009). Chemical Tracers of Particulate Emissions from Commercial Shipping. *Environmental Science & Technology*, 43(19), 7472–7477.  
<https://doi.org/10.1021/es901558t>
- Wang, Z., Sorooshian, A., Prabhakar, G., Coggon, M. M., & Jonsson, H. H. (2014). Impact of emissions from shipping, land, and the ocean on stratocumulus cloud water elemental composition during the 2011 E-PEACE field campaign. *Atmospheric Environment*, 89, 570–580.  
<https://doi.org/10.1016/j.atmosenv.2014.01.020>
- Yu, G., Zhang, Y., Yang, F., He, B., Zhang, C., Zou, Z., Yang, X., Li, N., & Chen, J. (2021). Dynamic Ni/V Ratio in the Ship-Emitted Particles Driven by Multiphase Fuel Oil Regulations in Coastal China. *Environmental Science & Technology*, 55(22), 15031–15039.  
<https://doi.org/10.1021/acs.est.1c02612>
- Yuan, T., Song, H., Wood, R., Wang, C., Oreopoulos, L., Platnick, S. E., Von Hippel, S., Meyer, K., Light, S., & Wilcox, E. (2022). Global reduction in ship-tracks from sulfur regulations for shipping fuel. *Science Advances*, 8(29), eabn7988. <https://doi.org/10.1126/sciadv.abn7988>
- Zetterdahl, M., Moldanová, J., Pei, X., Pathak, R. K., & Demirdjian, B. (2016). Impact of the 0.1% fuel sulfur content limit in SECA on particle and gaseous emissions from marine vessels. *Atmospheric Environment*, 145, 338–345. <https://doi.org/10.1016/j.atmosenv.2016.09.022>
- Zhao, M., Zhang, Y., Ma, W., Fu, Q., Yang, X., Li, C., Zhou, B., Yu, Q., & Chen, L. (2013). Characteristics and ship traffic source identification of air pollutants in China's largest port. *Atmospheric Environment*, 64, 277–286. <https://doi.org/10.1016/j.atmosenv.2012.10.007>