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Key Points:

- Shipping fuel regulations effectively reduced atmospheric vanadium concentrations along the US eastern coast over 15 years of measurements
- Low-sulfur fuel regimes make the V/Ni ratio unreliable for ship plume detection, but vanadium alone might represent a more suitable marker
- Vanadium from ship emissions over the western North Atlantic potentially catalyzes in-cloud and out-of-cloud oxidation reactions

Supporting Information:

Supporting Information may be found in the online version of this article.

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

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Abstract 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 fine particulate matter (PM_{2.5}) enriched in vanadium (V) and nickel (Ni). Near coasts, the International Maritime Organization (IMO) has implemented Sulfur Emission Control Areas where ships must operate on low sulfur marine fuel. In this study, we integrate 15 years of chemically speciated PM_{2.5} 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 V concentrations. We find statistically significant reductions in coastal atmospheric V (80%–89%) after IMO regulation implementation. Reductions in particulate Ni (67%–79%) and sulfate (53%–59%) levels were also observed. While the V/Ni ratio is traditionally used as a 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 V alone represents a stronger tracer. Under a low-sulfur fuel regime, cloud water V concentrations over the northwest Atlantic are an order of magnitude lower than in PM_{2.5} at coastal sites. Vanadium concentrations above the 75th percentile were observed in cloud droplets enriched in non-sea-salt sulfate (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 are a significant source of atmospheric pollution in coastal regions. These emissions contain sulfur oxides and fine particulate matter (PM_{2.5}) enriched with vanadium and nickel, which pose environmental concerns. To mitigate these impacts, the International Maritime Organization established control areas requiring vessels to transition to low-sulfur marine fuels. Our research examined the effectiveness of these regulations by analyzing 15-year data set of PM_{2.5} collected at IMPROVE monitoring sites along the U.S. east coast, and in-cloud measurements from the 2020 to 2022 NASA ACTIVATE flight campaign over the northwest Atlantic. The results demonstrate significant reductions in atmospheric pollutants following regulation implementation. The vanadium-to-nickel ratio, previously used as fingerprint for residual fuel oil combustion, is no longer a reliable marker in the current regulatory environment while vanadium concentration alone serves as a more reliable tracer. Additionally, our analysis indicates that cloud water vanadium concentrations over the northwest Atlantic are approximately an order of magnitude lower than in PM_{2.5} levels at coastal sites. These findings provide compelling evidences of the effectiveness of maritime regulations in reducing atmospheric pollutants and provide insights for future air quality monitoring methodologies in coastal environments.

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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 a 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., 2024; 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 are present 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 mostly of solid fractal soot (Agrawal et al., 2008; Corbin et al., 2018; Petzold et al., 2008). However, it has been observed that ship engine load conditions play a role in shaping the distribution of particles in the nucleation mode. 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 toward 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; 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. Thornton et al. (2017) hypothesized a causal relationship between CCN enhancement and lightning and/or marine convection through aerosol convective invigoration (Koren et al., 2005) over major shipping lanes in tropical regions. Consistent with this hypothesis, perturbations in cloud microphysics, including enhanced cloud droplet number concentrations, reduced cloud drop effective radius, and complex changes in liquid water path, have been observed concurrently with elevated below-cloud sulfate levels from ship exhaust (Christensen & Stephens, 2011; Diamond, 2023; Ferek et al., 2000; Hudson et al., 2000; Noone et al., 2000; Radke et al., 1989; Toll et al., 2017, 2019; Yuan et al., 2023). 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 SO_2 can appportion to 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 a catalyst in the aqueous phase oxidation of 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, the IMO established Sulfur 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 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: (a) 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% and (b) 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 SO_2 (Lehtoranta et al., 2019). Large decreases in SO_2 emissions in port and coastal cities and reduction in shiptrack occurrence in SECA regions have been observed following the implementations of the above-discussed regulations (Anastasopoulos et al., 2021; Gryspeerdt et al., 2019; 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 been reported after the implementation of SECAs (Cheng et al., 2022; Kotchenruther, 2015; Spada et al., 2018). Simultaneously, tests conducted on marine engines showed that the utilization of low-sulfur fuels resulted in the emission of smaller, hydrophobic particles that have a larger critical activation diameter (Santos et al., 2023). It is important to note that while the utilization of exhaust scrubbers with RFO combustion is reliable in decreasing ship exhaust SO_2 , particulate matter and metal emissions are only partially reduced (Lehtoranta et al., 2019; Passig et al., 2021). These studies have provided invaluable insights into the impact of shipping emission regulations on atmospheric perturbations. However, most of them only show data collected up to 3 years after the implementation of IMO 2015, and thus are not representative of the longer-term effect of FSC limit regulations. Nevertheless, direct measurements of cloud water sulfate and vanadium away from land remain scarce, limiting our understanding of the current influence of ship emissions on cloud droplet composition and their impacts on climate-relevant processes.

In this study, we leverage 15 years of chemically speciated $\text{PM}_{2.5}$ data (including SO_4 , $\text{PM}_{2.5}$, vanadium, and nickel) collected at Interagency Monitoring of Protected Visual Environments (IMPROVE) sites on the U.S. east coast, and we integrate them with in-cloud observations from the airborne NASA Aerosol Cloud meteorology Interactions oVer the western ATlantic Experiment (ACTIVATE) field campaign conducted over the northwest Atlantic ocean between 2020 and 2022, to: (a) examine the impact of marine vessel emissions along the U.S. North Atlantic coast and evaluate the potential effect of FSC limits on vanadium concentrations (Section 3.1), and (b) assess spatial distribution and seasonal variations of both airborne and cloud water vanadium within SECA after the implementation of the IMO 2015 (Section 3.2). With this work, we aim to achieve a quantitative understanding of the influence of ship emissions on atmospheric vanadium concentrations and to provide a starting point for more studies to examine vanadium's process-level activity in the study region, such as in catalyzing 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) (Hand, 2023, <http://vista.cira.colostate.edu/improve/>). In this study, we analyze fine particulate concentrations of vanadium (V), sulfate (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 2023. The sites selected are located in the vicinity of commercial ports and at elevations less than ~50 m 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 > ~250 km from commercial ports and at elevations > ~300 m) 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: (a) pre-regulations—data collected over a 4.5-years period between 1 January 2008 and 31 July 2012 prior to implementation of FSC, (b) 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 (FSC < 1.0%), (c) IMO 2015—data collected in the 8-years period between 1 January 2015 and 31 December 2023 after the implementation of the second FSC limit (FSC < 0.1%). In the case of fine particulate vanadium and nickel concentrations, datapoints below the minimum detection limit (MDL) were included in our analysis to avoid introducing bias that could result from their exclusion and to highlight that after the

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.	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
Inland Sites	Everglades (FL)	EVER	25.39 N, 80.68 W	1 m	60 km from Port of Miami (50 km from Port of Everglades)
	Dolly Sods Wilderness (WV)	DOSO	39.11 N, −79.43 W	1,182 m	250 km from Port of Baltimore
	Shenandoah (VA)	SHEN	38.52 N, 78.43 W	1,079 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	1,617 m	400 km from Port of Charleston and Savannah

Note. Distances are calculated as straight-line-distance.

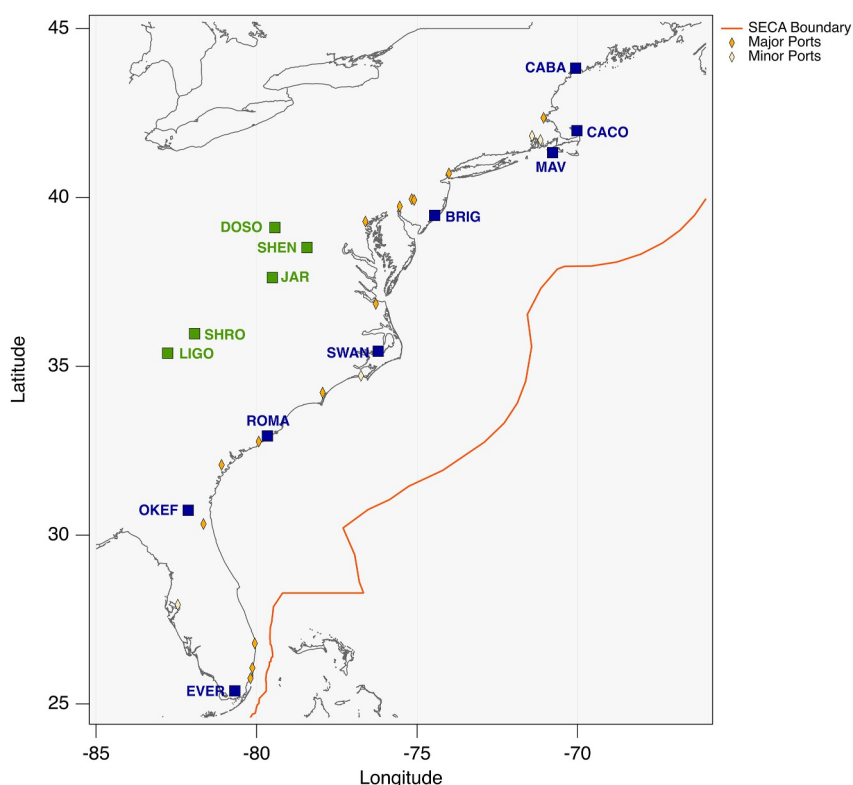


Figure 1. Map of coastal and inland IMPROVE sites (blue and green squares, respectively), major and minor U.S. commercial ports, and the Sulfur Emission Control Area (SECA) boundary.

implementation of IMO 2012 and IMO 2015, the percentage of datapoints below the MDL substantially increases. The percentages of datapoints below the MDL at each IMPROVE site associated with the implementation of IMO regulations are shown in Table S1 of Supporting Information S1. 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 $PM_{2.5}$ over the three periods of time analyzed.

2.1.1. Supporting Data Sets for IMPROVE Study

In order to identify any potential confounding effect of changes in 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). We analyzed individual ports throughout 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, 2023) sulfur dioxide 2023 emissions reduction 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 aerosols, clouds, and meteorology over the western North Atlantic Ocean (Sorooshian et al., 2025). 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's methodology and instrumentation 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 Section 3.2 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) (greater than 60% collection efficiency for cloud droplets with diameter $>20\text{ }\mu\text{m}$) (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 the 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 (NO_3^-), and sulfate (SO_4^{2-}), as well as cations including sodium (Na^+), and calcium (Ca^{2+});
- inductively coupled plasma mass spectroscopy (ICP-MS) for detecting aqueous mass concentrations of several trace metals including vanadium;
- pH analysis.

Samples contained variable volumes of cloud water due to different 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 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 $3\text{--}1,465\text{ }\mu\text{m}$ diameter. Nss-SO_4^{2-} concentrations were calculated following AzadiAghdam et al. (2019), where bulk SO_4^{2-} concentrations were corrected for sea salt contributions using measured sea salt sodium concentrations and the established mass ratio of 0.253 for $\text{SO}_4^{2-}:\text{Na}^+$ in sea salt.

3. Results and Discussion

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 and at five inland IMPROVE sites pre- and post-low-sulfur marine fuel regulations. The coastal 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 ($\sim 30\text{ km}$) and CABA the farthest ($\sim 180\text{ km}$). In a previous study, Agrawal et al. (2009) found that the concentration of fine particulates V and Ni at monitoring stations throughout southern California decreased 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 ~ 1.81 and $\sim 0.67\text{ ng m}^{-3}$ for V and Ni, respectively) observed at three IMPROVE sites (ROMA, EVER, and BRIG) located $< \sim 80\text{ km}$ from major commercial ports, and the lowest (as low as 0.94 and $\sim 0.37\text{ ng m}^{-3}$ for V and Ni, respectively) at SWAN and CABA, which are situated $> \sim 150\text{ km}$ from the closest major commercial port. The lower mean V concentration observed at OKEF (0.92 and $\sim 0.31\text{ ng m}^{-3}$ 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 ($\sim 30\text{ km}$), therefore supporting the hypothesis of stronger ship emission influences on coastal sites than in inland

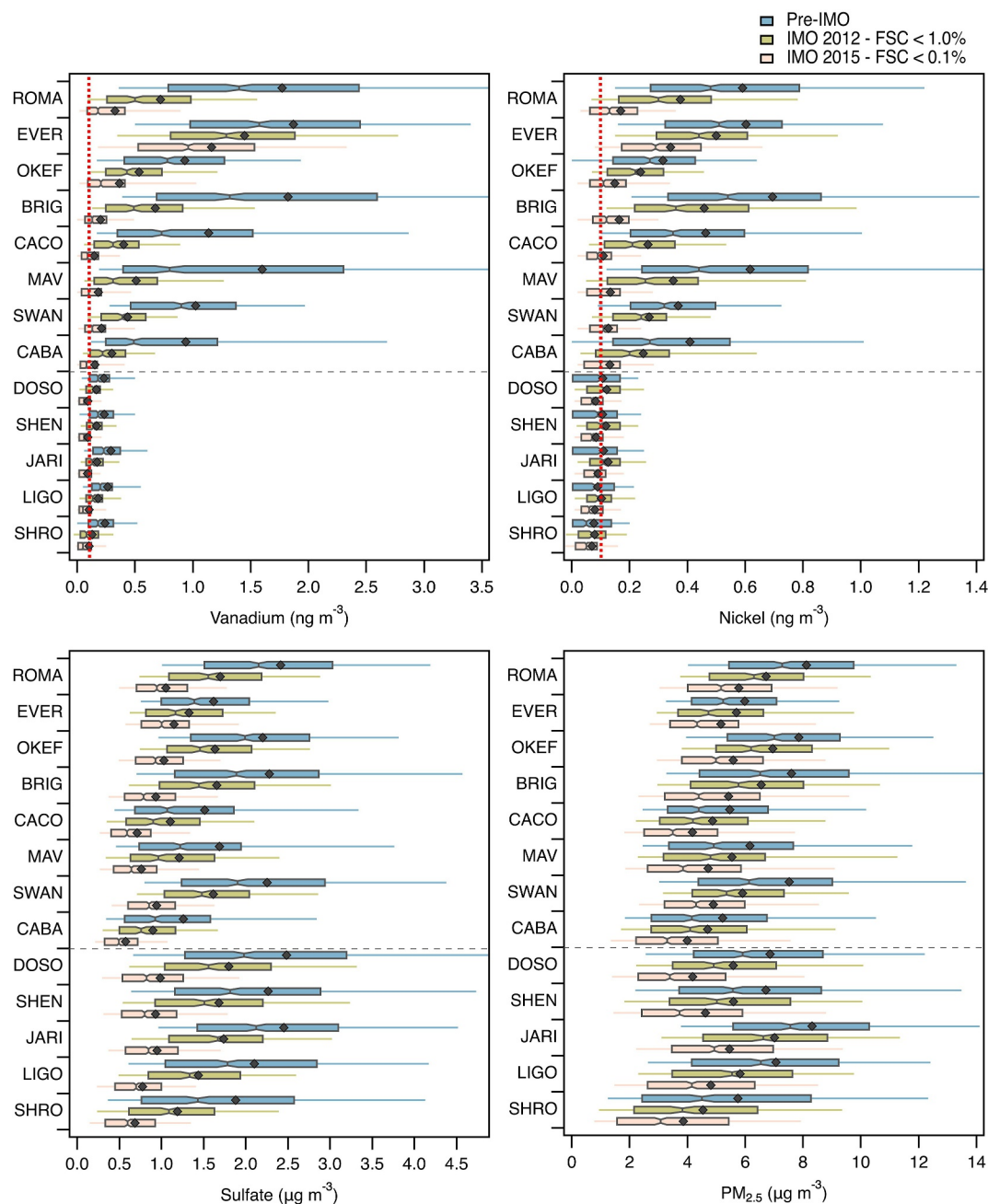


Figure 2. Box and whisker plots (central notch indicating the median, left box edge at 25%, right box edge at 75%, whisker left at 10%, and whisker right at 90%) and mean concentrations (black markers) of fine particulate vanadium, nickel, and sulfate, and $PM_{2.5}$ at coastal and inland IMPROVE sites pre-regulation (blue), and after the implementation of IMO 2012 (green) and 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). The black dashed line separates coastal (above) from inland (below) sites, while red dashed lines indicate the minimum detection limits for vanadium and nickel (MDL for sulfate and $PM_{2.5}$ were not included because their MDLs varied over the sampling periods).

cities. Interestingly, we found mean V and Ni concentrations (1.68 and ~ 0.61 $ng\ m^{-3}$ 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 concentrations. While local circulation patterns and wind direction likely influence the transport of ship emissions to the monitoring sites,

detailed meteorological analysis is beyond the scope of this study. At inland locations, mean V and Ni concentrations were overall ~5-fold lower than what was observed at the coastal IMPROVE sites. Furthermore, it is important to note that during the pre-IMO period analyzed here, between 12% and 18% of the V samples, and between 41% and 54% of the Ni samples collected at the inland sites, were below MDL (vs. <4% and <17% of the V and Ni samples, respectively, at the coastal sites) (Table S1 in Supporting Information S1), highlighting the impact of RFO combustion on V and Ni concentrations in the coastal environment.

In the case of fine particulate sulfate concentrations and $PM_{2.5}$, no clear trend between mean concentrations and distance from major commercial ports is observed. Particulate sulfate SO_4^{2-} and $PM_{2.5}$ mean concentrations varied across locations but no difference was observed comparing coastal and inland IMPROVE sites: SO_4^{2-} mean concentration ranged from 1.26 to 2.41 $ng\ m^{-3}$ at coastal sites and from 1.82 to 2.48 $ng\ m^{-3}$ at inland sites; $PM_{2.5}$ mean concentration included ranged from 5.22 to 8.12 $ng\ m^{-3}$ at coastal sites and from 5.74 to 8.31 $ng\ m^{-3}$ at inland sites. Indeed, while pre-regulation atmospheric concentrations of V in coastal areas are predominantly due to exhaust emissions from shipping, atmospheric sulfate and $PM_{2.5}$ originate from a wider array of sources, including industrial activities and coal-related operations, thus making the relative contribution from ship emissions comparatively minor.

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 coastal IMPROVE sites presented in this study (Figure 3). Changes in $PM_{2.5}$ concentrations were lower and statistically significant at all eight locations only after the implementation of IMO 2015, while following the implementation of IMO 2012, $PM_{2.5}$ reductions at EVER, CACO, MAV, and CABA were not significant. Inland IMPROVE sites showed similar trends to those at coastal locations only for particulate vanadium, sulfate, and $PM_{2.5}$. In contrast, for Ni, we observed a statistically significant increase after IMO 2012 (not statistically significant at SHRO) and subsequent reductions after IMO 2015 likely related to the implementation of regulations that did not directly target Ni but indirectly reduced its emissions.

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 coastal sites (vs. reductions between <45% and up to 69% between the 4.5-year period pre-regulation and the 8-year period after the implementation of IMO 2015, at the inland locations) 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 coastal 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 south eastern coast of Florida and the consequent arrival of shipping exhaust from outside SECAs (Figure 1). Consistent with our observations, Zhang et al. (2021) found through modeling studies that southern Florida experiences substantial ship emissions impacts from the Caribbean region, where vessels operate outside SECA regulations. Additionally, a previous study has shown that $PM_{2.5}$ 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 (a) farther inland compared to the other sites, and (b) approximately 65 km from the Seminole coal power plant.

Following IMO 2012 and IMO 2015, in January 2020, IMO implemented a new regulation (hereafter referred to as IMO 2020) imposing an FSC limit for vessels outside SECAs to be at or below 0.5%. To test the hypothesis of a possible residual Caribbean impact on EVER and OKEF, we divided the IMO 2015 data set into two time periods: (a) pre-IMO 2020 (01/01/2015 to 12/31/2019), and (b) post-IMO 2020 (01/01/2020 to 12/31/2020). Supporting our hypothesis of a possible residual Caribbean impact on EVER and OKEF, we observed that after the implementation of IMO 2020, mean V concentrations at EVER and OKEF were, respectively, 1.6- and 1.5-fold lower, while no changes were found at the other coastal sites (Figure S1 in Supporting Information S1). Mean Ni

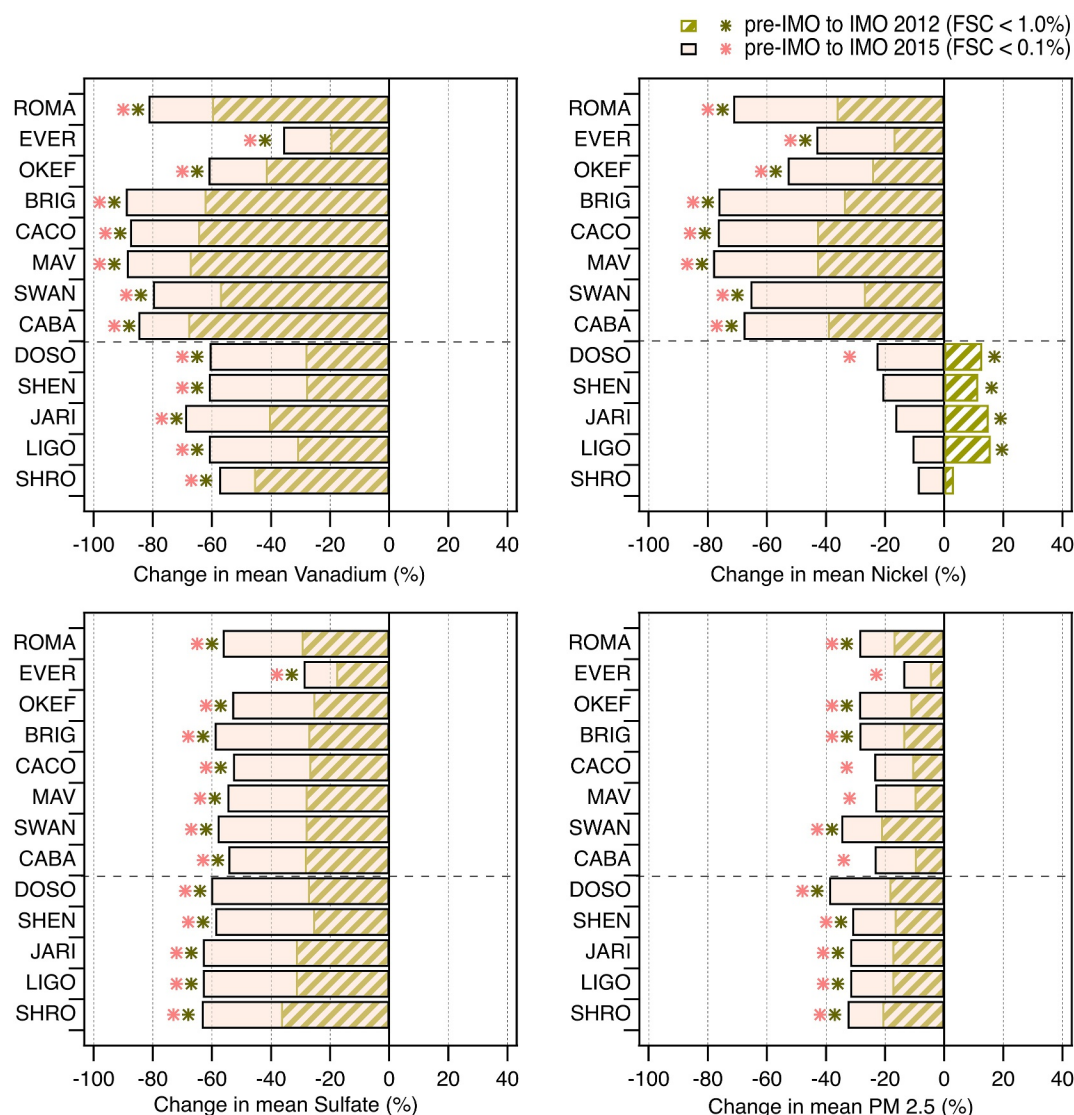


Figure 3. Changes in mean concentrations of fine particulate vanadium, nickel, and sulfate, and PM_{2.5} at coastal and inland IMPROVE sites between the 5-year period pre-regulation and the 2.5-year period after the implementation of IMO 2012 (green lines), and the 5-year period pre-regulation and the 8-year period after the implementation of IMO 2015 (pink). Asterisks indicate statistically significant changes in mean concentrations. 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). The black dashed line separates coastal (above) from inland (below) sites.

concentrations were only 1.3- and 1.2-fold lower at EVER and OKEF, respectively, in the post-IMO 2020 period and remained similar to the pre-IMO 2020 at the other coastal sites.

It is worth noting that after the implementation of IMO 2015, mean V levels at coastal locations (excluding EVER and OKEF) were still ~2.1-fold higher than those at inland sites. In comparison, mean Ni concentrations were only ~1.7-fold higher at the coastal IMPROVE sites. These results underscore the pervasive influence of vanadium, and to a lesser extent nickel, from shipping exhaust on coastal locations, even after the implementation of IMO regulations.

Reductions in particulate sulfate between the pre-regulation period and the IMO 2015 period were similar at all the sites (between 53% and 59% at coastal sites, and between 59% and 63% at inland sites) with the exception of EVER (30%). At coastal locations, 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 the 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 concentrations 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 potential importance of vanadium alone as a tracer for ship emissions. Our hypothesis is consistent with SO₂ emissions trend data from the Clean Air Markets Program Data (CAMPD) that show a larger decrease in mean SO₂ 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 (Figure S3 in Supporting Information S1).

Changes in PM_{2.5} levels between the pre-regulation and the IMO 2015 implementation periods were <34% at coastal locations and <39% at inland sites, and were statistically significant at all sites. However, lower mean PM_{2.5} reductions (<20%) were observed after the implementation of IMO 2012, and no statistically significant reductions were observed at EVER, CACO, MAV, and CABA. 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_{2.5} might be related to background PM_{2.5}. For example, Viana et al. (2009) found that in Europe, although the PM_{2.5} increase due to ship emissions is small, the relative contribution is large because of low PM_{2.5} background levels, while the opposite trend was observed in China. The lack of a statistically significant decrease in PM_{2.5} observed in this study might be due to elevated PM_{2.5} background levels due to plentiful sources of PM_{2.5} in the study region, which make the impact of regulations less noticeable (Anastasopoulos et al., 2021; Jang et al., 2023).

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 in shipping activities on the impact of the regulations (Figure S2 in Supporting Information S1).

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., 2024; 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 μm, <2.5 μm, and <10 μm) 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 PM_{2.5} and PM₁₀ 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 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 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 and 1.9 in coastal areas influenced by Ni-enriched emissions from stainless steel plants. We find that the ratio values decrease with increasing distance from the ports, with the

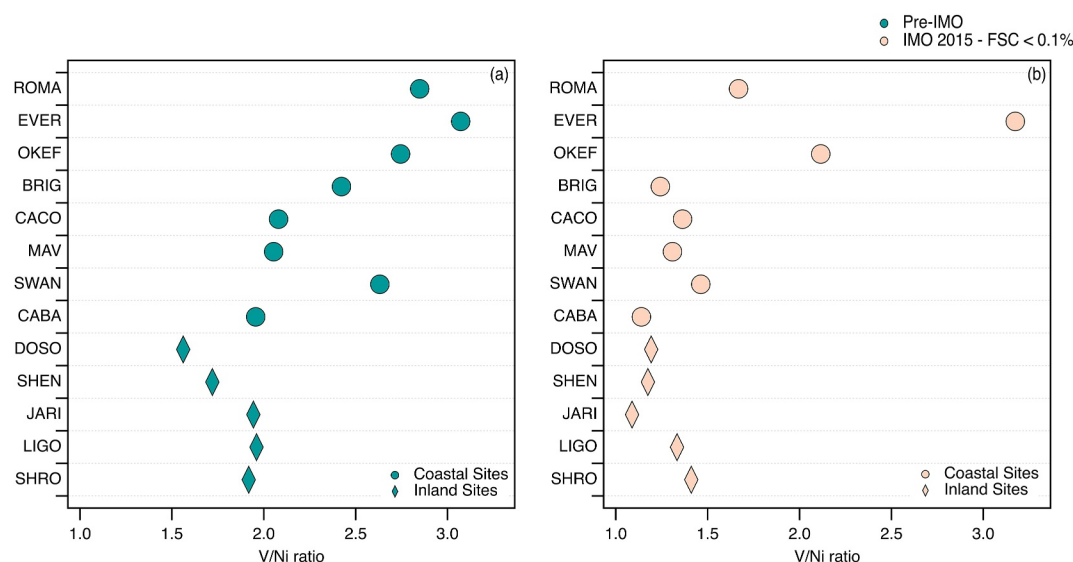


Figure 4. Median V/Ni ratios at coastal (circle) and inland (diamond) IMPROVE sites pre-regulation (blue) and after the implementation of IMO 2015 (pink). Coastal sites are displayed in order of distance from the closest major commercial port, with ROMA being the site located closest to a U.S. major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

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 ~80 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 2006–2009 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 were similar to those observed inland. However, median V/Ni values at the 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).

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 data sets, we show the spatial distribution of cloud water vanadium concentrations over the western North Atlantic Ocean (Figure 5). Measurements were made without targeting specific ship plumes, so samples reflect the area in and around major U.S. east coast shipping routes. 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 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 (Figure 6). Indeed, although particles emitted by ships have an important role in cloud formation, it is likely that not all of

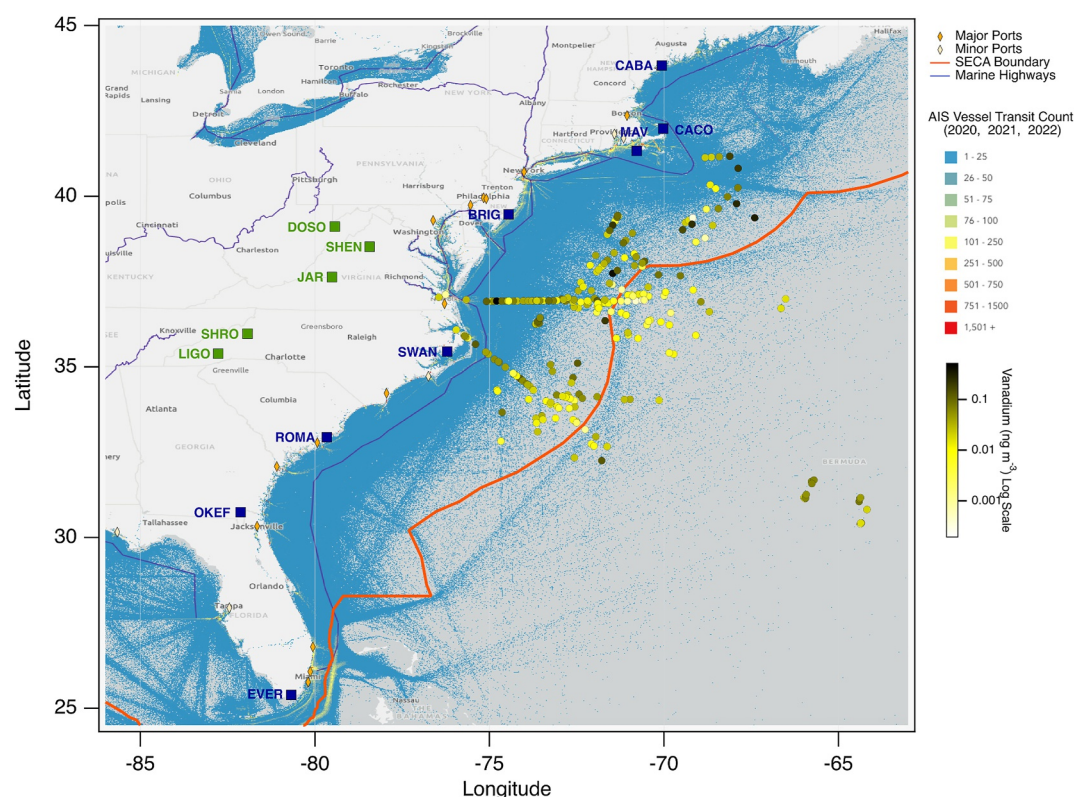


Figure 5. Map of spatial distribution of air equivalent mass concentrations of vanadium in cloud water over the western North Atlantic Ocean during ACTIVATE (yellow dots), major and minor U.S. east coast ports (diamonds), SECA boundary (red line), and marine highways (blue lines). Vessel transit counts for the years 2020, 2021, and 2022 from the Automatic Identification System (AIS) Marine Cadastre (<https://marinecadastre.gov/data/>) are summarized at a 100-m by 100-m geographic area with a single transit counted each time a vessel track passes through, starts, or stops within a 100-m grid.

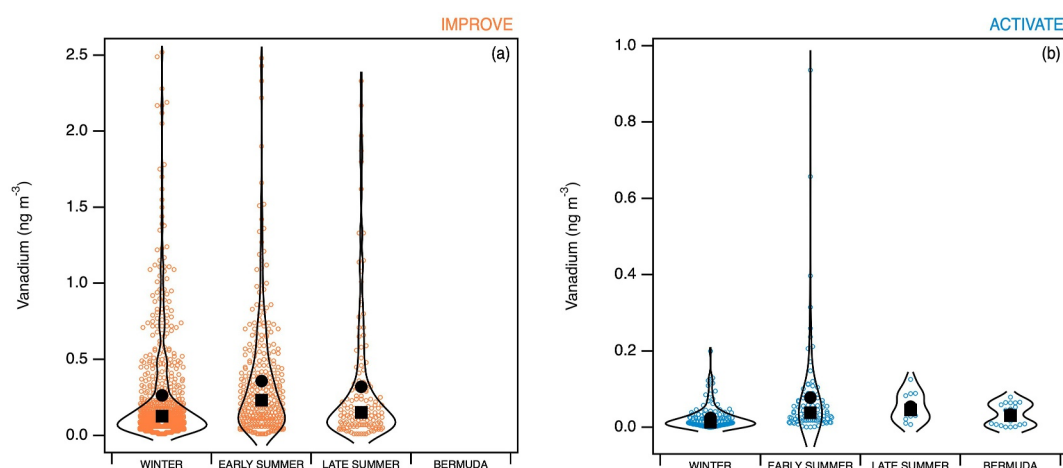


Figure 6. Violin plots, mean (circle), and median (square) of (a) atmospheric concentrations of V at coastal IMPROVE sites in winter (January–March 2020, 2021, and 2022), early summer (May and June 2020, 2021, and 2022), and late summer (August and September 2020); and (b) air equivalent mass concentrations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

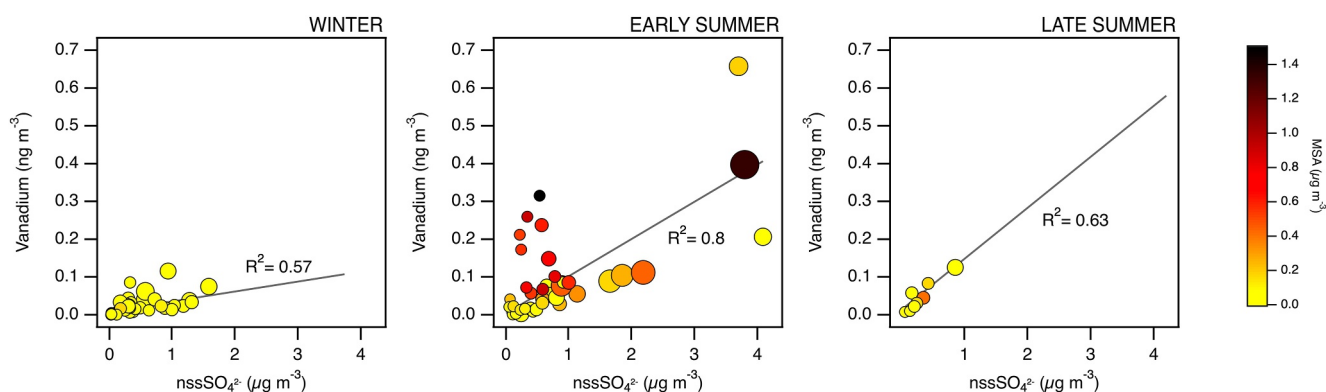


Figure 7. Scatterplots of air equivalent mass concentrations of in-cloud vanadium versus nssSO_4^{2-} over the western North Atlantic Ocean during ACTIVATE. Markers are colored as a function of air equivalent mass concentrations of MSA, while marker sizes are proportional to the air equivalent mass concentrations of nitrate.

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 have been reported in the free troposphere at altitudes up to 13 km (Abou-Ghanem et al., 2024). In another study, Corbin et al. (2018) observed that during fuel combustion, vanadium can become incorporated into insoluble soot particles which have low hygroscopicity, 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 $\text{PM}_{2.5}$ 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 (Figure 6), likely due to a shallower and more stable 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 were observed. 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 a 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 data sets 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 (Figures S2 and S4 in Supporting Information S1).

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 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, enhanced summer-time levels 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 (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) (Figure 7). Importantly, we found that in the early summer, mass concentrations of vanadium above the 75th percentile occur in cloud droplets enriched either in nssSO_4^{2-} and NO_3^- likely from anthropogenic sources (Figure 7), or in MSA at lower altitudes (<800 m) (Figure 8). These results underscore the potential 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. While this catalytic effect cannot unambiguously be shown with this data set, the results motivate future work to investigate this more deeply.

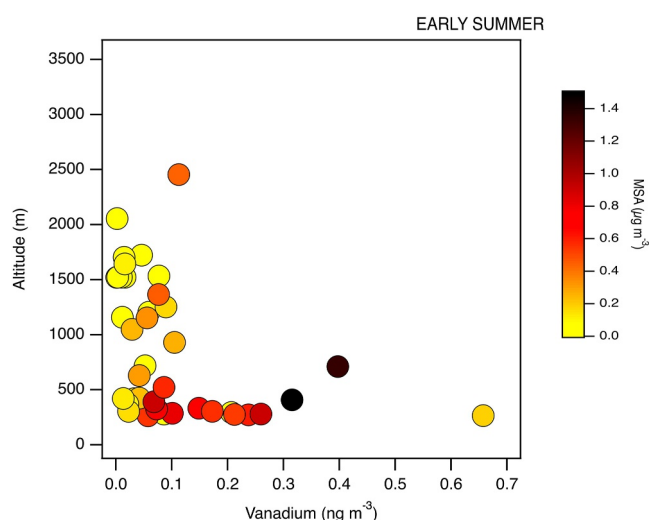


Figure 8. Vertical distribution of air equivalent mass concentrations of in-cloud vanadium over the western North Atlantic Ocean during early summer. Markers are colored as a function of MSA air equivalent mass concentration.

4. 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 provide 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 are 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 found distinctive V/Ni values consistent with previous literature focused on RFO combustions, while after the implementation 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 might represent a stronger tracer for ship emissions and V/Ni should only be used for marine engines operating on RFO. Future work is warranted for other regions to determine how reliable these various tracer species are for shipping emissions after IMO regulations began.

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 those 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 75th percentile correlated well with cloud water enriched in nssSO_4^{2-} and 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.

Conflict of Interest

The authors declare no conflicts of interest relevant to this study.

Availability Statement

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>). The Interagency Monitoring of Protected Visual Environments (IMPROVE) data sets are archived at the Federal Land Manager Environmental database (<https://views.cira.colostate.edu/fed/Pub/DatasetDetail.aspx?dssl=1&dsidse=10001>). 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>).

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