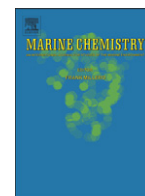


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Vanadium speciation and cycling in coastal waters

Deli Wang^{a,*}, Sergio A. Sañudo Wilhelmy^b^a State Key Laboratory of Marine Environmental Science, Xiamen University, 422 Siming Nanlu, Xiamen, 361005, China^b Department of Biological Sciences and Department of Earth Sciences, University of Southern California, Los Angeles, CA, 90089, USA

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ABSTRACT

Different chemical species of dissolved vanadium, V (IV) and V (V), were measured in the water column of the Long Island Sound (LIS), from the East River to the Atlantic boundary during spring and summer conditions. Our preliminary results showed seasonal and spatial changes in total dissolved V and its redox speciation along LIS. Levels of both V species were high in summer (V (IV), 2.2 ± 1.7 nM; V (V), 22.4 ± 3.9 nM), and low in spring (V (IV), 1.4 ± 1.4 nM; V (V), 11.1 ± 2.6 nM). A V-salinity mixing plot suggests a non-conservative behavior of total dissolved V (and V (IV)) during estuarine mixing.

Dissolved V (IV) occurred mostly in western LIS, accounting for 15–25% of the total dissolved V pool in summer hypoxic bottom waters of that region. In spring, V (IV) accounted for up to 40% of the total dissolved V pool in western LIS, likely from sewage inputs. Dissolved V (IV) was also measured near the Quinnipiac, Housatonic and Connecticut rivers (accounting for 10–20% of the total dissolved in summer), suggesting a local source of the reduced V (likely desorption from surficial sediments and resuspended particles). A positive trend between V (IV) and large size phytoplankton biomass suggests that levels of reduced V may be influenced by biological activity.

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1. Introduction

Vanadium is an essential element for many marine phytoplankton species (Moore et al., 1996), macroalgae (Patrick, 1978; Nalewajko et al., 1995), and other organisms (e.g., Taylor et al., 1997). Many enzymes contain V as their metal center in the active site, such as haloperoxidases (Butler and Carter-Franklin, 2004), nitrate reductases (Antipov et al., 1999), and nitrogenases (Robson et al., 1986; Rehder, 2000). Vanadium may also be involved in many metabolic processes such as chlorophyll synthesis (Meisch et al., 1977; Wilhelm and Wild, 1984), cell division (Meisch and Benzschawel, 1978), phosphate uptake kinetics (Lee, 1982), sulfoxidation (Andersson et al., 1997; ten Brink et al., 2001), cell motility and photosynthesis (Meisch and Becker, 1981; Gilmore et al., 1985). While V (V) is the thermodynamically stable form in oxygenated seawater, V (IV) commonly exists in intra-cellular media (Cantley and Aisen, 1979; Rubinson, 1981; Chasteen et al., 1986; Willsky, 1990). V (IV) ions, such as VO^{2+} , are generally internalized into the cytoplasm through passive diffusion (Yang et al., 2003), and biological uptake of V (IV) is more rapid than that of V (V) (Willsky et al., 1984). Once inside the cell, V (IV) is actively involved in phytoplankton metabolism and has a high reactivity with ADP, ATP, GDP, glutathione, amino acids, nucleic acids and lipids (e.g., Stern et al., 1993; Goc, 2006).

Vanadium is relatively abundant in open ocean waters (34–45 nM in oxygenated seawater) with a relatively conservative distribution

(Collier, 1984; Jeandel et al., 1987). Non-conservative behavior of V, however, is also quite common in coastal waters (e.g., Shiller and Mao, 1999; Auger et al., 1999), which has been attributed to ion exchange and deposition of particles (Paulsen and List, 1997), and/or scavenging by terrigenous and/or biogenic materials (e.g., Prange and Kremling, 1985; Yeats, 1992), ferric oxyhydroxide particles (e.g., Auger et al., 1999), manganese oxides (Takematsu et al., 1985), sedimentary and fluvial input (Shaw et al., 1990; Shiller and Mao, 1999), and possible V-redox changes and associated adsorption/desorption mechanisms (van der Sloot et al., 1985; Shiller and Mao, 1999).

Dissolved V generally exists in natural waters in two oxidation states, as V (IV) and V (V) (e.g., Wehrli and Stumm, 1989; Hirayama et al., 1992; Wang and Sañudo-Wilhelmy, 2008). The speciation of V may likely depend on redox conditions of the aqueous system (Taylor and van Staden, 1994; Elbaz-Poulichet et al., 1997; Giammanco et al., 1998; Pettersson et al., 2003). Different redox pairs such as $\text{NO}_3^-/\text{NH}_4^+$, $\text{Fe}^{3+}/\text{Fe}^{2+}$, $\text{MnO}_2/\text{Mn}^{2+}$, and $\text{SO}_4^{2-}/\text{H}_2\text{S}$ may potentially play an important role in V speciation and cycling in the water column. Thermodynamically, V (V) is stable in oxidized marine environments, while V (IV) is stable in moderately reducing environments (Sadiq, 1988). Both species have, however, been detected in natural waters (e.g., Hirayama et al., 1992; Bosque-Sendra et al., 1998; Wuilloud et al., 2001; Veschetti et al., 2007; Wang and Sañudo-Wilhelmy, 2008). In general, the solubility of V decreases with decreasing valence, and therefore V (IV) increases proportionally with decreasing total dissolved V pool as the environment becomes progressively more reducing (e.g., Sadiq, 1988). For example, compared to the Atlantic Ocean, dissolved V concentrations are depleted (by ~60%) in reducing

* Corresponding author. Tel.: +86 592 2182682; fax: +86 592 2184101.
E-mail address: deliwang@xmu.edu.cn (D. Wang).

deep waters of the Black Sea and the Cariaco Basin suggesting that reducing sediments may serve as a major sink for this element (e.g., Emerson and Husted, 1991; Nameroff et al., 2002).

While V concentrations in sediment cores are widely used as a geochemical proxy of anoxic events (e.g., Nijenhuis et al., 1998; Algeo and Maynard, 2004), it is unclear how V speciation is affected by water column redox changes, biological activity, and the concentrations of other trace metals that could act as potential reducers or oxidizers. In order to address some of those questions, a field study was conducted in the Long Island Sound (LIS). The LIS was chosen because periodic bottom water hypoxia and even anoxic events that could influence the redox chemistry of V have been observed in some portions of the LIS under summer conditions (Parker and O'Reilly, 1991). In this study, we applied the new method developed by Wang and Sañudo-Wilhelmy (2008) to establish the seasonal and spatial distributions of dissolved V (V) and V (IV) within LIS, and to further explore the potential mechanisms affecting the cycling of this trace element in coastal waters.

2. Materials and methods

Two cruises (April and September of 2005) were conducted across LIS from the East River in western LIS to the eastern part of the Sound adjacent to the Atlantic Ocean (Fig. 1). Spring and summer are seasonal extremes that reflect a wide range of environmental conditions within the LIS water column (high versus low river flows, water column stratification, oxic versus hypoxic conditions) (Parker and O'Reilly, 1991; Buck et al., 2005; Gobler et al., 2006). The April cruise was characterized by high river discharge and low water column temperature (water flux of Connecticut's rivers: 27 m³/s; water temperature: 6–10 °C; salinity: 21–29); while the September cruise took place under low river discharge and high water temperature (water flux of Connecticut's rivers: 3.4 m³/s; water temperature: 20–24 °C; salinity: 25–30).

Samples were collected using a peristaltic pump equipped with trace metal clean Teflon tubing attached to 10 m-long boom at two layers: surface (~2 m below surface), and bottom waters (~2 m above bottom). Dissolved samples were obtained by filtration through a trace metal clean polypropylene capsule filter (0.2 µm). Water temperature, salinity, pH and DO were measured at each location using a Seabird-19 CTD. Size-fractionated chlorophyll a (Chl-a) was analyzed by standard fluorimetric methods (Welschmeyer, 1994). Dissolved Fe was preconcentrated following the APDC/DDDC organic extraction technique (Bruland et al., 1985), and quantified by ICP-MS (ThermoFinnigan Element 2) using Indium as an internal standard (recoveries >95%).

All materials associated with the sampling, handling, and storage of seawater were acid-washed using established cleaning protocols

(e.g., Flegal et al., 1991; Breuer et al., 1999). The separation of different dissolved V species was carried out immediately after sample collection using the method of Wang and Sañudo-Wilhelmy (2008). The method includes a Chelex 100 resin solid-phase extraction of both V species from seawater at pH=4.5, elution with a base [for V (V)] and with an acid [for V (IV)], and subsequent quantification by graphite furnace atomic absorption spectrometry. All of the speciation V (IV) and V (V) samples were stored at –10 °C, and quantified via GF-AAS in the laboratory. The analytical precision was ~10% in the concentration range of 10 nM. Certified reference seawater CASS-4 was analyzed for total dissolved V with a recovery efficiency of >90%.

3. Results and discussion

3.1. Seasonal and spatial changes in vanadium speciation

Total dissolved V concentrations were significantly higher in summer (average: 25 ± 4.0 nM) than in spring (average: 13 ± 2.4 nM) (Fig. 2). These summer average concentrations of dissolved V were consistent with those reported for the Gulf of St. Lawrence (24 nM; Yeats, 1992), the Po-Adriatic mixing area (summer, 24 nM; Pettine et al., 1997), and the Sargasso Sea (summer, ~24 nM; Weisel et al., 1984).

Lower levels of dissolved V measured in the spring cruise were likely caused by high freshwater discharge from the Connecticut rivers (e.g., the Quinnipiac and Housatonic). Relatively high total V concentrations measured in the summer cruise near the East River and some Connecticut rivers (especially the Quinnipiac and Housatonic) (Fig. 2) indicated that there were some potential sources of dissolved V nearby such as sewage effluents (Wolfe et al., 1991; Balcom et al., 2004), and sedimentary releases (e.g., Aller, 1994; Mccray et al., 2000; Audry et al., 2006; Santos-Echeandia et al., 2009) under suboxic conditions. Slight differences in total V were observed among stations, but no consistent trend was observed for all stations (Fig. 2).

Higher levels of dissolved V under summer conditions have also been reported in other systems, e.g., Tokyo Bay and Shimizu Port (Sato and Okabe, 1978, 1982), Biwa Lake (Sugiyama, 1989), and Florida Bay (Caccia and Millero, 2003). Although the process(es) controlling seasonal changes in total dissolved V concentrations are still unknown, Harita et al. (2005) hypothesized that high levels of dissolved V in summer may result from the release from sediments and suspended particles due to increased biological activity. Santos-Echeandia et al. (2009) reported that the flux of dissolved V from surficial sediments may be very high during summer. Laboratory experiments suggest that water-particle interaction often results in the non-conservative behavior of dissolved V (Paulsen and List, 1997).

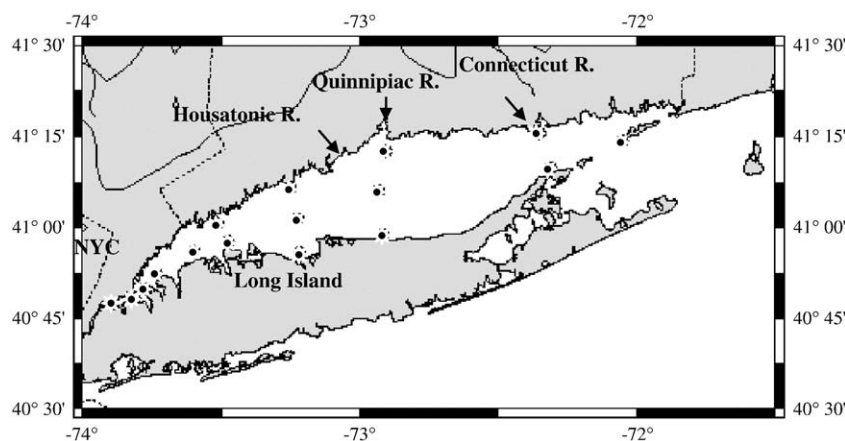


Fig. 1. Sampling stations in Long Island Sound.

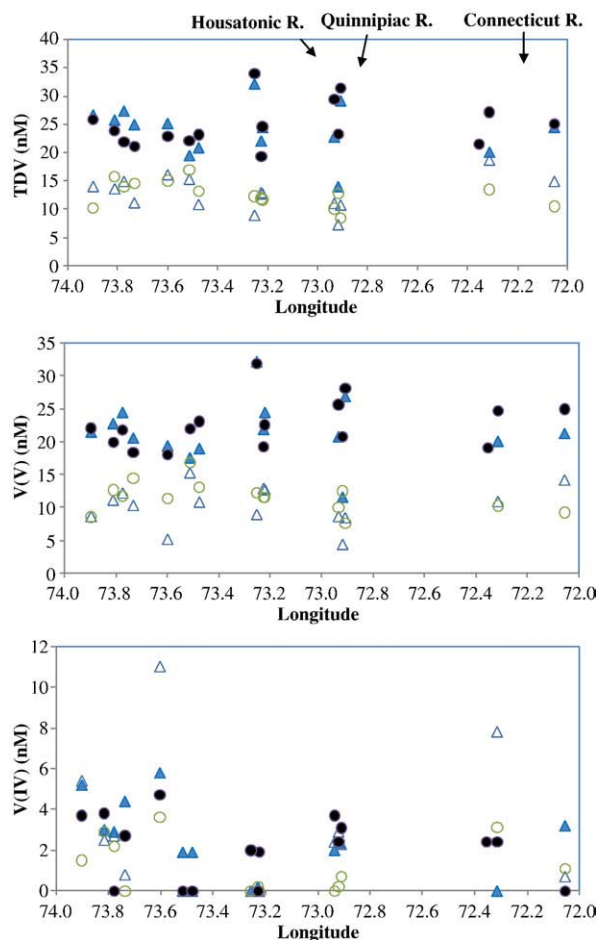


Fig. 2. Total dissolved vanadium (TDV), dissolved V(V) and V(IV) during spring and summer cruises (triangle and circle symbols represent surface and deep layers respectively; open and filled symbols denote spring and summer cruises respectively).

In summary, low levels of dissolved V measured in the LIS in spring may result largely from dilution due to increased freshwater input, and to some extent, from adsorption by suspended particles and organic materials in April, while desorption from particles and sediments under high temperature in September likely contributed

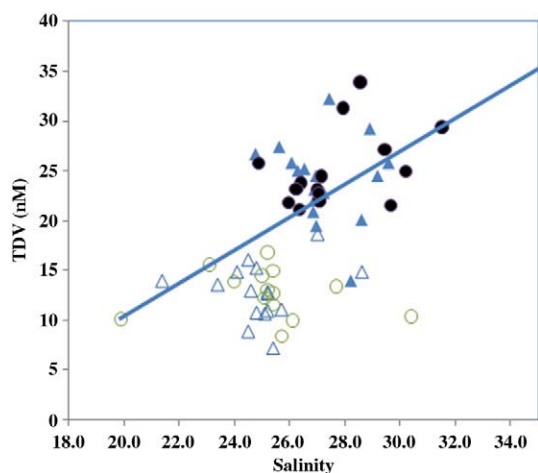


Fig. 3. Total dissolved vanadium (TDV) versus salinity in LIS. The solid line indicates expected trend for conservative mixing between Atlantic Ocean (35 nM at salinity of 35, Collier, 1984) and average river water (10 nM at salinity of 20) (triangle and circle symbols represent surface and deep layers respectively; open and filled symbols denote spring and summer cruises respectively).

to the relatively high levels of dissolved V in the Sound. Similar mechanisms have been invoked to explain temporal gradients in V concentrations in other systems (e.g., Francois, 1988; Mccray et al., 2000; Harita et al., 2005).

3.2. Non-conservative behavior of vanadium in coastal waters

Dissolved V generally behaves as a conservative component in open ocean waters (e.g., Morris, 1975; Jeandel et al., 1987). However, biological uptake or particle scavenging also occurs, albeit with a slight depletion in surface waters (Collier, 1984; Middelburg et al., 1988). Non-conservative behavior was commonly found in coastal waters, including the Louisiana Shelf (Shiller and Mao, 1999), English Channel (Auger et al., 1999) and Florida Bay (Caccia and Millero, 2003). Consistent with those studies, the V-salinity mixing plot suggests non-conservative behavior of total dissolved V in the LIS, when using the lowest salinity point in the LIS (10 nM at salinity of 20) and Atlantic Ocean (~35 nM; Collier, 1984) concentrations as end-members (Fig. 3).

Dissolved V (V) was also higher in summer (22.3 ± 3.9 nM) than in spring (11.0 ± 2.0 nM) (Fig. 2). Reduced V (IV) was measured in western LIS (Fig. 2) in both cruises (spring surface: 2.9 ± 1.9 nM; bottom: 2.0 ± 1.4 nM; summer surface: 4.3 ± 1.3 nM; bottom: 3.0 ± 1.8 nM). High levels of V (IV) were also detected near the East, Quinnipiac, Housatonic and Connecticut rivers (spring: 2.0 ± 2.0 nM; summer: 2.3 ± 1.3 nM), while levels of V (IV) were much lower in all other regions of the Sound. High levels of V (IV) may be attributed to several different sources, such as inputs from sewage and fluvial discharges (IPCS, 1988; ATSDR, 1992; Greig and Pereira, 1993; Caccia and Millero, 2003), sedimentary releases

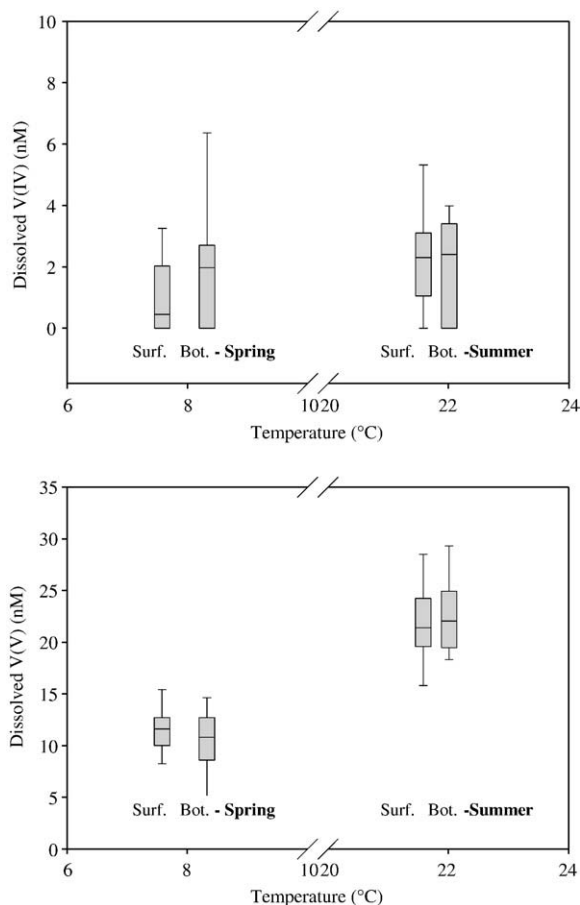


Fig. 4. Dissolved V(IV) and V(V) versus average water temperature in surface and bottom layers during spring and summer cruises.

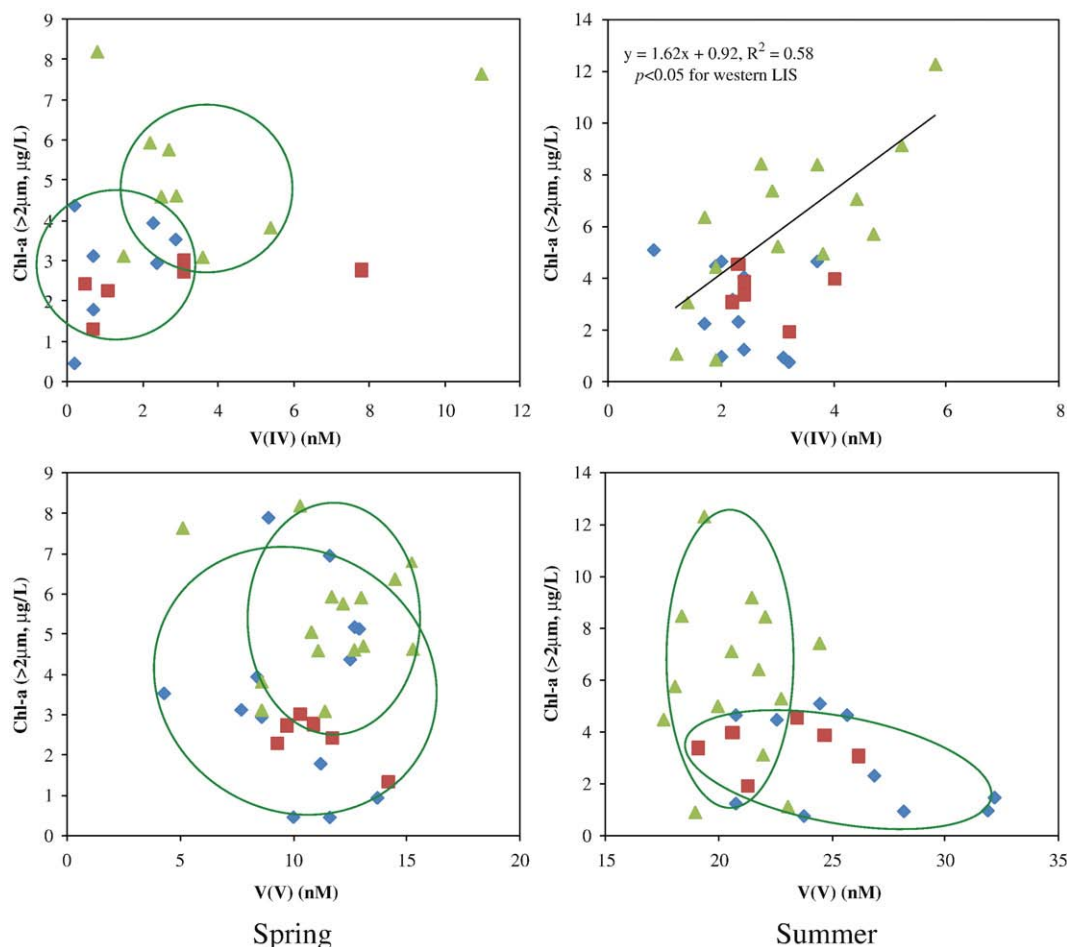


Fig. 5. Relationship between V(IV and V) and large size fraction chlorophyll a in LIS in spring and summer (■ Eastern LIS; ◆ Central LIS; ▲ Western LIS).

(e.g., Ouddane et al., 2004; Audry et al., 2006), and V (V) reduction in moderate reducing environments (Sadiq, 1988).

No consistent patterns in V speciation were found between surface and bottom waters of the LIS (Figs. 2–4), despite the fact that different sources may affect different parcels of water. Surface waters may receive V from river inflow and atmospheric fallout (rain water and airborne particles), while bottom waters may be influenced by sedimentary sources. On the other hand, particle scavenging, biogenic adsorption and uptake are assumed to be the major removal affecting V species in the whole water column. However, to some extent, the lack of surface and bottom water differences is consistent with the conservative behavior of this element reported for open ocean waters (Morris, 1975; Collier, 1984). This suggests that, once formed, reduced V species (likely as organic complexes) may remain for a long time in the water column, even during subsequent mixing.

3.3. Potential factors affecting vanadium cycling within the LIS

The geochemical behavior of V depends on the ambient redox conditions; V (V) is reduced to V (IV) with a decrease in the redox potential (Eh) (e.g., Szalay and Szilágyi, 1967; Breit and Wanty, 1991), and even to insoluble V (III) under strongly reducing conditions (e.g., Sadiq, 1988). V (IV) is also readily adsorbed onto particles or complexed with organic matter followed by deposition into sediments (e.g., Wanty and Goldhaber, 1992; Wehrli and Stumm, 1989).

Physico-chemical parameters such as water temperature, pH, DO, dissolved Fe, ammonium, and sulfide concentrations could be used as redox indicators for explaining V behavior. We found that dissolved V concentrations in the water column of the LIS (Fig. 4) were higher in

summer when water temperature was also higher (temp.: 22.1 ± 1.2 °C versus 7.9 ± 1.5 °C in spring). High levels of V (V) and V (IV) were also measured in summer [V (IV): 2.2 ± 1.7 nM; V (V): 22.4 ± 3.9 nM] than in spring [V (IV): 1.4 ± 1.4 nM; V (V): 11.1 ± 2.6 nM] (Fig. 4), suggesting that both species could be affected by temperature-dependent adsorption/desorption processes (e.g., Censi et al., 2006; Aller, 1994; Man et al., 2004). We hypothesized that in the LIS, besides freshwater dilution, weak adsorption processes occurred under cold spring conditions, with V (IV) being more readily adsorbed onto particles and removed from the water column (e.g., Rehder, 2008), while desorption of both V species from sediments and suspended particles dominated during warm periods (e.g., Harita et al., 2005), contributing to the high levels of both V species in summer (Fig. 4). High water temperature could also increase the release of V from surficial sediments (e.g., Aller, 1994; Beck and Sañudo-Wilhelmy, 2007), and this mechanism could also be responsible for the high levels of V detected in summer.

3.4. Impact of water column redox changes on vanadium cycling

Due to the influence of freshwater, the characterization of the redox environment in estuarine waters is likely to differ from those typical of open ocean environments (e.g., Turner et al., 1981). According to Emelyanov (2005), the redox conditions of the water column of estuarine waters such as the LIS can be roughly defined as: 1) oxic (Eh > 0.59 V); 2) moderately reducing suboxic (ranging from denitrification (Eh of 0.59 V) to iron reduction (0.24 V) conditions), and 3) strongly reducing (Eh of 0.24 to –0.38 V; sulfate reduction conditions). It should be noted that these definitions assume thermodynamic equilibrium.

The redox potentials in the LIS during both cruises were calculated using our measurements of pH, DO, nitrate, ammonium, dissolved Fe and sulfide concentrations from Cuomo et al. (2005). The calculated Eh values for the LIS ranged from -0.2 to 0.6 V, under which V (IV) was likely being produced in western LIS by V (III) oxidation and/or V (V) reduction. V (V) should exist as the only thermodynamically stable form under the oxic conditions prevalent in central and eastern LIS ($\text{DO} > 350 \mu\text{M}$; $\text{pH} = 8.0\text{--}8.3$; $\text{Eh} > 0.6$ V).

V (IV) may account for more than 50% of the total dissolved V in reducing groundwater (Nakano et al., 1990; Hirayama et al., 1992; Bosque-Sendra et al., 1998), and between 30 and 40% in waters affected by industrial effluents or volcanoes (e.g., Minelli et al., 2000; Banerjee et al., 2003). A low proportion of V (IV) ($< 10\%$) has also been reported in oxic river water and seawater (e.g., Emerson and Husted, 1991; Elbaz-Poulichet et al., 1997; Bosque-Sendra et al., 1998). Consistent with those reports, our results (Figs. 2–4) showed that V (IV) accounted for up to 40% of the total dissolved V in some areas of LIS. When less reducing conditions following summer hypoxia in western LIS are reestablished, V (III) in sediments may be re-oxidized back to soluble V (IV) and V (V) (Byerrum et al., 1974). High levels of both V (V) and V (IV) near the Connecticut rivers (the Quinnipiac, Housatonic and Connecticut) in summer suggest that desorption of both V species from sediments and suspended particles could also supply dissolved V in those waters despite being thermodynamically unfavorable.

3.5. Biological relevance of V (IV)

Although not fully elucidated yet, high levels of V stimulate the growth of diatoms and green algae in the laboratory (Patrick, 1978). Bellenger et al. (2008a) reported that dissolved vanadate concentrations of 10 to 1000 nM are suitable for the growth of nitrogen-fixing bacteria, and V may be limiting for nitrogen-fixing bacteria below 10 nM (Bellenger et al., 2008a). Under limiting conditions, these bacteria may also produce 'vanadophores' for taking up V (Bellenger et al., 2008b). Presumably, total dissolved V is unlikely to be a limiting nutrient for phytoplankton due to its high abundance in the LIS (above 10 nM, Fig. 2).

In our study, large phytoplankton ($> 2.0 \mu\text{m}$) abundance was generally high ($\sim 4\text{--}8 \mu\text{g/L}$) in the western LIS in spring (likely a spring bloom) but low ($< 4 \mu\text{g/L}$) in central and eastern LIS. Large phytoplankton was also prevalent ($\sim 4\text{--}8 \mu\text{g/L}$) near the Connecticut rivers (Quinnipiac, Housatonic and Connecticut) in summer (Fig. 5). The results presented in Fig. 2 showed very high levels of V (V) in central and eastern LIS in summer, which likely resulted from the advection of oxygenated seawater from Atlantic Ocean (Lee and Lwiza, 2005) with high V (V) concentrations. These high V (V) levels (associated with low Chl-a) suggest that the growth of those phytoplankton species may be unrelated to dissolved V (V) concentrations in LIS.

During our study, biomass of large phytoplankton (likely diatoms and dinoflagellates (Gobler et al., 2006) was directly related to the amount of V (IV) (relatively high biomass in western LIS with high V (IV) levels and low biomass in central and eastern LIS where low V (IV) concentrations were measured). A significant correlation ($r^2 = 0.58$, $p < 0.05$) between V (IV) concentrations and large phytoplankton (Chl-a $> 6.0 \mu\text{g/L}$) was detected in the western LIS in summer (Fig. 5). The positive relationship between biomass and V (IV) concentrations suggests that the concentrations of this V concentration could be influenced by biological uptake, as V (IV) is more easily taken up by phytoplankton (Willisky et al., 1984). Future studies should address that hypothesis with in-situ bottle incubation experiments using V (IV and V) additions.

3.6. Potential mechanisms influencing the geochemical behavior of vanadium

Our results showed that V speciation changed seasonally and spatially in LIS. The geochemical behavior of V seems to be affected by

water temperature, redox conditions, and biological activity. Supply of V to the LIS may include fluvial and sewage discharges, as well as releases from suspended particles and surficial sediments, while removal processes may include biological uptake and adsorption onto particles and sediments. Fig. 6 summarizes the major hypothetical mechanisms responsible for the seasonal and spatial variation in V speciation observed during our study in the LIS. The major differences in the two sampling seasons are a net removal of V in spring (mainly V (IV)) when riverine inputs and biomass are high, and desorption of this trace element (both V (IV) and V (V)) from suspended particles and bottom sediments in response to higher water temperature in summer (Fig. 6).

Vanadium speciation in the LIS seems to be also affected by point-sources (e.g., fluvial, sewage input) in addition to the ambient redox conditions. Therefore, enrichments or depletions of this element in the sedimentary record may not reflect only the redox conditions of the water column during sediment deposition. Further studies are needed to understand the biogeochemical behavior of this redox-sensitive element in the modern ocean to fully understand V enrichments in ancient sedimentary systems (e.g., Chaillou et al., 2002; Nameroff et al., 2002; McKay et al., 2007).

4. Summary

Consistent with thermodynamic calculations, V (IV) accounted for a significant fraction (as high as 40%) of the total dissolved V pool in western LIS during summer hypoxic conditions. V (IV) accounted for less than 5% in most of the other oxygenated waters of the LIS. Our preliminary results showed seasonal and spatial changes in total dissolved V and its redox speciation in LIS. Higher V (V), along with total V, was observed during the summer cruise, which likely resulted from oxygenated seawater intrusion from the Atlantic Ocean. Dissolved V (IV) was mostly detected in western LIS and near Connecticut rivers, suggesting that V speciation was influenced by point-sources, especially in summer. Dissolved V-salinity plots show a non-conservative behavior of this element, and a net removal in

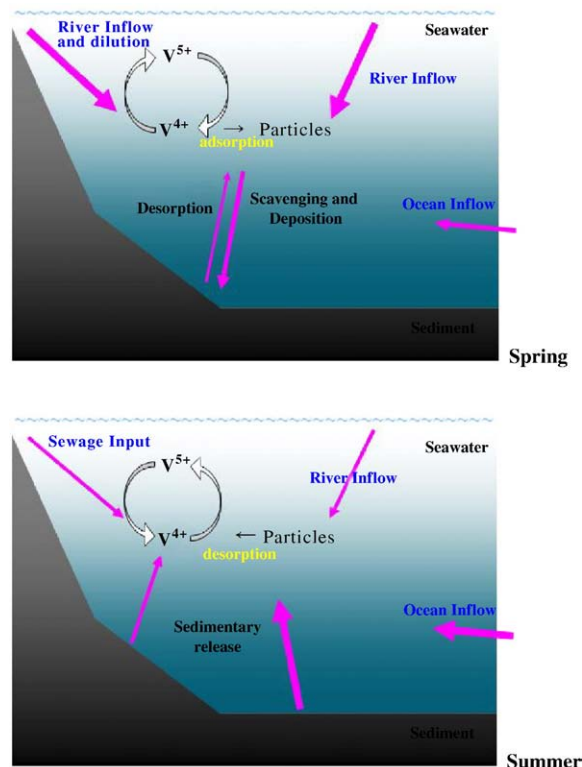


Fig. 6. Hypothetical mechanisms controlling vanadium speciation and cycling in Long Island Sound in spring and summer.

spring from particle adsorption and dilution by river input with low levels of dissolved V.

Water temperature seems to have an impact on the redox speciation of V, and the positive relationship between V (IV) and large size phytoplankton biomass suggested that V (IV) may be influenced by biological activity. Paleoceanographic studies that use V as a proxy for ancient redox chemistry, especially in coastal waters, should consider the complex geochemical behavior of this element. While the main objective of this project was to establish seasonal and spatial changes in V speciation in a marine system by direct measurements of V (IV) and V (V) concentrations, future studies are needed to confirm the bioavailability of V (V) and V (IV), and the exchange of the different V species between dissolved and solid phases.

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