

Development of an analytical protocol for the determination of V (IV) and V (V) in seawater: Application to coastal environments

Deli Wang^{a,b,*}, Sergio A. Sañudo-Wilhelmy^c

^a State Key Laboratory of Marine Environmental Science, Xiamen University, 422 Siming Nanlu, Xiamen, 361005, China

^b School of Marine and Atmospheric Sciences, Stony Brook University, Stony Brook, NY 11794-5000, USA

^c Department of Biological Sciences and Department of Earth Sciences, University of Southern California, Los Angeles, CA, 90089, USA

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ABSTRACT

A new method was developed for determining vanadium [V (IV) and V (V)] species in seawater by using a solid-phase extraction at pH 4.5 with Chelex-100 resin. Vanadium (V) was eluted with 0.1 M ammonium hydroxide and V (IV) was eluted with 0.2 N perchloric acid. The recovery of V species in synthetic seawater was >95% for V (V) and 92% for V (IV) at a concentration of 40 nM, typical of open ocean waters. Stability experiments showed V (IV) was relatively stable for over 24 h. The detection limit for V (IV) and V (V) was on the order of 0.5 nM. The analytical precision was ~10% in the concentration range of 10 nM.

The speciation method was applied to coastal water samples collected at the head of the Peconic River Estuary and in the Long Island Sound (LIS) during the Spring and Summer of 2005. Concentrations of dissolved total V ranged from 6.0 to 35 nM in both coastal environments. Consistent with thermodynamic considerations, the dominant V form in the study areas was V (V). However, V speciation varied seasonally and spatially in response to redox changes. Reduced V (IV) accounted for 5–20% of the total dissolved pool in coastal waters of LIS and about 40% of total V at the head of the Peconic River Estuary.

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1. Introduction

Thermodynamic considerations suggest that both V (IV) and V (V) should exist in fresh and seawater (e.g., Evans and Garrels, 1958; Kalk, 1963), although V (V) is expected to be the stable chemical form under oxic conditions and V (IV) should dominate in reducing environments (e.g., Peacock and Sherman, 2004). Total dissolved V concentrations are relatively low in freshwater (6–30 nM; Shiller, 1997; Shiller and Boyle, 1987; Shiller et al., 1998; Shiller and Mao, 1999, 2000), and higher in seawater (34–45 nM; Collier, 1984; Morris, 1975). Vanadium concentrations, however, are much lower in reducing waters (e.g., about 10 nM in water below 600 m in the Cariaco Trench and Black Sea; Emerson and Husted, 1991). In contrast, V concentrations are very high in anoxic sediments,

reaching concentrations as high as 4–8 mmol/kg (Emerson and Husted, 1991). In mildly reducing (suboxic) environments, V (V) as vanadate is first reduced to V (IV) as vanadyl, which may be adsorbed onto organic particles, and therefore removed from the water column (Szalay and Szilágyi, 1967; Emerson and Husted, 1991; Morford and Emerson, 1999). Under more strongly reducing (sulfidic) conditions, sulfides cause V to be further reduced to V(III), as solid V₂O₃ or hydroxide V(OH)₃ (Breit and Wanty, 1991; Wanty and Goldhaber, 1992; Algeo and Maynard, 2004). These chemical changes could explain the V enrichment observed in anoxic sediments (e.g., Emerson and Husted, 1991). While thermodynamic calculations have been used to describe these potential V speciation changes, the different chemical redox species of V in the ocean have never been reported.

Vanadium is an essential element, as lack of this element is lethal, but at high levels it is toxic (e.g., Taylor and van Staden, 1994). Toxicity and bioavailability of V, however, are much more dependent on speciation than on the total pool: V (V) being the more toxic form (e.g., Patel et al., 1990; Willsky et al., 1984;

* Corresponding author. State Key Laboratory of Marine Environmental Science, Xiamen University, 422 Siming Nanlu, Xiamen, 361005, China. Tel.: +86 592 2182682; fax: +86 592 2184101.

E-mail address: deliwang@xmu.edu.cn (D. Wang).

Taylor and van Staden, 1994). Both species of V are used by plants and animals, and both V (IV) and V (V) may exist in phytoplankton and bacteria (e.g., Crans et al., 1989; Baran, 2000). However, V (IV) is expected to be the dominant form in intercellular media (Willisky et al., 1985). Vanadium forms part of active centers in V-dependent enzymes, (e.g., V-nitrogenases and V-haloperoxidases; Rehder, 2003), and therefore, this element plays an important role in nitrogen fixation in some diazotrophs (e.g., *Azotobacter*; Dilworth et al., 1987), and the cycle of halides in diatoms and macroalgae (Moore et al., 1996; Butler, 1998).

Vanadium can be released to the environment from burning fossil fuels and from various industrial processes (e.g., Bertine and Goldberg, 1971; Zoller et al., 1974; Cessella et al., 2006) as this element is widely used in the production of special steels, temperature-resistant alloys, pigments and paints (e.g., Pyrzyńska and Wierzbicki, 2004; Ensafi et al., 2008).

In recent years, several studies have reported measurements of total dissolved V in environmental samples such as in seawater (Emerson and Husted, 1991), river water (Shiller and Mao, 2000), biological and sediment samples (Blotcky et al., 1979; Colina et al., 2005), using an array of different analytical techniques. Several studies have also attempted to measure V speciation in environmental samples (e.g., Starczewska, 2002; Filik et al., 2004; Fan et al., 2005) using various methods such as coprecipitation (Weisel et al., 1984; Fujiwara et al., 1986), solvent extraction (Remya and Reddy, 2004), ion exchange chromatography (Khuhawar et al., 2002; Huang et al., 2002; Zhang et al., 2003), capillary electrophoresis (Chen and Naidu, 2002), and liquid and solid-phase extraction (e.g., Nakano et al., 1990; Minelli et al., 2000; Cowan et al., 2000; Okamura et al., 2001; Pyrzyńska and Wierzbicki, 2004). However, most studies indirectly obtained V (IV) concentrations by subtracting V (V) levels from the total dissolved V pool (e.g., Zhao et al., 2006). In addition, all of the above studies were conducted under atmospheric conditions, without taking into consideration the kinetics of oxidation during sample manipulation and analysis. Therefore, the objective of this study was to develop a quick and precise method of measuring different chemical species of vanadium [V (IV) and V (V)] in oxic and suboxic seawater.

The technique to separate the different redox species of V is based on solid-phase extraction. This type of extraction has been widely used for differentiating metal species in aqueous solution (e.g., Minelli et al., 2000; Pyrzyńska and Wierzbicki, 2004) due to its efficiency and handling simplicity (Fang, 1991; Pyrzyńska and Trojanowicz, 1999). For example, the chelating resin Chelex 100 is a styrene divinylbenzene copolymer containing iminodiacetate ions, with a very strong attraction for transition metals, even in highly concentrated salt solution (e.g., Chan and Riley, 1966; Chandra et al., 1988; Dupont et al., 1991). Chelex 100 also acts as a cation exchanger at higher pH, and an anion exchanger at lower pH (Pyrzyńska and Wierzbicki, 2004). Both cations and anions can be adsorbed onto the Chelex 100 resin in the pH range of 4.0–7.4. Soldi et al. (1996) showed that, in a batch method, both vanadium species (V (V) in the form of H_2VO_4^- and V (IV) in the form of VO^{2+}) were adsorbed on Chelex 100 at pH of 3–6 in a nitrogen-enriched atmosphere. The two species were eluted under different pH conditions [V (V) at $\text{pH} > 10$ and V (IV) at $\text{pH} < 1$]. However, the choice of the best operational conditions for sorption and elution of different V ions is still a

problem, which has been mostly dealt with on a purely experimental basis using unrealistic high concentrations (millimolar) of this element (Soldi et al., 1996; Pyrzyńska and Wierzbicki, 2004). In addition, the batch method requires a very long sorption time of ~2 h, which increases the possibility of redox changes to V during the extraction protocol.

We have modified and optimized the original method of Soldi et al. (1996) for a quick, accurate and precise column procedure for separating V (V) and V (IV) in seawater. The method was successfully applied to measure both V oxidation states in coastal waters collected at the head of the Peconic River Estuary and in Long Island Sound (LIS) where summer hypoxia creates suboxic areas (Parker and O'Reilly, 1991; Breuer et al., 1999) suitable for the reduction of V (V) and the stability of V (IV).

2. Materials and methods

2.1. General description of the method for separating V (V) and V (IV)

A general protocol for separating V (V) and V (IV) species in natural water is summarized as below. Basically, 100 ml of a water sample was first adjusted to a pH of 4.5 with concentrated perchloric acid or with an acetate buffer (pH=4.5 in 0.1 M acetic acid and sodium acetate). This acid was chosen to adjust the pH of the sample because we found that other acids such as nitric oxidize the V (IV). After the pH adjustment, 10 ml of the water sample was immediately loaded, at a rate of 2 ml/min, onto a poly-prep column with H^+ form Chelex 100 resin (100–200 mesh, Bio-Rad) using a peristaltic pump with Teflon tubing extending from the head of the column to the water sample.

Both V (V) and V (IV) species absorbed onto Chelex 100 resin as in R-V (V) O_3 and R-V (IV) O (R: iminodiacetic groups in Chelex 100 resin). After rinsing with 20 ml of the acetate buffer and 20 ml of Milli-Q water, V (V) was eluted with 10 ml of 0.1 M ammonium hydroxide (0.1 M, pH=11.2) (10 elutions of 1 ml each). Following the V (V) elution, V (IV) was eluted with 10 ml (10 elutions of 1 ml each) of 0.2 N perchloric acid (pH=0.8). To avoid any changes in the V speciation during the handling of the samples, the loading and elution protocols were conducted under a nitrogen atmosphere. All of the collected eluents for both V (V) and V (IV) analyses were dried on a hot plate and re-dissolved in 2 ml 0.1 N HNO_3 . The quantification of both species of V was carried out by Graphite Furnace Atomic Absorption Spectrometry (GF-AAS).

Compared to previous studies (e.g., Soldi et al., 1996; Pyrzyńska and Wierzbicki, 2004), several analytical conditions needed to be optimized to achieve the best separation of V (V) and V (IV) species at the actual nanomolar concentrations at which V exists in seawater. Those modifications include sample volume, amount of Chelex 100 resin used in the separation, optimum pH of the water sample to do the chemical separation of both species, sample loading rate onto the resin, elution volumes required to obtain full extraction, and so on. The optimized analytical conditions, as well as a comparison of those conditions with other analytical protocols, are listed in Table 1.

The GF-AAS was also optimized for V analysis according to the following: thermal program or sequence: drying at 130 °C

Table 1

Comparison of the different analytical conditions used for separating different vanadium species in natural waters

	Previous studies	In this research
Water sample volume	400 ml (Soldi et al., 1996)	10 ml
Chelex 100 resin	0.2 g (Soldi et al., 1996)	2.0 g
Total operation time	>2 h (Soldi et al., 1996)	~10 min
Sample handling	Under nitrogen (Soldi et al., 1996)	Under nitrogen
	Under regular atmospheric conditions (e.g., Pyrzyńska and Wierzbicki, 2004) s	
Water sample pH	pH=3–5 (Chen et al., 1993) pH=4–6 (Soldi et al., 1996)	pH=4.5
pH buffer	Acetate buffer (Soldi et al., 1996)	Acetate buffer
Acid used for adjusting pH in water samples and in the acetate buffer	Nitric and/or perchloric acid (Soldi et al., 1996) Nitric acid (Pyrzyńska and Wierzbicki, 2004)	Perchloric acid only
Water sample loading rate	2.0–4.0 ml/min (Chen et al., 1993)	2.0 ml/min
PH in ammonium solution to elute V ⁵⁺	>10 (Soldi et al., 1996)	11.2
Volume of ammonium solution to elute V ⁴⁺	10 ml (Soldi et al., 1996)	10 ml
Acid to elute V ⁵⁺	Nitric and/or perchloric acid (Soldi et al., 1996) Nitric acid (Pyrzyńska and Wierzbicki, 2004)	Perchloric acid only
PH in acid to elute V ⁵⁺	<0.8 (Soldi et al., 1996)	0.8

for 30 s, ashing in ramp at 1600 °C for 10 s, hold for 20 s at 1600 °C, atomization at 2500 °C for 5 s, cleaning at 2550 °C for 3 s. The accuracy and precision of the V speciation analysis was obtained by analyzing certified reference seawater CASS-4 from the National Research Council, Canada.

2.2. Solid-phase extraction

Chelex 100 (particle size range of 100–200 mesh) in a Na form was converted to a H⁺ form by the procedure described by Pesavento et al. (1993). Two grams of Chelex-100 resin were transferred into a 10-ml poly-prep column (BIO-RAD) and washed with ~60 ml of Milli-Q water followed with ~20 ml of 0.1 N HClO₄. In order to obtain a full conversion to the H⁺ form, the resin was exposed to the acid for at least an hour. The resin was then rinsed with three 20 ml Milli-Q water aliquots each before starting the solid-phase extraction. The solid-phase extraction was carried out using a peristaltic pump with rotor heads (Cole-Parmer, Masterflex, Model 7553-12, 1–100 rpm), poly-prep columns containing the pre-prepared resin and Teflon tubing that extended from the head of the column into the bottom of a 30 ml acid-washed polyethylene bottle reservoir.

2.3. Recovery of different species of vanadium

In order to establish the operational conditions for the solid-phase extraction of the different V species, recovery experiments were carried out in degassed synthetic seawater. In contrast to previous studies where several mM concentrations of V were used in the recovery experiments (e.g., Soldi et al., 1996; Pyrzyńska and Wierzbicki, 2004), the synthetic

seawater was spiked with V concentrations typical of open ocean environments (40 nM of V (IV) only; 40 nM of V (V) only; and 40 nM of both V (V) and V (IV)).

Standard solutions of V (IV) and V (V) were prepared by diluting stock solutions (4 mM NaVO₃ in Milli-Q water, and 4 mM VOSO₄·5H₂O in 0.1 N perchloric acid) respectively to the desired concentration in synthetic seawater immediately before experiments. Synthetic seawater was prepared by dissolving sea salt (Sigma) in Milli-Q water with final salinity of 35, and pH was titrated to 4.5 by adding concentrated perchloric acid. The synthetic seawater was then passed through an acid-washed polypropylene filter (0.2 μm), and then through H⁺ Chelex 100 resin column (as described earlier) to remove any possible V ions. The synthetic seawater was finally degassed at least 1 h with nitrogen gas before use.

2.4. Stability of V (IV)

Stability of V (IV) at pH=4.5 was assessed in order to establish whether changes in V speciation occurs during the solid-phase extraction. For this test, a bottom water sample was collected at the head of the Peconic River estuary in September 2007 (water temperature=22 °C, salinity=14, pH=~7.5, and DO=~10 μM). The water samples (250 ml, two replicates) were adjusted to pH 4.5 immediately with perchloric acid, and incubated at room temperature (20 °C). V (IV) was determined at different time intervals (up to 4 h following collection). All other operations and handling followed the method described above.

In order to determine whether biological activity occurring inside the sample bottles could affect V speciation during the handling and operation, additional water samples were collected at the head of the Peconic estuary in September 2007 and incubated at 20° and at 0 °C (two replicates each). The hypothesis to be tested here is that any biological reduction or oxidation of V should be detected in the sample incubated at 20 °C. The concentration of V (IV) was determined at different time intervals over 24 h.

2.5. Coastal seawater sample collections at the head of the Peconic River Estuary and in Long Island Sound

Once the optimum operational conditions for the best recovery of both V (V) and V (IV) were established, the method was applied to the determination of both V species in filtered coastal seawater. The seawater samples were collected in April 2005 at the head of the Peconic River Estuary and in April and September 2005 in the LIS (Fig. 1).

The head of the Peconic River Estuary is located at Riverhead in eastern Long Island, NY. Due to damming at the head of the Peconic River, minimal riverine flow allows in situ processes (e.g., groundwater seepage, benthic remobilization and tidal exchange) to dominate trace metal geochemistry in this area (Schubert, 1988; Wilson, 1996; Breuer et al., 1999; Gobler, 1999). The local wastewater treatment plant in Riverhead, NY contributes the largest freshwater inputs to the estuary (NYDEC, 1992), and suboxic conditions are often observed at the head of this estuary (Breuer et al., 1999) (Fig. 1). The Long Island Sound (LIS) extends from the East River at New York City to the Race at the eastern end (Fig. 1),

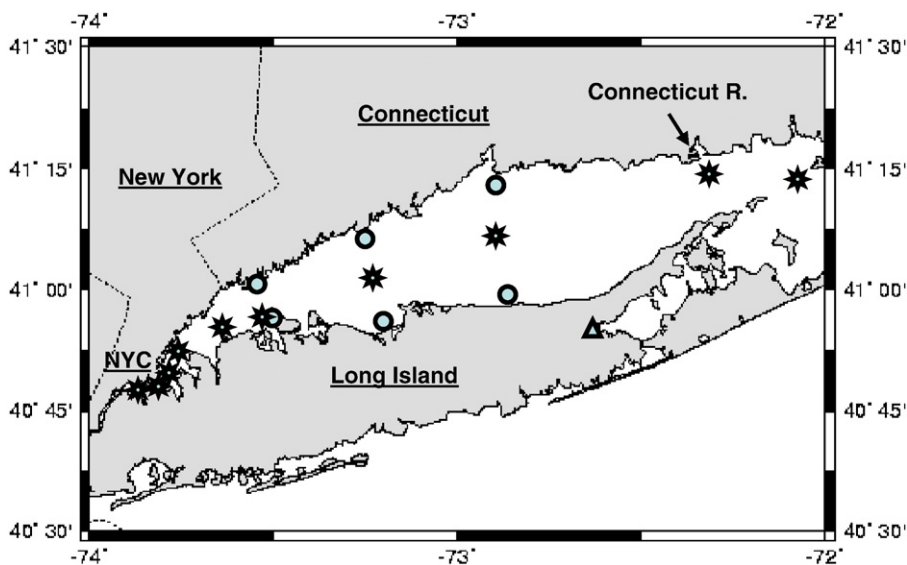


Fig. 1. Sampling locations (▲ = samples collected in April 2005 at the head of Peconic River Estuary; ○ = samples collected in April 2005 in Long Island Sound; ☆ = samples collected in September 2005 in Long Island Sound).

and it is the third-largest estuary in the United States, with a mean depth of 20 m and a total volume of $6.2 \times 10^{10} \text{ m}^3$ (Wolfe et al., 1991; EPA, 1994). Long Island Sound exchanges with lower salinity water through the East River at its western headwaters, and receives about 70% of its freshwater from its largest tributary, the Connecticut River. In the east, LIS is connected with the Atlantic Ocean, and deeper, more saline ocean water exhibits a net westerly flow as bottom and intermediate layers, while fresher water generally moves eastward in a surface layer through the Race (Riley, 1967). Periodic bottom water hypoxia events occur from June to September in the western LIS, and hypoxia has been observed even in eastern LIS (e.g., Parker and O'Reilly, 1991). The LIS and the head of the Peconic River estuary are suitable places for studying V speciation, as V(IV) is expected to exist under suboxic/anoxic conditions.

The water samples used in this study were collected at the head of the Peconic River Estuary (water depth of ~1 m), using a peristaltic pump equipped with Teflon tubing on a plastic pole and lowered to a depth of 0.2 m above the bottom. In the LIS, seawater samples were collected during two *R/V Seawolf* cruises; 6 bottom samples in April 2005 and surface and bottom samples at 11 locations from the East River to eastern LIS (middle layer water samples were also collected at stations in central and eastern LIS) in September 2005 (Fig. 1). Seawater samples in LIS were also collected using a peristaltic pump equipped with trace metal clean Teflon tubing attached to a 10 m trace metal clean boom.

For V speciation analysis, 100 ml water samples from each station were obtained by filtration through acid-washed polypropylene capsule filters (0.2 μm), and then processed immediately in situ according to the method described above. Once V(IV) and V(V) were isolated, samples were stored at -20°C in freezers until they were brought back to the laboratory and analyzed via GF-AAS within a week. All sampling material used in this study was prepared using trace metal clean techniques (Flegal et al., 1991).

3. Results and discussion

3.1. Recovery experiments of vanadium additions

The results of recovery experiments are summarized in Fig. 2. With both V(IV) and V(V) spiked, the cumulative recovery was 98% for V(V) and 96% for V(IV). With spiked V(V) only, the cumulative recovery was 95% for V(V) and no V(IV) was detected (Fig. 2). However, with spiked V(IV) only, the cumulative recovery of total V was 92% V(IV) and 9% V(V) (Fig. 2). The formation of a small amount of V(V) when only V(IV) was initially present shows that oxidation of free V(IV) ions occurred during handling under laboratory conditions, although steps were taken to prevent the introduction of oxygen. The detection limit for both V(V) and V(IV) was on the order of 0.5 nM. The precision was ~10% with concentrations of 10 nM.

3.2. Stability of V(IV)

The short-term stability study showed that the levels of V(IV) in the water sample collected in the Peconics remained unchanged for at least 4 h after collection and pH adjustment to 4.5. The results suggest that at pH 4.5, the

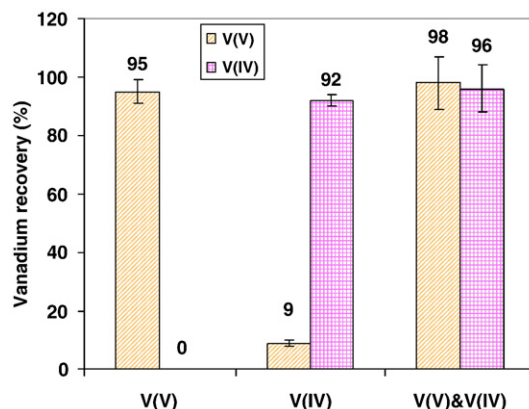


Fig. 2. Recoveries of different vanadium species in degassed synthetic seawater adjusted to pH 4.5 prior the spike. Recoveries of V(V) only, V(IV) only and both V(V) and V(IV) species (all additions: 40 nM) (Error bars represent the standard deviation, $n=4$).

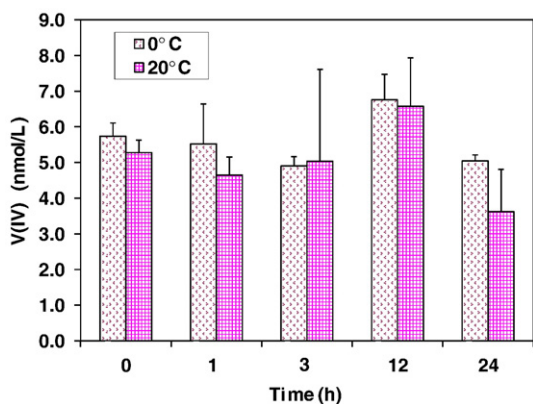


Fig. 3. Changes in V (IV) concentrations in water samples incubated at 0 and 20 °C for up to 24 h (error bars are standard deviation, $n=2$). The samples used in this experiment were bottom waters collected at the head of Peconic River Estuary with dissolved oxygen levels of $\sim 10 \mu\text{M}$ and $\text{pH} \sim 7.5$.

reduced form of V is stable for several hours. Furthermore, the similar results obtained in the different temperature incubation experiments (0° and 20 °C) (Fig. 3), suggest that, for at least 24 h, biological activity did not cause the reduction of V (V) or oxidation of V (IV). Our stability results seem to be consistent with the stabilization of V (IV) by organic ligands in natural environments (e.g., Szalay and Szilágyi, 1967; Baran, 2000; Zhou et al., 2005).

3.3. Variation of V speciation with pH in certified reference seawater CASS-4 and in the LIS

Since there are no certified reference materials for V (IV) yet, the certified reference seawater (SRSW) CASS-4 (23.1 ± 3.1 nM total dissolved V) from the National Research Council, Canada was analyzed for V speciation. Consistent with the fact that the CASS-4 has been acidified ($\text{pH}=1.6$), the speciation protocol recovered 93% of the total V as V (IV). The amount of V (V) found in the acidified SRSW ($\sim 7\%$) was within the 10% of the uncertainty of the analysis (Table 2). In order to measure V (V) in the SRSW, the pH was adjusted to 8.5 with 0.1 N NaOH for 5 h and reanalyzed for both V species. At this basic pH, V (V) was the dominant species, accounting for 96% of the total V (Table 2). The amount of V (IV) in the oxidized CASS-4 was only 4% of total V and within the uncertainty of the measurements (Table 2). The results on the effect of pH on V speciation were consistent with previous studies (e.g., Okamura et al., 2001; Nukatsuka et al., 2002) and validated the V speciation protocol.

The accuracy of the new speciation method was also established by comparing the concentration of total dissolved V (adding both V (IV) and V (V) species) measured in the LIS cruise using the new protocol with the V levels obtained using the APDC/DDDC organic extraction (e.g., Bruland et al., 1985) and ICPMS quantification (Fig. 4). The highly significant linear correlation obtained between the two protocols ($r^2=0.98$; $V(\text{IV}+\text{V})=0.998 * (V \text{ measured by APDC/DDDC extraction}) + 1.10$) clearly demonstrated that the new technique produced very reliable V results. The intercept of the linear regression between the two different analytical protocols suggests that our speciation technique overestimated the V concentration by about 1 nM, that is about 10% of the lowest concentration measured in the method inter-comparison presented in Fig. 4. This slight difference between the two protocols could be the result of differences in the precision of the instrumentation used in the V quantification (GF-AAS in the V speciation protocol vs ICPMS in the organic extraction).

Table 2

Dissolved V (IV) and V (V) concentrations measured in CASS-4 (all units in nM)

Samples	V (IV)	V (V)	Total V
CASS-4 reference material (total V: 23.1 ± 3.1)	24.1	1.8	25.9
Analyzed immediately			
CASS-4 reference material (total V: 23.1 ± 3.1)	1.0	21.8	22.7
After adjusting $\text{pH}=8.5$ for 5 h			

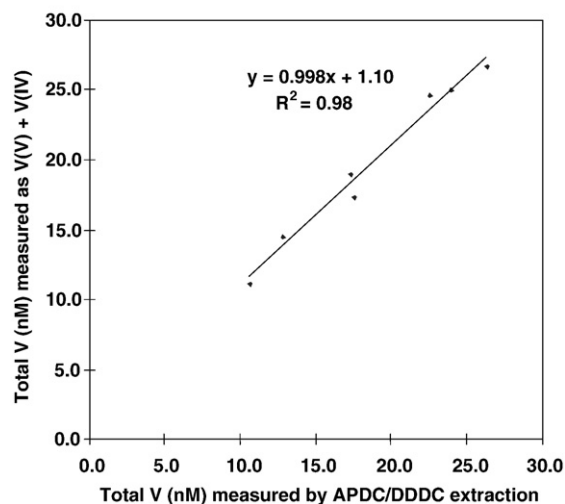


Fig. 4. Comparison of total vanadium concentrations measured by two different protocols: speciation by solid-phase extraction and APDC/DDDC extraction. Water samples collected in Long Island Sound during April and September 2005).

3.4. Redox speciation of vanadium at the head of the Peconic River Estuary and in the Long Island Sound

Total dissolved V concentrations in both study areas ranged from 6.1 to 18.0 nM in April 2005 (Fig. 5). Total dissolved V at the head of the Peconic River Estuary was more variable and relatively low (6.1–11.0 nM) in comparison to coastal waters of LIS (10.0–18.0 nM; April 2005; Fig. 5). When plotting against dissolved oxygen (DO), the lowest total V concentrations were measured in the Peconics at DO levels $< 250 \mu\text{M}$, while relatively high levels were measured in oxic waters of the LIS (Fig. 5). A similar pattern was also observed in bottom waters off the Louisiana Shelf in the Gulf of Mexico by Shiller et al. (1998). However, salinity in the LIS and the Peconics was lower than in the Louisiana Shelf bottom water. Consequently, total V concentrations in our area of study were also lower (Fig. 5), presumably due to mixing between freshwater with low total V concentrations, and high salinity waters with high levels of this element. However, further analyses are needed to substantiate that hypothesis, as we do not know the actual V concentrations in the freshwater end-members discharging into the LIS.

The results of the V speciation in the Peconics and in the LIS measured in April 2005 are shown in Fig. 6. Consistent with the redox conditions of the

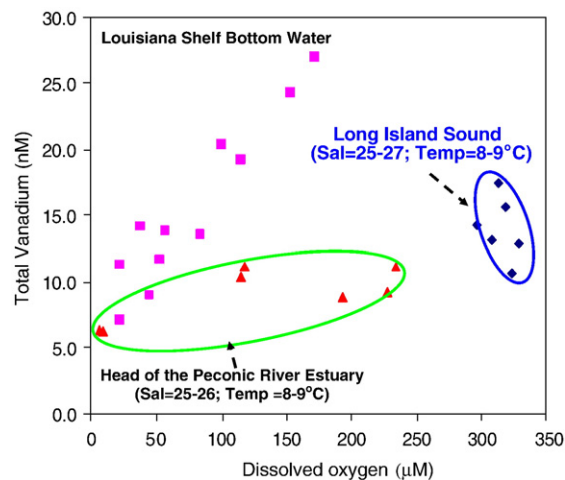


Fig. 5. Total vanadium concentrations versus dissolved oxygen in coastal waters (April 2005, —the head of Peconic River Estuary; —Long Island Sound; —Louisiana Shelf Bottom waters from Shiller et al., 1998 at salinity 35).

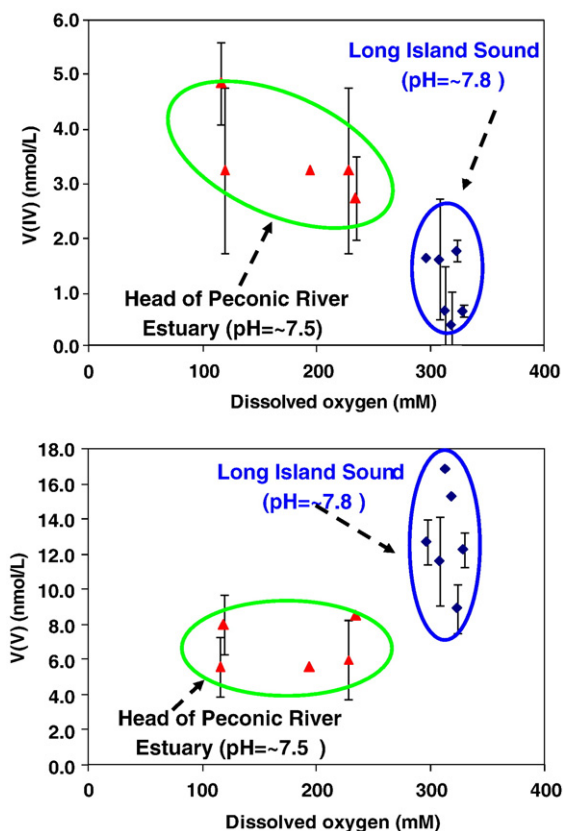


Fig. 6. Dissolved V (IV) and V (V) concentrations versus dissolved oxygen in coastal waters (April 2005, \blacktriangle at the head of Peconic River Estuary; \bullet in Long Island Sound).

different locations, V (V) was the dominant species under the oxic conditions of the LIS (range: 8–16.0 nM); reduced V (IV) (range: 0.5–3.0 nM) concentrations were <10% of the oxidized form. In contrast, in the suboxic

Peconic River estuary, dissolved V (V) concentrations ranged between 4.0 and 10.0 nM, and the levels of V (IV) (range: 2–5.5 nM) represented on average about 40% of the oxidized V (Fig. 6).

Low levels of total dissolved V under low oxygen conditions have been associated with V enrichments in sediments (Shiller et al., 1998; Shiller and Mao, 1999). Our results suggest that the reduction of V (V) to V (IV) occurred under low oxygen conditions, and therefore V (IV) cations (VO^{2+} or HVO^+ ; Pope et al., 1980) could be adsorbed onto particles and removed from the water column, leading to lower total V levels in seawater and high enrichment in sediments.

Distributions of V (IV) and V (V) in LIS measured in September 2005 are shown in Fig. 7. The average concentration of V (IV) was 3.0 nM (± 1.4 nM), ranging from undetectable to 6.1 nM. The average concentration of V (V) was 22.1 nM (± 4.0 nM), ranging from 11.6 to 32.2 nM. Overall, V (V) was the dominant V species found in the LIS, and V (IV) accounted for only 0–20% of the total V. The highest levels of V (V) were detected in the eastern and central regions of the LIS, especially in deep waters, which likely resulted from the input of oxic waters from the Atlantic Ocean (Fig. 7). In contrast, relatively low levels of V (V) were found in surface waters near river discharges and near New York City in the western region of the LIS (Fig. 7). To some extent, this is consistent with the low levels of dissolved V reported in rivers (e.g., Shiller and Mao, 2000).

The highest levels of V (IV) were measured in two areas: in the East River near New York City within the heavily contaminated western LIS (Buck et al., 2005), and near the Connecticut River (Fig. 7). High levels of V (IV) in the western LIS are consistent with the high volume of sewage being discharged in that area, and with the fact that sewage is anoxic with high levels of dissolved Mn and Fe that are reductants of V (V) to V (IV) (e.g., Myers and Myers, 1993, 1997; Myers et al., 2004). Similarly, high levels of Fe in the Connecticut River (Buck et al., 2005) could also be responsible for the high levels of reduced V measured near that river. However, other mechanisms such as the V (V) photo-reduction by peroxides (e.g., Voelker and Sedlak, 1995; Spokes and Liss, 1995) cannot be ruled out.

These field results confirmed the existence of V (IV) in coastal waters, although the reduced form of V was not the dominant species in the areas of study. The existence of V (IV) in natural waters is not uncommon. For example, V (IV) was measured in well-aerated river waters (Evans and Garrels, 1958; Kalk, 1963; Nakano et al., 1990; Wuilloud et al., 2001), waste water from power stations (Akl et al., 2005), volcanic water (Minelli et al., 2000), seawater (Hirayama et al., 1992; Wann and Jiang, 1997), groundwater (Veschetti et al., 2007), sediment and biological samples (Colina et al., 2005).

3.5. Thermodynamic considerations regarding vanadium speciation in the LIS

The different redox-pH conditions shown in the Eh-pH diagram for V speciation (Fig. 8) indicates that V (V) is the dominant species under oxic

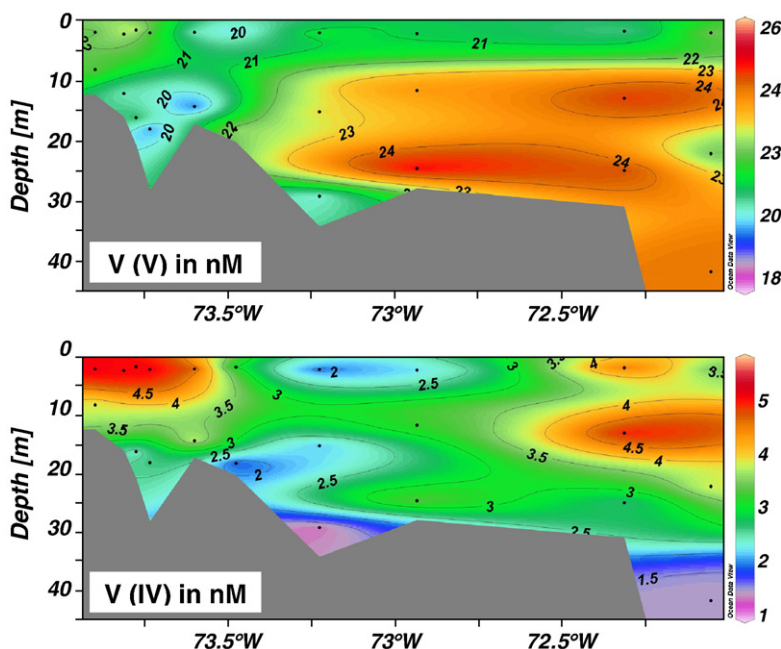


Fig. 7. Distribution of V (V) and V (IV) along a transect from the East River to eastern Long Island Sound (September 2005; all units in nM).

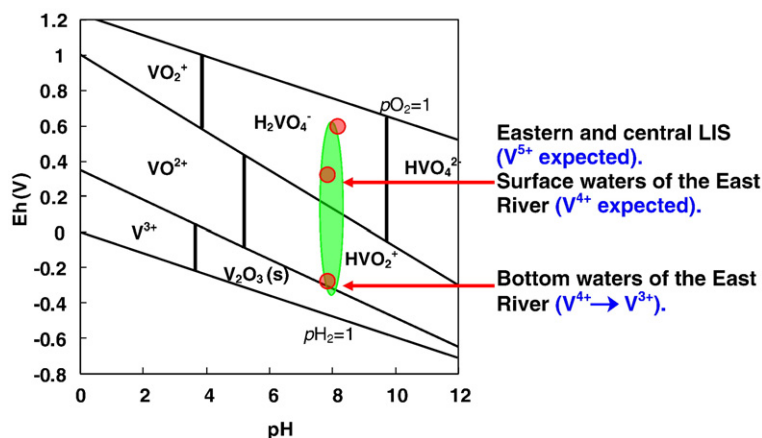


Fig. 8. Eh–pH diagram of vanadium in natural waters. The pH–Eh couple calculated for waters of the LIS, assuming activity for dissolved V of 10^{-7} M, is also shown. The diagram was modified from Peacock and Sherman (2004) and V (IV) species are from Pope et al. (1980).

condition, while V (IV) predominates in anoxic environments. Based on pH and oxygen measurements carried out during the September 2005 cruise in the LIS, dissolved V should exist only as V (V) under the oxic conditions prevalent in the central and eastern LIS (oxygen levels $>350 \mu\text{M}$; $\text{pH}=8.0\text{--}8.3$; $\text{Eh}>0.6$ V). In the East River, surface waters are close to the thermodynamic transition point (Fig. 8). Therefore, it would not be surprising to find more V (IV) here (suboxic conditions: $\text{NO}_3/\text{NH}_4 \sim 1$; $\text{pH}=7.5\text{--}7.8$; $\text{Eh} \sim 0.4$ V) than in oxic open ocean waters. These thermodynamic calculations are consistent with the geographical distributions of V (V) and V (IV) reported in Fig. 7.

While the lowest levels of dissolved oxygen occur in bottom waters of the East River, concentrations of reduced V (IV) were also relatively lower in that region (Fig. 7). Because bottom waters of the East River are highly sulfidic (1–10 mM; Cuomo, 2005) and less basic than seawater ($\text{pH}=7.5\text{--}7.8$), the calculated Eh value for those waters is ~ -0.2 V (Fig. 8). Those redox conditions are near the boundary between the V (IV)/(III) couple, suggesting that V (IV) was being reduced to solid V (III) in this area. Therefore, low levels of V (IV) in sulfidic bottom waters of the East River could be the result of sulfide precipitation of V (III) (e.g., Breit and Wanty, 1991; Wanty and Goldhaber, 1992). While these thermodynamic calculations are consistent with our field results, there are other important factors that can influence the concentrations of reduced V (IV) in some marine environments. For example, while free V (IV) ions are unstable under oxic conditions (Okamura et al., 2001), V (IV) is stabilized by organic ligands increasing the stability field of V (IV) to Eh values as high as +0.4 V under neutral pH (Wehrli and Stumm, 1989; Elbaz-Poulichet et al., 1997), close to the region where V (V) is stable (Fig. 8).

A low proportion of V (IV) has also been reported in oxic river water and seawater (e.g., Evans and Garrels, 1958; Kalk, 1963; Emerson and Husteded, 1991; Elbaz-Poulichet et al., 1997; Bosque-Sendra et al., 1998). However, V (IV) may be the dominant species in reducing environments. For example, Veschetti et al. (2007) reported that V (IV) accounted for $>90\%$ of total in anoxic ground water. Also, Wuilloud et al. (2001) found that V (IV) accounted for more than 50% of the total V in river water.

4. Conclusion

An analytical protocol has been developed for separating different redox species of V in sea water. Consistent with thermodynamic calculations, the dominant V species in oxic waters was V (V), but the reduced form of V as V (IV) was also detected in coastal waters. The redox speciation of V changed dynamically both seasonally and spatially during our study in response to different ambient redox conditions, and V (IV) may account for up to 40% of the total dissolved V in suboxic environments at the head of the Peconics, and between 5 and 20% in the LIS. The reduced form of V was detected in mildly reducing environments (suboxic conditions), where reductants such as H_2O_2 , Fe^{2+} , Mn^{2+} are expected to exist (e.g.,

Voelker and Sedlak, 1995; Spokes and Liss, 1995; Myers and Myers, 1993, 1997; Myers et al., 2004).

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