

CHANGES IN THE VANADIUM MIGRATION FORMS ON GEOCHEMICAL BARRIERS IN THE RIVER-SEA MIXING ZONES

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ABSTRACT

The article is devoted to the study of vanadium, a metal capable of stimulating the growth of phytoplankton *in situ* and has the greatest biological activity in dissolved form. The pattern of an increase in the concentration of vanadium dissolved forms in the mixing zones during the transition from river waters to seawaters is known. In this article, we examine the behavior, ratio and change in the concentrations of vanadium dissolved and suspended forms during the passage of geochemical barriers. The estuarine zone of the Razdolnaya River–Amur Bay (Sea of Japan) is considered as "river-sea" mixing zone. Modelling of physicochemical processes was carried out using the Selector-S and MINTEQA2/PRODEFA2 software systems. Ion-associative models of sea and river water were built and the modelling of the process of their mixing was carried out using the Selector-S software package. The sorption process was simulated using the MINTEQA2/PRODEFA2 software package. The results of modelling physicochemical processes occurring at geochemical barriers help to understand the reasons for changes in concentrations, both total vanadium and biologically active dissolved vanadium forms, during the passage of geochemical barriers in the "river-sea" mixing zones. The results showed that there is a change in the dissolved forms of vanadium migration, their transformation and an increase in the concentration of dissolved forms of vanadium at the geochemical barrier.

Keywords: *vanadium migration forms, vanadium dissolved forms, geochemical barrier, the Razdolnaya River*

INTRODUCTION

Estuaries and bays are mixing zones of river and sea waters, where the most of allochthonous suspended and dissolved organic matter of soil genesis is deposited. Here, at the geochemical barriers, there is a change in the migration forms of most elements. When river and sea waters mix, the processes of sorption and desorption of microelements, their transition from a dissolved to a suspended state and from a suspended to a dissolved state occur [1], [2].

Establishing the physicochemical forms of metal migration in various types of natural waters is one of the most important tasks in biogeochemistry, since the physicochemical form of their presence largely determines the degree of biometals assimilation by aquatic organisms. Concerning this, the transformation of the metal migration forms during mixing of river and sea waters, where geochemical barriers

are formed, in which not only a change in the migration forms occurs but also the removal of metals from solutions, is of considerable interest.

Most of the metals, including vanadium, enter these zones with river runoff from the catchment. Vanadium is a metal capable of stimulating phytoplankton growth *in situ* [3], and it has the greatest biological activity in a dissolved form; therefore, we aimed to study the behavior of vanadium forms on geochemical barriers in estuarine zones.

MATERIAL AND METHODS

Modelling of physicochemical processes of the behavior of vanadium forms during mixing of sea and river waters for the estuarine zone of the Razdolnaya River–Amur Bay (Sea of Japan) was carried out using the Selector-S and MINTEQA2/PRODEFA2 software packages [4]. The first software system was used to build ion-associative models of sea and river water and to model the process of their mixing; the second was used to simulate the sorption process based on the approach described in [5] and to determine the total vanadium concentration.

THEORY/CALCULATION

Vanadium form content calculation. Thus, vanadium is present in natural waters in various forms, the total vanadium concentration (V_{tot}) was calculated as the sum of the dissolved (V_{sol}) and suspended (V_{sorb}) forms. On average, about 98% of vanadium is in suspended form and only 2% migrate in dissolved form [6, 7]. Table 1 shows the vanadium various form concentrations, as well as its main chemical forms of presence in natural waters [2], [8].

Table 1. Mean concentrations of vanadium in river and ocean waters and its main chemical forms

Chemical element	Main chemical forms	River waters			Ocean waters	
		$\frac{V_{sorb}}{V_{sorb} + V_{sol}}$ (%)	V_{sorb} (%)	V_{sol} ($\mu\text{g/L}$)	V_{sorb} (%)	V_{sol} ($\mu\text{g/L}$)
Vanadium	$\text{VO}_2(\text{OH})_3^{2-}$, HVO_4^{2-} , H_2VO_4^- , NaH_2VO^-	98	$1.3 \cdot 10^{-2}$	1.0	$00.3 \cdot 10^{-2}$	1.5

The same amount of vanadium dissolved forms is contained, on average, in the river runoff is mentioned in the literary sources [1], [9]. In the reservoir of the final runoff (ocean), the fluctuations in vanadium concentrations are small, 1-2 $\mu\text{g/L}$, and the mean concentration is close to 1.5 $\mu\text{g/L}$. Suspended matter in the oceans contains about 0.008 $\mu\text{g/L}$ of vanadium or $3 \cdot 10^{-3}\%$ of vanadium of dry suspension. The surface suspension of the Indian Ocean can contain twice as much of this element – 0.016 $\mu\text{g/L}$ or $6 \cdot 10^{-3}\%$ of dry suspension, and in some cases the vanadium concentration increases to 0.28 $\mu\text{g/L}$ or $15 \cdot 10^{-3}\%$ of dry suspension [10].

Comparison of the mean concentrations of vanadium in the suspension of the world's rivers and in the lithosphere shows a significant amount of this element in the river suspension [6]. A distinctive geochemical feature of vanadium is the biophilic nature of behavior. River suspension is enriched with this element due to its participation in biological processes, as well as due to its ability to form strong organoelement complexes [8].

Assessment of the sorption effect on vanadium form content. River suspension is conventionally divided into three forms: 1) silicate – mineral particles; 2) biogenic – organic particles of the suspension, amorphous silica, calcium carbonate, nitrogen and phosphorus; 3) hydrogenic (readily soluble). The content of the latter is calculated as the difference between the total content of the suspension and the first two forms. These include the amount of metal adsorbed on mineral and organic particles of suspension, as well as for some elements (for example, iron) in the form of particles or films of hydroxide and precipitated with them.

Iron and manganese hydroxides covering the suspended matter particles can make up 40-50% of the total iron and manganese in the river suspended matter. In the experiment to study the ability of amorphous oxides of iron and manganese to sorption of various metals, a number of elements were investigated (according to the increasing role of sorption). The results showed that vanadium has the lowest sorption capacity [1].

The modelling of the process of the influence of sorption on the metal removal from the solution of the mixing zone was carried out under the following assumptions: the salinity is 5.33 ‰; up to 95% of suspended solids are lost at the geochemical barrier; the concentration of suspended matter in the estuary is 200 mg/L; the concentration of suspended matter in the river is 50 mg/L.

The degree of influence ($\Delta V_{\text{tot}}\%$) of sorption processes on the vanadium migration during mixing of sea and river waters was calculated by the formula

$$\Delta V_{\text{tot}}\% = 100\% \cdot (V_{\text{tot}}^{\text{New2}} - V_{\text{tot}}^{\text{sea}}) / V_{\text{tot}}^{\text{sea}}.$$

Where, $V_{\text{tot}}^{\text{New2}}$ is the total vanadium concentration formed at the geochemical barrier, $V_{\text{tot}}^{\text{sea}}$ is the total vanadium concentration in sea water.

RESULTS

At the first stage of the experiment on physicochemical modelling of the vanadium form behavior, the concentration of the element was determined in the form of simple and complexions, associates and ion pairs under the physicochemical conditions [11].

The overwhelming part of organic matter in river water is represented by humic and fulvic acids (more than 90%) [12], therefore, when modelling the interaction of metal ions with organic matter, only these substances were taken into account.

Concentrations of humic and fulvic acids in river water were $3.5 \cdot 10^{-7}$ mol/kg and $7.8 \cdot 10^{-7}$ mol/kg, respectively; only fulvic acids ($2.8 \cdot 10^{-7}$ mol/kg) were found in seawater [5]. The results of the experiment showed that the organic vanadium

compound amount in both types of waters is negligible. The contents of vanadium were $1.96 \cdot 10^{-8}$ mol/kg and $2.94 \cdot 10^{-8}$ mol/kg in the river and seawater, respectively [7]. The values of the total concentration of vanadium were $1.1115 \cdot 10^{-4}$ mol/kg and $4.6335 \cdot 10^{-7}$ mol/kg in the river and seawater, respectively.

Table 2 shows data on the distribution of physicochemical forms of vanadium in sea and river water, as well as in the estuary as a mixing zone.

Table 2. Vanadium chemical form concentrations and pH in river, estuary and sea waters

Vanadium chemical forms	River	Estuary	Sea
	pH		
	7.04	7.72	8.10
	Vanadium mass percentage (%)		
VO_2NO_3^0	0.2	0.02	0.0035
$\text{HV}_2\text{O}_7^{3-}$	0.21	1.153	2.04
H_2VO_4^-	90.5	51.32	22.75
HVO_4^{2-}	9.45	47.46	75.2

With the mixing of river and sea water, a sharp increase in pH values is observed (Fig. 1), which was regarded during the experiment as the formation of a geochemical barrier. At this barrier, there is a change in the dissolved forms of vanadium migration and their transformation (Table 2).

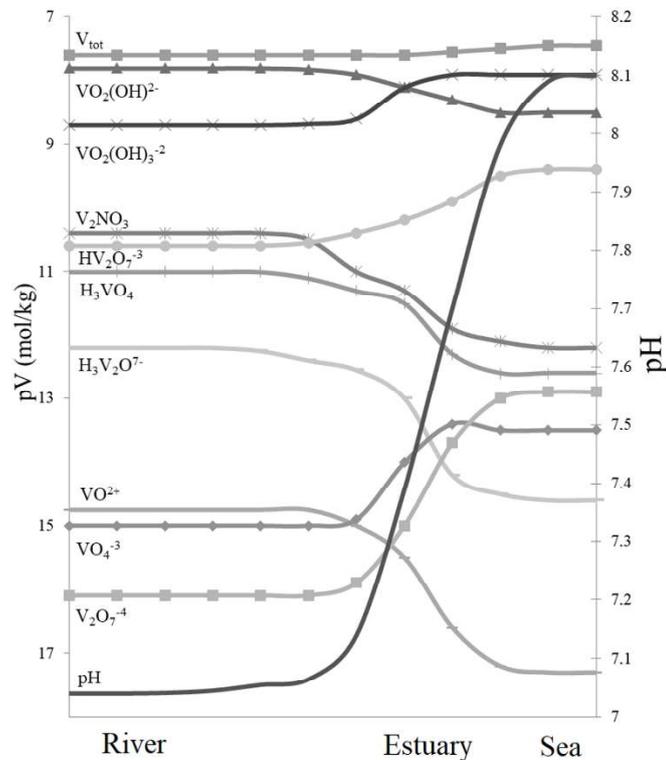


Fig. 1. Vanadium form distribution and concentrations at the river-sea geochemical barrier

At the next stage of the study, an attempt was made to assess the effect of physical sorption on the decrease in the total vanadium concentration during mixing at the geochemical barrier.

When sea and river waters mix, suspended matter of river water (and associated chemical elements) is deposited and new suspended matter is formed due to coagulation processes, which leads to an increase in turbidity.

Avalanche sedimentation and coagulation of colloids occurs at salinity from 2 to 5-6 ‰. In this area, up to 95% of suspended solids are lost. At a given salinity, the river suspended matter and newly formed suspended matter are removed, the concentration of the latter is calculated as the difference between the concentrations of suspended matter in the estuary and suspended matter in the river.

To simulate the sedimentation process, 95% of the microelements associated with suspended matter from the river are removed from the system. New values of the total vanadium concentration are obtained, which are used when calculating the sorption equilibrium with a concentration of newly formed suspended matter of 150 mg/L. Then, 95% of the vanadium associated with the newly formed suspended matter is removed from the system. The values of the total vanadium concentrations that should be in seawater when vanadium passes through the geochemical barrier

are obtained, provided that the change in contents is associated with physical sorption by 100%.

The results of modelling the vanadium behavior at the geochemical barrier are shown in Table 3.

Table 3. Vanadium form concentrations in river and sea waters

Vanadium concentrations (mol/kg)			
River water		Sea water	
V _{tot}	1.1115·10 ⁻⁴	V _{tot}	4.6335·10 ⁻⁷
V _{sol}	1.959·10 ⁻⁸ (0.05%)	V _{sol}	2.94·10 ⁻⁸ (6.5%)
V _{sorb}	1.111·10 ⁻⁴ (99.95%)	V _{sorb}	4.4405·10 ⁻⁷ (93.5%)

The results showed an increase in the concentration of vanadium dissolved forms by 1.5 times when passing the geochemical barrier.

As a result of experiments on physicochemical modelling of the behavior of vanadium forms [11], the role of sorption processes in the migration of vanadium, as well as the reasons for the change in their concentrations during the transition from river to sea waters, have been established.

CONCLUSION

As a result of the study, it was found that, during the transition from river to sea waters, an increase in the concentration of vanadium dissolved forms is observed, which is associated with the desorption of the latter with river suspended matter when passing through the geochemical barrier of the mixing zones of the river and sea waters.

In the study of estuarine zones, the main attention is paid to changes in the total element concentrations at the geochemical barrier, as well as the relationship between suspended and dissolved, organic and inorganic forms. At the same time, there is practically no information about the role of physicochemical biological processes in the formation of the acid-base barrier, where an increase in the concentration of vanadium dissolved forms play an important role in stimulating and enhancing biological processes.

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