

Coexisting Forms of Vanadium in Surface Water Objects (Review)

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The results of studies of the vanadium content and its coexisting forms in surface water bodies of various regions have been summarized. It has been shown that vanadium concentration in uncontaminated water bodies and rivers does not exceed several $\mu\text{g/L}$, whereas its concentration in water bodies which are subject to anthropogenic influence or located in the regions of volcanic activity reaches tens to hundreds of $\mu\text{g/L}$. The ratio of the suspended and dissolved forms of vanadium has been considered. The dissolved form of vanadium generally predominates in water bodies, whereas its migration as a constituent of suspended substances is characteristic of rivers, especially during the spring period. The studies of dissolved vanadium compounds concerning the ratio of its oxidized and reduced forms as well as complexation with dissolved organic matter have been discussed. It has been shown that V(V) dominates in the form of the H_2VO_4^- anion as the most stable form under oxidative conditions of surface waters. Several studies have noted the predominance of V(IV) in the form of oxocation VO^{2+} , although it is known as unstable in the natural aquatic environment and is rapidly oxidized to V(V). This process is decelerated in the presence of humic substances which exhibit reducing properties. Anionic, cationic and neutral complexes of vanadium with organic ligands are known. Humic substances play a major part in the complexation as established for certain water bodies of Ukraine. The results of studies on the molecular weight distribution of vanadium complex compounds have been also considered.

Keywords: vanadium, coexisting forms, the ratio V(V) and V(IV), complex compounds, humic substances, rivers, reservoirs, lakes

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INTRODUCTION

Bioavailability and toxicity of transition metals (Cr, Mn, Fe, Mo, V, etc.) depends on their forms of existing in the natural water as well as the oxidation state [1–3]. Therefore, for such metals it is not sufficient to determine their coexisting forms; on top of that, the conditions of their redox transformations should be considered.

Vanadium is among widespread elements in environmental objects (air, water, soil, and biota). Its content in the Earth's crust equals 0.016–0.02% [4, 5], close to this of zinc and nickel. However, in contrast to the latter elements, vanadium is more scattered, which determines its low concentration in natural waters

(0.01–20 $\mu\text{g/L}$) [6]. Vanadium concentration in rivers is of 0.2–4.5 $\mu\text{g/L}$ [7].

Leaching of vanadium from rocks and bottom sediments is a natural route of vanadium to surface water objects [8]. However, anthropogenic factor is crucial in environmental pollution with vanadium compounds. Transport, chemical, metallurgical, rubber, paper, textile, and paintwork factories, oil refineries, and thermal power plants are among major anthropogenic sources of vanadium determining its content in environmental objects, including water ones [9–14]. Oil and its processing products are the major sources of surface waters pollution with vanadium [7, 12, 13].

The functional role of vanadium in living organisms has not been solidly determined so far [15, 16]. Its immunotoxic, mutagenic, and carcinogenic properties have been marked [17–19]. At the same time, vanadium is a biogenic element essential for normal cells growth [20]. It is known to participate in the regulation of carbohydrates metabolism and human heart and circulatory systems [21]. Vanadium compounds have been used in medicine as stimulants in the treatment of anemia, tuberculosis, rheumatism, and other diseases. Toxic action of high concentrations of vanadium is due to the metabolism disfunction. The negative action of vanadium is reflected in the hematological and biochemical disfunctions, toxic action on the kidney and genital system [18]. Toxicity of the most widespread forms of V(IV) and V(V) is significantly different. V(V) compounds are known for the higher toxicity; they suppress the activity of enzymes catalyzing hydrolysis of ATP [3, 9, 22, 23] and can induce inflammatory processes and development of oncological diseases [24].

Experimental studies of the action of anionic form of vanadium(V) on certain biochemical and hydrochemical parameters of natural water of r. Don have been performed [25]. Reduction of activity of extracellular phosphatase of seston, the increase in the BOD₅ value as a marker of intensity of microbiological processes, and the decrease in the concentration of phosphates as well as ammonium and nitrite nitrogen in water [25] have been revealed; these effects have become more prominent with the increase in vanadium concentration from 0.5 to 100 µg/L.

The state of vanadium in natural waters has been scarcely studied, due to its high reactivity, low concentration, and wide variety of the coexisting forms, fractions of which depend on many factors including the metal concentration, pH, redox potential, the presence of complexing ligands, etc. [4, 26–28].

The studies on the coexistence of vanadium forms in aquatic ecosystems have been limited to the data on its oxidation state, with V(IV) and V(V) as the most probable states of vanadium in natural waters [29–31]. The state of vanadium is strongly dependent on the redox conditions in an aquatic environment [32, 33]. Vanadium(V) is thermodynamically stable under oxidative conditions, whereas V(IV) dominates under reductive conditions. V(V) exists in surface water objects in the anionic forms: H₂VO₄⁻ or HVO₄²⁻ (much less commonly, at pH above 9.0). It is believed that

V(V) in a complex with dissolved organic matter (DOM), for example, with humic substances (HS), can be reduced into V(IV) at pH < 6.0 owing to reductive properties of the ligands [34, 35]. Under reductive conditions, V(IV) exists in the form of the VO²⁺ oxocation, yet at very low pH. The stability of VO²⁺ is enhanced in more alkaline medium and in the complexes with natural organic ligands, even under oxidative conditions.

Vanadium in different oxidation states has been detected in natural waters, but the ratio of V(IV) and V(V) has been a matter of debate. Some researchers have mentioned V(IV) as the dominating form [36], whereas others have stated that both oxidation states coexist, the V(V) form being somewhat predominant [37, 38]. The vanadyl cation VO²⁺ is rapidly oxidized into V(V) in water saturated with oxygen, and it can be hardly possible that V(IV) dominates under such conditions.

Total content of vanadium in surface water objects. The data in Table 1 show that vanadium concentration in non-polluted surface water objects is about several µg/L. Higher content of vanadium is typical of the water objects which are subject to anthropogenic factors or these located in the regions of volcanic activity [12, 22, 39–41]. Thermo-electrical power plants consuming solid or liquid fuels (coal and petroleum products) contribute significantly to the pollution of water objects [12–14]. Coals contain 7 to 100 mg/kg of vanadium, whereas its content in oil is up to 1600 mg/kg [12].

Suspended and dissolved forms of vanadium. Analysis of limited data on the routes of vanadium migration in surface water objects evidences the predominance of its dissolved form (Table 2). Only in certain cases the suspended form of vanadium has been found prevailing; this is mainly the case of mountain rivers, for example rivers of Georgia (mass fraction of vanadium in the form of suspended particles V_{susp} reaching 96.4–99.6% of V_{total}) and rivers exhibiting high water turbidity (r. Danube and others) [6, 55, 56]. It has been mentioned that rivers transfer vanadium in the form of suspended matter [51, 52, 56, 57], especially during spring high water period [52, 58]. Predominance of V_{susp} has been related to the enhanced content of vanadium in rocks, soils, inorganic substances, and river suspended particles [57]. It has been noticed that V(IV) (as VO²⁺) is more prone to the adsorption on the suspended particles in natural waters [59, 60].

Table 1. Concentration of vanadium in different surface water objects

Water objects	V_{total} , $\mu\text{g/L}$	References
Rivers of Earth	<u>0.10–2.04</u> 0.71	[42]
Rivers of Africa	0.590–0.645	
Rivers of Europe	0.400–2.850	
Rivers of North America	0.009–2.055	
Rivers of different regions	0.23–3.7	[43]
r. Hrazdan, Armenia	<u>1.2–10.6</u> 4.4	[44]
r. Volga, lower course, delta, Russia	2.09–2.78	[18]
r. Bilina, Czech Republic	2.5–85.6	[41]
r. Warri, Nigeria	<u>0.0–260</u> 24.6	[45]
r. Conchos, Mexico	412–687	[40]
Rivers of the USA	0.2–49.2	[46, 47]
Basin of r. Bagmati, Nepal	<u>0.26–3.74</u> 1.37	[48]
r. Tama, Japan	1.22–2.72	[49]
r. Don, Russia	0.24–0.45	[50]
Rivers of Black Sea basin	n.d.–4.5	[51]
Rivers of Sweden	0.061–6.67	[52, 53]
Lakes of different regions of Russia	(0.35±0.23)–(3.18±2.80)	[18]
lake Imandra, Russia	0.05–0.24	
lake Weija, Ghana	<u>190–430</u> 140±10	[39]
Reservoirs of the Volga cascade, Russia	0.58–1.36	[18]
	1.2–3.8	[54]
Kuchurganskoe reservoir, Moldova	3.5–14.9	[13]
Surface waters near ash disposal areas of thermoelectrical power stations, Russia	0.5–150	[14]
Coastal sea waters	0.31–2.8	[48]

Dissolved forms of vanadium. Ratio of different oxidation states of vanadium. As has been shown above, vanadium is majorly found in the dissolved state in surface waters. Since vanadium is a transition metal, the ratio of its oxidized and reduced forms is an important issue. The corresponding data are collected in Table 3.

Many of the available reports lack the data on the ratio between V(V) and V(IV), due to the complicated procedure of their separate determination. The available data evidence the predominance of V(V) in the dissolved forms of vanadium, since V(IV) is readily oxidized by dissolved oxygen, if not in the form of a complex with DOM. However, some researchers have

Table 2. Total concentration of vanadium and its dissolved and suspended forms in different surface water objects^a

Water objects	V_{total} , $\mu\text{g/L}$	V_{dissolv}		V_{susp}		References
		$\mu\text{g/L}$	% V_{total}	$\mu\text{g/L}$	% V_{total}	
r. Danube (mouth), Ukraine	–	2.3–4.5	–	10.8–18.6	–	[56]
r. Volga, Russia	–	1.8–18.6	–	2.3–6.5	–	[54, 56, 61]
Rivers of Azov region, Russia	6.6–16.0	–	55.8–83.5	–	–	[62]
Rivers of Georgia	53.9–121.4	0.4–1.9	0.4–3.5	52.0–121	96.4–99.6	[55]
Rivers of Central Siberia, Russia	1.06–13.41	0.66–8.79	35.4–74.1	0.40–6.04	25.9–64.6	[57]
r. Severnaya Dvina, Russia	–	0.412–0.812	27.7–82.5	–	17.5–72.3	[58]
r. Neva and tributaries, Russia	2.42–22.30	2.32–14.83	67.8–96.0	0.086–7.191	4.0–32.2	[63]
r. Pearl, the USA	0.36	0.30	83.3	–	–	[64]
r. Tamma, Japan	1.22–2.72	0.67–1.96	54.9–72.1	0.55–0.76	27.9–45.1	[49]
r. Kalix, Sweden	–	<u>0.077–0.140</u> 0.108	–	<u>0.068–0.330</u> 0.160	–	[52, 65]
r. Torne älv, Sweden	–	<u>0.076–0.163</u> 0.106	–	<u>0.108–0.270</u> 0.166	–	
Estuaries of rivers of Sweden	–	<u>0.067–0.256</u> 0.156	–	<u>0.022–0.333</u> 0.117	–	[52, 65]
lake Biwa, Japan	<u>0.092–0.28</u> 0.16	<u>0.076–0.26</u> 0.126	<u>62.7–94.7</u> 78.8	<u>0.012–0.056</u> 0.034	<u>5.3–37.3</u> 21.2	[66]
Lakes of China	–	1.0–4.36 (V^V) 0.25 (V^{IV})	–	–	–	[67]
Baltic Sea, Sweden	–	0.096–0.200	–	0.0005–0.020	–	[65]

^a Here and in Table 3: extreme values are given above-the-line, average values are given below-the-line; (–) the data are not available.

marked that V(IV) can exist in surface waters in the presence of excess of organic compounds capable of V(V) reduction. Under such conditions, oxidation of V(IV) is decelerated owing both to the predominance of the reduction and the decrease in the dissolved oxygen concentration (due to its consumption on oxidation of organic matter).

Earlier experiments have revealed (Fig. 1) that 90% oxidation of V(IV) with dissolved oxygen at pH 5 and vanadium concentration 50.0 $\mu\text{g/L}$ occurs within 40 min, whereas at pH ≥ 7 (typical of surface waters) the process occurs within less a minute [84]. These data

explain why V(IV) has not been detected in the samples of water even using highly sensitive chemiluminescence method [85].

The addition of HS decelerates oxidation of V(IV). At concentration of humic acids (HA) and fulvic acids (FA) 10 mg/L and pH 8.5, 90% oxidation of V(IV) has required 13 and 11 min, respectively. The rate of V(IV) oxidation has been significantly reduced upon increase in the HS concentration to 30 mg/L. At higher concentration of FA (30–50 mg/L), the rate of oxidation has been seemingly increased, as judged by the decrease in the V(IV) concentration in the solution.

Table 3. Concentration of dissolved forms of vanadium in natural waters

Water objects	V_{dissolv} , $\mu\text{g/L}$	V(IV)		V(V)		References
		$\mu\text{g/L}$	% V_{dissolv}	$\mu\text{g/L}$	% V_{dissolv}	
Coastal waters, the USA	(0.66±0.12)– (1.27±0.20)	(0.15±0.097)– (0.22±0.066)	11.6–28.2	(0.56±0.10)– (1.14±0.20)	71.8–88.4	[30]
Churchill river estuary, Monitoba, Canada	(0.24±0.18)– (1.39±0.96)	–	–	–	–	[8]
Rivers of the Earth	0.76	–	–	–	–	[68]
Lake Hafik, Turkey	19.58±0.46	5.70	29.1	13.88±0.42	70.9	[69]
Stream, Imranla region, Turkey	38.44±0.53	14.32	37.3	24.12±0.50	62.7	
East Lake, Wuhan, China	(4.48±0.13)– (4.65±0.22)	n.d.	n.d.	(4.48±0.13)– (4.65±0.22)	100	[70]
lake Biwa, Japan	<u>0.066–0.59</u> 0.16	–	–	–	–	[66]
Rivers of Africa	0.59–0.65	–	–	–	–	[42]
Rivers of Europe	0.4–2.9	–	–	–	–	
Rivers of North Americas	0.4–1.84	–	–	–	–	
Rivers of basin of r. Amazon	0.04–1.71	–	–	–	–	[42, 68]
Gironde river estuary, France	0.89–2.76	–	–	–	–	[71]
r. Missisipi and tributaries, the USA	0.23–2.27	–	–	–	–	[68, 72]
Rivers of Argentina	0.91–2.19	(0.33±0.02)– (1.21±0.02)	36.3–55.3	(0.58±0.03)– (1.16±0.02)	44.7–63.7	[73]
lake Chasicó, Argentina:						
rainy season	44.0–86.0	–	–	–	–	[74]
drought season	96.0–366	–	–	–	–	
stream Chasicó:						
rainy season	68.0–94.0	–	–	–	–	
drought season	184–252	–	–	–	–	
r. Neva and tributaries, Russia	2.32–14.83	–	82–89	–	11–18	[63]
Surface waters near lake Bracciano, Italy	<u>10.0–30.0</u> 23.1	–	–	–	–	[22]
Subsoil waters of volcanic regions of Italy:						
Castelli Romani area	<u>13.0–82.0</u> 39.6	<u>2.0–33.0</u> 11.9	<u>3.8–53.2</u> 30.1	<u>8.0–54.0</u> 27.7	<u>46.8–96.2</u> 69.9	[22]
Mount Etna area	<u>33.0–138</u> 57.1	<u>5.0–114</u> 31.3	<u>15.2–89.2</u> 54.8	<u>7.0–70.0</u> 25.8	<u>10.8–84.8</u> 45.2	[22]
	15.6–182	–	–	–	62.8–98.9	[75]

Table 3. (Contd.)

Water objects	V_{dissolv} , $\mu\text{g/L}$	V(IV)		V(V)		References
		$\mu\text{g/L}$	% V_{dissolv}	$\mu\text{g/L}$	% V_{dissolv}	
Rivers of Japan	(0.22±0.04)– (39.8±0.03)	–	–	–	–	[76]
	0.32–0.44	0.27–0.40	85.7–92.0	0.035–0.045	8.0–14.3	[77]
Lakes of Japan	(0.56±0.02)– (5.78±0.07)	–	–	–	–	[76]
	0.16–0.50	0.12–0.42	71.9–84.8	0.045–0.075	15.2–28.1	[77]
r. Yangtze, China	1.55–2.05	–	–	–	–	[68]
Lakes of the USA	1.7–22.9	–	–	–	–	[78]
Well water, Southern Nevada, the USA	(7.0±0.1)– (82.6±0.5)	(0.07±0.02)– (0.47±0.06)	0.6–0.9	(6.9±0.01)– (82.1±0.05)	98.7–99.4	[79]
Lakes of Japan: epilimnion	0.14–0.95	–	–	–	–	[80]
hypolimnion	0.08–0.31	–	–	–	–	[80]
Surface waters of Argentina	0.93–3.14	0.4–0.6	19.1–43.0	0.9–3.1	96.8–98.7	[81]
Basin of r. Amazon, the USA	(0.66±0.04)– (1.03±0.08)	–	–	–	–	[82]
Myrtle Grove channel, delta of r. Missisipi, the USA	1.0–3.04	–	–	–	–	[83]
Lakes of China	–	0.25	–	1.4–4.36	–	[67]
Sea waters: near-bottom	1.58–2.04	–	–	–	–	[59]
interstitial water	8.19–71.77	–	–	–	–	[59]

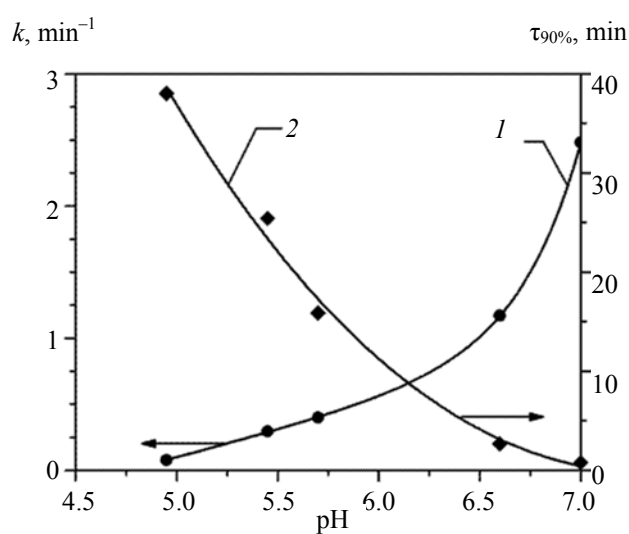


Fig. 1. Rate of oxidation (1) and time to 90% oxidation of V(IV) (2) with dissolved oxygen as functions of pH. $C_{V(IV)} = 50.0 \mu\text{g/L}$.

However, it has been later found that the decrease in V(IV) concentration has been due to its complexing with FA, as confirmed by the data of gel permeation chromatography [84]. At the same time, a fraction of V_{dissolv} exists in the form of HVO_4^{2-} oxoanions in natural surface waters.

Complexation of vanadium in surface waters. It should be noted that the studies of the complexation of vanadium in surface waters have been scarce. Predominant existence of vanadium in the form of HVO_4^{2-} oxoanion is likely among the major reasons of its weak complexing with natural ligands found in surface waters. Complexation is more typical of the reduced form, V(IV) [67].

The most attention has been paid to the complexation of vanadium with HS, for example, with HA and FA [34, 35, 69, 86–88]. It has been marked that the formation

Table 4. Concentration of dissolved forms of vanadium in selected water objects of Ukraine [84]

Water objects	V_{dissolv} , $\mu\text{g/L}$	V(V)		Organic complexes of vanadium	
		$\mu\text{g/L}$	% V_{dissolv}	$\mu\text{g/L}$	% V_{dissolv}
r. Yuzhnii Bug, v. Kostyantynovka	6.4±0.4	1.1	17.2	5.3	82.8
Cooling reservoir of Southern-Ukrainian nuclear power station	6.0±0.5	1.5	25.0	4.5	75.0
Same place, v. Bugskoe	4.4±0.8	1.4	31.8	3.0	68.2
Same place, v. Aleksan- drovka					
above dam	6.1±0.4	2.2	38.0	3.9	62.0
below dam	6.5±0.5	2.2	33.8	4.3	66.2
Same place, v. Pribuzh'e	7.7±0.5	3.8	49.4	3.9	50.6
r. Ros, spring	8.3±0.7	2.4	28.9	5.9	71.1
summer	3.3±0.5	0.3	9.1	3.0	90.9
r. Stugna, spring	5.4±0.4	1.4	25.9	4.0	74.1
summer	2.5±0.4	0.1	4.0	2.4	96.0
Kanevskoe reservoir, Obolon bay, summer	0.49±0.06	$<5 \times 10^{-3}$	Not determined	0.49±0.06	100

of V(V) complexes with HS is less typical, since negative charge of HVO_4^{2-} inhibits the formation of strong electrostatic bonds with HS which are also negatively charged (the covalent bonding is, however, possible) [87]. The ESR studies have revealed that fulvate complexes of vanadium contain the VO^{2+} ions. Since HA and FA exhibit reducing properties, V(V) is likely first reduced into V(IV) and then the formed vanadyl ions are bound into the complexes [34, 87]. 1 g of HA can reduce 1.53 mg (0.03 mmol) of vanadium from the VO_3^- anionic form into VO^{2+} [35]. It has been found that 35 to 50% of VO_3^- can be reduced at the FA: VO_3^- ratio of 10 : 1 [89].

Formation of VO^{2+} complexes with FA fractions (molecular mass 750 and 300 Da) has been studied [86]. Binding of vanadyl ions has been accompanied by the aggregation of the FA and almost six-fold increase in its molecular mass (to 4.0 kDa at pH 5). The complexation has involved strong as well as weak binding sites of FA. The low-molecular fraction of FA (MM 300 Da) has formed weaker complexes with VO^{2+} than the high-molecular fraction. The binding of VO^{2+} has occurred mainly via carboxylic and phenol

hydroxyl groups of FA, in line with stronger binding of V(IV) and V(V) with donor oxygen atoms [87]. The formation of the $(\text{VO})_2(\text{FA})_6$ fulvate complexes has been suggested [86]. The formation of vanadium-containing complexes with DOM has been marked in some other studies [8, 53]. It has been shown that the concentration of dissolved vanadium (V_{dissolv}) is positively correlated with total dissolved organic carbon (DOC) ($r = 0.48$) and with HS ($r = 0.39-0.66$) [8]. At the same time, the correlation between concentrations of V_{dissolv} and the protein-like compounds has been weak [8].

The formation of stable vanadium complexes with organic ligands in coastal seawater has been confirmed in Ref. [90]. However, their mass fraction has not exceeded 5–10%, and the major part of vanadium has been found in the form of colloidal particles with size below 0.45 μm ; such particles has been considered unstable. The minor role of the complexation in migration of vanadium has been stated in Ref. [68].

The presence of anionic (0.0–30.0% V_{dissolv}), cationic (38.0–74.2% V_{dissolv}), and neutral (21.2–27.0% V_{dissolv}) vanadium compounds in the water of r. Neva

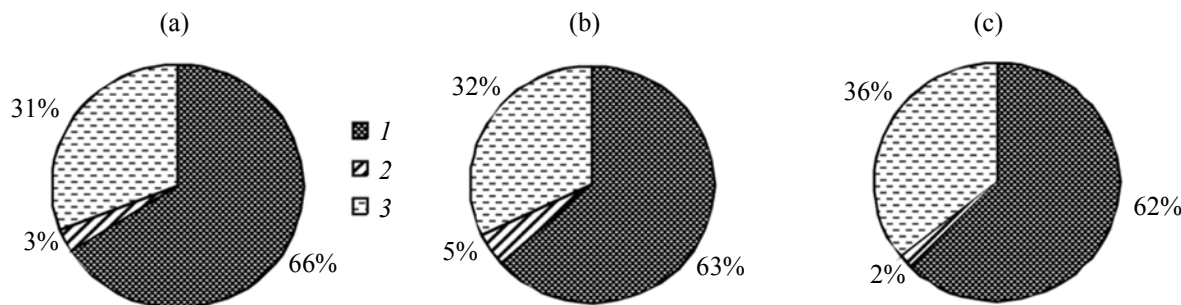


Fig. 2. Distribution of vanadium between the complexes with anionic (1), cationic (2), and neutral (3) groups of DOM in water of rivers Ros (a) and Stugna (b), and upper part of Kanevskoe reservoir (c) during summer of 2003 [84].

and its tributaries has been confirmed by means of electro dialysis and electromigration [63]. The anionic and cationic compounds have contained high-molecular ($0.0\text{--}17.8\%$ V_{dissolv}) as well as low-molecular ($55.5\text{--}74.2\%$ V_{dissolv}) ones, the latter prevailing.

Extraction of more than 90% of V_{dissolv} using a column based on anion-exchange cellulose DEAE (diethylaminoethylcellulose) has evidenced the predominance of anionic compounds of vanadium in the water of lake Pavin (France) [91]. The authors have marked that these can be negatively charged organic complexes of vanadium as well as its oxoanions H_2VO_4^- which are also adsorbed by the DEAE cellulose anionite. Association of vanadium with organic macromolecules has been confirmed by means of dialysis and ultrafiltration. The relative content of the colloidal fraction of vanadium was of 55% of V_{dissolv} . The compounds with molecular weight below 10 kDa have contained about 70% of V_{dissolv} , and 45% of them have been low-molecular compounds (< 1 kDa), likely, oxoanions H_2VO_4^- . The share of the colloidal fraction (1 kDa– $0.22\ \mu\text{m}$) of V_{dissolv} in the water of r. Severnaya Dvina has ranged between 18% in winter and 26% in spring [58]. The low-molecular fraction (< 1 kDa) has remained the major one, giving 80–90% of V_{dissolv} .

Our earlier reported studies have shown that a significant part of V_{dissolv} in the studied water objects has existed in the form of complexes with DOM (Table 4). Degree of the complexation has been 50.6 to 96–100%.

The organic complexes of vanadium have been mainly anionic and neutral compounds (Fig. 2). Hence, the binding of vanadium majorly involves HS (for example, FA) and carbohydrates. The main part in the complexation was played by FA (the predominant form of DOM in surface waters); they have bound 62 to 66% of V_{dissolv} .

CONCLUSIONS

The content of vanadium in non-polluted surface water is of several $\mu\text{g/L}$, being increased to tens or hundreds of $\mu\text{g/L}$ in waters subject to anthropogenic or volcanic action. Thermal power plants consuming coal or petroleum products (containing vanadium) play significant part in the environmental pollution with vanadium.

Dissolved form of vanadium determines its migration in most of water objects. However, suspended vanadium-containing substances prevail in river water. The dissolved forms of vanadium have been the best studied so far. Significant attention has been paid to the investigation of the ratio between oxidized and reduced forms of vanadium: V(V) and V(IV), since their toxicity to the hydrobionts is different. V(V) is more toxic than V(IV). V(V) is predominant in surface waters as the most stable form of vanadium. Vanadyl ions (VO^{2+}) are unstable in natural waters, being oxidized by dissolved oxygen. However, the oxidation is decelerated in the presence of humic substances. This is due to the reductive as well as complex forming properties of these compounds. V(IV) has been identified in the complexes with humic substances, and it is believed that their interaction involves the reduction of V(V) into V(IV), followed by the complexation.

The data on molecular weight distribution of the vanadium complexes with dissolved organic compounds have been limited. Certain reports have mentioned the presence of vanadium compounds with molecular weight of 1 kDa or 10 kDa to size of $0.22\ \mu\text{m}$. Likely, they can be related to colloidal (disperse) form of vanadium.

The data on the distribution of vanadium between the differently charged complexes are available. Anionic complexes of vanadium with humic substances are the prevailing ones, as evidenced by the

study of selected water objects of Ukraine (62 to 66% of V_{dissolv}). A portion of vanadium has been found also in the form of neutral complexes, likely with carbohydrates.

In summary, the state of vanadium in surface water objects has revealed a variety of the coexisting metal forms. The relevant information is essential in view of ecological issues and for the understanding of the ways of vanadium migration in water objects and possible transformation of the vanadium forms under the action of environmental factors.

CONFLICT OF INTEREST

No conflict of interest was declared by the authors.

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