

Article



Adsorbed Chemical Elements of River Runoff of Solids and Their Role in the Transformation of Dissolved Matter Runoff into the Ocean

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Abstract: A procedure for experimental modeling of sorption–desorption processes in the mixing zone of river and sea waters, which excludes the determination of the absolute concentrations of adsorbed chemical elements, has been proposed. Based on experimental data, quantitative characteristics of the ion-exchange transformation of dissolved matter runoff during the penetration of terrigenous material into the marine environment were obtained. The real input of calcium into the ocean as a result of desorption from the solid substances of river runoff increases by 8.3–8.7%, while input of sodium, potassium, and magnesium decreases by 14.0–14.6, 22.2–23.3, and 3.0–3.2% of their dissolved river runoff. For trace elements, sorption–desorption processes lead to an increase in the runoff of dissolved manganese, cobalt, nickel, cadmium, thallium, barium, and ammonium by 98.6–103.5, 20.6–21.6, 3.8–4.0, 15.6–16.5, 4.7–4.9, 20.3–21.3, and 0.8% and to a decrease in the runoff of dissolved lead and cesium by 9.1–9.4 and 2.6–2.8%.



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Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). **Keywords:** sorption–desorption processes; mixing zone of river and sea waters; major cations; trace elements

1. Introduction

One of the main inputs in the geochemical balance of the ocean is the river runoff of dissolved and solid matter, the chemical composition of which has been studied quite well [1–5]. It is generally accepted that dissolved substances are directly involved in the formation of the seawater salt composition, while solid phases affect seawater mainly indirectly through reactions of authigenic mineral formation (reverse weathering and diagenesis). At the same time, there are many facts indicating that due to sorption–desorption processes in the mixing zone of river and sea waters, the real amounts of dissolved forms of chemical elements entering the ocean can differ significantly from the calculated values based on data on the chemical composition and water discharges in the river's outlet [4,6].

The adsorbed and dissolved forms of chemical elements are in a mobile dynamic equilibrium, and composition of the adsorbed complex, which is understood as the sum of adsorbed components, is easily and relatively quickly transformed when the composition of the aqueous medium in contact with the solid phase changes. According to experimental modeling data, the transition of terrigenous material from freshwater to marine environment leads to the replacement of most of the calcium by sodium, potassium, and magnesium [7–9]. This markedly increases the estimated river runoff for dissolved calcium and reduces the corresponding estimates for potassium, sodium, and magnesium [10]. However, the existing methods for determining the adsorbed complex composition have a number of irremediable disadvantages that do not allow considering the results obtained with their help to be sufficiently reliable. Such disadvantages include the distortion of the adsorbed complex composition during the preliminary removal of soluble substances, the

possibility of chemical interaction of desorbing solutions with the studied solid phases, etc. Quantitative estimates of the sorption–desorption transformation of the river runoff of dissolved trace elements are based mainly on field observations on the distribution of their concentrations in the mixing zone and the form of the concentration–salinity relationship, which allow for ambiguous interpretation due to the simultaneous occurrence of various physical, chemical, and biological processes in nature [4].

Recently, the authors have developed an original procedure for experimentally determining the balance of sorption-desorption processes in the mixing zone of river and sea waters, which is maximally similar to natural conditions. This manuscript describes this procedure and presents the first results of its application.

2. Materials and Methods

The procedure for determining the balance of sorption–desorption processes in the mixing zone of river and sea waters is as follows.

A weighted portion of the solid phase (terrigenous material) is brought to the state of sorption equilibrium with fresh water, an analog of the river runoff, after which 1/3 of settled equilibrium solution is filtered and separated into two aliquots. In the first aliquot, the content of macro and trace elements is analyzed, which corresponds to the initial equilibrium concentration of their dissolved forms in suspension solid phase–fresh water. Artificial seawater with a salinity of 105‰ is added to the second aliquot in the amount of 1/2 of its volume (to prepare 105‰ seawater, the three-fold amounts of salts contained in normal 35‰ seawater are taken, minus the masses of salts contained in the two-fold volume of fresh water used in the experiment, so that when mixing one volume of 105‰ seawater and two volumes of fresh water, the composition of the mixed solution exactly corresponded to normal seawater with a salinity of 35‰). The obtained solution "A" has a salinity of 35‰, and its composition reflects the integral, not related to sorption–desorption, result of the chemical transformation of the river runoff of dissolved substances at their penetration into the sea basin (in this case, the factors of chemical transformation will be, for example, the processes of coagulation and flocculation).

To the remaining equilibrium suspension, from which 1/3 of liquid phase has been extracted, an appropriate amount of 105‰ artificial seawater is added, and with continuous stirring in the presence of air, the system is brought to the state of sorption equilibrium. The salinity of the obtained solution "B" is 35‰, and its composition is determined by both changes in the composition of the river runoff of dissolved matter and the transformation of the composition of the adsorbed complex. It is obvious that the difference between the compositions of solutions "B" and "A" corresponds to the integral balance of the sorption–desorption transformation of the adsorbed complex of the solids of river runoff.

This procedure was applied to determine the balance of macro and trace elements (Na, K, Mg, Ca, N-NH₄, Cs, Ba, Mn, Co, Ni, Cd, Tl, and Pb) in the mixing zone of river and sea waters.

Samples of freshwater terrigenous material were selected according to the principle of similarity to the mineralogical composition of the global runoff of solids. Five samples of freshwater bottom sediments prewashed by distilled water from pore solutions were used in the experiments: dark-gray silt (creek, Nizhny Novgorod Region, Russia), two samples of silty sand (Remna and Seima Rives in the same place), and two samples of sandy brown silt (Lake Pes'vo, Tver Region, Russia). According to the data of X-ray phase analysis, clay minerals in the samples are mainly represented by hydromicas (40–60%), kaolinite (20–30%), and chlorite (10–15%). This is close to the relative abundance of clay minerals in the suspended matter of world rivers, where the proportion of hydromicas, smectite minerals, kaolinite, and chlorite averages 50, 25, 15, and 10% [11].

Plastic vessels with 15 g of air-dry sediments were poured with 150 mL of water from the Mozhaisk Reservoir (Moscow Region, Russia), filtered through an autoclaved dense paper filter and containing 0.43, 0.05, 0.61, and 1.50 mg-eq/L of sodium, potassium, magnesium, and calcium, as well as 0.12, 0.28, and 2.05 mg-eq/L of chlorides, sulfates, and

hydrocarbonates. The suspensions were bubbled with air for 8 h and kept without stirring for 16 h for settling of the fine fraction. This was enough time to establish sorption equilibrium between Mozhaisk Reservoir water and freshwater sediments. After that, 50 mL of settled solution was taken from each plastic vessel and filtered through a membrane filter 0.22 µm. To 40 mL of the filtrate was added 20 mL of 105‰ artificial seawater containing 1436.7, 31.3, 326.9, and 61.6 mg-eq/L of sodium, potassium, magnesium, and calcium, as well as 1683.4 and 173.2 mg-eq/L of chlorides and sulfates, so that at mixing the latter with water from the Mozhaisk Reservoir in proportion 1:2, the composition corresponded to normal seawater with a salinity of 35%. The obtained solutions "A" were filtered once again through a membrane filter $0.22 \,\mu m$ into two polypropylene flasks each: (1) without preservation for the determination of major cations and ammonium, and (2) with preliminarily added aliquots of 5 N high-purity nitric acid (0.25 mL per 10 mL solution) for trace element analysis. The remaining 100 mL of water from the Mozhaisk Reservoir with 15 g of sediments were poured with 50 mL of 105% seawater, and the suspensions were brought to an equilibrium state with continuous air bubbling (also ~8 h). The obtained solutions "B", similarly to solutions "A", were filtered through a membrane filter 0.22 µm into polypropylene flasks without preservation and with preservation by 5 N nitric acid.

The concentrations of major cations and ammonium were measured by capillary electrophoresis. The concentrations of dissolved trace elements (Cs, Ba, Mn, Co, Ni, Cd, Tl, and Pb) were determined by mass-spectrometry with inductively coupled plasma. The relative measurement error was $\pm 3\%$. The trueness of the analyses was assessed using the international standards of river water SLRS-4 and SLRS-5 and the standard of estuarine water with a salinity of 15‰ SLEW-3, for which the discrepancy between the measured and certified concentrations of the studied elements did not exceed 20%.

3. Results and Discussion

3.1. Major Cations

According to the experimental data summarized in Table 1, the ion-exchange balance of major cations during the interaction of freshwater terrigenous material with seawater is maintained with a high accuracy. The mean sum of the amounts of sodium, potassium, and magnesium removed from the solution (-14.67 mg-eq/100 g) almost exactly corresponds to the amount of calcium entering the solution (14.54 mg-eq/100 g): the residual is only 0.9%.

For correct comparison of the results of experiments and field observations, it is better to use not absolute values but their equivalent amounts, because changes in the absolute concentrations of exchangeable ions depend on the total exchange capacity of mineral phases, which is subject to strong variability [10]. To eliminate the influence of this factor, the changes in the concentrations of adsorbed ions $\Delta[i]$ were normalized to the change in the content of adsorbed calcium $\Delta[Ca]$ (Table 2). The ratios $\Delta[i]/\Delta[Ca]$ do not depend on the dispersion degree and other properties of solid phases, which affect the value of their total exchange capacity, and unambiguously characterize the process of chemical transformation of the adsorbed complex.

Comparison of calcium-normalized changes in the composition of the adsorbed complex of terrigenous material (Table 2) shows good agreement between field and experimental data. The dissolution of 1.0 mg-eq of calcium from the adsorbed complex of terrigenous material is accompanied, on average, by the uptake of 0.72, 0.13, and 0.15 mg-eq of sodium, potassium, and magnesium from seawater. This relation can be used to calculate the global ion-exchange balance at the river–sea geochemical barrier.

	Equilibrium Concentrations [i], mg-eq/L			
Solid Phase	Solution "A" (Mixing in the Absence of Solid Phase)	Solution "B" (Mixing in the Presence of Solid Phase)	Difference $\Delta[i] = [i]_{B} - [i]_{A}$	
	Ν	a		
Dark-gray silt	480.5	466.8	-13.7	
Sandy brown silt, sample 1	479.6	467.0	-12.6	
The same, sample 2	479.1	467.3	-11.8	
Silty sand, sample 1	479.6	472.1	-7.5	
The same, sample 2	479.9	472.1	-7.8	
Mean			-10.68	
	K			
Dark-gray silt	10.55	8.60	-1.95	
Sandy brown silt, sample 1	10.48	8.76	-1.72	
The same, sample 2	10.29	8.68	-1.61	
Silty sand, sample 1	10.39	9.42	-0.97	
The same, sample 2	10.19	9.20	-0.99	
Mean			-1.45	
	М	g		
Dark-gray silt	110.6	107.4	-3.2	
Sandy brown silt, sample 1	109.0	106.4	-2.6	
The same, sample 2	110.1	107.5	-2.6	
Silty sand, sample 1	109.5	107.5	-2.0	
The same, sample 2	111.6	109.3	-2.3	
Mean			-2.54	
	С	a		
Dark-gray silt	20.56	38.85	18.28	
Sandy brown silt, sample 1	21.15	36.83	15.68	
The same, sample 2	20.76	37.44	16.68	
Silty sand, sample 1	20.82	31.27	10.45	
The same, sample 2	20.38	32.01	11.63	
Mean			14.54	

Table 1. Changes in the composition of the adsorbed complex of freshwater terrigenous material at the interaction with seawater ¹.

¹ Under the experimental conditions (mass ratio solid phase/solution 1:10), the difference in the concentrations of ion *i* in the solution in mg-eq/L with the opposite sign corresponds to the change in the content of this ion in the adsorbed complex in mg-eq/100 g.

Table 2. Calcium-normalized changes in the composition of the adsorbed complex of terrigenous material during the transition from freshwater to marine environment.

Material	Ratio of the Equivalent Concentrations Difference in Solution $\Delta[i]/\Delta[Ca]$				Reference
_	Na	К	Mg	Ca	_
Terrigenous material of river runoff, natural observations	-0.67	-0.19	-0.15	1.00	[10]
Soil and clay minerals, experimental modeling	-0.77	-0.09	-0.14	1.00	"
Freshwater bottom sediments, experimental modeling	-0.73	-0.10	-0.17	1.00	This study
Mean	-0.72	-0.13	-0.15	1.00	"

According to [10], the average specific value of the exchange capacity of solids of river runoff is 28 mg-eq/100 g (280 g-eq/t), and the calcium proportion in the adsorbed complex decreases from 74.8 to 14.5% when freshwater conditions change to marine environment. This leads to the input from the adsorbed complex to the dissolved state of 168.8 g-eq, or 3.38 kg of calcium from each ton of terrigenous material entering the ocean. With the most probable mass of river runoff of solid substances being 15.0–15.7 Gt/yr [12,13], desorption of calcium is equal to 50.7–53.1 Mt/yr. The ratios of the difference between equivalent concentrations of dissolved sodium, potassium, and magnesium to the similar difference in calcium concentrations $\Delta[i]/\Delta[Ca]$, given in Table 2, make it possible to determine the global ion-exchange balance of cations of the main salt composition at the river–sea geochemical barrier (Table 3). The input of calcium increases by 8.3–8.7%, while the runoff of other cations decreases by 14.0–14.6% for sodium, by 22.2–23.3% for potassium,

and by 3.0–3.2% for magnesium. It follows that the sorption–desorption transformation noticeably changes the runoff of the major cations, which must be taken into account in the geochemical balance of the ocean.

Table 3. Input of dissolved cations of the main salt composition with river runoff into the ocean with correction for the ion exchange in the adsorbed complex of solid substances.

		Contribution of the Ion		
Ion	River Runoff [14]	Ion Exchange in the Adsorbed Complex of the Solids of River Runoff ¹	Input with Correction for the Ion Exchange ¹	Ocean (% of the Input with the River Runoff) ¹
Na	300	$-\frac{41.9}{43.9}$	$\frac{258.1}{256.1}$	$-\frac{14.0}{14.6}$
Κ	58	$-\frac{12.9}{13.5}$	$\frac{45.1}{44.5}$	$-\frac{22.2}{23.3}$
Mg	152	$-\frac{4.6}{4.8}$	$\frac{147.4}{147.2}$	$-\frac{3.0}{3.2}$
Ca	613	$\frac{50.7}{53.1}$	$\frac{663.7}{666.1}$	$\frac{8.3}{8.7}$

 1 The numerator and denominator are the values calculated for the global river runoff of solid substances, equal to 15.0 Gt/yr [13] and 15.7 Gt/yr [12].

3.2. Trace Elements

Experimental determination of the sorption–desorption balance of dissolved trace elements at the interaction of freshwater terrigenous material with seawater is shown in Table 4. For all trace elements, the measured concentrations of dissolved forms both in fresh and sea water are significantly lower than those in equilibrium with the least soluble solid phases [15–20]. Due to this, the processes of dissolution–precipitation of solid phases cannot take part in the chemical transformation of the studied elements runoff in the mixing zone of river and sea waters, and biogeochemical and sorption–desorption processes come to the fore.

Table 4. Sorption–desorption balance of dissolved trace elements at the interaction of freshwater terrigenous material with seawater ¹.

	Equilib	Enceific Decomption (1)			
Solid Phase	Solution "A" (Mixing in the Absence of Solid Phase)	Solution "B" (Mixing in the Presence of Solid Phase)	Difference $\Delta[i] = [i]_{\rm B} - [i]_{\rm A}$	or Sorption (–), μg/g (g/t)	
		N-NH ₄			
Dark-gray silt	257	305	48	0.48	
Sandy brown silt, sample 1	179	211	32	0.32	
The same, sample 2	185	217	32	0.32	
Silty sand, sample 1	157	177	20	0.20	
The same, sample 2	162	182	20	0.20	
Mean			30	0.30	
		Cs			
Dark-gray silt	0.198	0.044	-0.154	-0.0015	
Sandy brown silt, sample 1	0.063	0.005	-0.058	-0.0006	
The same, sample 2	0.085	0.007	-0.078	-0.0008	
Silty sand, sample 1	0.099	0.039	-0.060	-0.0006	
The same, sample 2	0.080	0.024	-0.056	-0.0006	
Mean			-0.081	-0.0008	
Ba					
Dark-gray silt	32	1650	1618	16.2	
Sandy brown silt, sample 1	66	1450	1384	13.8	
The same, sample 2	87	1510	1423	14.2	
Silty sand, sample 1	32	1090	1058	10.6	
The same, sample 2	64	1100	1036	10.4	
Mean			1304	13.0	

$\begin{tabular}{ c c c c c c c c c c c c c c c c c c c$		Equilib	Specific Description (1)				
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	Solid Phase	Solution "A" (Mixing in the Absence of Solid Phase)	Solution "B" (Mixing in the Presence of Solid Phase)	Difference $\Delta[i] = [i]_{\rm B} - [i]_{\rm A}$	or Sorption (–), μg/g (g/t)		
$\begin{array}{c c c c c c c c c c c c c c c c c c c $			Mn				
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Dark-gray silt	1540	17780	16240	162.4		
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	Sandy brown silt, sample 1	680	13140	12460	124.6		
	The same, sample 2	880	17110	16230	162.3		
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	Silty sand, sample 1	120	1770	1650	16.5		
Mean 9350 93.5 Dark-gray silt 1.91 22.15 20.24 0.202 Sandy brown silt, sample 1 1.25 8.81 7.56 0.0076 The same, sample 2 2.13 8.86 6.73 0.067 Silty sand, sample 1 0.51 3.70 3.19 0.032 The same, sample 2 0.94 6.47 5.53 0.086 Mean 0.865 0.086 0.086 Dark-gray silt 13.92 35.28 21.36 0.214 Sandy brown silt, sample 1 7.21 17.59 10.38 0.104 The same, sample 2 1.659 24.95 8.36 0.086 Silty sand, sample 1 0.71 2.27 1.56 0.016 The same, sample 2 1.97 2.88 0.91 0.009 Mean 0.22 2.61 2.39 0.024 The same, sample 1 0.13 2.03 1.90 0.019 Mean 0.32 0.72 0.400 0.	The same, sample 2	80	260	180	1.8		
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	Mean			9350	93.5		
$\begin{array}{c c c c c c c c c c c c c c c c c c c $			Со				
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Dark-gray silt	1.91	22.15	20.24	0.202		
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Sandy brown silt, sample 1	1.25	8.81	7.56	0.076		
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	The same, sample 2	2.13	8.86	6.73	0.067		
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	Silty sand, sample 1	0.51	3.70	3.19	0.032		
Man 8.65 0.086 Dark-gray silt 13.92 35.28 21.36 0.214 Sandy brown silt, sample 1 7.21 17.59 10.38 0.104 The same, sample 2 16.59 24.95 8.36 0.084 Silty sand, sample 1 0.71 2.27 1.56 0.016 The same, sample 2 1.97 2.88 0.91 0.009 Mean Cd 0.085 Dark-gray silt 0.14 7.54 7.40 0.074 Sandy brown silt, sample 1 0.22 2.61 2.39 0.024 The same, sample 2 0.40 5.65 5.25 0.052 Silty sand, sample 1 0.13 2.03 1.90 0.019 The same, sample 2 0.32 0.72 0.40 0.004 Mean 10.03 0.40 0.37 0.0037 The same, sample 1 0.01 0.33 0.32 0.0037 Sandy brown silt, sample 1 0.01 0.07	The same, sample 2	0.94	6.47	5.53	0.055		
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	Mean			8.65	0.086		
$\begin{array}{c c c c c c c c c c c c c c c c c c c $			Ni				
$\begin{array}{c ccccc} Sandy brown silt, sample 1 7.21 17.59 10.38 0.104 \\ The same, sample 2 16.59 24.95 8.36 0.084 \\ Silty sand, sample 1 0.71 2.27 1.56 0.016 \\ The same, sample 2 1.97 2.88 0.91 0.009 \\ \hline Mean & 8.51 0.009 \\ \hline Mean & 8.51 & 0.085 \\ \hline \\ \hline \\ \hline \\ Dark-gray silt & 0.14 7.54 7.40 0.074 \\ Sandy brown silt, sample 1 0.22 2.61 2.39 0.024 \\ The same, sample 2 0.40 5.65 5.25 0.052 \\ Silty sand, sample 1 0.13 2.03 1.90 0.019 \\ The same, sample 2 0.32 0.72 0.40 0.004 \\ \hline \\ Mean & 3.47 0.035 \\ \hline \\ \hline \\ \hline \\ \hline \\ \hline \\ Dark-gray silt & 0.07 & 0.50 & 0.43 0.0043 \\ Sandy brown silt, sample 1 0.03 & 0.40 0.33 0.32 0.0035 \\ \hline \\ $	Dark-gray silt	13.92	35.28	21.36	0.214		
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	Sandy brown silt sample 1	7 21	17 59	10.38	0.104		
International sample 1 0.71 2.27 1.56 0.016 The same, sample 2 1.97 2.88 0.91 0.009 Mean Cd 0.085 0.085 Cd Dark-gray silt 0.14 7.54 7.40 0.074 Sandy brown silt, sample 1 0.22 2.61 2.39 0.024 The same, sample 2 0.40 5.65 5.25 0.052 Silty sand, sample 1 0.13 2.03 1.90 0.019 The same, sample 2 0.32 0.72 0.40 0.004 Mean TI Dark-gray silt 0.07 0.50 0.43 0.0043 Sandy brown silt, sample 1 0.03 0.40 0.37 0.0037 The same, sample 2 0.01 0.33 0.32 0.0032 Silty sand, sample 1 0.01 0.00 0.009 0.0009 The same, sample 2 0.01 0.07 0.007 Mean <td colspa<="" td=""><td>The same sample ?</td><td>16 59</td><td>24.95</td><td>8.36</td><td>0.084</td></td>	<td>The same sample ?</td> <td>16 59</td> <td>24.95</td> <td>8.36</td> <td>0.084</td>	The same sample ?	16 59	24.95	8.36	0.084	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Silty sand sample 1	0.71	2 27	1.56	0.016		
Mean 2.00 0.01 0.005 Mean 8.51 0.005 Dark-gray silt 0.14 7.54 7.40 0.074 Sandy brown silt, sample 1 0.22 2.61 2.39 0.024 The same, sample 2 0.40 5.65 5.25 0.052 Silty sand, sample 1 0.13 2.03 1.90 0.019 The same, sample 2 0.32 0.72 0.40 0.004 Mean 7 0.035 0.035 0.035 Dark-gray silt 0.07 0.50 0.43 0.0043 Sandy brown silt, sample 1 0.03 0.40 0.37 0.0037 The same, sample 2 0.01 0.33 0.32 0.0026 The same, sample 1 0.01 0.10 0.09 0.0007 Silty sand, sample 1 0.01 0.07 0.07 0.0026 Mean Pb Dark-gray silt 5.05 0.92 -4.13 -0.041 Sandy brown silt, sample 1 3.16 0.92 -2.24 -0.022 The same, sam	The same sample 2	197	2.88	0.91	0.009		
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	Mean	107		8.51	0.085		
$\begin{array}{c ccccc} \text{Dark-gray silt} & 0.14 & 7.54 & 7.40 & 0.074 \\ \hline Sandy brown silt, sample 1 & 0.22 & 2.61 & 2.39 & 0.024 \\ \hline The same, sample 2 & 0.40 & 5.65 & 5.25 & 0.052 \\ \hline Silty sand, sample 1 & 0.13 & 2.03 & 1.90 & 0.019 \\ \hline The same, sample 2 & 0.32 & 0.72 & 0.40 & 0.004 \\ \hline Mean & & & & & & & & & & & & & \\ \hline & & & & &$			Cd				
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Dark-gray silt	0.14	7.54	7.40	0.074		
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Sandy brown silt, sample 1	0.22	2.61	2.39	0.024		
Silty sand, sample 10.132.031.900.019The same, sample 20.320.720.400.004Mean 3.47 0.035TIDark-gray silt0.070.500.430.0043Sandy brown silt, sample 10.030.400.370.0037The same, sample 20.010.330.320.0032Silty sand, sample 10.010.100.090.0009The same, sample 2<0.01	The same, sample 2	0.40	5.65	5.25	0.052		
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Silty sand, sample 1	0.13	2.03	1.90	0.019		
Mean 3.47 0.035 TI Dark-gray silt 0.07 0.50 0.43 0.0043 Sandy brown silt, sample 1 0.03 0.40 0.37 0.0037 The same, sample 2 0.01 0.33 0.32 0.0032 Silty sand, sample 1 0.01 0.10 0.09 0.0009 The same, sample 2 <0.01 0.07 0.07 0.0007 Mean 0.26 0.0026 0.0026 Pb Dark-gray silt 5.05 0.92 -4.13 -0.041 Sandy brown silt, sample 1 3.16 0.92 -2.24 -0.022 The same, sample 2 3.39 1.45 -1.94 -0.019 Silty sand, sample 1 3.08 2.44 -0.64 -0.006 The same, sample 2 3.22 2.17 -1.05 -0.010	The same, sample 2	0.32	0.72	0.40	0.004		
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	Mean			3.47	0.035		
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$							
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	Dark-gray silt	0.07	0.50	0.43	0.0043		
The same, sample 2 0.01 0.33 0.32 0.0032 Silty sand, sample 1 0.01 0.10 0.09 0.0009 The same, sample 2 <0.01	Sandy brown silt, sample 1	0.03	0.40	0.37	0.0037		
Silty sand, sample 1 0.01 0.01 0.02 0.002 Silty sand, sample 1 0.01 0.10 0.09 0.0007 Mean 0.26 0.0007 Pb Dark-gray silt 5.05 0.92 -4.13 -0.041 Sandy brown silt, sample 1 3.16 0.92 -2.24 -0.022 The same, sample 2 3.39 1.45 -1.94 -0.019 Silty sand, sample 1 3.08 2.44 -0.64 -0.006 The same, sample 2 3.22 2.17 -1.05 -0.010	The same, sample 2	0.01	0.33	0.32	0.0032		
The same, sample 2 <0.01 0.07 0.007 Mean 0.007 0.0007 Dark-gray silt 5.05 0.92 -4.13 -0.041 Sandy brown silt, sample 1 3.16 0.92 -2.24 -0.022 The same, sample 2 3.39 1.45 -1.94 -0.019 Silty sand, sample 1 3.08 2.44 -0.64 -0.006 The same, sample 2 3.22 2.17 -1.05 -0.010	Silty sand, sample 1	0.01	0.10	0.09	0.0009		
Mean Other Other Other Other Mean 0.26 0.0026 Pb Dark-gray silt 5.05 0.92 -4.13 -0.041 Sandy brown silt, sample 1 3.16 0.92 -2.24 -0.022 The same, sample 2 3.39 1.45 -1.94 -0.019 Silty sand, sample 1 3.08 2.44 -0.64 -0.006 The same, sample 2 3.22 2.17 -1.05 -0.010	The same, sample 2	< 0.01	0.07	0.07	0.0007		
Pb Dark-gray silt 5.05 0.92 -4.13 -0.041 Sandy brown silt, sample 1 3.16 0.92 -2.24 -0.022 The same, sample 2 3.39 1.45 -1.94 -0.019 Silty sand, sample 1 3.08 2.44 -0.64 -0.006 The same, sample 2 3.22 2.17 -1.05 -0.010	Mean	0.001		0.26	0.0026		
Dark-gray silt5.050.92-4.13-0.041Sandy brown silt, sample 13.160.92-2.24-0.022The same, sample 23.391.45-1.94-0.019Silty sand, sample 13.082.44-0.64-0.006The same, sample 23.222.17-1.05-0.010	Ph						
Sandy brown silt, sample 1 3.16 0.92 -2.24 -0.022 The same, sample 2 3.39 1.45 -1.94 -0.019 Silty sand, sample 1 3.08 2.44 -0.64 -0.006 The same, sample 2 3.22 2.17 -1.05 -0.010	Dark-grav silt	5.05	0.92	-4.13	-0.041		
The same, sample 2 3.39 1.45 -1.94 -0.019 Silty sand, sample 1 3.08 2.44 -0.64 -0.006 The same, sample 2 3.22 2.17 -1.05 -0.010	Sandy brown silt, sample 1	3.16	0.92	-2.24	-0.022		
Silty sand, sample 1 3.08 2.44 -0.64 -0.006 The same, sample 2 3.22 2.17 -1.05 -0.010	The same, sample 2	3.39	1.45	-1.94	-0.019		
The same, sample 2 3.22 2.17 -1.05 -0.010	Silty sand, sample 1	3.08	2.44	-0.64	-0.006		
	The same, sample 2	3.22	2.17	-1.05	-0.010		
Mean -2.00 -0.020	Mean			-2.00	-0.020		

Table 4. Cont.

¹ Mass ratio solid phase/solution 1:10.

The obtained data indicate that the penetration of freshwater terrigenous material into the marine environment causes the desorption of ammonium, barium, manganese, cobalt, nickel, cadmium, and thallium, as well as the sorption of cesium and lead. In absolute terms, the effect of sorption-desorption processes in the first approximation is proportional to the relative abundance of trace elements (mean values of desorption (+) or sorption (-) in μ g/g or g/t are denoted in brackets):

Mn (93.5) > Ba (13.0) >> Ni (0.085) ≈ Co (0.086) >> Tl (0.0026),

Pb (-0.020) > Cs (-0.0008).

Table 4 also shows that the absolute values of sorption and desorption increase in the passage from coarse-grained (silty sands) to fine-grained (silts) sediments. For manganese and nickel, the differences are maximal (17–18 times); for cobalt, cadmium, thallium, and

lead they are equal to 5–6 times; and for ammonium, cesium, and barium, as well as for the major cations, they do not exceed 2.5 times. This is in agreement with the well-known regularity of an increase in the specific sorption capacity of solid phases with an increase in their dispersion degree and, consequently, the specific surface area.

Based on experimental data, it is possible to make approximate estimates of the transformation of the dissolved trace elements runoff under the influence of exchange processes in the adsorbed complex of freshwater terrigenous material at the river–sea geochemical barrier. Multiplying the most probable mass of river runoff of solid substances equal to 15.0-15.7 Gt/yr [12,13] by the mean values of specific desorption (sorption) of components *i* (Table 4), we calculated the amounts of the latter that pass into the solution, or, on the contrary, are removed from it as a result of sorption–desorption processes in the mixing zone of river and sea waters. Then, the contribution of ion exchange to the input of the considered components into the ocean was estimated as a percentage of their input with river runoff (Table 5).

Table 5. Input of dissolved trace elements with river runoff into the ocean with correction for the ion exchange in the adsorbed complex of solid substances.

		Input into the Ocean, Thous. t/yr			Contribution of the Ion
Ion	Concentration in the River Runoff, μ g/L ¹	River Runoff ²	Ion Exchange in the Adsorbed Complex of the Solids of River Runoff ³	Input with Correction for the Ion Exchange ³	Exchange to the Input into the Ocean (% of the Input with the River Runoff) ³
N-NH ₄	14	584	$\frac{4.5}{4.7}$	<u>588.5</u> 588.7	0.8
Cs	0.011	0.46	$-\frac{0.012}{0.013}$	$\frac{0.448}{0.447}$	$-\frac{2.6}{2.8}$
Ba	23	959	$\frac{195}{204}$	$\frac{1154}{1163}$	$\frac{20.3}{21.3}$
Mn	34	1420	$\frac{1400}{1470}$	$\frac{2820}{2890}$	$\frac{98.6}{103.5}$
Co	0.15	6.26	$\frac{1.29}{1.35}$	$\frac{7.55}{7.61}$	$\frac{20.6}{21.6}$
Ni	0.80	33.4	$\frac{1.28}{1.33}$	$\frac{34.68}{34.73}$	$\frac{3.8}{4.0}$
Cd	0.08	3.34	$\frac{0.52}{0.55}$	3.86 3.89	$\frac{15.6}{16.5}$
Tl	(0.02)	0.83	$\frac{0.039}{0.041}$	$\frac{0.869}{0.871}$	$\frac{4.7}{4.9}$
Pb	0.079	3.29	$-\frac{0.30}{0.31}$	$\frac{2.99}{2.98}$	$-\frac{9.1}{9.4}$

¹ N-NH₄ [21], other trace elements [5]. ² The volume of water runoff into the World Ocean taken to be equal to 41,700 km³/yr [22]. ³ The numerator and denominator are the values calculated for the global river runoff of solid substances, equal to 15.0 Gt/yr [13] and 15.7 Gt/yr [12].

As can be seen in Table 5, the change from freshwater to marine conditions is accompanied by desorption of manganese, cobalt, nickel, cadmium, thallium, barium, and ammonium in the amounts of 98.6–103.5, 20.6–21.6, 3.8–4.0, 15.6–16.5, 4.7–4.9, 20.3–21.3, and 0.8% of the input of dissolved forms of these elements into the ocean without taking into account their transformation on the river–sea geochemical barrier. Lead and cesium, conversely, are adsorbed and removed from the solution, resulting in that the global runoff of their dissolved forms decreasing by 9.1–9.4 and 2.6–2.8%, respectively. This suggests that sorption–desorption processes in the mixing zone of river and sea waters lead to a significant transformation of the runoff of dissolved trace elements.

Thus, the presented experimental results in comparison with the data of natural observations for major cations allows for establishing that the described procedure of experimental modeling of sorption–desorption processes at the river–sea geochemical barrier is suitable for estimating their real contribution to the transformation of dissolved matter runoff into the ocean.

4. Conclusions

The proposed procedure for experimental modeling of the transformation of the adsorbed complex of terrigenous material in the mixing zone of river and sea waters makes it possible to study this process under conditions maximally similar to those in nature.

As a result of sorption-desorption processes at the river–sea geochemical barrier, the input of dissolved sodium, potassium, and magnesium into the ocean decreases by 41.9–43.9, 12.9–13.5, and 4.6–4.8 Mt/yr, and the input of dissolved calcium increases by 50.7–53.1 Mt/yr, which is equal to $-(14.0\div14.6)$, $-(22.2\div23.3)$, $-(3.0\div3.2)$, and $8.3\div8.7\%$ of their river runoff, respectively.

Penetration of solid substances of river runoff into the marine environment causes desorption of manganese, cobalt, nickel, cadmium, thallium, barium, and ammonium equal to 98.6–103.5, 20.6–21.6, 3.8–4.0, 15.6–16.5, 4.7–4.9, 20.3–21.3, and 0.8%, respectively, of the input of dissolved forms of these elements into the ocean without taking into account their transformation on the river–sea geochemical barrier. Lead and cesium, on the contrary, passed into the adsorbed complex and were removed from the solution, which reduces the global runoff of their dissolved forms by 9.1–9.4 and 2.6–2.8%.

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