Phosphorus Transport in World Rivers

Subjects: Geochemistry & Geophysics

Contributor: Alla Savenko

Data on the geochemistry of phosphorus in the continental runoff of dissolved and solid substances were systematized and generalized, with a separate consideration of the processes of runoff transformation in river mouth areas. It has been established that atmospheric deposition, which many authors consider to be an important source of phosphorus in river runoff and not associated with mobilization processes in catchments, actually contains phosphorus from soil-plant recycling. This is confirmed by the fact that the input of phosphorus from the atmosphere into catchments exceeds its removal via water runoff. An analysis of the mass ratio of phosphorus in the adsorbed form and in the form of its own minerals was carried out. It was shown that the maximum mass of adsorbed phosphorus is limited by the solubility of its most stable minerals. The minimum concentrations of dissolved mineral and total phosphorus were observed in the rivers of the Arctic and subarctic belts; the maximum concentrations were confined to the most densely populated temperate zone and the zone of dry tropics and subtropics. In the waters of the primary hydrographic network, the phosphorus concentration exhibited direct relationships with the population density in the catchments and the mineralization of the river water and was closely correlated with the nitrogen content. This strongly suggests that economic activity is one of the main factors in the formation of river phosphorus runoff. The generalization of the authors' and the literature's data on the behavior of phosphorus at the river–sea mixing zone made it possible to draw a conclusion about the nonconservative distribution of phosphorus, in most cases associated with biological production and destruction processes. The conservative behavior of phosphorus was observed only in heavily polluted river mouths with abnormally high concentrations of this element.

geochemistry of phosphorus continental runoff river mouth

1. Phosphorus Mobilization at the Stage of River Runoff Formation

The initial stage in the formation of the chemical composition of surface waters is often associated with atmospheric precipitation on the earth's surface and their subsequent interaction with soil and vegetation cover and rocks. However, due to the constant presence of terrigenous aerosols (mainly the products of the wind erosion of soils) in the surface air layers, this interaction begins already in the atmosphere immediately after the condensation of water vapor. Therefore, it is expedient to divide the mobilization of dissolved substances at the initial stage of river runoff formation into the mobilization in the atmosphere and in the catchments.

1.1. Phosphorus Mobilization in the Atmosphere

Chemical elements are delivered from the atmosphere to the catchments in the form of wet (rain, snow) and dry (aerosols) precipitation. The chemical composition of wet precipitation is due to leaching from the atmosphere and the partial dissolution of aerosols, which are represented by substances of terrigenous and marine genesis. The contribution of marine aerosols to the transport of phosphorus into the land is apparently small. This is indicated by an exponential decrease in the content of aerosol phosphorus in the lower atmosphere when moving from the coast to the central regions of the ocean and a significantly lower content of phosphorus in the rains over the ocean compared to land [1][2][3]. The estimates of phosphorus input into the atmosphere from various sources confirm this conclusion and show that the main role is played by the aeolian erosion of the soil cover and the combustion of terrestrial vegetation (**Table 1**). Another source associated with the products of plant metabolism (spores, pollen, volatile organic compounds, and small particles of plant residues) is currently not quantifiable, but observations unambiguously indicate the widespread occurrence of plant metabolism products present in atmospheric aerosols.

Table 1. Sources of phosphorus in the atmosphere [4].

Source	Mass of Aerosols Entering the Atmosphere, Gt/yr	Phosphorus Content in Aerosols, %	Phosphorus Input into the Atmosphere, Mt/yr
Aeolian soil erosion	4.6–8.3	0.08	3.7–6.6
Splashing of seawater	1.8–1.9	0.001	~0.02
Burning of vegetation	0.15–0.60	1.5 [1]	2.3–9.0
Volcanism	–	–	≤0.003
Combustion of solid fuels	0.03–0.06	0.1	0.03–0.06
Combustion of liquid fuels	0.003	0.01	0.0003

[1] By the composition of terrestrial vegetation at 10% ash content.

The total phosphorus concentration in aerosols varies from 600 to 4700 µg/g, averaging ~2000 µg/g [5], which is 2–5 times higher than the phosphorus content in the rocks of the earth's crust and soils, the main sources of terrigenous material in the atmosphere. The increased phosphorus concentrations in atmospheric aerosols are logically explained by the presence of the solid products of plant biomass combustion in the amount of 0.6–1.1% of the total aerosol mass [4]. A significant part of the phosphorus in aerosols is present in water-soluble form, which, as a rule, accounts for 20–50% of its total content [6]. Apparently, the soluble forms of phosphorus in aerosols are associated with the products of combustion of plant biomass and its destruction.

In atmospheric precipitation, the concentrations of mineral and total phosphorus (P_{min} and P_{total}) are distributed in accordance with the lognormal law. The average median concentrations of these forms are 15 and 33 µg/L and the values of their input with atmospheric precipitation to the earth's surface are 0.11 and 0.25 kg/ha yr (**Table 2**). The percentage of the soluble forms of the total phosphorus in atmospheric precipitation is in the range of 20–80%, with an average value of 55% [6], which is in good agreement with the percentage of soluble phosphorus in aerosols, the main source of dissolved substances.

Table 2. Concentration of phosphorus in atmospheric precipitation and its input on the earth's surface with wet precipitation [7].

Parameter	Concentration, µg/L		Input, kg/ha yr	
	P_{min}	P_{total}	P_{min}	P_{total}
Number of observation sites	130	97	104	77
Arithmetic mean	30	73	0.22	0.36
Median mean	13	34	0.093	0.23
Geometric mean	15	33	0.11	0.25

Atmospheric precipitation is considered by many authors as an important source of phosphorus in river runoff, which is not associated with the processes of its mobilization in the catchments. However, the balance of total phosphorus in the catchments shows that the input of this element with atmospheric precipitation usually exceeds the removal with water runoff [4]. The opposite situation, when the phosphorus runoff exceeds its input, is observed, as a rule, under the conditions of a strong anthropogenic load. The positive value of the difference between the phosphorus input from the atmosphere and its removal from the catchments is an artifact that is associated with the lack of reliable methods for quantifying the masses of substances remobilized from the earth's surface into the atmosphere and returned back as a part of atmospheric precipitation (**Figure 1**).

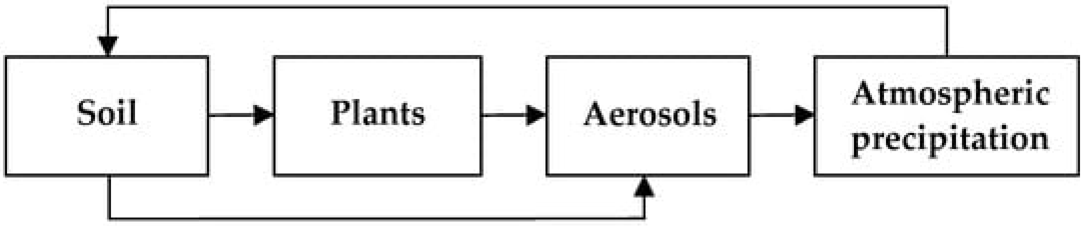


Figure 1. Scheme of phosphorus fluxes in the catchments.

1.2. Phosphorus Mobilization in the Catchment Areas

The primary sources of phosphorus are igneous, metamorphic, and sedimentary rocks, which differ significantly in the content of this element (**Table 3**). The maximum phosphorus concentrations are characteristic of basic and intermediate magmas; with an increase and decrease in acidity, the phosphorus content in igneous rocks decreases. In sedimentary rocks, the phosphorus concentration does not vary so much, and in general, for the sedimentary deposits it is slightly higher than in granites. In metamorphic processes, phosphorus behaves as an inert component, and its content is inherited from the parent rocks.

Table 3. Content of phosphorus in rocks [8][9].

Rock	[P], µg/g	Rock	[P], µg/g
Igneous rocks:		*Sedimentary rocks:*	
Ultrabasic rocks	280	Sands and sandstones	620
Basic rocks	1300	Clays and clay shales	790
Andesites, diorites	1350	Carbonate rocks	480
Granodiorites	980	Siliceous rocks	660
Granites	600	Evaporites	4
Syenites	800	Volcanic rocks	900
Volcanic rocks	900	Sedimentary deposits in general	710
		Surface of the continental lithosphere [1]	690

[1] Based on results of [9].

Apatite is the main phosphorus mineral in all types of igneous, metamorphic, and sedimentary rocks. The abundance of two other important phosphorus minerals, xenotime YPO_4 and monazite $CePO_4$, is 100–1000 times lower than that of apatite and can reach 10% only in acid rocks [10]. According to mineralogical analysis, in igneous rocks, apatite accounts for 1.7–5.7% of the total phosphorus, whereas in sedimentary carbonate, clayey, and sandy rocks, apatite contains 22.9, 0.5, and 7.1% of phosphorus, respectively [10][11]. In magmatic and metamorphic silicates, phosphorus can isomorphically replace silicon with charge compensation ($Na^+ + P^{5+} = Ca^{2+} + Si^{4+}$ and $Al^{3+} + P^{5+} = 2\ Si^{4+}$) or with the formation of cation vacancies. In the Critical Zone, the bulk of phosphorus is in the sorbed state, as well as in the form of apatite and various iron and aluminum phosphates. The composition of apatite is different for various types of rocks. Fluorapatite predominates in igneous and metamorphic rocks, with fluoro-carbonate-apatite pervading in sedimentary rocks, and bone phosphate is represented by hydroxyl-apatite and carbonate-hydroxyl-apatite.

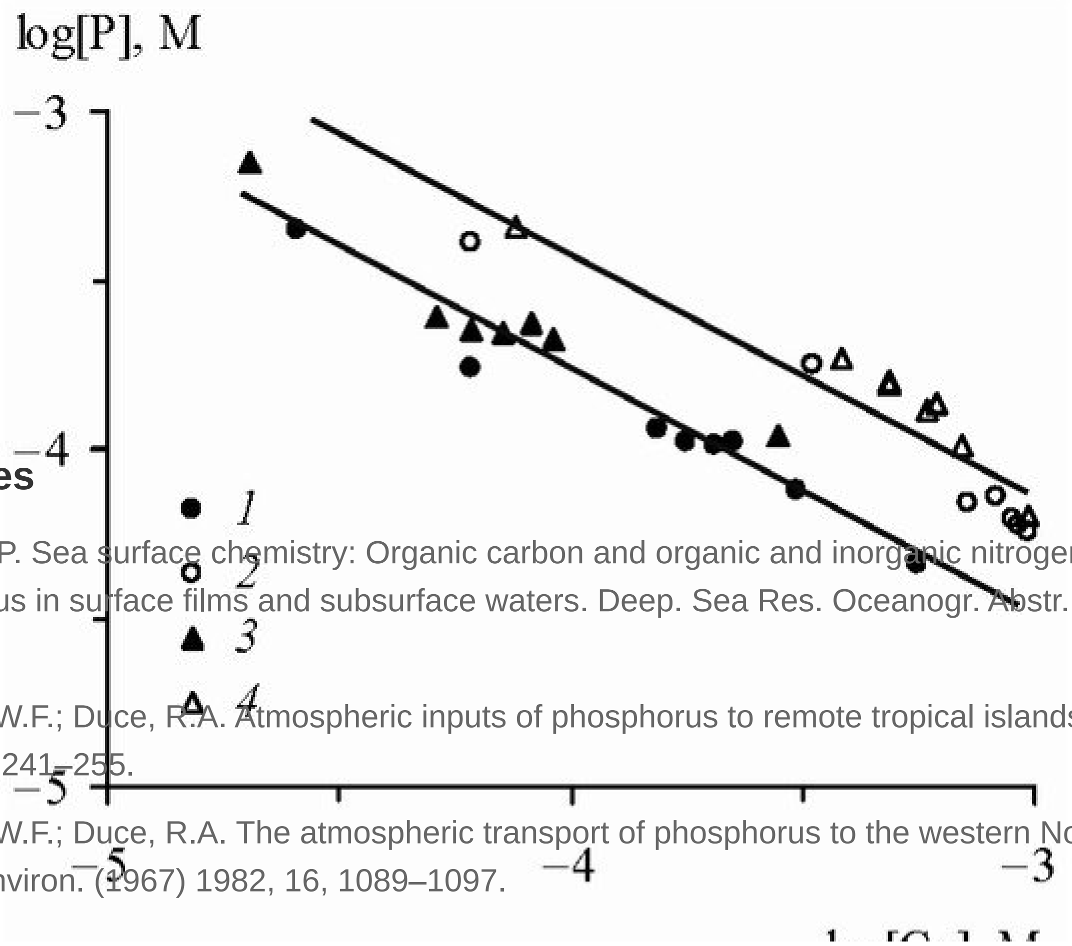
Biological metabolites and the products of dead organisms’ destruction are an important source of phosphorus in continental runoff. The phosphorus content in land plants (on average 1500–2000 µg/g dry weight) is almost an order of magnitude lower than the content in animals and bacteria [12][13][14]. Therefore, the destruction of animal and bacterial biomasses can lead to the emergence of high local concentrations of dissolved phosphorus.

The most obvious factor in phosphorus mobilization is the solubility of the phosphorus-containing mineral phases. According to calculations [15], the concentration of dissolved mineral phosphorus in the waters of the Rhine and Rhone rivers is controlled by the solubility of hydroxylapatite. However, under the conditions of the earth's surface, hydroxylapatite is unstable and transforms into a less soluble fluoro-carbonate-apatite. The dissolution of fluorapatite in fresh waters leads to a concentration of dissolved mineral phosphorus at the level of 14 ± 3 μg/L [16], which, as will be shown below, approximately corresponds to the average median value for the world rivers.

The acidity of the aquatic environment is apparently the main factor controlling the stability of the mineral forms of phosphorus. In a moderately alkaline medium, the stable phase is fluoro-carbonate-apatite; in a moderately acidic medium, iron (III) and aluminum phosphates are stable under oxidizing conditions and iron (II) and aluminum phosphates are stable under reducing conditions [6]. According to the experimental data [17], in waters with a reaction close to neutral, the monophosphates of iron (III) and aluminum transform into more stable iron-calcium and aluminum-calcium phosphates with the hypothetical chemical formulas $CaFe(OH)_3HPO_4$ and $CaAl(OH)_3HPO_4$. In the neutral medium, the dissolved iron (III) and aluminum are mainly in the form of the electroneutral hydroxocomplexes Fe(OH)3 and Al(OH)3, and the bulk of the phosphorus is represented by HPO4. Therefore, in accordance with the dissolution reactions

$$CaFe(OH)_3HPO_4 = Ca^{2+} + Fe(OH)_3^0 + HPO_4^{2-},$$

an inverse relationship between the logarithms of the concentrations of mineral phosphorus and calcium is observed (**Figure 2**).



References

1. Williams, P. Sea surface chemistry: Organic carbon and organic and inorganic nitrogen and phosphorus in surface films and subsurface waters. Deep. Sea Res. Oceanogr. Abstr. 1967, 14, 791–800.
2. Graham, W.F.; Duce, R.A. Atmospheric inputs of phosphorus to remote tropical islands. Pac. Sci. 1981, 35, 241–255.
3. Graham, W.F.; Duce, R.A. The atmospheric transport of phosphorus to the western North Atlantic. Atmos. Environ. (1967) 1982, 16, 1089–1097.

Figure 2. Relationship between logarithms of the concentrations of dissolved phosphates and calcium in the interactions of $FePO_4$ and $AlPO_4$ with freshwaters [17]: $FePO_4$ (1) water from the Moscow River, (2) water from the Don River mouth; $AlPO_4$ (3) water from the Moscow River, (4) water from the Don River mouth.

In equilibrium with iron-calcium and aluminum-calcium phosphates, the concentration of dissolved mineral phosphorus is significantly higher than its content in river and ground waters. Therefore, it should be assumed that the presence of these solid phases is possible only where high local concentrations of dissolved phosphorus can be maintained for a long time. These can be bottom sediments with an extremely slow rate of water exchange or soils in which a high concentration of dissolved phosphorus is provided by the destruction of organic matter during the biological cycle. In all other cases, iron-calcium and aluminum-calcium phosphates must be replaced by hydroxides containing adsorbed phosphorus.

At sufficiently high concentrations of phosphates, arising, for example, during the destruction of animal or bacterial biomass, the silicate phosphatization reaction can occur, in which the silicon of the solid phase is replaced by phosphorus from the solution. This process was experimentally studied by us, using rock-forming minerals of different structural types (hornblende, orthoclase, labradorite, kaolinite, and montmorillonite) and background buffer solutions with variable concentrations of orthophosphates (0.25–6.0 mM), maintaining the pH at ~1.8, 3.7, 4.9, 6.8, 7.8, and 8.8 [18][19][20].

The results of the experiments demonstrated the following features. First, all the samples were characterized by approximately equivalent variations in the concentrations of phosphorus and silicon in the solution in the pH range of 3.7–8.8: $\Delta\,[\mathrm{Si}] \approx -\Delta[\mathrm{P}]$,

whereas at pH 1.8 the supply of the dissolved silicon was 1.3–2 times higher than the removal of the phosphates (**Figure 3**), which was likely explained by the change in the stoichiometry of the phosphatization reaction. Second, the amount of phosphorus absorbed by the silicates was linearly dependent on its final concentration in the solution;

$$-\Delta\,[\mathrm{P}] = k[\mathrm{P}]_{\mathrm{final}}$$

with almost the same values of the proportionality coefficient *k* for the different minerals, slightly decreasing with a decrease in the acidity of the medium (**Table 4**).

4. Savenko, V.S. Atmospheric Input of Phosphorus and Its Runoff from Catchment Areas; Transactions Doklady Russian Academy of Sciences Earth Science Sections; Scripta Technica, Inc., A Wiley Company: New York, NY, USA, 1997; Volume 5, pp. 783–785.
5. Savenko, V.S. Atmospheric aerosols as a source of phosphorus in aquatic ecosystems. Water Resour. 1995, 22, 170–179.
6. Savenko, V.S.; Savenko, A.V. Geochemistry of Phosphorus in the Global Hydrological Cycle; GEOS: Moscow, Russia, 2007; pp. 1–248. (In Russian)
7. Savenko, V.S. Phosphorus in atmospheric precipitation. Water Resour. 1996, 23, 169–179.
8. Ovchinnikov, L.N. Applied Geochemistry; Nedra: Moscow, Russia, 1990; pp. 1–248. (In Russian)
9. Ronov, A.B.; Yaroshevsky, A.A.; Migdisov, A.A. Chemical Constitution of the Earth’s Crust and Geochemical Balance of the Main Elements; Nauka: Moscow, Russia, 1990; pp. 1–182. (In Russian)
10. Grigor’ev, N.A. The average mineral composition of the sedimentary layer of the continental crust’s. Lithosphere 2003, 3, 3–14. (In Russian)
11. Grigor’ev, N.A. Average concentrations of chemical elements in rocks of the upper continental crust. Geochem. Int. 2003, 41, 711–718.
12. Bowen, H.J.M. Environmental Chemistry of the Elements; Acad. Press: London, UK, 1979; pp. 1–333.
13. Romankevich, E.A. Living matter of the Earth (biogeochemical aspects of the problem). Geochemistry 1988, 2, 292–306. (In Russian)
14. Frossard, E.; Brossard, M.; Hedley, M.J.; Metherell, A. Reactions controlling the cycling of P in soils. In Phosphorus in the Global Environment; Tiessen, H., Ed.; J. Willey: Chichester, UK, 1995; pp. 107–137.
15. Golterman, H.L.; Meyer, M.L. The geochemistry of two hard water rivers, the Rhine and the Rhone, Part 4: The determination of the solubility product of hydroxyl-apatite. Hydrobiologia 1985, 126, 25–29.
16. Savenko, A.V.; Savenko, V.S. Stability of accessory fluorine minerals in the process of formation of dissolved matter continental runoff. Process. GeoMedia 2019, 1, 82–86. (In Russian)
17. Savenko, A.V. Experimental study of the transformations of iron and aluminum phosphates at the river–sea geochemical barrier. Geochem. Int. 2005, 43, 414–419.
18. Savenko, A.V. The possibility of phosphatization of silicates in the supergene zone. Geochem. Int. 2014, 53, 87–94.

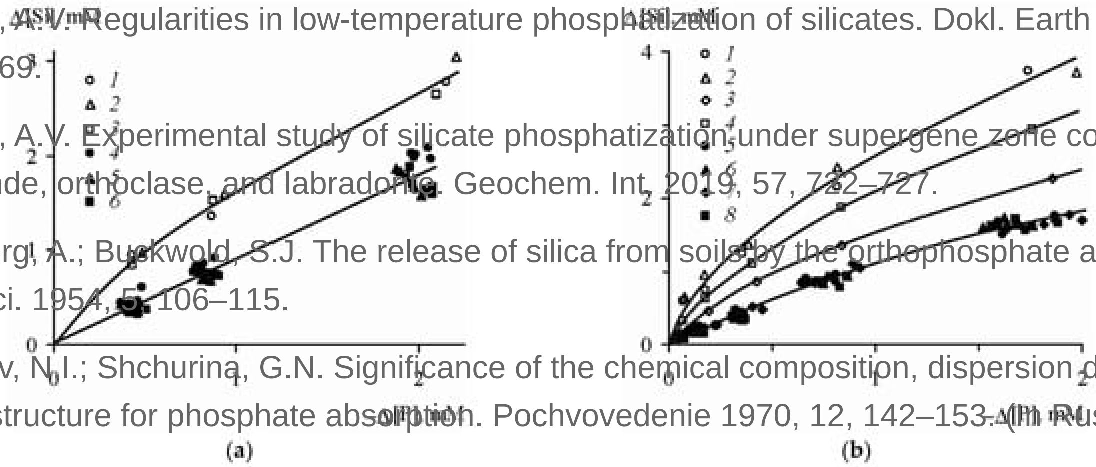


Figure 3. Correlation between variations in the concentrations of phosphorus and silicon in the solution upon phosphotization of silicates [19]. (**a**) pH 1.8: (*1*) hornblende, (*2*) orthoclase, (*3*) labradorite; pH 3.7–8.8: (*4*) hornblende, (*5*) orthoclase, (*6*) labradorite. (**b**) pH 1.8: (*1*) kaolinite, Glukhovetsk, (*2*) the same, Podol'sk, (*3*) montmorillonite, Askania, (*4*) the same, near Askania; pH 3.7–8.8: (*5*) kaolinite, Glukhovetsk, (*6*) the same, Podol'sk, (*7*) montmorillonite, Askania, (*8*) the same, near Askania.

Table 4. Proportionality coefficient *k* in Equation (4) as a function of solution pH.

pH	1.8	3.7	4.9	6.8	7.8	8.8
k	0.57	0.57	0.54	0.51	0.46	0.46

According to the data in Table 5, in the experiments on phosphatization of silicates at the maximum initial concentration of phosphates at pH 3.7–8.8 replaced 6%–11.0% of the initial silicon in the minerals. Even more silicon (up to 9.4–19.9%) entered the solution at pH 1.8, when the process of phosphatization was accompanied by the acid

Table 5. Amount of silicon removed from the studied silicates and replaced by phosphates at the concentration [1], % of the initial content in the mineral [19].

Mineral	pH	
	1.8	**3.7–8.8**
Hornblende	19.4	11.0
Orthoclase	11.2	8.1
Labradorite	12.3	8.0
Kaolinite, Glukhovetsk	18.0	7.8
As above, Podol'sk	19.9	8.6
Montmorillonite, Askania	9.4	6.5
As above, near Askania	12.4	6.9

[1] 5 mM for hornblende, orthoclase, and labradorite; 6 mM for kaolinite and montmorillonite.

19. Savenko, A.V. Regularities in low-temperature phosphatization of silicates. Dokl. Earth Sci. 2018, 478, 67–69.

20. Savenko, A.V. Experimental study of silicate phosphatization under supergene zone conditions: Hornblende, orthoclase, and labradorite. Geochem. Int. 2019, 57, 722–727.

21. Reifenberg, A.; Buckwold, S.J. The release of silica from soils by the orthophosphate anion. Eur. J. Soil Sci. 1954, 5, 106–115.

22. Gorbunov, N.I.; Shchurina, G.N. Significance of the chemical composition, dispersion degree, and mineral structure for phosphate absorption. Pochvovedenie 1970, 12, 142–153. (In Russian)

23. Rajan, S.S.S. Phosphate adsorption and the displacement of structural silicon in an allophane clay. J. Soil Sci. 1975, 26, 250–256.

24. Rajan, S.S.S.; Fox, R.L. Phosphate adsorption by soils. II. Reactions in tropical acid soils. Soil Sci. Soc. Am. J. 1975, 39, 846–851.

25. Rajan, S.S.S.; Perrott, K.W. Phosphate adsorption by synthetic amorphous aluminosilicates. J. Soil Sci. 1975, 26, 257–266.

26. Remezov, N.P. On the relationship between biological accumulation and the eluvial process under 58, 6,

27. World Water Balance and Water Resources of the Earth; Gidrometeoizdat: Leningrad, Russia, 1974; pp. 1–525. (In Russian)

28. Meybeck, M. Carbon, nitrogen, and phosphorus transport by world rivers. Am. J. Sci. 1982, 282, 401–450.

29. P and 193.

30. ia,

31. 1973,

32. off.

33. –72. (In Russian)

34. Nazarov, G.V.; Kuznetsov, V.K. Zonal features of the nutrients removal from natural and agricultural lands. In Proceedings of the 5th All-Union Hydrological Congress, Leningrad, Russia,

In previous studies [21][22][23][24][25], the negative correlation between the variations in the concentrations of dissolved phosphates and silicon was associated with the adsorption exchange of phosphate ions and silica on the surface of silicates. Since the duration of the experiments did not exceed several days, this time was sufficient to establish the adsorption equilibrium but was not long enough for noticeable progress in the phosphatization reaction of the bulk silicate phase. The experiments proceeded for more than one year, so the amount of phosphorus absorbed from the solution and the silicon displaced from the solid phase indicated the participation in the process of not only the surface layer, but also the volume of the solid phase.

The same quantitative characteristics of the process of phosphatization for all the studied silicates, corresponding to different structural types and with different chemical compositions, were an unusual result. It can be assumed that the initial minerals were not subject to phosphatization, but that the secondary silicate phases formed during the interaction of the silicates with water and were stable in a certain pH range. The parameters of the phosphatization reaction at pH 1.8 varied due to the stability under these conditions of the surface silicate phase, which was different to that in the area of higher pH values.

A powerful factor of the phosphorus mobilization in the Critical Zone is the activity of living organisms. Primary producers annually synthesize about 140 Gt of dry organic matter on land, 98–99% of which is mineralized. With the average phosphorus content in plants equal to ~1500 μg/g dry matter, about 210 Mt of phosphorus participates in the biotic cycle, which forms soluble phosphates at the stage of mineralization and becomes a potential source of dissolved phosphorus in continental runoff. However, mineralized phosphorus is almost completely reincluded in the biotic cycle and used to create new organic matter. The highest degree of completeness of the biotic cycle is inherent in mature biogeocenoses (**Table 6**).

Table 6. Phosphorus input with litter and removal with subsurface runoff in forest biogeocenoses [26].

Process	Oak Forest	Aspen Forest
Input with litter, kg/ha yr	7.85	9.9
Removal with subsurface runoff, kg/ha yr	~0.001	~0.0015
Phosphorus removal, % of input with litter	0.013	0.015

If all mineralized phosphorus was a part of river runoff, the volume of which is 41,700 km³/yr [27], its concentration due to this source alone would be 5 mg/L. Such high concentrations of dissolved phosphorus are extremely rare and usually associated with the reducing conditions of the environment or anthropogenic pollution. The average concentration of dissolved phosphates in unpolluted river waters is equal 30–50 μg P/L [28][29][30], which is 0.6–1.0% of the calculated value of 5 mg P/L. This means that continental runoff contains a very small portion of the labile phosphorus that is formed as a result of organic matter degradation.

20–24 October 1986; Gidrometeoizdat: Leningrad, Russia, 1991; Volume 5, pp. 184–189. (In Russian).

35. Sharpley, A.N.; Hedley, M.J.; Sibbesen, E.; Hillbricht-Ilkowska, A.; House, W.A.; Ryszkowski, L. Phosphorus transfers from terrestrial to aquatic ecosystems. In Phosphorus in the Global Environment; J. Willey: Chichester, UK, 1995; pp. 171–199.
36. Perel'man, A.I.; Kasimov, N.S. Geochemistry of Landscape; Astreya-2000: Moscow, Russia, 1999; pp. 1–768. (In Russian)
37. Savenko, V.S. Geochemistry of continental link of the global hydrological cycle. In Global Changes in the Natural Environment—2001; Publ. House of the Siberian Branch of RAS: Novosibirsk, Russia, 2001; pp. 274–287. (In Russian)
38. Dillon, P.; Kirchner, W. The effects of geology and land use on the export of phosphorus from watersheds. Water Res. 1975, 9, 135–148.
39. Lozovik, P.A.; Basov, M.I.; Litvinenko, A.V. Assessment of chemical input into the drainage network from Karelian river basins. Water Resour. 2005, 32, 532–536.
40. Gardner, L. The role of rock weathering in the phosphorus budget of terrestrial watersheds. Biogeochemistry 1990, 11, 97–110.
41. Conley, D.J.; Stalnacke, P.; Pitkanen, H.; Wilander, A. The transport and retention of dissolved silicate by rivers in Sweden and Finland. Limnol. Oceanogr. 2000, 45, 1850–1853.
42. Savenko, V.S.; Zakharova, E.A. Phosphorus in the water of the primary hydrographic network. Water Resour. 1997, 24, 266–273.
43. Savenko, V.S. Phosphorus discharge with suspended load. Water Resour. 1999, 26, 41–47.
4 load of s.;
4 Coast. Mar. Sci. 1980, 11, 383–391.
46. van Eck, G.T.M. Forms of phosphorus in particulate matter from the Hollands Diep/Haringvliet, The Netherlands. In Sediment/Freshwater Interaction. Developments in Hydrobiology; Dumont, H.J., Ed.; Junk Publ.: Hague, The Netherlands, 1982; Volume 9, pp. 665–681.
47. Kohonen, T. Influence of sampling frequency on the estimates of runoff water quality. Publ. Water Res. Inst. 1982, 27, 1–30.
48. Prairie, Y.T.; Kalff, J. Particulate phosphorus dynamics in headwater streams. Can. J. Fish. Aquat. Sci. 1988, 45, 210–215.

It is known that when phosphorus fertilizers are applied to soils, the behavior of the phosphorus differs significantly depending on the properties of the soil and the fertilizers themselves. Poorly soluble phosphorite flour increases the content of biologically available phosphorus if the soil conditions are conducive to the transformation of apatite into more soluble forms. With the addition of highly soluble fertilizers, over time, phosphorus immobilization occurs due to chemosorption and the formation of poorly soluble compounds, including apatite phases. It is assumed that phosphates of iron, aluminum, and calcium make up ~90% of the immobilized phosphorus of fertilizers [31].

Whereas the final products of the transformation of fertilizers are represented by poorly soluble mineral phases, there is usually no direct relationship between the amount of applied phosphorus and its removal. The amount of removed phosphorus from fertilizers, as a rule, does not exceed 1–2% [32][33][34][35].

Formally, the mobility of chemical elements in the Critical Zone is characterized by the coefficients of water migration K_i, equal to the ratio of the concentrations of element *i* in the dry residue of water (a_i) and in drained rocks

$$K_i = a_i / m_i .$$

Phosphorus belongs to the group of low-mobility elements with $0.01 < K_i < 0.1$ [36].

In (5), it is implicitly assumed that all the substances in the dry residue of water enter it as a result of the dissolution of drained rocks. However, there are two other powerful sources of dissolved matter: cyclic sea salts, transported from the ocean to land through the atmosphere, and anthropogenic substances. Taking into account the contribution of these sources leads to a significant change in the values of the coefficients of water migration, in particular, to an approximately tenfold increase of this coefficient for phosphorus (**Table 7**).

Table 7. Coefficients of water migration of chemical elements in the Critical Zone taking into account the contribution of cyclic sea salts and anthropogenic substances [37].

Cl	S	Na	F	C	Mg	Ca	K	P	Si	Mn	Fe	Ti	Al
9.6	9.2	4.0	3.3	3.3	2.4	2.4	0.93	0.81	0.27	0.22	0.02	0.01	0.01

2. Phosphorus in River Runoff

2.1. Phosphorus in the Waters of the Primary Hydrographic Network

The primary hydrographic network consists of small catchments, which are characterized by the significant spatial variability of the chemical composition of the waters, caused by the territorial heterogeneity of geomorphological, lithological, and biological soil conditions. The enlargement of rivers and pooling of small catchments leads to the

49. Savenko, V.S. Chemical Composition of World Rivers's Suspended Matter; GEOS: Moscow, Russia, 2006; pp. 1–175. (In Russian)

50. Savenko, V.S.; Zakharova, E.A. Phosphorus in river runoff. Doklady Akademii Nauk. 1995, 345, 682–685. (In Russian)

51. Savenko, V.S.; Zakharova, E.A. Principal features of phosphorus behavior in river flow. Water Resour. 1997, 24, 139–147.

52. Caraco, N.F. Influence of human populations on P transport to aquatic systems: A regional scale study using large rivers. In Phosphorus in the Global Environment; Tiessen, H., Ed.; J. Willey: Chichester, UK, 1995; pp. 235–244.

53. Justić, D.; Rabalais, N.N.; Turner, R. Stoichiometric nutrient balance and origin of coastal eutrophication. Mar. Pollut. Bull. 1995, 30, 41–46.

54. Tarasov, M.N.; Smirnov, M.P.; Kryuchkov, I.A.; Laki, G.I. River runoff of nutrients from the territory of the USSR and its change in time (1936–1980). Hydrochem. Mater. 1988, 103, 49–66. (In Russian)

55. Fraser, A.S. Tributary and point source total phosphorus loading to Lake Erie. J. Great Lakes Res. 1987, 13, 659–666.

56. Behrendt, H. Estimation of the nutrient inputs into medium and large river basins—A case study for German rivers. LOICZ Newsl. 1999, 12, 1–4.

57. Shvartsev, S.L. Hydrogeochemistry of the Hypergenesis Zone; Nedra: Moscow, Russia, 1998; pp. 1–366. (In Russian)

58. Dedkov, A.P.; Mozzherin, V.I. Erosion and Sediment Yield on the Earth; Kazan University Publ. House: Kazan, Russia, 1984; pp. 1–264. (In Russian)

59. Dedkov, A.P.; Mozzherin, V.I.; Safina, G.R.; Gusarov, A.V. Global sediment yield and its variability. [illegible] ouse:

60. Gordeev, V.V. River Runoff into the Ocean and Specifics of Its Geochemistry; Nauka: Moscow, Russia, 1983; pp. 1–160. (In Russian)

61. Lisitzin, A.P. Ocean Sedimentation; Nauka: Moscow, Russia, 1974; pp. 1–438. (In Russian)

62. Gordeev, V.V.; Dzhamalov, R.G.; Zektser, I.S.; Zhulidov, A.V.; Bryzgalo, V.A. Assessment of nutrient discharge with river and groundwater flow into marginal seas of the Russian Arctic regions. Water Resour. 1999, 26, 206–211.

63. Savenko, V.S. Global hydrological cycle and geochemical balance of phosphorus in the ocean. Oceanology 2001, 41, 360–366.

“averaging” of the geochemical conditions for runoff formation. Therefore, the large-scale regularities associated with the implementation of the periodic law of geographic zonality are acquiring decisive importance.

The lithological characteristics of the catchments have a strong influence on the phosphorus concentration in the waters of the primary hydrographic network, because rocks are the main source of dissolved phosphorus. The highest concentrations of dissolved mineral phosphorus are found in catchments located on basalts, in which the phosphorus content is greater than in other types of rocks (Table 8). The runoff of dissolved phosphorus from drainage basins composed of sedimentary rocks is usually greater than for igneous rocks. In the small, almost completely forested catchments on the Canadian Crystalline Shield, the dissolved phosphorus runoff was 4.8 (2.5–7.7) mg/m^2 yr for igneous rocks and twice as large (10.7 (6.0–14.5) mg/m^2 yr) for sedimentary rocks [38].

Table 8. Relationship between the concentration of dissolved mineral phosphorus in the waters of the primary hydrographic network and phosphorus content in the catchment rocks

Lithological Composition of Catchments	Phosphorus Concentration	
	in Water, µg/L [29]	in Rock, µg/g [8][9]
Sandstones	2	620
Granites	3	600
Limestones	2	480
Basalts	20	1300
Carbonaceous shales	3	–
Mica schists	4	550
Gypsum-bearing clays	1	–

Another important factor of phosphorus migration is the climate, which affects the rate of weathering and, consequently, the intensity of the phosphorus mobilization from rocks. For example, the runoff of dissolved phosphorus from the territory of Karelia (NW Russia, temperate climate) due to the pure weathering of crystalline rocks is 2 mg/m^2 yr [39], while the average intensity of dissolved phosphorus removal during the weathering of crystalline rocks for three catchments in Brazil (humid tropical climate) is 5 times higher: 10 (5–14) mg/m^2 yr [40].

The presence of areas with slow water exchange in catchments leads to a decrease in the phosphorus content in the waters of the primary hydrographic network. Indeed, Conley et al. [41] showed an exponential dependence of the concentration of total dissolved phosphorus ([P_{total}], µg/L) on the relative area of lakes (S, %) in catchments:

$$[P_{total}] = 2.18e^{-0.096S}$$

Data on the content of dissolved phosphorus in the waters of the primary hydrographic network, to which catchments with an area ≤50 km^2 were assigned, were collected during observations that lasted for at least a year

64. Prego, R. Biogeochemical pathways of phosphate in a Galician ria (north-western Iberian Peninsula). Estuar. Coast. Shelf Sci. 1993, 37, 437–451.

65. Morris, A. The chemistry of the Severn Estuary and the Bristol Channel. Mar. Pollut. Bull. 1984, 15, 57–61.

66. Mackay, D.W.; Leatherland, T.M. Chemical processes in an estuary receiving major inputs of industrial and domestic wastes. In Estuarine Chemistry; Burton, J.D., Liss, P.S., Eds.; Academic Press: London, UK, 1976; pp. 185–218.

67. van Bennekom, A.J.; Wetsteijn, F.J. The winter distribution of nutrients in the Southern Bight of the North Sea (1961–1978) and in the estuaries of the Scheldt and the Rhine/Meus. Netherl. J. Sea Res. 1990, 25, 75–87.

68. Kronberg, B.I.; Lammers, U.; Schutt, M.; Jonge, V.N. Valdivia Cruise October 1981: Mineral nutrients in the Elbe, Weser and Ems Rivers and German Bight. Mitt. Aus Dem Geol.-

6 imo, K.; d and

7 alaksha

7

7 runoff in the mouth areas of small watersheds of the southern coast of the Kola Peninsula. Oceanology 2011, 51, 785–795.

73. Savenko, A.V.; Demidenko, N.A.; Pokrovskii, O.S. Chemical transformation of the runoff of dissolved matters in the mouth areas of the Onega and Mezen' rivers. Geochem. Int. 2016, 54, 439–448.

74. Savenko, A.V.; Shevchenko, V.P. Seasonal variability of the distribution of dissolved forms of biogenic elements and alkalinity in the Northern Dvina mouth. Water Resour. 2005, 32, 417–421.

75. Savenko, A.V.; Demidenko, N.A.; Pokrovsky, O.S. Spatial and temporal variability of the transformation of dissolved matter runoff in the Mezen River estuary. Oceanology 2019, 59, 199–207.

76. Hydrometeorology and Hydrochemistry of the Seas of the USSR. Vol. II. Barents Sea. Issue II. Hydrochemical Conditions and Oceanological Foundations of Bioproductivity Formation; Gidrometeoizdat: Leningrad, Russia, 1992; pp. 1–265. (In Russian)

and were systematized in[42]. Based on the differences in the sources of phosphorus input, the conditions of runoff formation, and the processes in the catchments, all catchments were divided into four groups: (1) natural (forest) catchments; (2) mixed agricultural–forest catchments with land use <50%; (3) agricultural catchments with land use >50%; (4) urban catchments. For a number of catchments, the group could not be determined due to the lack of the necessary data.

Table 9 shows that the values of the arithmetic and median mean concentrations of mineral and total phosphorus in solution for all the accounted catchments differed several times, indicating the positive asymmetry of the probability distribution functions, which corresponds to the lognormal law. When the small catchments were combined into groups, the asymmetry of the probability distribution functions for the phosphorus concentrations remained. Therefore, the average median concentrations of mineral and total phosphorus, equal to 31 and 95 μg/L, can be considered as the global average concentrations of these forms of dissolved phosphorus in the waters of the primary hydrographic network under modern conditions.

Table 9. The average content and concentration range of dissolved phosphorus (μg/L) in the waters of the primary hydrographic network [42].

Component	Number of Catchments	Arithmetic Mean	Median Mean	Minimum	Maximum
Forest catchments					
P_{min}	67	15	7	0	114
P_{total}	40	58	28	3	806
Mixed agricultural–forest catchments					
P_{min}	23	88	48	6	435
P_{total}	24	142	90	17	589
Agricultural catchments					
P_{min}	34	218	116	2	1145
P_{total}	26	535	250	7	3255
Urban catchments					
P_{min}	6	708	700	101	1572
P_{total}	5	1605	1500	163	3300
All accounted catchments, including catchments of unknown type					
P_{min}	137	115	31	0	1572

77. Rachold, V.; Beeskow, B.; Gordeev, V.V. Geochemistry of the Ob and Yenisey estuaries: A comparative study. Ber. Polar-Meeresforsch. 2007, 565, 1–235.

78. Savenko, A.V.; Pokrovsky, O.S. Distribution of dissolved matter in the Yenisei estuary and adjacent Kara Sea areas and its inter-annual variability. Geochem. Int. 2019, 57, 1201–1212.

79. Arfi, R. Hydrologie et charge nutritive à l'embouchure du Rhône (Saison froide). Bull. Ecol. 1987, 18, 123–130.

80. Pagnotta, R.; Blundo, C.M.; La Noce, T.; Pettine, M.; Puddu, A. Nutrient remobilisation processes at the Tiber River mouth (Italy). Hydrobiologia 1989, 176, 297–306.

81. Badyukov, D.D.; Korneeva, G.A.; Savenko, A.V. Transformation of structural and functional characteristics of the mainland runoff of the river Chernaya and the sea waters of the Sevastopol Bay in winter. Probl. Reg. Ecol. 2014, 3, 69–75. (In Russian)

82. Savenko, A.V.; Pokrovsky, O.S. Transformation of major and trace element composition of the dissolved matter runoff in the mouths of medium and small rivers of the Black Sea coast of Russia. Oceanology, 2022; 62, in press.

Estuar. Coast. Shelf Sci. 1993, 37, 27–41.

Component	Number of Catchments	Arithmetic Mean	Median Mean	Minimum	Maximum
P_{total}	103	301	95	3	3300

(7 and 28

ic activity

intensified, the phosphorus content increased. For the mixed agricultural-urban catchments, the average concentrations of P_{min} and P_{total} were 48 and 90 µg/L, while for the agricultural catchments they increased to 116 and 250 µg/L. A very high content of dissolved phosphorus was characteristic of the urban catchments, where the average concentrations of P_{min} and P_{total} reached 700 and 1500 µg/L. In general, there was a tendency towards an increase in the concentrations of P_{min} and P_{total} in the surface waters of the small catchments as the population density increased (**Figure 4**).

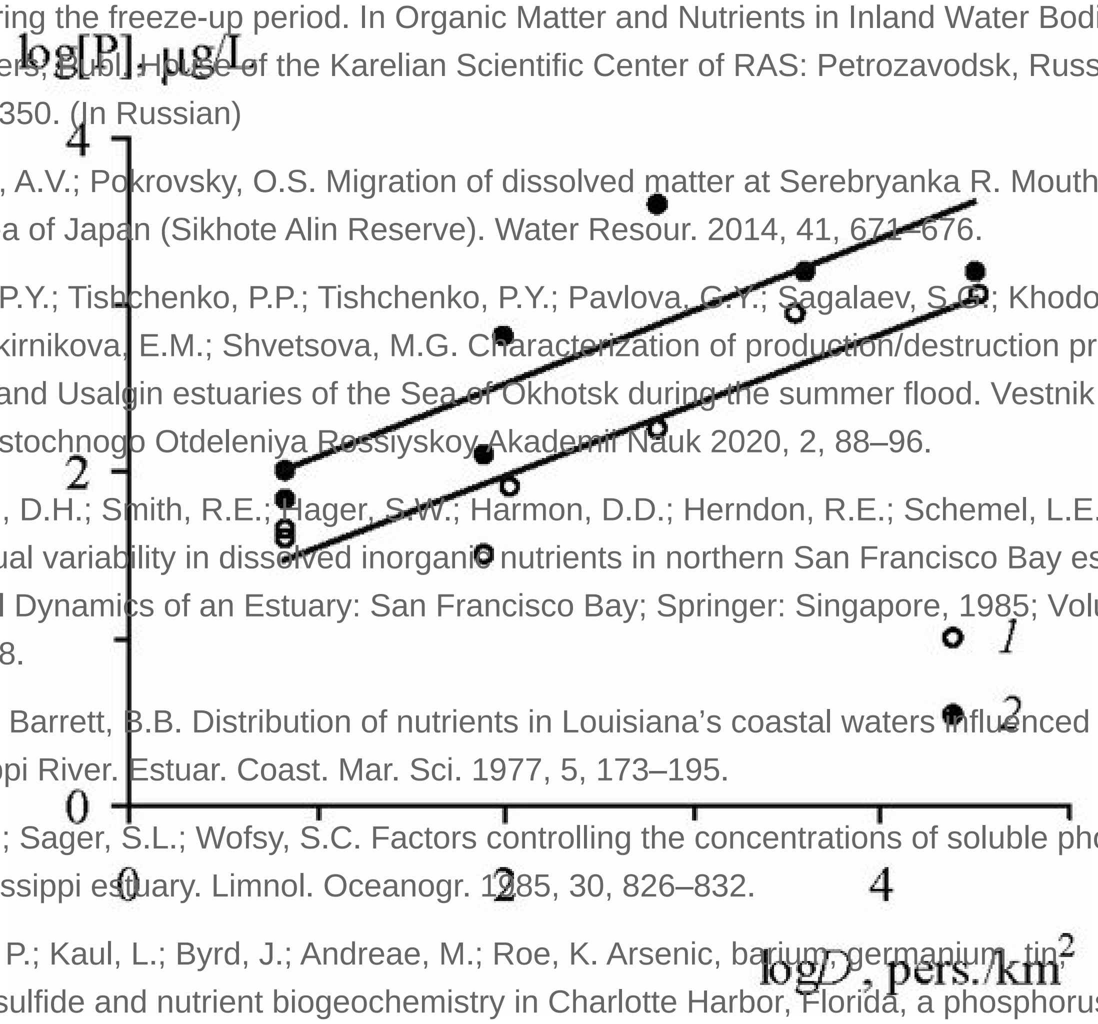


Figure 4. Relationship between the average annual concentrations of dissolved forms of mineral (*1*) and total (*2*) phosphorus in the waters of the primary hydrographic network and the population density *D* [6].

2.2. Phosphorus in River Waters

The rivers of the world carry into the ocean ~3 Gt/yr of dissolved matter and 15–20 Gt/yr of solid matter. The phosphorus runoff in the form of particulate suspended matter significantly exceeds its dissolved flux, which plays an extremely important role for biota and biogeochemical processes.

utrients

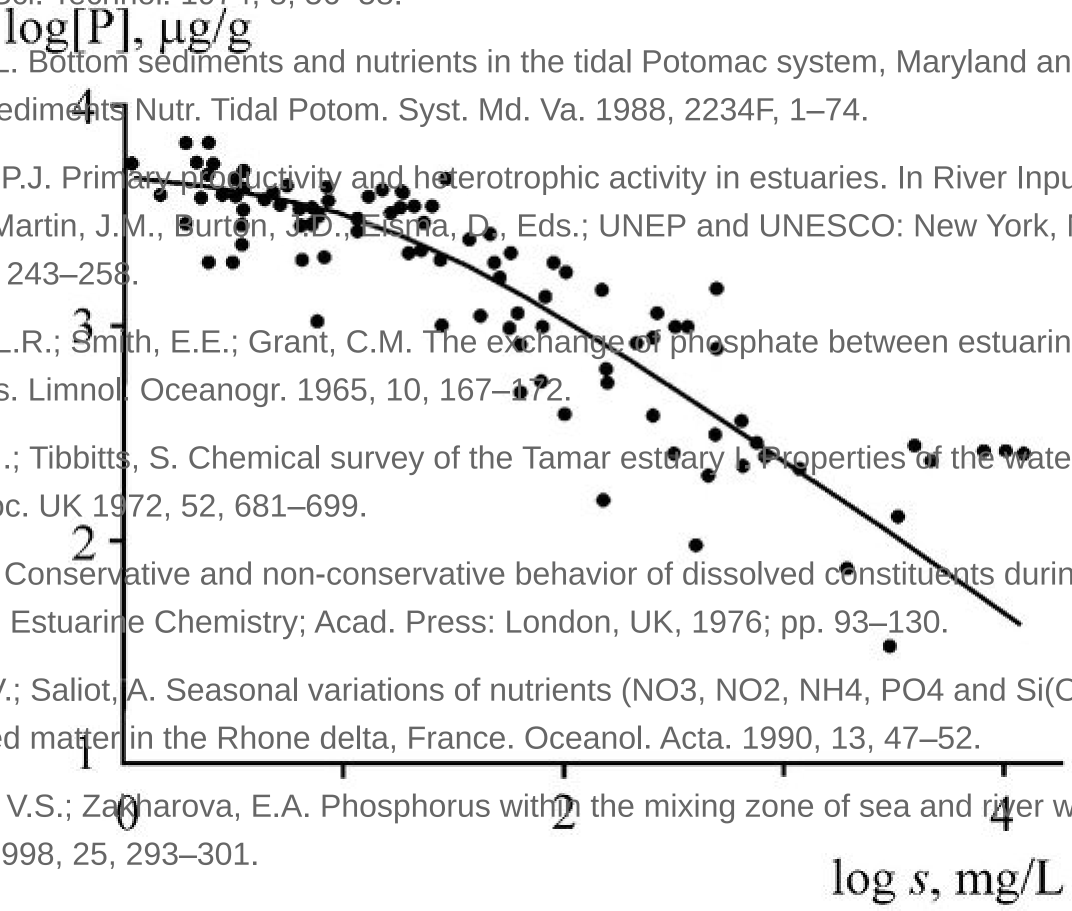
Russ.

92. Zvalinsky, V.I.; Tishchenko, P.P.; Tishchenko, P.Y.; Lobanov, V.B.; Sagalaev, S.G.; Shvetsova, M.G.; Volkova, T.I.; Sergeev, A.F.; Propp, L.N. Hydrochemical and production parameters of Amursky Bay during of high water of Razdol'naya River in August 2005. In Current Environmental Condition and Tendencies of Its Change in the Peter the Great Bay, Sea of Japan; GEOS: Moscow, Russia, 2008; pp. 199–229. (In Russian)
93. Maryash, A.A.; Zvalinsky, V.I. Production–destruction processes in the estuary of the Razdol'naya River during the freeze-up period. In Organic Matter and Nutrients in Inland Water Bodies and Sea Waters; Publ. House of the Karelian Scientific Center of RAS: Petrozavodsk, Russia, 2012; pp. 346–350. (In Russian)
94. Savenko, A.V.; Pokrovsky, O.S. Migration of dissolved matter at Serebryanka R. Mouth, the basin of the Sea of Japan (Sikhote Alin Reserve). Water Resour. 2014, 41, 671–676.
95. Semkin, P.Y.; Tishchenko, P.P.; Tishchenko, P.Y.; Pavlova, G.Y.; Sagalaev, S.G.; Khodorenko, N.D.; Shkirnikova, E.M.; Shvetsova, M.G. Characterization of production/destruction processes in the Uda and Usalgin estuaries of the Sea of Okhotsk during the summer flood. Vestnik Dal'nevostochnogo Otdeleniya Rossiyskoy Akademii Nauk 2020, 2, 88–96.
96. Peterson, D.H.; Smith, R.E.; Hager, S.W.; Harmon, D.D.; Herndon, R.E.; Schemel, L.E. Interannual variability in dissolved inorganic nutrients in northern San Francisco Bay estuary. In Temporal Dynamics of an Estuary: San Francisco Bay; Springer: Singapore, 1985; Volume 30, pp. 37–58.
97. Ho, C.L.; Barrett, B.B. Distribution of nutrients in Louisiana's coastal waters influenced by the Mississippi River. Estuar. Coast. Mar. Sci. 1977, 5, 173–195.
98. Fox, L.E.; Sager, S.L.; Wofsy, S.C. Factors controlling the concentrations of soluble phosphorus in the Mississippi estuary. Limnol. Oceanogr. 1985, 30, 826–832.
99. Froelich, P.; Kaul, L.; Byrd, J.; Andreae, M.; Roe, K. Arsenic, barium, germanium, tin, dimethylsulfide and nutrient biogeochemistry in Charlotte Harbor, Florida, a phosphorus-enriched estuary. Estuar. Coast. Shelf Sci. 1985, 20, 239–264.
100. Maest, A.S.; Crerar, D.A.; Stallard, R.F.; Ryan, J.N. Metal and nutrient behavior in the Raritan estuary, New Jersey, USA: The effect of multiple freshwater and industrial waste inputs. Chem. Geol. 1990, 81, 133–149.
101. Clark, J.F.; Simpson, H.J.; Bopp, R.F.; Deck, B. Geochemistry and loading history of phosphate and silicate in the Hudson estuary. Estuar. Coast. Shelf Sci. 1992, 34, 213–233.

2.2.1. Phosphorus of Suspended Matter and Bed Load

The distribution function of the phosphorus content in suspensions of 77 large, medium, and small rivers of the world corresponds to a lognormal law; the arithmetic and geometric mean concentrations of phosphorus equal 1500 and 1000 µg/g [43], respectively, which is close to the estimate [44]: 1270 µg/g. About 3% of the phosphorus in river suspended matter is represented by bioavailable soluble/exchangeable forms that can be used by living organisms [45][46].

Phosphorus runoff in the form of suspended solids is affected by the ratio of fine and coarse fractions. The phosphorus content in the fine fractions of the suspended matter and bottom sediments of rivers is 2–10 times higher than that in the coarse fractions. The consequence of this is apparently a decrease in the phosphorus concentration in river suspensions with an increase in the total content of suspended solids (turbidity), which is accompanied by an increase in the proportion of the coarse fractions (**Figure 5**). The highest phosphorus concentrations (~4000 µg/g) are observed at a turbidity <20 mg/L, while at a turbidity >100 mg/L, the phosphorus concentration begins to decline sharply, reaching 400 µg/g at a suspended matter content of 1000 mg/L. The same reason leads to an inverse relationship between the concentration of phosphorus in suspended matter and the water discharge or erosion rate. At small discharges during the low-water period, the relative contribution of fine suspensions increases and the phosphorus concentration reaches its maximum values, while in the high-water period, the bulk of suspended solids are represented by coarse suspensions with low phosphorus content.



102. Eastman, K.W.; Church, T.M. Behavior of iron, manganese, phosphate and humic acid during mixing in a Delaware salt marsh creek. Estuar. Coast. Shelf Sci. 1984, 18, 447–458.

103. Edmond, J.; Boyle, E.; Grant, B.; Stallard, R. The chemical mass balance in the Amazon plume I: The nutrients. Deep. Sea Res. Part A Oceanogr. Res. Pap. 1981, 28, 1339–1374.

104. Fox, L.E.; Sager, S.L.; Wofsy, S.C. The chemical control of soluble phosphorus in the Amazon estuary. Geochim. Cosmochim. Acta 1986, 50, 783–794.

105. van Bennekom, A.J.; Berger, G.W.; Helder, W.; Vries, R.T.P. Nutrient distribution in the Zaire estuary and river plume. Netherl. J. Sea Res. 1979, 12, 296–323.

106. Kudo, I.; Matsunaga, K. Behavior of nutrients and heavy metals in a high productive estuary. Bull. Jpn. Soc. Sci. Fish. 1989, 55, 957–962.

107. Chambers, R.M.; Fourqurean, J.W.; Hollibaugh, J.T.; Vink, S.M. Importance of terrestrially-derived, particulate phosphorus to phosphorus dynamics in a west coast estuary. Estuaries 1995, 18, 518–526.

108. Dubinin, A.V. Geochemistry of iron–calcium hydroxophosphates in pelagic sediments: Origin and compositional evolution in the course of diagenesis. Geochem. Int. 2001, 39, 585–596.

109. Upchurch, J.B.; Edzwald, J.K.; O'Melia, C.R. Phosphates in sediments of Pamlico Estuary. Environ. Sci. Technol. 1974, 8, 56–58.

110. Glenn, J.L. Bottom sediments and nutrients in the tidal Potomac system, Maryland and Virginia. Bottom Sediments Nutr. Tidal Potom. Syst. Md. Va. 1988, 2234F, 1–74.

111. Williams, P.J. Primary productivity and heterotrophic activity in estuaries. In River Input to Ocean System; Martin, J.M., Burton, J.D., Eisma, D., Eds.; UNEP and UNESCO: New York, NY, USA, 1981; pp. 243–258.

112. Pomero, L.R.; Smith, E.E.; Grant, C.M. The exchange of phosphate between estuarine water and sediments. Limnol. Oceanogr. 1965, 10, 167–172.

113. Butler, E.I.; Tibbitts, S. Chemical survey of the Tamar estuary I. Properties of the waters. J. Mar. Biol. Assoc. UK 1972, 52, 681–699.

114. Liss, P.S. Conservative and non-conservative behavior of dissolved constituents during estuarine mixing. In Estuarine Chemistry; Acad. Press: London, UK, 1976; pp. 93–130.

115. Denant, V.; Saliot, A. Seasonal variations of nutrients (NO3, NO2, NH4, PO4 and Si(OH)4) and suspended matter in the Rhone delta, France. Oceanol. Acta. 1990, 13, 47–52.

116. Savenko, V.S.; Zakharova, E.A. Phosphorus within the mixing zone of sea and river waters. Water Resour. 1998, 25, 293–301.

Figure 5. Relationship between the phosphorus content in suspended matter and the turbidity (s) of river waters [43].

The use of fertilizers is accompanied by an immobilization of the phosphorus in the upper soil horizons, which are the main supplier of suspended matter. As a result, the phosphorus content in suspensions denudated from cultivated lands is approximately 2 times higher than the runoff soils from forest catchments: 2500 and 1100 μg/g, respectively [47].

Forests prevent the erosion of the earth's surface and should reduce phosphorus runoff. This is confirmed by the data for seven small catchments in Southern Quebec [48], where the relationship between the concentration of suspended phosphorus ($[P_{susp}]$, μg/L) and the degree of forest coverage of the territory (X, %) was established:

$$[P_{susp}] = 10.2 - 0.056X.$$

Deforestation should lead to an increase in suspended phosphorus runoff on a global scale, but it is still very difficult to quantify this effect.

It is estimated that 10 to 30% of the river runoff of solid matter is carried in the form of bed load, in which the phosphorus content is on average 800 μg/g [49]. This value is lower than the phosphorus content in river suspended matter (1000 μg/g), which corresponds to the larger hydraulic size of the bed load.

2.2.2. Dissolved Phosphorus

In [50][51], the average annual and long-term average annual data on the content of the dissolved forms of mineral and total phosphorus in 179 rivers of the world (>200 observation stations) are summarized. The arithmetic and median mean concentrations of dissolved mineral phosphorus are 113 and 28 μg/L, respectively, and those of total dissolved phosphorus are equal to 241 and 85 μg/L (**Table 10**). The distribution of the concentrations of dissolved phosphorus obeys the lognormal law; therefore, the median mean concentrations are preferred for obtaining average values.

Table 10. The average content of dissolved phosphorus (μg/L) in the river waters of different geographic zones [50][51].

Geographic Zone	Number of Stations	Arithmetic Mean	Median Mean
P_{min}			
Arctic and subarctic zones	7	76	6
Temperate zone	123	132	32
Humid tropics and subtropics	19	39	16
Dry tropics and subtropics	33	93	31

117. Arenas, V.F.; de la Lanza, G.E. Annual phosphorus budget of a coastal lagoon in the northwest of Mexico. Environ. Biogeochem. Ecol. Bull. 1983, 35, 341–440.

118. Matsukawa, Y.; Sasaki, K. Budgets of nitrogen, phosphorus and suspended solid in an intertidal flat. Bull. Japan. Soc. Sci. Fish. 1986, 52, 1791–1797.

119. Yurkovskis, A.; Wulff, F.; Rahm, L.; Andruzaitis, A.; Rodriguez-Medina, M. A nutrient budget of the Gulf of Riga; Baltic Sea. Estuar. Coast. Shelf Sci. 1993, 37, 113–127.

120. Lebo, M.E.; Sharp, J.H. Modeling phosphorus cycling in a well-mixed coastal plain estuary. Estuar. Coast. Shelf Sci. 1992, 35, 235–252.

121. Bennett, J.P. Nutrient and sediment budgets for the tidal Potomac River and Estuary. IAHS Publ. 1983, 141, 217–227.

Geographic Zone	Number of Stations	Arithmetic Mean	Median Mean
Whole world	182	113	28
P_{total}			
Arctic and subarctic zones	3	235	19
Temperate zone	68	247	106
Humid tropics and subtropics	12	226	91
Dry tropics and subtropics	14	228	175
Whole world	97	241	85

Most of the natural factors affecting the content of chemical elements in river water are closely related to the geographic zonality, which determines the features and intensity of the weathering processes, biological activity, etc. In this regard, to analyze the spatial distribution of phosphorus content, all rivers were divided into four groups according to their geographical zones: Arctic region and subarctic zone, temperate zone, humid tropics and subtropics, and dry tropics and subtropics.

The minimum median mean concentrations of the dissolved forms of mineral and total phosphorus were observed in the rivers of the Arctic and subarctic belts, where the biological cycle of elements is much slower and the anthropogenic impact on the aquatic environment is not pronounced, given that there are no extensive sources of phosphorus input associated with agricultural industries, fewer large cities, and, therefore, less industrial and domestic wastewater. The highest median mean concentrations of dissolved mineral phosphorus were characteristic of the rivers of the temperate zone and the zone of dry tropics and subtropics. This is explained by the powerful anthropogenic impact on the nature of these regions, as well as the favorable conditions for the involvement of phosphorus in the biological cycle and its rapid turnover therein. A similar situation is typical for total dissolved phosphorus.

The average annual concentrations of the dissolved forms of mineral and total phosphorus for the rivers of the world correlate with the mineralization of river water (r = 0.94 and 0.89, respectively) and with the concentration of total nitrogen (r = 0.81 and 0.79, respectively) [51]. The cycles of nitrogen and phosphorus are closely linked in the biological cycle of matter and liable to similar anthropogenic changes. Like phosphorus, nitrogen is used in mineral fertilizers and its concentration in wastewater also increases tens and hundreds of times. A rather close correlation between dissolved phosphorus and the mineralization of waters is interesting. It can be assumed that it arises due to an increase in the mineralization of river water in the north–south direction parallel to an increase in the population density, which is an indicator of the anthropogenic load and, in particular, of the intensity of anthropogenic phosphorus sources. Indeed, the average concentrations of mineral and total phosphorus in the river water regularly increase with an increase in the population density in the catchments (**Table 11**).

Table 11. The average content of dissolved phosphorus in the water of rivers with different population densities in their catchments [51].

Population Density *D*, pers./km^2	Concentration, µg/L	
	P_{min}	P_{total}
<1	21	81
1–10	28	76
10–50	34	157
50–100	39	139
100–200	193	120
200–700	556	598

According to [52], for large rivers there is only a weakly expressed tendency towards an increase in the runoff of dissolved mineral phosphorus with an increase in the population density in the catchments. However, if one takes into account the presence of a directly proportional dependence of phosphorus removal from catchments on the value of specific water discharge, a significant correlation ($r = 0.78$) is found between the runoff of dissolved mineral phosphorus and the population density in the catchments, normalized to the specific water discharge.

The intensification of economic activity is accompanied by an increase in the phosphorus content in river runoff. Systematic observations carried out in 1936–1980 on the territory of the USSR showed a noticeable increase in the concentration and runoff of dissolved mineral phosphorus over time (**Table 12**). The same was established for other large rivers of the world, including the coastal parts of the sea basins into which these rivers flow [53].

Table 12. Change in water runoff (Q, km^3/yr), concentration ([P_{min}], µg/L) and runoff (J_{Pmin}, thous. t/yr) of dissolved mineral phosphorus in the USSR in 1936–1980 [54].

Drainage Basin	1936–1970			1970–1980		
	Q	[P_{min}]	J_{Pmin}	Q	[P_{min}]	J_{Pmin}
Arctic Ocean	2746	6.2	16.9	2849	13.5	38.5
Pacific Ocean	866	12.8	11.1	726	27.2	19.8
Atlantic Ocean	261	24.6	6.4	235	38.2	9.0
Aral–Caspian	381	29.4	11.2	315	45.3	14.2
Former USSR territory	4250	10.7	45.6	4120	19.8	81.5

Environmental protection measures can not only stop the increase in dissolved phosphorus concentrations but also cause its significant decrease. In particular, due to a reduction in the volumes of municipal wastewater and the use of phosphorus-containing detergents, the total phosphorus runoff into Lake Erie decreased from 27.9 to 10.5 thous. t/yr during 1968–1981 [55]. The deepening of wastewater treatment and a decrease in its volume led to a decrease in the phosphorus runoff into the Rhine and Elbe rivers from 51.1 and 20.5 thous. t/yr, respectively, in 1983–1987 to 20.5 and 12.5 thous. t/yr in 1993–1997 [56].

2.3. Phosphorus in Groundwater in the Zone of Active Water Exchange

The surface waters of the primary hydrographic network, rivers and lakes, are in direct hydrodynamic connection with groundwater, which plays an important role in the formation of the chemical composition of the continental runoff of dissolved matter. The greatest influence is exerted by the groundwater of the zone of active water exchange, the discharge of which is the main source of river runoff during the low-water period. The phosphorus content in groundwater is of the same order of magnitude as in the waters of the primary hydrographic network.

The average content of dissolved mineral phosphorus in the groundwater of the Critical Zone varies within the same order of magnitude: from 18 to 191 µg/L (**Table 13**). The maximum concentrations (191 and 127 µg P/L) were found in the waters of bog landscapes and steppes (dry savannah). The lowest phosphorus content was observed in the waters of permafrost zones and mountainous areas, in which the fluorine mobilization from rocks is impeded by the low temperature and relatively high water velocity, respectively. The concentrations of dissolved mineral phosphorus in the groundwater in areas of leaching and continental salinization, despite the significant difference in their mineralization, are relatively equal, amounting to 56.9 and 62.6 µg/L, respectively.

Table 13. The content of dissolved phosphorus in groundwater of the Critical Zone [57].

Groundwater Type	[P_{min}], µg/L
Groundwater of the provinces of permafrost	
Northern bog landscapes	26.3
Tundra landscapes	19.1
Northern taiga landscapes	21.7
Groundwater of the provinces of temperate climate	
Bog landscapes	191
Mixed forest landscapes	59.5
Southern taiga landscapes	57.1
Forest-steppe and steppe landscapes	75.8
Groundwater of the provinces of tropical and subtropical climate	
Wet savannah landscapes	29.4
Rainforest landscapes	65.3

Groundwater Type	[P_{min}], µg/L
Subtropical forest landscapes	58.7
Landscapes of dry savannah and steppes	127
Groundwater of the provinces of arid climate	
Landscapes of the temperate continental zone:	
soda waters	20.6
sulphate waters	63.3
chloride waters	21.7
Landscapes of the dry tropical zone	76.7
Groundwater of the mountainous areas	
High-mountain and mountain–meadow landscapes	18.0
Mountain–forest and mountain–taiga landscapes	40.1
Mountain–steppe landscapes	46.8
Average concentrations	
Groundwater of the leaching areas:	56.9
permafrost	22.6
temperate climate	98.2
tropical and subtropical climate	71.8
mountainous areas	34.9
Groundwater of the areas of continental salinization	62.6
Average for groundwater of the Critical Zone	58.0

2.4. Integral Characteristic of the Phosphorus River Runoff

2.4.1. Phosphorus Runoff in the Composition of Suspended Matter and Bed Load

The average phosphorus concentrations in the suspended matter and bed load of world rivers are 1000 and 800 µg/g, respectively [49]. The most detailed calculations of the global runoff of suspended matter give a value of 15.5 Gt/yr [58][59]. The mass of the bed load, according to various estimates, is from 10 to 30% of the mass of suspended matter, and 20% can be taken as an average value. Hence, the total continental runoff of suspended and drawn phosphorus is equal to 18.0 Mt/yr. This value is in close agreement with earlier estimates, 16.1 [44] and 20.4 [60] Mt P/yr; however, these did not take into account the runoff of bed load.

Phosphorus is also carried out from land via ice runoff and coastal abrasion. Here, phosphorus is mainly contained in the lithogenic material, while the contribution of its dissolved forms is negligible. The phosphorus content in the products of glacial erosion and coastal abrasion can be taken to equal that in the rocks of the land surface: 690 µg/g. A.P. Lisitsyn [61] estimates the removal of the solid products of ice runoff and coastal abrasion to be 1.5 and 0.5 Gt/yr, which corresponds to a phosphorus mass of 1.4 Mt/yr.

2.4.2. Dissolved Phosphorus in River Runoff

A detailed assessment of river phosphorus runoff was made in [50][51], where data for more than 100 medium and large rivers of the world were used and a correction for the value of the accounted water runoff for each continent was applied (**Table 14**). The total volume of continental water runoff in these works was taken to be equal to 38,500 km^3/yr. The more correct value is 41,700 km^3/yr [27], which would mean that the river runoff of dissolved mineral and total phosphorus increases to 1.6 and 4.5 Mt/yr, respectively.

Table 14. River runoff of dissolved forms of mineral and total phosphorus [50][51] [1].

Continent	Water Runoff, km^3/yr	% of Accounted Water Runoff		Phosphorus Runoff, thous. t/yr			
		P_{min}	P_{total}	P_{min}		P_{total}	
				Accounted	Full	Accounted	Full
Europe	2365	80	52	92.3	116	160	310
Asia	10,152	53	–	484	913	–	1094
North America	7840	12	24	9.8	82	237	988
South America	11,700	84	22	124	148	286	1300
Australia and Oceania	2370	4	1	1.9	48	1.2	205
Africa	4110	49	34	58	120	85	249
Whole world	38,537 (41,700)	52	19	770	1481 (1603)	769	4154 (4495)

[1] Values in parentheses are calculated for water runoff of 41,700 km^3/yr.

2.4.3. Dissolved Phosphorus in Groundwater Runoff

Groundwater phosphorus runoff is difficult to estimate due to the limited amount of available information. According to calculations [62], the proportions of the dissolved forms of mineral and total phosphorus in the groundwater and river runoff into the seas of the Russian Arctic are approximately the same, at 11–13% (**Table 15**). A similar proportion of dissolved mineral phosphorus in groundwater and river runoff also follows from the global estimates [63]. With an average concentration of phosphorus in the groundwater of the Critical Zone of 58 μg/L [57] and a groundwater runoff value of 2200 km^3/yr, the phosphorus removal into the ocean is 0.13 Mt/yr, or ~8% of the river runoff of dissolved mineral phosphorus.

Table 15. The proportion of dissolved phosphorus in groundwater and river runoff into the marginal seas of the Russian Arctic [62].

Receiving Water Body	Proportion of Groundwater Runoff from River Runoff, %		
	Water	P_{min}	P_{total}
White and Barents Seas	14.6	15.3	15.5
Kara Sea	10.3	12.3	–
Laptev Sea	7.6	6.9	5.1
East Siberian Sea	6.7	5.8	6.6
Average for the Arctic seas of Russia	10.0	12.8 [1]	10.7 [1]

[1] Weighted mean for water runoff.

3. Phosphorus in the Mixing Zone of River and Sea Waters

The final stage of the transformation of the river runoff of dissolved and suspended matter is carried out in the mouth area of rivers, as a result of which the ratio of the dissolved and suspended forms of chemical elements entering the ocean changes.

The dissolved components with conservative behavior are involved in intrabasin chemical and biological processes to an insignificant extent, and their content linearly depends on the ratio of the proportions of the sea and river water masses in the mixing zone. The components with nonconservative behavior are also added into the solution or are removed from it as a result of their involvement in different processes occurring in the water column or at the water–air and water–bottom boundaries. In this case, the linearity of the relationship between the component concentration and the ratio of the water mass proportions is violated. The best indicator of the ratio of the sea and river water mass proportions is the isotopic composition of water; however, the concentration of chemically inert chlorides, which is more accessible for measurements, is used more often.

The conservative behavior of the dissolved component *i* in the mixing zone of river and sea waters is described by the linear relationship between its concentration $[i]_{mix}$ and chloride content $[Cl]_{mix}$:

$$[i]mix = a + b[Cl]mix,$$

where *a* ≈ [i]rw is a constant parameter; *b* is the slope ratio taking positive or negative values at a higher or lower concentration of the component *i* in seawater in comparison with river runoff; and the subscript "*rw*" denote the concentrations in river water. If the component*i* is removed from the solution or, on the contrary, its internal source is present, the line showing the actual distribution of the concentrations of the relevant component is located, respectively, below or above the calculated line of conservative behavior (**Figure 6**). This equation is widely used to determine the type of behavior of chemical components in the mixing zones of river and sea waters.

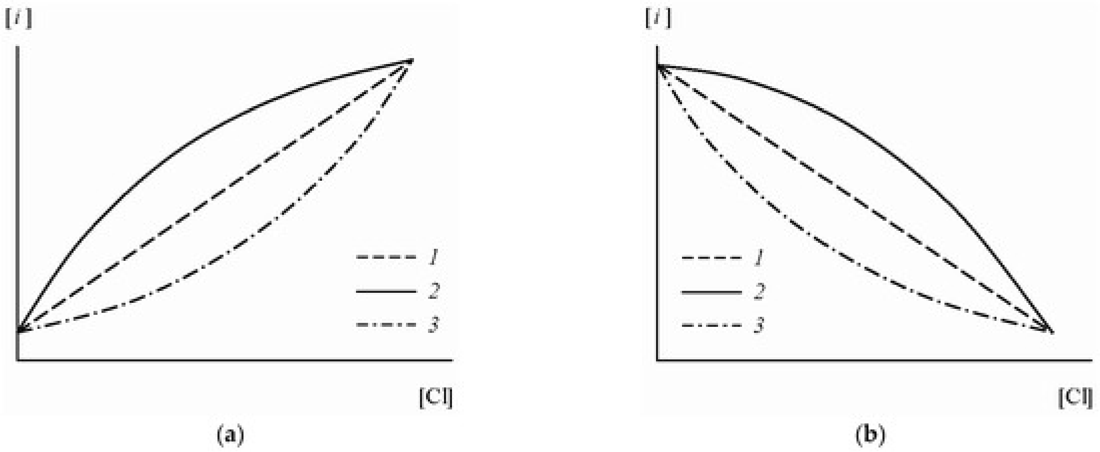


Figure 6. Relationships between the concentration of dissolved component *i* and chloride content by the conservative behavior (*1*) and availability of processes of additional input (*2*) or removal (*3*) of this component in the mixing zone of river and sea waters: (**a**,**b**) are cases when the concentration of component *i* in the river water is accordingly below or above that in the seawater.

Active participation in biological processes brings about the nonconservative behavior of phosphorus, which is observed in most river mouths of the world. The consumption of dissolved mineral phosphorus by phytoplankton leads to a decrease in its content in the water down to "analytical zero". The mineralization of the precipitated organic detritus causes the input of phosphorus into a solution in the lower layers of the water column and at the water–bottom boundary. Approximately half of the phosphorus entering the bottom as part of the organic detritus, after the mineralization of organic matter, can return back to the water with circulating currents or during the stirring up of the bottom sediments [64]. In addition to the production–destruction processes, an important role in the transformation of dissolved phosphorus runoff in the mixing zone of river and sea waters is played by the transformation processes of phosphorus-containing solid phases, sorption–desorption, and coprecipitation, as well as the diagenetic processes that control the phosphorus fluxes at the water–bottom boundary [6].

Table 16 summarizes the data on the distribution of the concentrations of the dissolved forms of mineral, organic, and total phosphorus in the mouth areas of large and small rivers of the world. The behavior of phosphorus in river mouths can be both nonconservative and conservative. In some cases, a complex type of phosphorus distribution was established exhibiting different behavior in various parts of the mixing zone.

Table 16. The behavior of dissolved phosphorus in the mouth areas of world rivers.

River	Receiving Sea Area	Phosphorus Form	Observation Period	Salinity, ‰		[P], μg/L		Phosphorus Runoff Transformation, %	Supposed Cause of nonconservative Behavior	Reference
				Observation Zone	Transformation Zone	River Boundary	Sea Boundary			
Severn	Bristol Channel of the Atlantic Ocean	P_{min}	June 1975	0–28	16–26	610	80	+10	Wastewater inflow	[65]
		“	February 1976	0–32	5–28	310	100	+20	As above	“
Clyde	Irish Sea	P_{min}	April 1973	0–32	1–8	242	15	−68	Sorption on suspended matter	[66]
		“	March 1974	0–32	–	40	242	~0	–	“
Scheldt	North Sea	P_{min}	January 1978	0–35	–	280	62	~0	–	[67]
Rhine–Meuse	As above	P_{min}	“	0–35	–	465	62	~0	–	“
Ems	“	P_{min}	October 1981	14–30	–	–	40	~0	–	[68]
Weser	“	P_{min}	“	0–32	–	520	62	~0	–	“
Elbe	“	P_{min}	“	0–31	–	200	68	~0	–	“
Neva	Baltic Sea	P_{min}	August 1990	0–5	0–3	13	31	−82	Biological consumption	[69]
		P_{total}	“	0–5	0–3	36	17	−49	As above	“
Keret	White Sea	P_{total}	July 1992	0–23	0–18	5.0	14	−62	“	[70]
Pulonga	As above	P_{total}	“	0–25	0–5	7.0	14	−48	“	“
Knyazhaya	“	P_{min}	June 2000	0–26	–	5.3	3.3	~0	–	[71]
Niva	“	P_{total}	July 1992	0–20	–	9.0	11	~0	–	[70]
		P_{min}	“	0–20	0–10	3.8	1.3	−33	Biological consumption	“
		“	June 2000	0–27	0–10	9.7	3.5	−46	As above	[71]
		“	June 2016	0–19	0–13	5.5	12	+35	Destruction of organic matter	A.S.[1]

River	Receiving Sea Area	Phosphorus Form	Observation Period	Salinity, ‰		[P], µg/L		Phosphorus Runoff Transformation, %	Supposed Cause of nonconservative Behavior	Reference
				Observation Zone	Transformation Zone	River Boundary	Sea Boundary			
Kolvitsa	“	P_{min}	June 2000	0–28	–	5.7	3.3	~0	–	[71]
		“	June 2016	0–21	0–13	5.4	12	+35	Destruction of organic matter	A.S.
Stream in the Por’ya Inlet	“	P_{min}	July 2008	0–23	0–12	4.4	2.1	−21	Biological consumption	[72]
Kuzreka	“	P_{min}	February 2020	0–23	0–2	2.5	6.8	+70	Destruction of organic matter	A.S.
Indera	“	P_{min}	September 2008	0–24	0–12	5.6	2.1	−25	Biological consumption	[72]
Chavanga	“	P_{min}	“	0–24	0–12	3.0	2.1	−46	As above	“
Strelna	“	P_{min}	February 2010	0–10	0–10	4.3	2.5	−18	“	A.S.
Onega	“	P_{min}	August 2004	0–21	0–12	11	4.7	−20	“	“
		“	June 2011	0–18	0–2	1.4	0.5	−43	“	[73]
		“	January 2017	0–6	–	6.9	12	~0	–	A.S.
		“	August 2017	0–18	0–10	3.0	5.0	+56	Destruction of organic matter	“
		P_{org}	June 2011	0–18	0–10	3.9	5.6	+51	As above	[73]
		“	January 2017	0–6	0–4	43	7.0	+100	“	A.S.
		“	“	0–6	4–6	43	7.0	−30	Mineralization	“
		“	August 2017	0–18	0–6	16	6.0	−21	As above	“
		P_{total}	June 2011	0–18	0–10	5.3	6.1	+26	Biological consumption and destruction of organic matter	[73]

River	Receiving Sea Area	Phosphorus Form	Observation Period	Salinity, ‰		[P], μg/L		Phosphorus Runoff Transformation, %	Supposed Cause of nonconservative Behavior	Reference
				Observation Zone	Transformation Zone	River Boundary	Sea Boundary			
		“	January 2017	0–6	0–4	50	19	+44	Destruction of organic matter	A.S.
		“	“	0–6	4–6	50	19	−40	Mineralization	“
		“	August 2017	0–18	0–4	19	11	−10	As above	“
Kyanda	“	P_{min}	August 2016	0–21	0–18	16	5.3	−8	Biological consumption	“
		P_{org}	“	0–21	0–4	25	6.5	−15	Mineralization	“
		P_{total}	“	0–21	0–14	41	12	−18	Biological consumption and mineralization	“
Northern Dvina	“	P_{min}	April 2003	0–25	0–18	32	9.0	−17	Biological consumption	[74]
		“	June 2003	0–23	0–6	18	7.3	−22	As above	“
		“	July 2016	0–14	0–2	3.1	2.3	−22	“	A.S.
		P_{org}	“	0–14	0–7	11	5.3	+110	Destruction of organic matter	“
		P_{total}	“	0–14	0–7	14	7.6	+93	As above	“
Mezen	“	P_{min}	July 2009	0–21	0–1	27	10	+88	Input from bottom sediments	[73]
		“	August 2015	0–21	0–1	25	6.0	+93	As above	[75]
		P_{org}	July 2009	0–21	–	2.5	0.5	~0	–	[73]
		P_{total}	“	0–21	0–1	30	11	+82	Input from bottom sediments	“
Semzha	“	P_{min}	August 2018	0–17	–	8.7	6.6	~0	–	A.S.
Indiga	Barents Sea	P_{min}	April 1981	0–30	–	2.0	18	~0	–	[76]

River	Receiving Sea Area	Phosphorus Form	Observation Period	Salinity, ‰		[P], μg/L		Phosphorus Runoff Transformation, %	Supposed Cause of nonconservative Behavior	Reference
				Observation Zone	Transformation Zone	River Boundary	Sea Boundary			
		“	September 1981	0–30	–	6.0	4.0	~0	–	“
Pechora	Pechora Sea	P_{min}	July 1984	0–30	0–7	16	20	−75	Biological consumption	“
Ob	Kara Sea	P_{min}	September 1993	0–34	0–20	43	50	−28	As above	[77]
		“	“	0–34	20–34	43	50	+120	Destruction of organic matter	“
		“	August 1999	0–33	0–15	45	90	−33	Biological consumption	“
		“	“	0–33	15–33	45	90	+150	Destruction of organic matter	“
Yenisei	As above	P_{min}	September 1993	0–34	0–20	5.0	50	~0	–	“
		“	“	0–34	20–34	5.0	50	+50	Destruction of organic matter	“
		“	September 2009	0–30	0–12	20	33	−30	Biological consumption	[78]
		“	“	0–30	12–30	20	33	+100	Destruction of organic matter	“
		“	September 2010	0–17	0–2	7.1	1.5	−57	Biological consumption	“
		“	April 2016	0–26	0–10	19	22	−6	As above	“
		“	“	0–26	10–26	19	22	+47	Destruction of organic matter	“
Rhone	Mediterra-nean Sea	P_{min}	1983–1984	1–37	–	170	6	~0	–	[79]
Tiber	Tyrrhenian Sea	P_{min}	July 1984	0–37	–	93	280	~0	–	[80]
		“	November 1984	0–37	–	93	22	~0	–	“
		P_{total}	July 1984	0–37	–	93	310	~0	–	“

River	Receiving Sea Area	Phosphorus Form	Observation Period	Salinity, ‰		[P], µg/L		Phosphorus Runoff Transformation, %	Supposed Cause of nonconservative Behavior	Reference
				Observation Zone	Transformation Zone	River Boundary	Sea Boundary			
		“	November 1984	0–37	–	155	22	~0	–	“
Salgir	Azov Sea	P_{min}	February 2016	0–15	0–8	540	116	−29	Biological consumption	A.S.
		P_{org}	“	0–15	0–4	70	90	+54	Destruction of organic matter	“
		P_{total}	“	0–15	0–4	610	206	−19	Biological consumption and destruction of organic matter	“
Chernaya (Crimea)	Black Sea	P_{min}	February 2004	0–17	0–2	7.1	1.8	−65	Biological consumption	[81]
Anapka	As above	P_{min}	May 2014	0–16	0–3	18	13	+700	Input from bottom sediments	[82]
		P_{org}	“	0–16	0–7	8.8	0.7	−58	Mineralization	“
		P_{total}	“	0–16	0–3	27	14	+450	Input from bottom sediments	“
Ashamba	“	P_{min}	July 2010	0–15	0–11	14	11	+35	Destruction of organic matter	“
		“	August 2010	2–13	2–9	82	25	−11	Biological consumption	“
		“	January 2011	0–10	0–3	2.2	14	+950	Input from bottom sediments	“
		P_{org}	July 2010	0–15	0–11	1.0	5.0	−320	Mineralization	“
		“	August 2010	2–13	2–9	21	6.4	−8	As above	“
		“	January 2011	0–10	0–1	1.7	1.4	−80	“	“
		P_{total}	July 2010	0–15	0–11	15	16	~0	–	“

River	Receiving Sea Area	Phosphorus Form	Observation Period	Salinity, ‰		[P], µg/L		Phosphorus Runoff Transformation, %	Supposed Cause of nonconservative Behavior	Reference
				Observation Zone	Transformation Zone	River Boundary	Sea Boundary			
		“	August 2010	2–13	2–9	103	31	−8	Biological consumption	“
		“	January 2011	0–10	0–3	3.9	15	+430	Input from bottom sediments	“
Mezyb	“	P_{min}	September 2010	0–15	2–9	5.5	7.7	+180	Desorption from suspended matter	“
		P_{org}	“	0–15	0–11	4.0	5.3	−37	Mineralization	“
		P_{total}	“	0–15	2–5	9.5	13	+100	Desorption from suspended matter	“
Hotetsai	“	P_{min}	September 2010	0–12	2–9	4.7	7.1	+170	As above	“
		P_{org}	“	0–12	–	0.3	0.3	~0	–	“
		P_{total}	“	0–12	2–9	5.0	7.4	+170	Desorption from suspended matter	“
Vulan	“	P_{min}	July 2006	0–16	0–2	8.0	1.9	−32	Biological consumption	“
Volga	Caspian Sea	P_{min}	August 2003	0–11	0–1	37	10	−60	As above	[83]
		“	August 2004	0–10	0–1	12	4.0	−63	“	“
		“	August 2005	0–5	0–1	41	2.6	−91	“	“
		“	September 2006	0–9	0–1	14	3.4	−64	“	“
Ural	As above	P_{min}	April 2016	0–8	0–5	16	29	+150	Input from bottom sediments	[84]
		“	April 2017	0–5	0–3	1.6	1.1	+300	As above	“

River	Receiving Sea Area	Phosphorus Form	Observation Period	Salinity, ‰		[P], μg/L		Phosphorus Runoff Transformation, %	Supposed Cause of nonconservative Behavior	Reference
				Observation Zone	Transformation Zone	River Boundary	Sea Boundary			
Mandovi	Arabian Sea	P_{min}	February 1981	0–36	0–12	3.0	6.0	−100	Sorption on suspended matter	[85]
Cauvery	Bay of Bengal	P_{min}	July 1986	0–15	0–2	267	108	−98	Unspecified	[86]
Chilka Lake	As above	P_{min}	November 1988	0–21	0–6	22	14	−24	Sorption on suspended matter	[87]
Mekong	South China Sea	P_{min}	November 1987	0–26	0–2	25	9.0	−84	As above	[88]
		“	“	0–26	2–15	25	9.0	+300	Desorption from suspended matter	“
Yangtze	East China Sea	P_{min}	June 1980	0–27	18–22	15	<3	−100	Biological consumption	[89]
		“	November 1981	0–33	0–24	7.0	11	+63	Desorption from suspended matter	“
		“	August 1981	0–32	25–28	23	<1	−44	Biological consumption	[90]
Razdolnaya	Sea of Japan	P_{min}	July 2001	0–32	0–25	60	<5	−27	Biological consumption	[91]
		“	“	0–32	0–9	80	<3	−70	As above	“
		“	August 2005	0–32	0–24	25	<3	−52	“	[92]
		“	February 2008	0–34	0–7	75	15	−28	“	[93]
Serebryanka	As above	P_{min}	July 2009	1–18	1–15	8.4	8.4	+13	Desorption from suspended matter	[94]
		P_{org}	“	1–18	–	0.3	5.2	~0	–	“
		P_{total}	“	1–18	1–15	8.7	14	+12	Desorption from suspended	“

River	Receiving Sea Area	Phosphorus Form	Observation Period	Salinity, ‰		[P], μg/L		Phosphorus Runoff Transformation, %	Supposed Cause of nonconservative Behavior	Reference
				Observation Zone	Transformation Zone	River Boundary	Sea Boundary			
									matter	
Usalgin	Sea of Okhotsk	P_{min}	July 2016	0–25	–	54	9.0	~0	–	[95]
		P_{total}	“	0–25	–	70	25	~0	–	“
Uda	As above	P_{min}	“	0–27	0–24	9.0	29	+100	Destruction of organic matter	“
		P_{total}	“	0–27	0–24	10	30	+70	As above	“
Sacramento	Pacific Ocean	P_{min}	May 1976	0–29	0–20	84	43	+74	Unspecified	[96]
		“	July 1976	0–30	0–30	77	43	+56	As above	“
		“	September 1976	0–30	0–28	81	15	+108	“	“
		“	November 1976, March 1977	0–29	0–18	62	62	+125	“	“
Mississippi	Gulf of Mexico	P_{min}	March 1971	10–33	–	71	15	~0	–	[97]
		“	January 1973	6–33	–	81	5.0	~0	–	“
		“	May 1973	0–20	8–20	90	5.0	−68	Biological consumption	“
		“	October 1983	0–34	0–3	248	3.0	+24	Dissolution of calcium phosphates	[98]
Peace	As above	P_{min}	October 1981	0–30	0–25	2790	496	−80	Biological consumption	[99]
Raritan	Atlantic Ocean	P_{min}	June 1982	0–22	0–3	12	50	−100	Sorption on suspended matter	[100]
		“	October 1982	0–27	0–9	600	31	−50	As above	“
Hudson	As above	P_{min}	March 1974	0–29	0–4	25	46	+156	Wastewater inflow	[101]

River	Receiving Sea Area	Phosphorus Form	Observation Period	Salinity, ‰		[P], μg/L		Phosphorus Runoff Transformation, %	Supposed Cause of nonconservative Behavior	Reference
				Observation Zone	Transformation Zone	River Boundary	Sea Boundary			
		“	August 1974	0–29	0–15	50	56	+250	As above	“
		“	August 1988	0–29	0–12	62	68	+90	“	“
Old Mill Creek	“	P_{min}	December 1978	0–27	0–9	6.0	12	+195	Desorption from suspended matter	[102]
Orinoco	“	P_{min}	November 1979	0–35	0–6	7.0	<3	+42	As above	[89]
		“	“	0–35	6–20	7.0	<3	−100	Biological consumption	“
Amazon	“	P_{min}	May 1976	0–35	8–15	15	3.0	−80	Biological consumption	[103]
		“	December 1982	0–36	0–2	20	6.0	−15	Sorption on suspended matter	[104]
		“	“	0–36	2–20	20	6.0	+118	Desorption from suspended matter	“
		“	May 1983	0–32	–	28	12	~0	–	“
Zaire (Congo)	“	P_{min}	November 1976	0–35	0–20	28	6.0	+100	Desorption from suspended matter	[105]
		“	May 1978	0–36	0–25	28	6.0	+100	As above	“

[1] Data of A.V. Savenko.

3.1. Nonconservative Behavior of Phosphorus

Biological processes are the main reason for the nonconservative behavior of dissolved phosphorus in the mixing zones of river and sea waters. This is shown in the interrelated change in the phosphorus content and the various characteristics of the biological processes: the concentrations of nutrients, oxygen, chlorophyll, and organic detritus, and the pH value.

The leading role of production–destruction processes in the transformation of dissolved phosphorus runoff has been established for the mouths of many rivers (**Table 16**): Neva, the small rivers of the Kandalaksha Bay of the White Sea, Onega, Kyanda, Northern Dvina, Mezen, Pechora, Ob, Yenisei, most of the small rivers in the Black and the Azov Sea catchments, Volga, Ural, Yangtze, the Far Eastern rivers Razdolnaya and Uda, and Peace (USA). Due to the seasonal and interannual dynamics of phytoplankton development, the distribution of nutrients in the mixing zones of river and sea waters is also subject to seasonal and interannual variability.

The consumption of dissolved mineral phosphorus by biota occurs in the surface layer or in the vertically mixing water column throughout the entire salinity range and varies from 6 to 100% of its content in river runoff. The most intensive consumption of mineral phosphorus by aquatic organisms is observed during the vegetative season and is most often accompanied by the extraction from the solution of another biogenic element, silicon [71][72][73][74][82][83][91][92]. Along with this, in the mouths of some rivers (Strelna of the Kandalaksha Bay of the White Sea, Chernaya of the Sevastopol Bay of the Black Sea, and Razdolnaya of the Amur Bay of the Sea of Japan), the removal of dissolved mineral phosphorus was found even in winter, with relatively low biological activity.

Under stratification conditions, the plots of river and sea water mixing show the influence of two processes that regulate the concentration of dissolved mineral phosphorus at different depths. Either the behavior of phosphorus in surface waters is conservative, or it is removed as a result of biological assimilation, while in the deep layers, phosphorus, on the contrary, enters the solution due to the destruction of the organic matter deposited on the bottom. As a result, the relationships between the concentration of dissolved mineral phosphorus and the chlorinity (salinity) acquire orderliness only when the points are grouped along the horizons [77][78][103][106]. This distribution is typical for the estuaries of the Ob and Yenisei Rivers, in which aquatic organisms consume 6–57% of the mineral phosphorus supplied via river runoff, and the destruction of organic matter provides an increase in its concentration by 50–150%, relative to the content in the river water. A distinctive feature of the release of mineral phosphorus into the solution during the destruction of organic matter is the simultaneous entry into the water column of the mineral forms of nitrogen [77][96].

The predominance of destruction processes over production processes is also often found throughout the entire water column, periodically occurring in the mouths of the Onega River, some rivers of the Kandalaksha Bay of the White Sea, the Ashamba River of the Black Sea coast of Russia, and the Uda River of the Sea of Okhotsk, and leading to an increase in the flux of dissolved mineral phosphorus by 35–100%. An even greater transformation of river runoff under the influence of destruction processes occurs when pore solutions from stirred up sediments enter the mixing zone. This situation is typical for the mouths of the Mezen and the Ural Rivers and in some periods is observed in the mouths of the Black Sea rivers Anapka and Ashamba, where the additional input of mineral phosphorus into the solution exceeds its removal via river runoff by 90%, 150–300%, 7.0 times, and 9.5 times, respectively. Firstly, the organic matter in the bottom sediments is remineralized with the release of phosphates, and secondly, it can reduce iron (III) phosphates to iron (II) phosphates, which causes the input of part of the phosphorus into a dissolved state.

The behavior of dissolved organic phosphorus characterizes the process of the destruction of organic matter in the mixing zone of river and sea waters. Its additional intake indicates the excess of the rate of the release of dissolved organic forms over the rate of complete phosphorus recycling and is observed in the mouths of the Northern Dvina and Salgir Rivers. A decrease in the concentration of dissolved organic phosphorus relative to the line of the conservative mixing of water masses occurs at a higher rate of its mineralization than its release into the solution during destruction and was noted in the mouths of the Kyanda River and rivers of the Black Sea coast of Russia (Anapka, Ashamba, Mezyb, and Hotetsai). Both losses and excesses of dissolved organic phosphorus were recorded at the mouth of the Onega River in different periods and at different salinity intervals. The distribution of dissolved organic phosphorus is close to conservative at the Mezen River estuary and the Serebryanka River mouth (Sikhote Alin Reserve).

A significant part of the phosphorus in suspended matter in rivers is represented by reactive mineral and organic compounds, which can be sources of dissolved phosphorus in the mixing zones of river and sea waters. From the experimental data [107], it follows that the amount of phosphorus passing from river suspensions into the dissolved state increases with an increasing salinity.

Some curves of the distribution of dissolved phosphorus concentration have a deflection in the salinity range from 0 to 9‰ [103]. In this case, the similar form of such relationships for dissolved iron and aluminum in the absence of clear signs of the biological consumption of phosphorus indicates the physicochemical removal of the latter from the solution as a result of coprecipitation with iron and aluminum hydroxides.

It can be expected that the terrigenous hydroxophosphates of iron and aluminum in the marine environment will be unstable due, firstly, to an increase in the pH value, accompanied by the displacement of phosphates by hydroxyl ions, and, secondly, to an increase in the concentration of dissolved calcium, which promotes the formation of apatite phases typical for ocean sediments. This assumption is confirmed by the results of observations [108], which showed that iron–calcium hydroxophosphates in oceanic pelagic sediments decompose during diagenesis into more stable iron oxyhydroxides and apatite. The replacement of the terrigenous hydroxophosphates of iron and aluminum with apatite should begin already in the river mouth areas and cause an increase in the concentration of dissolved phosphorus. Therefore, the input of iron and aluminum phosphates into the salinized portion of the river mouth area as a component of the suspended matter and bed load can lead to a partial release of dissolved phosphorus and, in some cases, be the cause of its nonconservative behavior. From these positions, one can explain the decrease in phosphorus content with the increase in salinity in the bottom sediments of the mouths of the Pamlico and Potomac Rivers [109][110].

Phosphorus removal as a result of sorption and coprecipitation processes occurs, as a rule, at the initial stage of river and sea water mixing during the period of low biological activity and is observed in the mouths of the rivers Clyde (Great Britain), Mandovi and Chilka Lake (India), Mekong (Vietnam), Raritan (USA), and Amazon, accounting for 15–100% of the removal of dissolved mineral phosphorus via river runoff (**Table 16**). The input of dissolved phosphorus due to desorption from river suspensions penetrating into the marine environment is also a common phenomenon established for the mouths of the Black Sea rivers Mezyb and Hotetsai, Mekong in the area of medium salinity, Yangtze, Serebryanka (Sikhote Alin Reserve), Old Mill Creek (USA), Orinoco (Venezuela), Amazon at medium salinity, and Zaire (**Table 16**). The maximum desorption values (13–300% of the content in river water, or 1–75 µg P/L) are reached at a salinity of 7–15‰, and the mixing curves have a convex shape.

The spatial separation of the processes of phosphorus sorption and desorption (predominance of sorption in the freshwater part of the mixing zone, and desorption in the area of intermediate salinity) confirms the distribution of phosphorus and iron in the bottom sediments of the river mouth areas. Thus, at the Pamlico River mouth, the concentrations of phosphorus and iron in the bottom sediments of the riverine part of the mixing zone closely correlate with each other (*r* = 0.98), whereas when approaching the sea boundary of the mouth area, this relationship becomes less pronounced (*r* = 0.86–0.77). The same concentrations of iron correspond to lower phosphorus concentrations in the marine part of the mouth, which indicates the release of the latter from the bottom sediments [111]. This combination of sorption and desorption in the estuaries is called the phosphate buffer mechanism [60][112][113][114]. Many authors have tried to determine the concentration of dissolved mineral phosphorus at which an equilibrium between the water and bottom sediments is established. According to experiments [99][112][113], the equilibrium concentrations of dissolved phosphates are in the range of 22–46 µg P/L. Convincing results of field observations proving the existence of such a concentration limit have not yet been obtained, although in the studied estuaries, with the exception of the Mekong River mouth, the concentrations of desorbed phosphorus do not really exceed the values recorded in the experiments and amount to 1–28 µg/L [82][89][94][102][104][105].

3.2. Conservative Behavior of Phosphorus

Despite the active participation of phosphorus in the intrabasin biological and chemical processes, cases of its conservative behavior were established (**Table 16**), which were observed either under conditions of the severe pollution of the aquatic environment (the mouths of the European rivers Clyde, Scheldt, Rhine–Meuse, Ems, Weser, Elbe, Rhone, and Tiber), or during periods of low biological activity (the mouths of the Mississippi River; Amazon River; the rivers of the Arctic; and the Far Eastern rivers Knyazhaya, Niva, Kolvitsa, Onega, Semzha, Indiga, Pechora, and Usalgin).

The concentration of dissolved mineral phosphorus in the waters of polluted rivers (93–520 µg/L) is an order of magnitude higher than its average content in the rivers of the world. Increased concentrations of dissolved mineral phosphorus were also found at the sea boundary of the mouth areas of these rivers: up to 242 and 280 µg/L on the near-shore zone of the Clyde and Tiber River mouths. The conservative behavior of phosphorus in the mouths of these European rivers can be explained by the fact that the absolute values of the fluctuations in its concentration in the mixing zones at such a high content in river or sea waters are comparable to the amount of phosphorus involved in the intrabasin processes. In addition, most of the observations in which the conservative behavior of phosphorus was recorded were carried out in the autumn–winter period, when the intensity of production processes in the temperate zone decreases with the intensification of the biological processes, and the conservative behavior of phosphorus can turn into nonconservative behavior within several weeks, which was noted, for example, for the Rhone River delta [115]. The conservative distribution of dissolved mineral phosphorus in the mouths of the Onega, Mississippi, and Amazon Rivers that appeared in the winter–spring period is also, apparently, caused by the low activity of aquatic organisms.

Separately, it should consider the conservative behavior of dissolved phosphorus during the vegetative season in the mouths of the small Arctic and Far Eastern rivers that are not subject to strong anthropogenic impact. The concentration of suspended matter in the mouths of these rivers in spring and early summer is small due to the slow thawing of soils in the catchments and the low water temperature preventing phytoplankton development, which limits the participation of phosphorus in physicochemical and biological processes.

Thus, the conservative behavior of dissolved phosphorus in the mixing zone of river and sea waters is an atypical phenomenon and occurs in special conditions when the biological and chemical processes at river mouths are suppressed as a result of an unfavorable combination of natural and anthropogenic factors.

3.3. Phosphorus Balance in the Mixing Zones of River and Sea Waters

An analysis of the mixing curves indicates the complex nature of the dynamics of dissolved phosphorus fluxes in river mouth areas, with the combination of conservative and nonconservative distribution and the spatiotemporal variability of the latter, including a change in the direction of transformation. Therefore, the calculations of the values of the removal or input of phosphorus in the mixing zones of river and sea waters based on data for relatively short time intervals turn out to be insufficiently representative for balance estimates.

To obtain more reliable estimates, Savenko and Zakharova [116] summarized the results of balance studies carried out in river mouths and bays for a year or more (**Table 17**). As follows from the data presented, on average, a significant part of the phosphorus is removed per year. The maximum removal (80–94%) is characteristic of the total phosphorus, including the suspended fraction (P_{dissol} + P_{susp}), and only a third of this value is associated with physical sedimentation, while the rest of the phosphorus is removed as a result of biosedimentation [117][118]. Biological processes also play a major role in the extraction of mineral phosphorus from the solution (40–80%) due to its transfer to the composition of suspended organic matter, which is subsequently deposited at the bottom. Total dissolved phosphorus (P_{total}) is retained in river mouths in much smaller amounts (7–38%). This is corresponds to the observational data presented in **Table 16**, according to which the losses of the dissolved forms of mineral and total phosphorus during biological consumption in the mixing zones of river and sea waters are on average 46 and 25%.

Table 17. Balance estimates of phosphorus losses in the river mouth areas and bays.

Object	Phosphorus Form	Observation Period	[P], μg/L River Boundary	[P], μg/L Sea Boundary	Phosphorus Balance, %	Supposed Cause of Transformation	Reference
Gulf of Riga, Baltic Sea	P_{min}	1989	–	–	−57	Biological consumption	[119]
	P_{total}	“	–	–	−7	As above	“

Object	Phosphorus Form	Observation Period	[P], µg/L		Phosphorus Balance, %	Supposed Cause of Transformation	Reference
			River Boundary	Sea Boundary			
Vigo Bay, Spain	P_{min}	1986	394	12	−40	Biological consumption and sedimentation	[64]
	P_{total}	“	–	–	−38	As above	“
Mikawa River mouth, Japan	P_{dissol} + P_{susp}	July 1983	930	–	−80	“	[118]
Delaware River mouth, USA	P_{min}	April 1986–July 1988	–	–	−61	Biological consumption	[120]
	“	As above, winter	–	–	−75	As above	“
	“	As above, spring	–	–	−135	“	“
	“	As above, summer	–	–	−70	“	“
	“	As above, autumn	–	–	+33	Destruction of organic matter	“
	P_{total}	April 1986–July 1988	–	–	−23	Biological consumption	“
	“	As above, winter	–	–	−53	As above	“
	“	As above, spring	–	–	−56	“	“
	“	As above, summer	–	–	−37	“	“
	“	As above, autumn	–	–	+52	Destruction of organic matter	“
Potomac River mouth, USA	P_{min}	1979–1981	–	–	−81	Biological consumption	[121]
Huizache-Caimanero	P_{dissol} + P_{susp}	1969–1981	93	170	−94	Biological consumption	[117]

Object	Phosphorus Form	Observation Period	[P], μg/L		Phosphorus Balance, %	Supposed Cause of Transformation	Reference
			River Boundary	Sea Boundary			
Lagoon, Mexico						and sedimentation	

4. Conclusions

The formation of the chemical composition of surface waters begins already in the atmosphere during the interaction of aerosols with the condensates of water vapor: cloudy water and the water of atmospheric precipitation. The average median concentrations of mineral and total phosphorus in atmospheric precipitation are 15 and 33 μg/L, respectively; the values of the input of these forms into the earth's surface are equal to 0.11 and 0.25 kg/ha yr. The content of the soluble forms of total phosphorus in atmospheric precipitation is in the range of 20–80%, with an average value of 55%.

The average median concentrations of dissolved mineral and total phosphorus in the waters of the primary hydrographic network are 31 and 95 μg/L, respectively. The concentrations of both forms increase with an increasing anthropogenic load: natural (forest) catchments < agricultural–forest catchments with land use less than 50% < agricultural catchments with land use over 50% < urban catchments. The concentration of dissolved mineral phosphorus, all other conditions being equal, increases with an increase of the phosphorus content in the catchment rocks.

The average median concentrations of dissolved mineral and total phosphorus in world rivers are 28 and 85 μg/L, respectively. The minimum values are observed in the rivers of the Arctic and subarctic zone; the maximum values are found in the most densely populated temperate zone and the zone of dry tropics and subtropics. The anthropogenic load is a dominant factor for riverine export, which is confirmed by the presence of a direct relationship between the concentrations of mineral and total phosphorus, on the one hand, and the population density, on the other hand.

The distribution of dissolved mineral and total phosphorus in the mixing zones of river and sea waters in the overwhelming majority of cases corresponds to nonconservative behavior. The conservative type of distribution is rarely observed and is found in the mouths of polluted rivers with high phosphorus concentrations, which significantly exceed the possible changes that occur as a result of biological and chemical processes. The decreases in the fluxes of dissolved mineral and total dissolved phosphorus at the river–sea geochemical barrier are 40–80% and 7–38%, respectively.