The aquasoils humus of the Ussuri Bay in the Sea of Japan

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Abstract. The study investigates the main characteristics humus of aquasoils (organic carbon, type of humus, content of humic and fulvic acids, E4/E6, acid-base properties, total nitrogen) in the Ussuri Bay shelf zone of the Sea of Japan. A strong (close) relationship is observed in organic carbon with carbon of humic acids and carbon of non-hydrolysable residue. The average content of organic carbon throughout the entire water area of the Ussuri Bay was 0.91%. Most of the water area of the Ussuri Bay is represented by a humate type of humus.

1 Introduction

The study of the patterns of transformation, distribution and general circulation of organic matter in the ocean, as well as its accumulation in sediments, is of great importance for geochemistry, lithology, geography, and biogeocenology [1]. Humus formation processes in bottom sediments occur "in situ", which in turn leads to the formation of underwater soils – "aquasoils". Aquasoils are the result of a special type of soil formation, where organic matter, both autochthonous and allochthonous, serves as the basis for humus formation processes [2].

The humus of the oceans is the largest carbon reservoir. If for some reason it decreases, an additional amount of CO_2 enters the atmosphere. The deposition of organic carbon in bottom sediments can occur both due to terrigenous runoff and synthesis and decomposition of organic matter in the oceanic column. The composition of the products of catagenesis of organic matter is largely inherited from the composition of the organic matter itself, which entered the bottom and was changed by biogeochemical processes in diagenesis [3, 4].

Studies of the content of the organic environment in aquasoils of the Ussuri Bay and the full composition of humus play a major role in circulation models in the system of bottom and benthic ecosystems.

The need to study underwater soils is dictate by time itself. in addition to the fundamental tasks associated with the problems of classifying these objects by soil scientists, the need to develop principles and methods for diagnosing their soil and ecological state, assessing the

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dynamics of this state, which makes up a certain inventory of certain indicators, there are also purely applied tasks - the need to develop a theory of mapping, zoning, and sanitation. Underwater soil science is still in its infancy, in fact, that is why it is so necessary to study the properties and modes of aquasoils in order to identify patterns of their formation [5].

The Ussuri Bay is the largest of the bays of the second order, which are part of the Peter the Great Bay of the Sea of Japan, occupies its northeastern part. Among the waters of Peter the Great Bay, the Ussuri Bay is the largest. At the same time, it is less studied than Amur and Nakhodka Bay, since it is deeper and more open and, as a result, more dynamic. The coast of the Ussuri Bay is less developed by man than the Amur and Nakhodka, however, there are and continue to be areas of intense anthropogenic impact on it.

From December to March, the Ussuri Bay near the northern shores partially freezes, the ice cover is insignificant. The Ussuri Bay is considered colder than the neighboring Amur Bay. Currently, the Ussuri Bay receives wastewater from the cities of Vladivostok, Bol'shoy Kamen' and many coastal settlements, the drains of which are supplied by the rivers of the eastern coast [6].

2 Materials and Methods

The object of the study was aquasoils, samples of which were collected during the expedition on the research ship "Professor Gagarinsky" in the shelf zone of Ussuriysky Bay, located in Peter the Great Bay, Primorsky Krai. Sampling was carried out using shipboard devices that ensure sampling of bottom sediments without violation of stratification (stratimeters, tubes of various designs) from depths from 11 m to 72.7 m (depth excluding ship deposition of 4.25 m). The sampling design provided the possibility of transportation, operation and mechanisms for lifting and lowering under water and reliable sealing of the sample in sampling devices without violating stratification. A total of 28 samples were selected, located throughout the entire water area of the Ussuri Bay (Figure 1). The laboratory studies described below characterize the upper 10 cm (surface horizon) aquasoils [7].

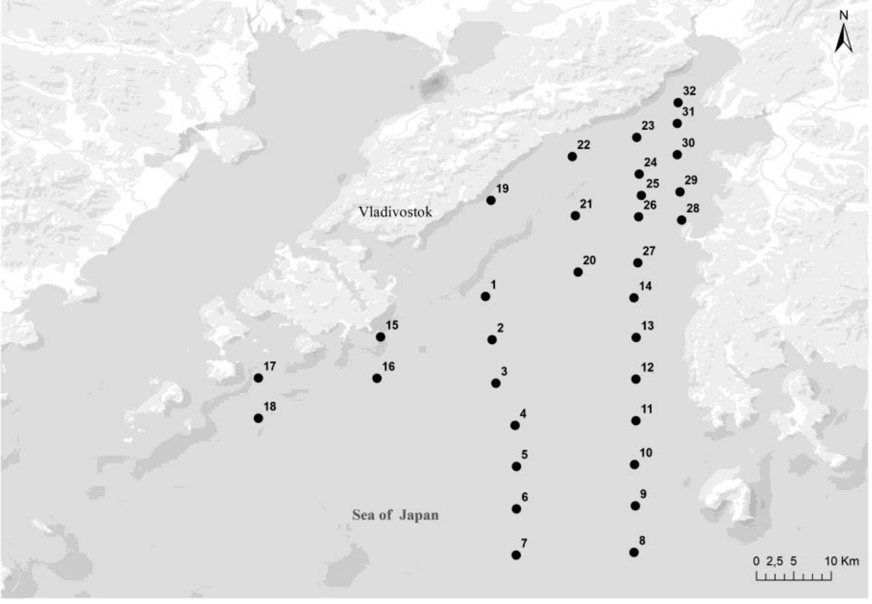

Fig. 1. Map-scheme of aquasoils sampling in the Ussuri Bay of the Sea of Japan.

Soil organic carbon (Corg) content was measured using the wet combustion method - oxidation of soil organic matter (SOM) by a mixture of 0.07 mol dm^{-3} $H2_SO_4$ and $K_2Cr_2O_7$ with titration using Mohr's salt [8]. The method used is based on the oxidation of carbon of soil organic matter by potassium dichromate in the presence of sulfuric acid. Sample preparation included grinding of aquasoils samples and sieving through a 0.25 mm diameter sieve; purification of ground samples from organic residues. The qualitative composition of humus of aquasoils was determined using the accelerated method of determining the composition of humus of mineral soils by the Kononova and Belchikova method [9]. This method was developed by the authors in relation to various types and subtypes of mineral soils. It can be use to identify three main groups of humic substances: humic acids, fulvic acids and insoluble residue of humic substances, also the mobility of humus and the nature of humic acids can be characterized. Humic substances are extracted with a mixture of a solution of sodium pyrophosphate and alkali [9].

The optical density of humic acids of aquasoils was determined using a Shimadzu UV 1800 spectrophotometer. The humic acid solution obtained during the analysis of the qualitative composition of humus was measured at two wavelengths: 465 (E4) and 665 (E6). As a result, we obtained the value of the E4/E6 ratio, the so-called chromaticity coefficient, which allows us to judge the maturity of the humic acids of the studied samples [9].

The determination of the granulometric composition was carried out by the sieve method according to Mathieu Cl. et. all [10]. The method is based on the laws of falling solid particles in calm water. The analysis of fine-grained soil is carried out by the pipette method. The rate of incidence of granulometric particles depends on their diameter and density of the solid phase. In addition, the temperature of the water has a certain effect, affecting its connectivity. Sample preparation was carried out on the recommendation of the V.V. Dokuchaev Soil Institute, using a 4% solution of sodium pyrophosphate. The principle of the method is that after the time required for a particular fraction to settle below a certain depth, a sample is taken from this depth – a certain volume of soil suspension. To establish the full name of the soil by granulometric composition, it is necessary to take 4 samples [10].

The total nitrogen in the studied samples was determined by the Kjeldahl method on a programmable infrared digester IDU 6. The method is based on the decomposition (salinization) of soil organic matter with concentrated sulfuric acid during boiling and subsequent quantitative accounting of the resulting nitrogen [11].

Standard soil analyses were used to determine the parameters, such as: soil pH was analyzed potentiometrically (Five Easy Plus FP20, Mettler Toledo, Russia) in suspension with 1 mol dm^{-3} KCl solution ratio 1:2.5 [12, 13]. The method is based on the ability of sodium hydroxide to neutralize hydrogen ions displaced into the soil solution by a solution of potassium chloride. The total potential acidity was determined by the potentiometric method, by measuring the pH on a stationary ionometer (Five Easy Plus FP20, Mettler Toledo, Russia) [13].

3 Results and Discussion

In the studied samples, the content of organic carbon (Table 1) ranged from 0.24% – the sampling point near cape Polosaty up to 1.94% located near Muravinaya Bay and Sukhodol Bay and further south-west to the center of the bay area. The average organic carbon content throughout the entire Ussuri Bay was 0.91%. In principle, the northeastern part of the bay contains the highest content of organic carbon, which can be caused by the cones of freshwater rivers flowing into Muravinaya and Sukhodol bays, respectively as well as the hydrochemical conditions of the estuaries of the Artemovka and Shkotovka rivers flowing into Muravinaya Bay. In the central part of the bay and further to the southeast, the content of organic carbon in the studied samples ranged from 0.52% to 1.22%.

In the studied samples, the proportion of humic acids from the total organic carbon content ranges from 15.75% to 60.58%, the proportion of fulvic acids varies from 1.12% to 36.17% (Table 1).

Table 1. Parameters of aquasoils of the Ussuri Bay of Primorsky region.

Samples	C_{org},%	Cha	Cfa	C_{gumin}	C_{ha}/C_{fa}	E_4/E_6	N, %	pH_{H2O}	pH_{KCl}
01	0.76	40.99	8.15	50.86	5.03	4.00	0.32	5.96	5.95
02	0.52	29.86	4.06	66.09	7.36	3.67	0.16	6.62	5.73
03	0.77	17.90	17.94	64.16	1.00	4.43	0.12	6.73	5.70
04	1.12	15.75	19.03	65.22	0.83	3.73	0.17	6.58	5.85
05	1.22	37.85	5.14	57.01	7.36	4.21	0.15	6.50	6.15
06	0.97	42.54	14.58	42.87	2.92	4.27	0.08	6.52	5.86
07	0.93	23.76	16.12	60.13	1.47	4.17	0.33	6.52	5.45
08	0.62	60.58	16.55	22.88	3.66	4.00	0.16	6.29	6.72
09	0.72	42.96	26.16	30.88	1.64	4.14	0.26	5.81	5.63
10	0.86	48.81	7.93	43.27	6.16	4.14	0.08	6.55	5.95
11	1.08	36.82	2.94	60.24	12.54	4.50	0.30	6.10	5.93
12	0.55	50.21	10.11	39.68	4.96	4.46	0.28	6.53	5.79
13	0.65	37.39	18.16	44.45	2.06	4.50	0.22	6.78	5.92
14	0.24	73.64	15.81	10.55	4.66	3.71	0.08	6.61	6.26
16	1.06	28.14	21.58	50.29	1.30	4.13	0.02	6.46	5.60
18	0.34	50.21	11.89	37.90	4.22	4.24	0.07	6.66	5.88
19	0.88	34.73	3.50	61.77	9.94	4.07	0.20	6.71	6.17
20	0.35	38.99	12.67	48.34	3.08	3.50	0,14	6.96	5.84
21	1.94	42.13	1.12	56.74	37.50	4.18	0,94	6.04	5.84
22	0.68	59.91	1.28	38,80	46.64	3.88	0.29	6.51	6.39
23	1.94	15.91	12.20	71.90	1.30	6.33	0.22	6.13	5.99
24	1.18	39.57	36.17	24.26	1.09	4.38	0.41	6.19	5.61
25	1.25	56.58	14.82	28.60	3.82	3.79	0.14	6.80	6.52
26	0.67	31.56	3.83	64.61	8.25	4.33	0.12	5.98	6.39
27	0.28	42.16	4.02	53.82	10.48	4,13	0.12	6.56	5.94
29	0.82	40.99	8.15	50.86	5.03	4,00	0.23	6.41	5.79
31	1.82	29.86	4.06	66.09	7.36	3.67	0.56	5.88	5.67
32	1.31	17.90	17.94	64.16	1.00	4.43	0.63	6.45	5.95

The ratio of carbon of humic acids to carbon of fulvic acids (Sgc/Sfc) is 0.83 - 46.64. Based on the results of the Sgk/Sfk ratio, we can say. most of the water area of the Ussuri Bay is represented by a humate type of humus. This is the ratio of Cha/Cfa is a distinctive feature of underwater soils. The predominance of the humate type of humus indicates the predominance of allochthonous organic matter in the formation of the studied thickness of the aquasoils of the Ussuri strait. There is also a humate-fulvate type of humus in places.

The content of non-hydrolyzable residue (humin) from the total humus content ranges from 10.55% to 71.9%. Half of the studied samples have a non-hydrolyzable residue content of more than 50%. It can be assumed that insoluble organic substances can be represented by chitin, since the water area of the bay is quite rich in biodiversity of animal fauna.

In the extracts studied by us, humic acids of aquatic origin had a rather weak color or were almost colorless. This is most likely due to the absence of lignin and tannins in the composition of the sources of organic matter of aquasoils. The E4/E6 indicator varied in values from 3.5 to 6.33, the average value was 4.2 (Table 1). Approximately along the entire sampling line along the southeastern part of the bay, E4/E6 indicators of 4.65 ± 0.13 are observed.

The total nitrogen content in the samples under study varies from 0.03% to 0.95%. On average, indicators in the region of 0.1–0.2% prevail. Such values are included in the norm of the average total nitrogen content in the soils of the land. A sufficiently high content of total nitrogen relative to the rest of the sample is observed in a pair of samples near

Muravinaya Bay, which is 0.57% and 0.63%, respectively. Which, in turn, has something in common with a sufficiently large percentage of organic carbon in relation to the entire water area.

According to the granulometric composition, the underwater soils of the studied water area are mostly represented by sandy loam – 19 samples, as well as light loam – 4 samples, light clay and cohesive sand 2 samples each, medium loam and heavy loam 1 sample, respectively. From the southwestern part of the bay, near the island Russian and east to the cape Polosatik, further south into the bay, the studied samples are sandy loam.

Among the studied samples, there is a pattern of decreasing the percentage of coarse and medium sand fractions during the removal of sampling points towards the exit from the bay. At the same time, the opposite pattern of increasing the percentage of coarse dust fraction is observe in the same samples. The same situation of increasing the percentage of coarse dust fraction is observe along the eastern coast of the gulf from north to south (samples 10 to 14). A little higher to the north along the east coast, one can observe a moment of a regular increase in the percentage of coarse and medium sand fractions from north to south (samples 25 - 27). It is quite difficult to identify any pattern of distribution of fractional particles in the western coastal part of the bay.

In the studied samples, the index of actual acidity (pH_{H2O}) varies from 5.81 to 6.80, which indicates a slightly acidic degree of acidity. In turn, this may probably contribute to a positive trend for precipitation of humic acids and predominantly humic humus type in the study area. The potential acidity (pH_{KCl}) varies from 5.45 to 7.72, which indicates the degree of acidity of the studied samples from slightly acidic to neutral. Most of the samples have a degree of acidity close to neutral. Since our samples were taken from the surface of the sedimentary strata, then, naturally, oxidative processes prevail there.

Let's consider the relationship between the studied parameters and the percentage of organic carbon in the aquasoils of the Ussuri Bay, we will trace the dependence on the parameters of the granulometric composition, the content of gross nitrogen and acidity in the studied samples. In the course of describing the results presented earlier, it is possible to make an assumption about the possible dependence of the content of organic matter on such indicators as the content of gross nitrogen and sludge fraction.

The structural relationships between nitrogen and carbon in the aquasoils of the Ussuri Bay indicate the unity of their sources of supply and are confirm by a moderate correlation coefficient (r) equal to 0.62. A strong (close) bond is observed in organic carbon with carbon of humic acids (r = 0.75) and carbon of non-hydrolysable residue (r = 0.95), but there is no bond with carbon of fulvic acids (r = -0.16). There is also no dependence of Corg on the chromaticity coefficient of humic acids (r = 0.21). There is no dependence of $Corg_{hum}$ on potential acidity (r = -0.15), but there is a moderate feedback with actual acidity (r = -0.46). On the basis of which it can be concluded that the lower the potential acidity, the more likely it is to increase the percentage of $Corg_{hum}$. In other words, the more acidic the sedimentation medium, the more likely it is to have a higher organic carbon content. Moreover, this is more likely due to precipitation of humic acids, which is confirmed by a moderate feedback between pH_{H2O} and carbon of humic acids (r = -0.48). We also observe a direct relationship between the accumulation of $Corg_{hum}$ and the silty fraction of aquasoils (r = 0.84), and in principle with the content of physical clay (r = 0.84). Which in turn indicates a strong feedback of Corg from the fraction of physical sand (r = -0.84) – the lower the percentage of physical clay, the higher the Corg content.

4 Conclusions

The organic carbon content in aquasoils varies from 0.24% to 1.94%. The average content of organic carbon in aquasoils throughout the entire water area of the Ussuri Bay was 0.91%.

The content of humic acids from the total organic carbon content ranges from 15.75% to 60.58%, the content of fulvic acids varies from 1.12% to 36.17%. The content of non-hydrolysable residue from the total humus content varies from 10.55% to 71.90%. Half of the studied samples have a non-hydrolysable residue content of more than 50%. The ratio of humic acids carbon to carbon of fulvic acids (Cha/Cfa) is 0.83–46.64. Most of the water area of the Ussuri Bay is represented by a humate type of humus.

The color coefficient varies in values from 3.50 to 6.33, the average value was 4,20.

The content of gross nitrogen in the studied samples varies from 0.03% to 0.95%. On average, indicators in the region of 0.1–0.2% prevail, which is normal for the average total nitrogen content in land soils.

The indicator of humus enrichment with nitrogen in aquasoils ranges from 2 to 11, a rare exception is a sample with a mineralization index. In most of the studied samples, the enrichment of humus of aquasoils with nitrogen is estimated to be very high (C:N aquasoils, respectively <5).

According to the granulometric composition, the studied samples are mostly represented by sandy loam.

The index of actual acidity (pH) varies from 5.81 to 6.80, which indicates a slightly acidic degree of acidity. The potential acidity (pH_{KCl}) varies from 5.45 to 7.72, which indicates the degree of acidity of the studied samples from slightly acidic to neutral. Most of the samples are represented by a degree of acidity close to neutral.

The relationship between the content of organic carbon (Corg) and total nitrogen in aquasoils is confirmed by a moderate correlation coefficient (r) equal to 0.62. A strong (close) relationship is observed in organic carbon with carbon of humic acids (r = 0.75) and carbon of non-hydrolysable residue (r = 0.95). The content of Corg with pH_{H2O} has a moderate feedback (r = -0.46). There is also a direct relationship between the accumulation of $Corg_{hum}$ from the silty fraction of aquasoils (r = 0.84), and in principle from the content of physical clay (r = 0.84). Which in turn indicates a strong feedback of the Corg from the fraction of physical sand (r = -0.84).

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