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# Natural remediation of surface water systems used as deposits of nuclear industry waste by humic substances

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# Acknowledgement

# Abstract

Radionuclides are found in all parts of the environment, including the atmosphere, aquatic and terrestrial systems, and throughout the biosphere. As with other chemicals, the fate and transport of radionuclides in the environment results from the interaction of physical, chemical, and biological processes. Similarly to metals in general, and unlike organic compounds, theses processes do not change the chemical into a benign end product. The radionuclides are still radioactive. Radionuclide transport from highly contaminated water reservoirs is of great importance for human exposure. In turn, radionuclide dispersal is connected with the problem of radioactive waste disposal. Spatially extended dispersal of radionuclides can lead to severe contamination of human water resources and to contamination of biota, which again are part of ecological food chains with humans as end members. Different natural processes exert high influence on contamination patterns, which partly exhibit elevated radionuclide concentrations in areas remote to the primary radionuclide sources.

In South Ural, nuclear production industry is located and therefore, a large number of water reservoirs have been contaminated as a result of this industrial activity. These reservoirs are diverse in morphology and function. Several reservoirs have been used as a depository of radioactive waste. Another group of reservoirs were significantly contaminated only once during a Kyshtym accident in 1957. The third group of reservoirs that are relatively pure have been unaffected by nuclear industry and subsequent dispersal in the environment in the region of South Ural.

In all reservoirs, the long-lived radionuclides $^{137}$Cs and $^{90}$Sr occur in measurable concentrations. Moreover, industrial reservoirs keep a high radioactivity of α-emitting radionuclides, such as $^{235}$U, $^{238}$U, $^{239}$Pu, $^{240}$Pu. In order to understand and estimate how these radionuclides migrate from nuclear waste and influence the contamination of the environment, and what mechanisms exist decreasing or retarding the radionuclide migration, the sorption behaviour of radionuclides in water bodies of differently contaminated water reservoirs, each of them typical of one of the types mentioned above was examined.

Based on the originating experimental data, the sorption of radionuclides was investigated and the relevant processes and significant parameters were found. Among different processes, the interaction of radionuclides with humic substances appreciably influences on binding of radionuclides to mineral solids in water solution that promotes their immobilization in nuclear waste. The accumulation of radionuclides by solid phase was mathematically expressed in a form of modified Henry's law that was calculated for the first time: the local increase in the

concentration of humics results in proportional increasing of the local content of adsorbed radionuclides. As shown in this thesis, the influence of humic substances on radionuclide sorption is provided by their special properties of a reversible transform into micelles. Multipole molecules and associates of humic substances form a single ensemble with humic substance micelles. An increase of the local humic substance concentration causes microphase conversion of some portion of humic substances multi-pole molecules into micelles with additional capture of radionuclides by micelle granule. The theoretical approach based on consideration of protons ($H^+$) as fermion gas in water solution was assumed and applied to this phenomenon, being due to the duel nature of humic substances molecules. Combining of all assumed models allows for understanding observed phenomenon of remediation effect of humic substances in the radioactively contaminated reservoirs. Investigation of changing of electrostatical status of micelles leads to modelling of remediation effect of humic substances in respect to influence on fish in contaminated waters. This effect was interpreted and quantified, based on properties of proteins of gill's cell membranes to lose $H^+$ under certain conditions in water solution

Thus, the formation of radionuclide complexes with humic substances removes and converts radionuclides to a less hazardous form, and is followed by a decrease in radionuclide bioavailability to fresh water biota, especially fish and benthos. It provides to reduce potential risk to ecological receptors by altering the concentration, mobility, toxicity, and bioavailability of environmental contaminants, and should be considered as an alternative to manage radioactive materials released into the environment.

Presented investigation and quantification of natural remediation of highly contaminated surface water systems located in South Ural via humic substances is the first step for sustainable developing of nuclear industry. In the surface water systems, humic substances are shown to promote the immobilization of radionuclides and, thus, decrease the bioavailability for fish contamination in the investigated water bodies. Humic substances appreciably influence the chemical and biological interactions between radionuclides and the environment that has experienced increasing interest concerning the remedial uses of humic materials.

# Erklärung über die Eigenständigkeit der erbrachten wissenschaftlichen Leistung

Ich erkläre hiermit, dass ich die vorliegende Arbeit ohne unzulässige Hilfe Dritter und ohne Benutzung anderer als der angegebenen Hilfsmittel angefertigt habe. Die aus anderen Quellen direkt oder indirekt übernommenen Daten und Konzepte sind unter Angabe der Quelle gekennzeichnet.

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# Chapter 1

# Aim and Scope[1]

In view of the principles of sustainable development it has to be ensured that the production, use, and disposal of nuclear industry waste do not pose unacceptable risk to men and the environment, nor alter the function of ecosystems – nowhere on the world and never in the future.

The problems of nuclear waste disposal have appeared in 40-ies years of the 20th century when the nuclear production began to develop. There wasn't a good understanding what stress this nuclear production and its wastes exert on human and environment. The first industrial nuclear reactor (PA Mayak) on Eurasia Continent was started up in South Ural (Russia) in 1948. The production association (PA) "Mayak" (South Ural, Russia, Figure 1.1) had the task to produce weapon's grade plutonium (Malyshev et al., 1997).

Its nuclear wastes have been partially deposited in surface water systems: lakes, industrial reservoirs and rivers. During the working period from the beginning of the 50-ties up to present days, some contaminated water was filtrated through the bed of lakes, and a lens of highly contaminated water was formed with the area of 10 km$^2$. The maximal values of groundwater contamination amount to $8 \cdot 10^5$ Bq·l$^{-1}$ with $^{90}$Sr, 10 mg·l$^{-1}$ with summary isotopes of uranium, and 2.05 Bq·l$^{-1}$ with summary isotopes of plutonium (Ivanov and Postovalova, 2003; Novikov, 2006). Also, the highly radioactive contamination of large areas of soils, water, and biota took place. At present, plutonium production is closed. Reprocessing and vitrification facilities of radioactive materials are in progress, releasing part of nuclear waste into the same reservoirs (Glagolenko et al., 2006). Strong impact on the environment was affected not only by the past and present activity of Mayak PA but also by accidents at production. As a result of accident in 1957, 20 Million Ci of radionuclides were released into the environment (Figure 1.2, Malyshev, 1997). 90% of this value settled in the

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[1] This chapter is partially published in Aleksandrova et al (2008a, b) and partially in Aleksandrova et al. (2009).

immediate vicinity of the explosion site. The remaining 2 Million Ci was dispersed by the wind and caused the radioactive trace along the path of the plume.
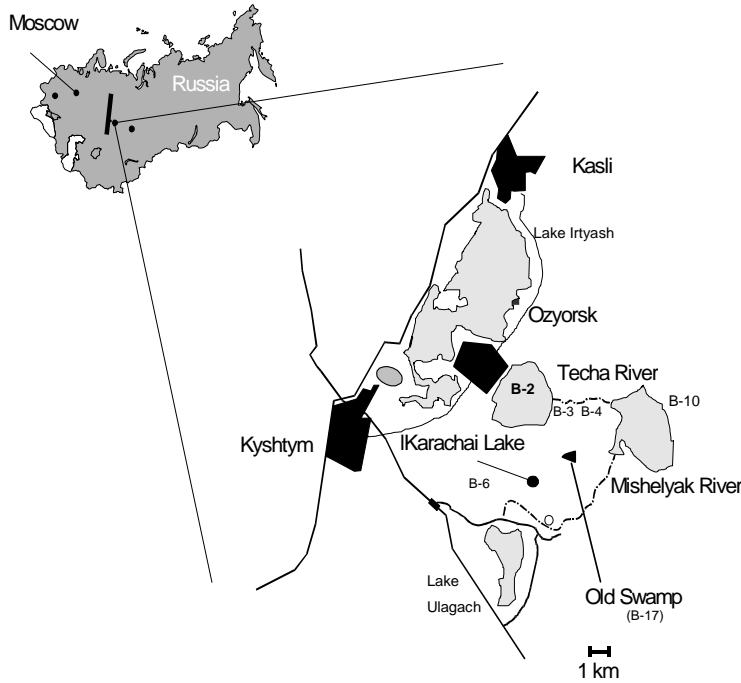


Figure 1.1 – Map of study site
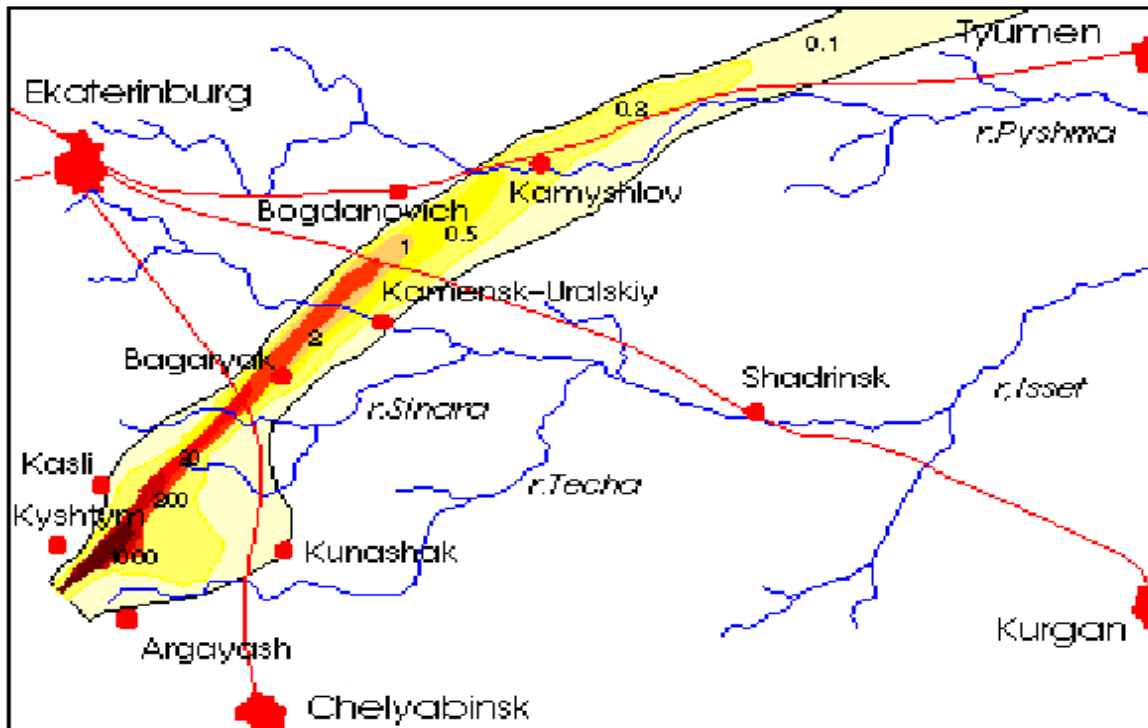


Figure 1.2 - The Eastern Ural Radioactive Trace formed as a result of the accident in 1957 (The numbers on the map corresponds to density of contamination with $^{90}$Sr $Ci \cdot km^{-2}$ ).

As a result, numerous natural lakes were significantly contaminated. Among them, there were the Lake Berdenish (the total contamination amounts to $1.58 \cdot 10^5$ Ci), the Lake Uruskul (the total contamination is about $6.25 \cdot 10^4$ Ci), and the Lake Kazhakul (the total contamination is about 292 Ci). The incident in 1967 was caused by the wind transport of contaminated sediments from exposed shores of Lake Karachay and Old swamp. The early spring was dry, with strong gusty winds, and it caused the exposure of sediments of the lakes shore. Some 6000 Ci of radioactivity associated with the fine particles of sediments was dispersed and caused an additional contamination of lakes and rivers of South Ural.

The problems caused by past and present nuclear activities that threaten the environment are substantial (Malyshev, 1997). This highly contaminated region is always under detailed consideration. A lot of different data was sampled but sufficient and multi-aspect interpretation of these data is yet not finished. However, generalizing of originating data of long-term ecological monitoring allowed for definition of influence of humic substances on the radioactive contamination of the environment and biota.

Making a comparison of radioactive contamination of South Ural Region, one should stress that there isn't other region in the world that is so highly radioactively contaminated. Chopping (2005) stated that nuclear test explosion and reactor wastes have deposited an estimated $16 \cdot 10^{15}$ Bq of plutonium into the world's aquatic systems. The current total contamination of α-radionuclides of the Lake Karachay (one of industrial reservoirs of Mayak PA) accounts to about $3.7 \cdot 10^{16}$ Bq, and 10 – 20% from this contamination is due to plutonium. According to Chopping (2005), controlled and uncontrolled releases of radioactivity from nuclear reactor systems amount to a total of $5.3 \cdot 10^{18}$ Bq. The inventory made at Mayak PA in 1990 showed that some $2.96 \cdot 10^{19}$ Bq of liquid and solid radioactive waste had been accumulated during its past activity (Malyshev et al., 1997). A part of the liquid waste was deposited in the industrial reservoirs.

Presented data of radioactive contamination of South Ural region obviously proves the necessity to investigate and study the problem of behavior of accumulated nuclear waste in the environment as well as to state precautionary principles of current sustainable development of nuclear industry in South Ural and current management of nuclear waste. These principles must take into account the ecosystem fundamental property of self-organization. Among these principles first, one should consider the natural remediation of the large-scale highly contaminated surface water system. As shown by a lot of investigations (Swindoll et al., 2000, Perminova & Hartfield, 2005, Aleksandrova et al., 2008), the remediation activity of humic substances in contaminated surface water systems can be used as prospective tool for the natural remediation of water and fresh water biota. This

approach includes the investigation of an influence of humic substances on radionuclide migration, sorption, precipitation, and their accumulation in biota, as well as the quantification of these effects.

## 1.1 Impact of radioactive contamination on biota of the surface water system of South Ural

Highly radioactively contaminated surface waters not only affect aquatic ecological communities and other ecosystems in their neighborhood, but also have ecological impact on large scales. A wide range of radioactive isotopes and their potential hazard has to be considered for a great variety of biota and ecosystem types over long time scales. As shown by the experimental investigation in 1951- 1952, a significant part of crayfish, worms and mollusks became extinct in Techa river from discharge point over distance about 100 - 160 km (Marey, 1976), Bivalvia - over distance in 79 km from discharge point. The maximal contamination of their shell amounts to about 104.4 µCi kg$^{-1}$ d.m. The contamination of worm accounts to 160.2 µCi kg$^{-1}$ w.m., of crawfish - to 33.042 µCi kg$^{-1}$ d.m. The contamination of water and sediments of Metlinskiy pond (B-4) caused high exposure of fish and benthos, and their extinction. In 1951 - 1953, specific activity of fish (Table 1.1) accounts to 10 – 400 µCi kg$^{-1}$ w.m. (Aleksandrova et al., 2005).

Table 1.1: The accumulated activity in fish of Metlinskyi pond experimentally measured in 1951

| Fish | Sampled quantity of fish | Averaged specific activity [$\mu Ci \cdot kg^{-1}$ w.m.] | Fish parameters | |
| --- | --- | --- | --- | --- |
| | | | Averaged weight [g] | Averaged length[sm] |
| Tinca tinca & Carassius | 3 | 407 | 112 | 16 |
| Perca | 4 | 183 | 45 | 15 |
| Esocidae | 5 | 148 | 78 | 26 |
| Rutilus rutilus | 25 | 271 | 34 | 13 |

In lakes contaminated as a result of accident in 1957, the total contamination of fresh water biota reached about 1% (e.g. the accumulated in biota activity amounts to 1.58 kCi of ^{90}Sr for Lake Berdenish, and 0.625 kCi of ^{90}Sr for Lake Uruskul) of the total contamination of the water system (Table 1.2).

Table 1.2: Partitioning of radionuclides between water, sediments and fresh water biota

| Radionuclide | Part of radionuclide content in sediments [%] | Part of radionuclide content in water [%] | Part of radionuclide content accumulated in fish [%] |
|---|---|---|---|
| Results averaged on experimental data of 13 lakes obtained during period from 1958 to 1959 | | | |
| $^{90}$Sr | 89.0 | 10.4 | 0.86 |
| $^{137}$Cs | 98.85 | 1.15 | - |
| $^{106}$Ru | 92.04 | 7.96 | - |
| $^{144}$Ce | 99.31 | 0.40 | 0.29 |
| Results averaged on experimental data of 2 lakes obtained during period from 1960 to 1970 | | | |
| $^{90}$Sr | 89.45 - 91.35 | 7.70 - 9.34 | 0.94 - 1.20 |
| Results averaged on experimental data of 4 lakes obtained in 1985 | | | |
| $^{90}$Sr | 99.8 - 99.99 | 0.01 - 0.2 | - |
| $^{137}$Cs | 99.9 - 99.99 | 0.001 - 0.1 | - |

## 1.2 Environmental Relevance of Natural Remediation of Radioactively Contaminated Surface Water Systems

Several water reservoirs used as deposits of highly radioactive waste are strongly connected with other surface waters via channel network, wind-driven transport, runoff, and groundwater pathways, especially at extreme meteorological conditions, such as flood and storm events (Albrecht, 2003). In addition to lateral surface transport, the invasion of radionuclides into groundwater may cause external and internal exposures to humans.

In aquatic systems, radionuclides become adsorbed to suspended matter and subsequently settled, disintegrated, or consumed by biota. This all leads to a purification of the pelagial water body. At the same time, profundal sediments accumulate and keep radionuclides. Assessment of the natural remediation in surface water often focuses on reducing contaminant concentration in surface sediments. However in the case of nuclear deposits, the sediment layer is the main keeper of nuclear waste. Thus, the principles of natural remediation defined as the sum of the nano-anthropogenic chemical, physical, and biological processes that reduce potential risk to ecological receptors should

be used to decrease the radionuclide concentration in water solution, their mobility from sediments, and bioavailability for biota. Therefore, all of the physical, chemical, and biological processes that determine the fate of radionuclides in surface water system have to be the subject of extensive scientific investigation, which should allow for understanding of their biogeochemical transport.

## 1.3 Physical and geochemical isolation of radionuclides in water reservoirs

To restrict the radionuclide transport into the open hydrographic system, the natural *physical and geochemical isolation* of radionuclides should be considered. The most contaminated water reservoirs, as Lake Karachay and Old swamp, have no outlet. Reservoir beds of loams are mostly little permeable but there is a little part of the bed with good water permeability. The filtration coefficient of contaminated water of the Lake Karachy and Old swamp is about 1 m/a. It means that $\sim 10^5$ m$^3$ of contaminated water go to groundwater. In this case, the main mechanism to restrict radionuclide spreading is found to be their immobilization by solids in the water body of waste deposits. Other reservoirs and rivers are not so highly contaminated as Lake Karachay and Old swamp and not so isolated. In general case, the contamination is gradually spreading into the environment.

*Geochemical isolation* of radionuclides means to keep them in the restricted volume of environment medium, not excluding direct interaction of radionuclides with the environment. It is possible under certain hydrochemical conditions. For these purposes, one can mark humic substances (HS) and their remediation effect. In industrial reservoirs with the value pH $\sim 8\pm1$, they bind radionuclides to solids, define the value of the partition coefficient of radionuclide $K_{d\_RN}$ between the solid and liquid phases, and affect the surrounding environment with the protective action.

## 1.4 Influence of humic substances on immobilization and bioavailability of radionuclides in surface water systems

In the water body, there are a lot of mechanisms to bind radionulide directly to mineral solids or by mediation of other substances. The mechanisms to bind radionuclide to solids include electrostatic interaction, sorption, intercalation, chemical reactions, induction and dispersion interaction, and isomorphous substitution. To form organo-mineral complexes including radionuclides and their compounds, HS is believed to play significant role in solution. HS compose from 60 to 80 % of

non-living organic matter in both soil and water ecosystems. HS are product of chemical-microbiological synthesis occurring during decomposition of mortal remains of living organisms and organic matter. Formation of humic molecules doesn't have a genetic code and proceed stochastically. The structure of HS resists further microbial and chemical decomposition. As a result, intrinsic features of HS are non-stoichiometric elemental compositions, irregular structures, heterogeneous structural units, and polydisperse molecular weights (Perminova et al., 2006). Example of humic substance is shown in Figure 1.3.
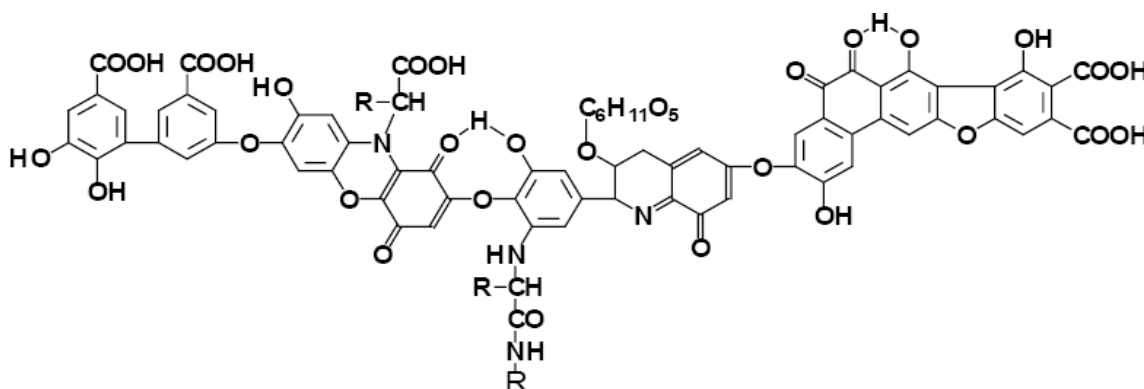


Figure 1.3 – Hypothetic structure of a part of humic acid (Stevenson, 1982) (R- alkyl residue)

HS of different origin have a very similar structural organization. A humic macromolecules consist of an aromatic core highly substituted with functional groups (among those dominant oxygen functionalities – carboxyls, hydroxyls, carbonyls) and of peripheral aliphatic units composed mostly of polysaccharidic and polypeptidic chains, terpenoids, etc (Stevenson, 1994).

The main rule to classify HS is based on solubility in alkali and acids (Perminova et al., 2006). In accordance to this rule, HS is divided into three general groups: humin (not soluble in alkali and acids), humic acids (HA) and fulvic acids (FA). HA are soluble in alkali and precipitate at pH<2. FA are soluble in alkali and acids. HA are not so mobile in the water system as FA. Compounds of HA with radionuclides foster to be bound to solids or precipitate. As found in experiment, about 16-41% of plutonium of released radionuclides are bound to humic acids and not mobile. FA and their compounds with radionuclides are mobile in ecosystems and take an active part in environment transport processes (Sorokina, 2004). So, 11% of plutonium and 88% of americium released into disposal and found in the ground water, being bound to fulvic acids and low-molecular compounds. Complex structure of HS provides for their diverse reactivity. Hydrophobic aromatic core and hydrophilic peripheral moieties determine amphiphylic character and surface activity of humics. The connection between HS and radionuclides is provided by ionic donor-acceptor (including

hydrogen bonding and charge transfer complexes) and hydrophobic bonding. Ionic bonds are fostered by cations of alkaline and alkaline-earth metals to form simple heteropolar salts with HA (humates). The substitution of protons with radionuclides in carboxyl and phenolic groups depends on pH and Eh conditions of the solution. A general formula of such a simple heteropolar salt can be written as follows (Orlov et al., 2005):

$$R \Big\langle \begin{matrix} (COO^-)_m (Me^{m+}) \\ (O^-)_p (Me^{p+}) \end{matrix}$$
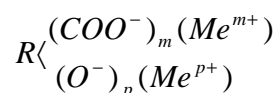
where $Me^{m+}, Me^{p+}$ can be substituted with cations: $Na^+$, $K^+$, $Cs^+$, $NH_4^+$, $Ca^{2+}$, $Sr^{2+}$, and $Mg^{2+}$, corresponding to its valency $m, p$.

Humates of alkalines ($Na^+$, $K^+$, $Cs^+$) and ammonium are highly soluble, but are enriched at the boundary with the solid phase. Humates of calcium and strontium are not soluble in water at pH < 12. Humates of magnesium are slightly soluble. Humates of calcium and strontium precipitate, forming a film on the surfaces of suspended particles that can be observed on radiographical pictures of water samples (Bachur et al., 2005).

As well, the interaction of metals, radionuclides and their complexes with HS may result in the formation of complex salts with metal ions incorporated into the anionic part of HA molecules, and unoccupied carboxyl and phenol groups also interact with radionuclide. It results in the formation of complex heteropolar salts. The general formula of this composition can be written as follows:

$$\left[ R \Big\langle \begin{matrix} COO \\ OH \end{matrix} {}^{\diagdown}_{\cdot\cdot} M \right] \begin{matrix} (COOH)_p^- Me^{p+} \\ O_m^- Me^{m+} \end{matrix}$$
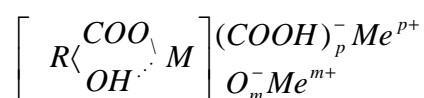
where M can be substituted with $Al(OH)_2^+$, $Al(OH)^{2+}$, $Fe(OH)^{2+}$.

Under certain conditions, HA can bind not only heavy metals and radionuclides but also polar and highly hydrophobic organic compounds released into environment. Being chemically bound to radionuclides, humates form strong complexes with mineral solids, using radionuclides or other cations as "bridge" with acceptor-donor bonds.

As shown in many works in the environment, humic substances operate as binding agents and detoxicants, sorbents and flushing agents, redox mediator of abiotic and biotic reactions, nutrients carriers, bioadaptogens, and growth-stimulator (Perminova & Hatfield, 2005). These functions possess significant utility in the remediation of contaminated environments.

## 1.5 Summary of experimental investigations of contaminated surface water systems

Several monitoring programs were carried out to investigate the water body of different reservoirs during the entire period of the past and present activities of PA Mayak. In these campaigns, physicochemical, sedimentary, and biotic parameters, such as contamination of different types of fresh water biota (benthos and fish), were measured in high spatial resolution. To calculate the spatial distribution of radionuclides in water systems, water and sediment samples were taken at some locations in the reservoirs at various depths, using the freeze core technique (Stukalov et al., 2007). The freeze core technique was applied to some industrial open water systems (Old swamp (B-17), Kisliy canal, Mishelyak River). The long cored pipes were submerged in water straight down to loam at several locations of reservoir, and frozen. The frozen cores were cut into smaller parts and subsequently analyzed for chemical and physical properties.

The water body samples were divided into two parts (solids and solution), using filter with $2 \cdot 10^{-6}$ m diameter porous. Solid and solution parts were analyzed separately. The solid parts were dried, heated to $100^0$ C and then to $600^0$ C. Physicochemical analyses were carried out at each step. The analytical results of the physicochemical parameters were correlated to the concentrations of radionuclides applying single regression analyses. Further characteristics of the samples were obtained applying radiographical, radiochemical, electron microscopic, and spectroscopic investigations of suspended matter, sediments and loam (Antonova et al., 1999; Bachur et al., 2005).

### 1.5.1 Investigation of radionuclide depth profiles in Old swamp

In March 2006, water and sediment samples were taken at 20 locations in the reservoirs at various depths. Physicochemical and sedimentary parameters were investigated in high spatial resolution using the freeze core technique. The frozen cores were cut into 15 parts and subsequently analyzed for chemical and physical properties. The data include information on concentrations of microelements (sodium, potassium, calcium, magnesium, manganese, uranium), anions (carbonate, sulphate, chloride, bicarbonate, acetate), content of total organic matter, physico-chemical water parameters (hardness, bichromate oxidizability, permanganate oxidizability), content of solids, volumetric activities of dissolved and adsorbed radionuclides ($^{90}$Sr, $^{137}$Cs, $^{134}$Cs, $^{60}$Co, $^{106}$Ru, $^{154}$Eu, $^{241}$Am, $^{244}$Ci, sum of plutonium isotopes $^{239}$Pu and $^{240}$Pu, sum of uranium isotopes $^{235}$U and $^{238}$U),

and granulometric and mineral composition of solids. Depth profiles of several radionuclides, the volumetric content of SR, and OM are presented in Figures 1.4. In water reservoirs, OM was found to consist mainly of HS (Stukalov and Simkina, 2003).
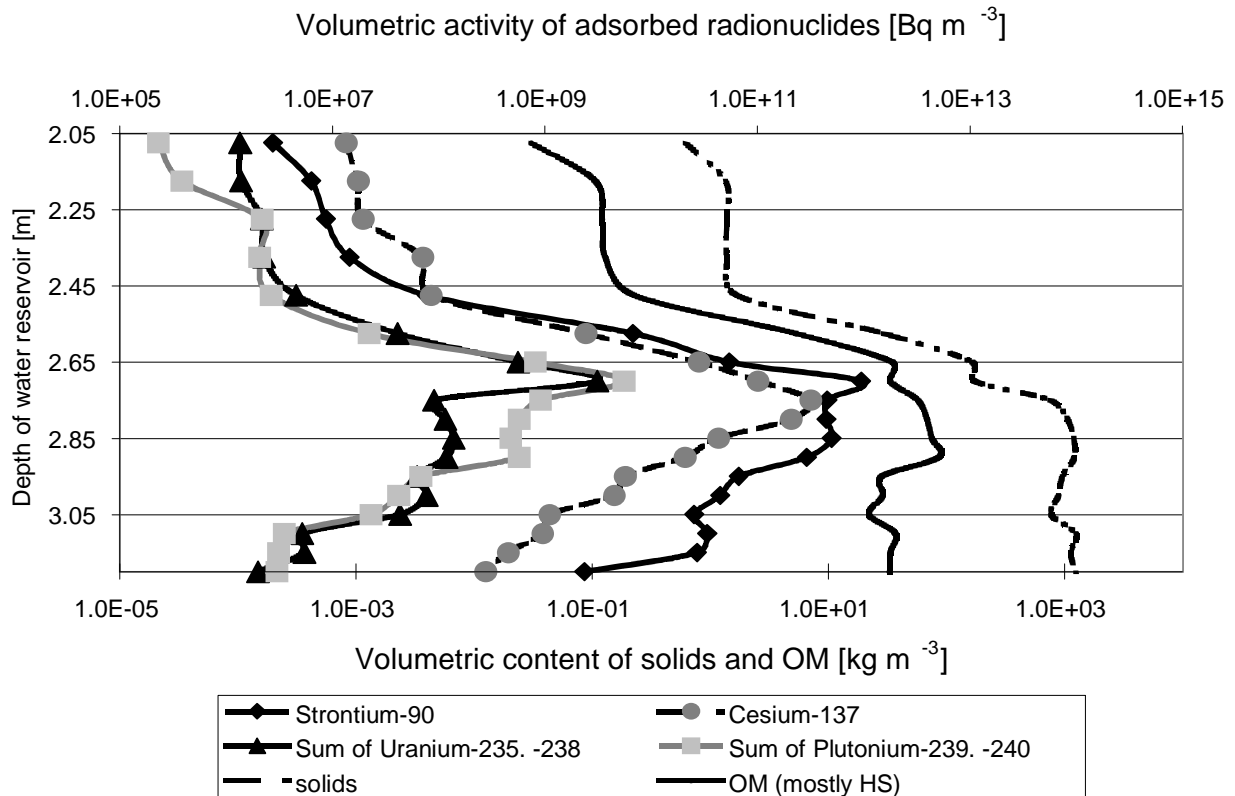


Figure 1.4 - Depth profiles of the volumetric activity of $^{90}$Sr, $^{137}$Cs, sum of uranium isotopes $^{235}$U, $^{238}$U, and plutonium isotopes $^{239}$Pu, $^{240}$Pu bound to solids and the volumetric content of solids (SR) and organic matter (OM)

Applying radiographical, radiochemical, electromicroscopic, and spectroscopic investigations of suspended matter, sediments and loam, Bachur et al. (2005) showed that the major part of radionuclides is adsorbed by fine–grained particles, such as clay minerals, hydroxyls of iron, and OM (Figure 1.5). In all samples, the following chemical forms of radionuclides were found: adsorbed, isomorphous substitutions, and proper radionuclide phases. As found, the main stable and meta-stable forms of radionuclides were incorporated in a gel structure. All samples of the monitoring program contained a gel of different structure with mono- and multi-component composition including the radionuclides $^{137}$Cs, $^{90}$Sr, uranium and plutonium isotopes, and fractions of calcium, sodium, chlorine, and sulfur. Depth profiles of several cations are presented in Figure 1.6.
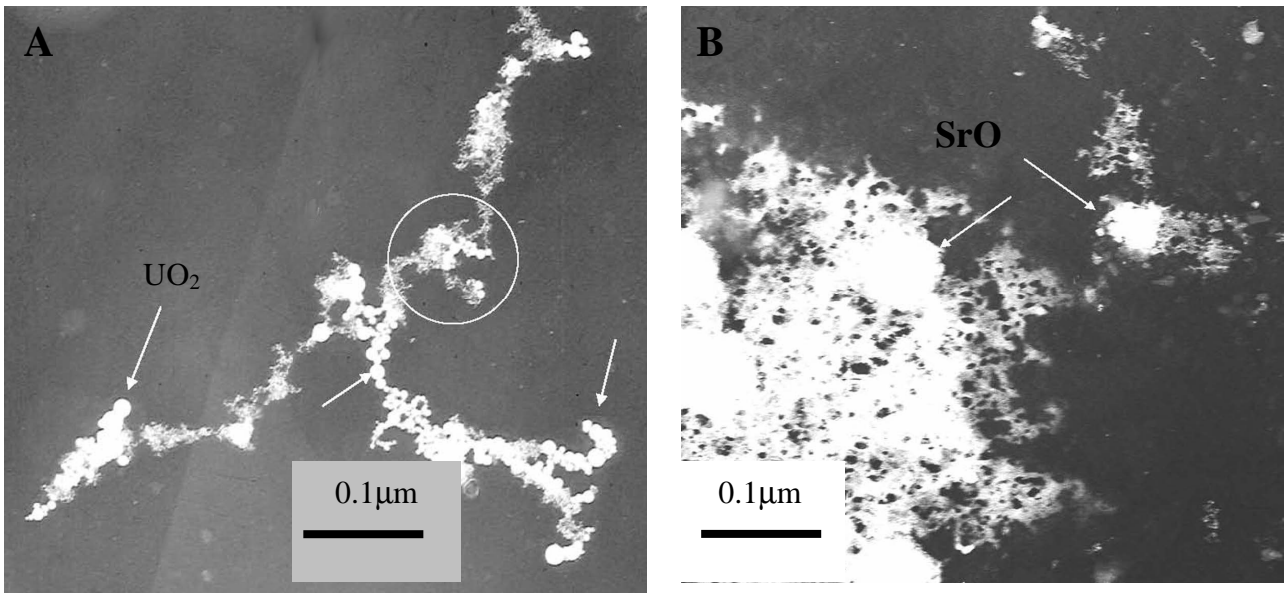
Figure 1.5 - Extracted replicas from sediments containing $UO_2$ (A) and SrO (B) repeats humic substance fractal
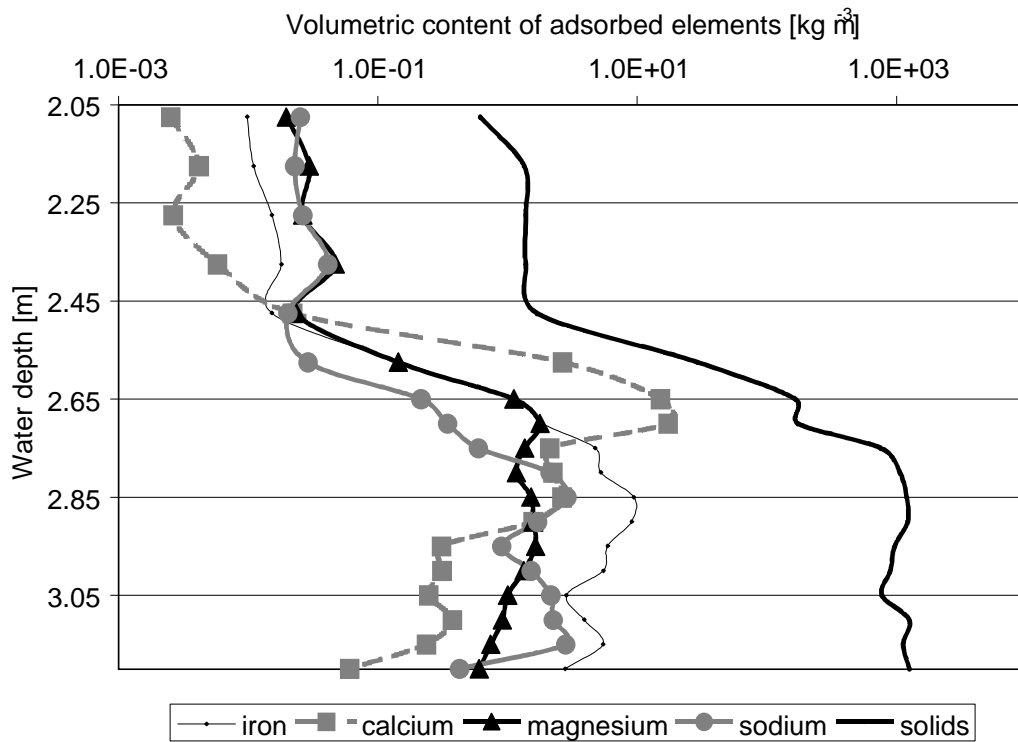


Figure 1.6 - Depth profiles of adsorbed microelements and solids (SR)

The dependences of adsorbed activity (AA) of $^{90}$Sr and a sum of plutonium isotopes $^{239}$Pu, $^{240}$Pu on the activity of the same dissolved radionuclides were presented in Figure 1.7. For $^{90}$Sr, we observe an S-type change of sorption isotherms in accordance with Jails theory (Orlov, 2005). For plutonium, a non-typical sorption process was found.
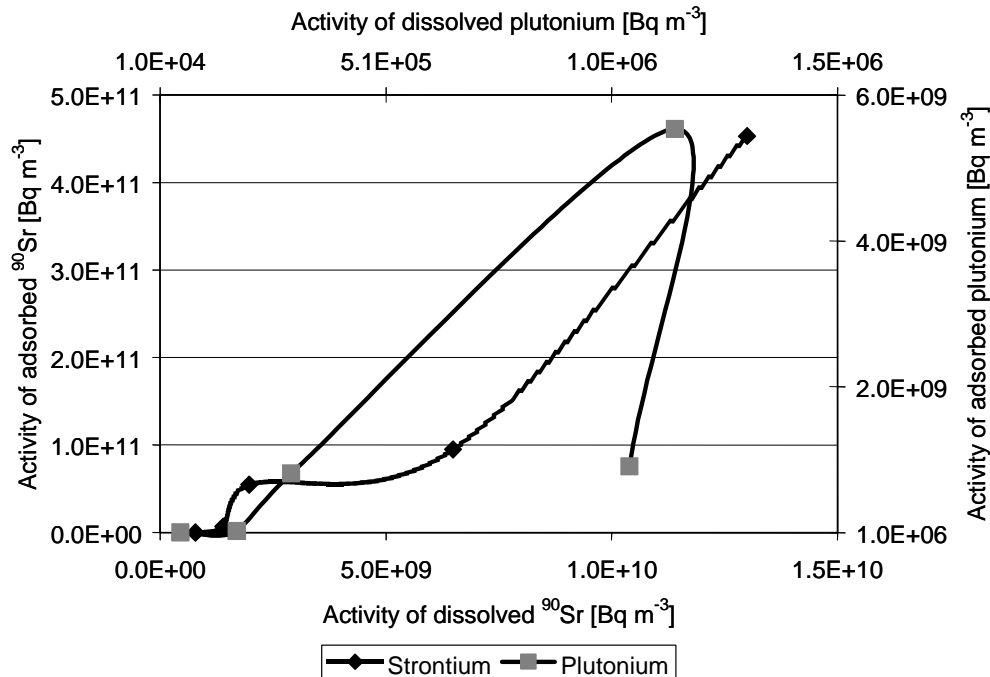


Figure 1.7 - Dependence of the volumetric activity of adsorbed radionuclide on the volumetric activity of dissolved radionuclide shown for $^{90}$Sr and sum of plutonium isotopes $^{239}$Pu, $^{240}$Pu

## 1.5.2  Test-investigation of radionuclide depth profiles in Kisliy canal

Based on the results of investigations carried out and described by Aleksandrova et al. (2008), regression analyses was applied to the contaminated Kisliy canal. Depth profiles of the volumetric content of organic matter (OM) and solids (SR) and the volumetric adsorbed activities (AA) of several radionuclides (RN) $A_{RN\_sorb}$ were examined. The same radionuclides are investigated: $^{90}$Sr, $^{137}$Cs, sum of uranium ($^{235}$U, $^{238}$U) isotopes, and sum of plutonium ($^{239}$Pu, $^{240}$Pu) isotopes (Figure 1.8).

Volumetric content of organic matter and solids [kg m$^{-3}$]
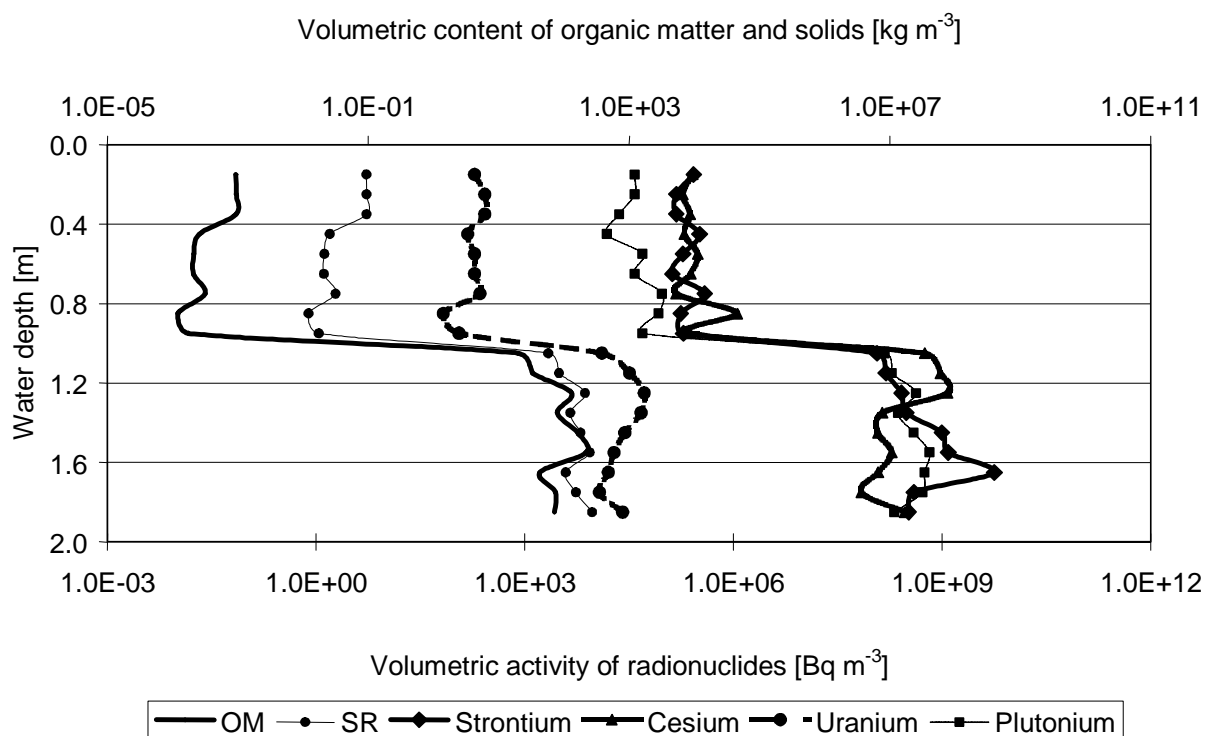
Figure 1.8 - Vertical profiles of the contents of solids (SR) and organic matter (OM) per volume and the volumetric activities of $^{90}$Sr, $^{137}$Cs, sum of uranium isotopes $^{235}$U, $^{238}$U, and plutonium isotopes $^{239}$Pu, $^{240}$Pu in Kisliy canal.

As shown in Figure 1.8, the depth profiles of the local content of adsorbed radionuclide, organic matter and solids look similar. Correlation coefficients $r_{Kisliy}$ between OM, mostly consisting of HA, and AA of radionuclides account to 0.241 for $^{90}$Sr, 0.344 for $^{137}$Cs, 0.66 for sum of uranium isotopes, and 0.84 for sum of plutonium isotopes at n = 18, p < 0.05 in each case. The values of $r_{Kisliy}$ are not as high as in Old swamp for all investigated radionuclides: $r_{Old\_swamp} \geq 0.67$ (Aleksandrova et al., 2008).

## 1.6 Summary of experimental data of radionuclide accumulation in fish

Among all lakes, the following sub-group of lakes with sub-equal content of calcium (0.032 – 0.042 $kg \cdot m^{-3}$) was considered: Lake Large Kasli, Lake Kirety, Lake Small Nanoga, Lake Large Nanoga, Lake Akakul, Lake Ulagach, Lake Irtyash, Lake Alabuga, Lake Kazhakul, Town Pond.

Sampling of fish was carried out once a year at the end of biological summer. An accumulation of $^{90}$Sr in the entire wet weight of the fish specie *Rutilus rutilus* was considered in the case of the sub-group of reservoirs with sub-equal content of calcium. Concerning enlarged group of reservoirs, we considered the following fish species: *Rutilis rutilus*, *Perca*, *Tinca tinca*, *Cyprinus*, *Coregonus* and *Carassius*. The wet weight of each fish amounted to 3 – 5 kg. Fish was examined with the ichthyological method and subsequently dismembered into bones, muscles, and carcass. These three parts were dried at $105^{0}$C and burned up at $450^{0}$C. At each step, samples were analyzed for radionuclide contents in different tissues (Ternovskiy et al., 1985; Antonova et al., 1999; Trapeznikov & Trapeznikova, 2006; Antonova et al., 2007). The comparison of contamination of water and fish is presented in Figure 1.9.
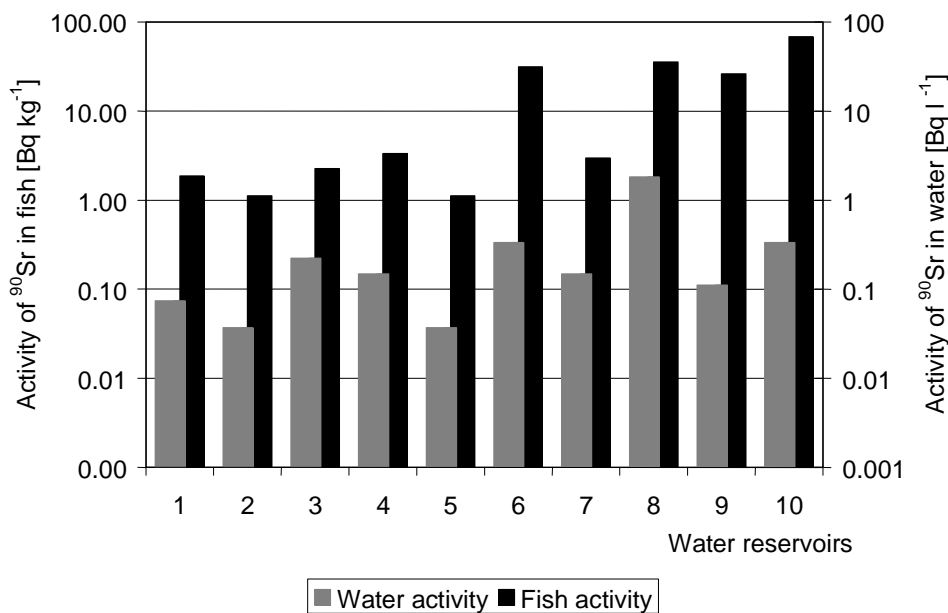


Figure 1.9 - Activity of $^{90}$Sr in solution and accumulated in fish in the following South Ural lakes: Lake Large Kasli (1), Lake Kirety (2), Lake Small Nanoga (3), Lake Large Nanoga (4), Lake Akakul (5), Lake Ulagach (6), Lake Irtyash (7), Lake Alabuga (8), Lake Kazhakul (9), and Town Pond (10). Matched numbers correspond to numbers in Figure.

## 1.7 Legal aspects

Each nuclear waste storage or disposal facility has its own WARs (Waste Acceptance Requirements) for ensuring that the facility meets the requirements of the regulatory bodies (IAEA, Technical report series No. 421, 2004)[1]. The main criterion of a waste storage or disposal facility is that of minimizing the potential for the release of contaminants from the waste to the environment and thus minimizing exposure of humans. It requires detailed scientific investigation of processes taking place at radioactive waste disposal. The International Commission on Radiological Protection (ICRP), the International Atomic Energy Agency (IAEA) and other international organizations have encouraged information exchange on this subject. On Table 1.3, the water quality standards defined by World Health Organization[2] are presented. These standards are general principles to state the nation and regional standards for every country (World Health Organization).

Table 1.3: Radiological standards of drinking water quality

| Parameter | Units | WHO | US EPA | Russian Standard |
|---|---|---|---|---|
| Total $\alpha$ -radioactivity | Bq l$^{-1}$ | 0,1 | 0,555 | 0,1 |
| Total content of $\beta$ radionuclidesd | Bq l$^{-1}$ | 1,0 | - | 1,0 |
| Total content of uranium isotopes | $10^{-6}$ g l$^{-1}$ | - | 30 | - |

Freshwater contamination due to environmental releases of radioactivity is an issue of global concern. On Table 1.4, the content of Uranium –Thorium series in drinking water for some countries is presented[3]. Comprehensive planning of resource protection strategies requires the characterization of radionuclide migration patterns and processes in terrestrial and aquatic environments[4].

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[1] IAEA, Technical Reports SeriEs No. 42I/ International Atomic Energy Agency, Vienna, 2004, 120 p.
[2] http:// www.who.int/
[3] UNSCEAR – 2000. Volume I Sources OCR
[4] IAEA-TECDOC-1314, 2002

Table 1.4: Content of Uranium – Thorium series in drinking water (2000), mBq kg$^{-1}$

| Region/Country | $^{238}$U | $^{230}$Th | $^{232}$Th | $^{228}$Ra | $^{235}$U |
|---|---|---|---|---|---|
| Northern America/ USA | 0,3-77 | 0,1 | 0,05 | 0-0,5 | 0,04 |
| Asia/China  India | 0,1 - 700  0,09-1,5 | | 0,04-12 | | |
| Europe  Finnland  France  Germany  Itanily/Poland  Rumania  Switzerland  Spain  Great Britain | 0,5-150000  4,4-930  0,4-600  0,5 - 130  7,3  0,4 - 37  0-1000  3,7-4,4 | 1,4 | 0-4,2    0,06; 0,04-9,3 | 18-570      0-200 | 0-50 |

Radioactive contamination of the aquatic environment may result in ingestion doses by three pathways: drinking of freshwater from both surface and ground sources, consumption of biota living in the water, typically fish, and consumption of terrestrial foods that have been contaminated by the use of freshwater for irrigation, by the application of sediments as soil conditioners, or by the application of aquatic plants as fertilizer. Water consumed by animals may also form a pathway for the transfer of radionuclides to the human diet. Shoreline deposits of contaminated sediments can contribute to external exposures[1].

Immobilization of radionuclides in waste disposal is one of the options for dealing with radioactive waste. The objective of immobilization is to convert radioactive waste into a stable form, which minimizes the probability of radionuclide release to the environment during interim storage, transport and final disposal[2]. Therefore, an investigation of immobilization of radionuclides by solids in water systems is urgent problem requiring to be solved.

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[1] UNSCEAR, 2000
[2] IAEA, Technical report series No. 421, 2004

## 1.8 Objectives

The overall objective of this thesis is to develop the concept of natural remediation based on remediation effect of humic substances to reduce potential risk of deposited in the surface water reservoirs radionuclides. Application of this approach requires to describe and interpret the observed behavior of radionuclides in contaminated reservoirs, define a key processes and develop a physicochemical model predicting temporally resolved concentrations of mobile radionuclides in reservoir water and their subsequent influence on fish. Before combining all observed processes in one complex model, it is necessary to understand the mechanisms of relevant processes and quantify the influence of their parameters. Therefore, important processes governing the fate of radionuclides in the surface water reservoir shall be identified chemically and physically, and described mathematically. Partition coefficients, mitigating degree of contamination of water and fish, and other process variables shall be estimated from originating experimental data of ecological monitoring. Influences of environmental conditions and humic substances properties on radionuclide fate that change with increasing of the volumetric content of humic substances shall be figured out, and the physicochemical transformation of humic substance molecules shall be linked to biological effects. This thesis is subdivided into chapters, which are structured according to following processes. Since the environmental conditions in water solution and conditions of industrial usage define processes of radionuclide partitioning between solution and solids, their immobilization by solids, bioaccumulation in fish, detailed description of relevant experimental data is expected to allow for understanding significant correlations between different substances (Chapters 2.1 - 2.2). Peculiarities of radionuclide partition between solid and liquid phases in the surface water reservoirs are described in Chapter 2.3. Intrinsic features of humic substances, such as polydisperse molecule weights, duel nature of structural units in respect to water as solvent, very diverse reactivity, especially of dominate oxygen functionalities, will be taken into account, and the mediating action of humic substances will be reviewed and investigated based on available data (Chapter 2.4). To understand observed phenomena of remediation effect of humic substances on the radioactively contaminated aquatic system, the system data analyses of the mutual local changing of the humic substances concentration and volumetric content of adsorbed activity of considered radionuclides are accomplished, and results are presented in Chapters 3.1 – 3.2. To quantify the influence of the humic substance content in water on radionuclide accumulation in fish, correlation and regression analyses of originating experimental data was carried out (Chapters 3.3 – 3.4).

 A link between the humic substance behavior, on the one hand, and radionuclide immobilization and decreasing of their biological effect, on the other hand, shall be realized by combining the effect of the local concentration of adsorbed radionuclides, the statistical model of humic substances, and the model of microphase transformation of humic substance associates into micelles. The phase transformation of humic substances is interpreted via Fermi – Dirac statistics of protons with increasing of humic substance concentration in the water solution (Chapter 4). The presented interpretation is the originating approach that is supposed to apply the Fermi – Dirac statistics of protons to describe changing environmental conditions in aquatic systems with increasing of humic substance concentration in solution. This approach successfully integrates complex properties of humic substances and radionuclide fate in the water body of highly contaminated reservoirs into a consistent model describing biospherical functions of humic substances in biogeochemical cycle of radionuclides in the aquatic environment.

# Chapter 2

# Data and Methods[1]

## 2.1  Study Site

The "Mayak" Production Association facility has played a central role in the development of both the military and the civil nuclear industries of the former Soviet Union. It is located in the Chelyabinsk region of the Southern Urals area of Russia, situated between the lakes Irtash and Kyzyltash. Lake Irtash north of "Mayak" is the source of the river Techa, the largest water course in the region. The nearest cities to the site are Kyshtym (15 km to the west), Chelyabinsk (70 km to the south) and Ozersk (10 km to the north) (Lavyorov et al., 2007). The Chelyabinsk district has a total population of over 3.5 million, one million of whom live in Chelyabinsk city.

Construction at the "Mayak" site began in 1945. The first reactor became operational in 1948. «Mayak» Production Association (PA) is the first Russian (Soviet) industrial site for weapon plutonium production and fissile materials reprocessing. The PA included reactor, radiochemical and chemical-metallurgical productions (Malyshev et al., 1997):

♦ uranium-graphite reactor operating with natural uranium;

♦ radiochemical production on $^{239}$Pu extraction from the uranium blocks exposed in the reactor;

♦ chemical-metallurgical production of extra pure metallic plutonium.

Currently «Mayak» PA is a large modern enterprise of the nuclear industry (Glagolenko et al., 1997). Weapon plutonium production at the radiochemical plant at «Mayak» PA was stopped in 1987. In 1977, the facility for reprocessing of the spent fuel was started up. Also, the facility for solidification of the liquid radioactive waste via vitrification (phosphate glass) is in operation. Here, there is the production of different radioisotopes, using two operating reactors.

The activity of Mayak PA has affected areas of three Ural regions: the Northern part of the Chelyabinsk Region, the southern part of Sverdlovsk Region and a small part of the Kurgan Region

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[1] This chapter is partially published in Aleksandrova et al (2008a, b) and Aleksandrova et al (2009).

along the Techa and Iset Rivers. The affected regions are situated in the Eastern slopes of the Central and Southern Urals and the Western Siberian lowlands. The southwestern and central parts of this area are located within the abrasion-erosion platform with absolute altitude of 220 – 250 m above sea level. The northeastern part is situated in the erosion-accumulative plain.

The geographical features of the Mayak region as geology, hydrology, climate, etc. have influenced the atmospheric dispersion and the extension with groundwater of radioactive releases, and then have played a role in the formation of the current contamination of considered areas and their hydrographical system.

## 2.1.1      Geological structure

Considered region is situated on the eastern slope of the Southern Urals belt. The geological setting of the area consists of complex combinations of sedimentary, metamorphic and igneous Palaeozoic rocks, overlaid mainly by more recent thin Meso-Cainozoic sediments (Malyshev et al., 1997). The Mayak site itself is bounded to the west and east by systems of contiguous mobile regional faults of a sub-meridional direction.

The western marginal faults are marked by zones of schist formation and folding, and by gabbro and peridotite intrusives. In the folded basement of the area, three structural complexes may be identified: gneiss-magmatite, schist-amphibolite and sedimentary. The northwestern part of the site is comprised of an independent tectonic block represented by gneisses and crystalline schists, containing intercalations of carbonate rocks and siliceous schist. These rocks have not been accurately dated, but are normally assigned to the Late Pre-Cambrian-Early Palaeozoic ($PR_3$-$PZ_1$).

The central part of the site (i.e. the area around Lakes Kyzyltyash and Karachay, Reservoirs 3 and 4 and Lake Ulagach) lies within the Kyzyltyash syncline, comprising igneous and sedimentary rocks of Silurian and Early Devonian age. The sedimentary rock complex is comprised of the Nazirov ($S_{1-2}$nz) and Sergaidy ($S_2$-$D_1$sr) suites. Nazirov's suite comprises tuffaceous sandstones, tuffaceous siltstones and shale. Lavas and tufflavas of andesite-basalt porphyrites are not so common. The formations are plicated into folds of various orders, and may be traced as bands of sub-meridional trend. The rocks of Sergaidy suite make up the main part of the major Gornensky syncline. They consist mainly of tuff-like components (psammitic and gravelly-psammitic tuffs), alternating with lavas and tufflavas of andesite-basalt porphyrites.

The eastern part of the site has tuffs, tuffaceous-sedimentary and sedimentary intrusive rocks of Silurian, Devonian and Carboniferous age, and intrusive rocks of the Middle Paleozoic age.

Throughout the considered area, the common weathering crust was formed as a result of hypergenesis of the Paleozoic rocks. In Figure 2.1, the geological structure of the weathering crust of considered site part is presented.
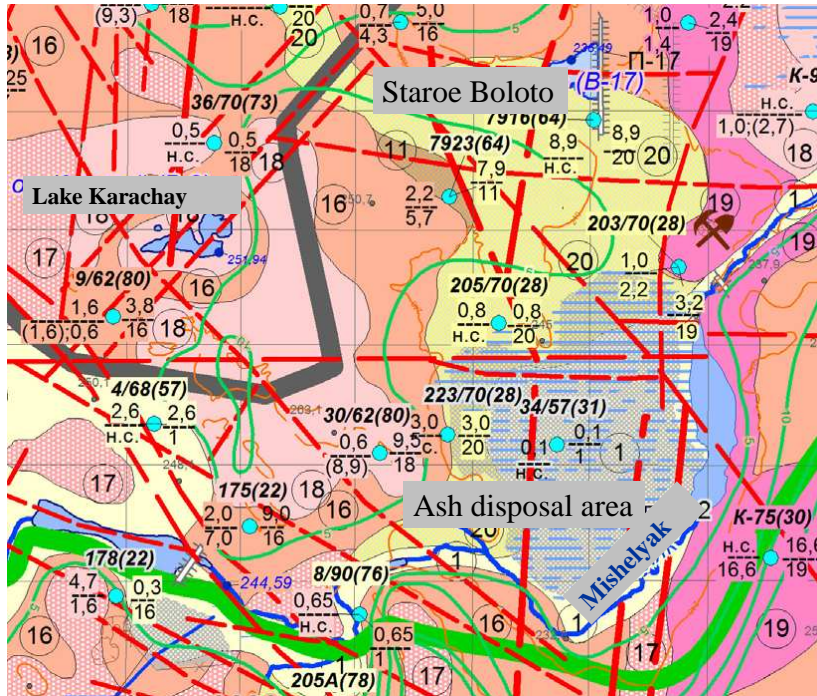


Figure 2.1 – Geological structure of considered site of Mayak PA
Map of signs and geomorphological structure are shown on Tables 2.1 – 2.2.

Table 2.1: Legends of map signs of geomorphological structure of the Mayak PA site

| Geological index | Location with number[1] | Lithologic-stratigraphical profile | Depth interval [m] | Description of rock |
|---|---|---|---|---|
| Geomorphological complex: Surface of denudation and accumulatively denudation for levelling | | | | |
| edQ$_{3-4}$ 2edMZ-KZ 1edMZ-KZ | (16) | | 3.0 - 20.0 | 1. Loams, loamy sand, loam with gruss; 2. Silt loams with gruss and detritus including relic structure of mother rock; 3. Crumbly- rubbly rock of Palaeozoic |

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[1] Map signs are matched with localization numbers on the map part presented in Figure 2.1
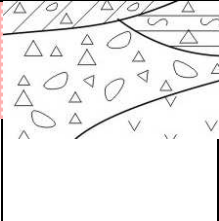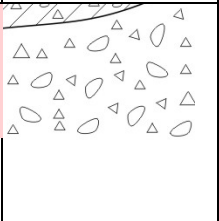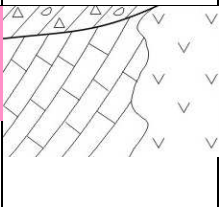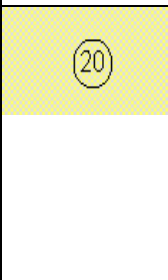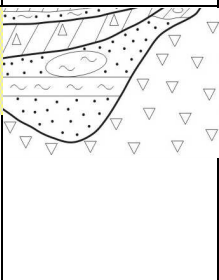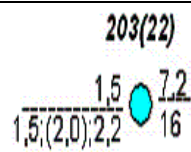
| | | | | |
|---|---|---|---|---|
| edQ$_{3-4}$<br>2edMZ-KZ<br>1edMZ-KZ<br>Pz | ⑰ | | 3.0-11.6 | 1. Loams, loamy sand, loam with gruss and pebble;<br>2. Silt loams with gruss and detritus;<br>3. Crumbly- rubbly rock of Palaeozoic |
| edQ$_{3-4}$<br>1edMZ-KZ | ⑱ | | 3.0-12.0 | 1. Loams, loamy sand, loam with gruss and pebble;<br>2. Silt loams with gruss and detritus, including sandy loams (~ 30% of volume) |
| edQ$_{3-4}$<br>Pz | ⑲ | | Till 21.6 | 1. Loams, loamy sand, loam with gruss and pebble; 2. Chalkstone, porphyry deposit and other rock of Paleozoic |
| a,lhQ$_4$; aQ$_3$<br>edQ$_{3-4}$<br>N-Q<br>1edMZ-KZ | ⑳ | | 0.3-12 | 1. Interleaved peat, loams, sand with pebble; 2. Loams with gruss; 3. Loams with gravel pebbles of quarz, and lens of sand and loams located in eroded incut; 4. Loams with gruss and detritus. |

Table 2.2: Meaning of signs on the geomorphological map

| Map Sign | Meaning of sign |
|---|---|
| 203(22)<br>$\frac{1,5}{1,5;(2,0);2,2}$ ◆ $\frac{7,2}{16}$ | Borehole. Upper index is the well number. Depth of stratigraphic layers of sedimentary is situated at numerator of left fraction. At denominator of this fraction, there is depth of clay - 2edMZ-KZ, crumbly -1edMZ-KZ in brackets; residual soil of rocky soil of Paleozoic base. The total depth of airing zone of rock is situated at nominator of the right fraction, and a number of the location on the map is at denominator. |
| ～～ | Boundaries between locations of different types of geological structure of airing zone. |
| ～～ | Isopach of rock of airing zone with its number, m. |
| ━━ | Stratigraphical boundaries between layers of lithostratigraphic column sampled out typical locations. |
| ━━ | Lithologic boundaries between layers of lithostratigraphic column sampled |

| | |
|---|---|
| | out typical locations. |
| | Argayash thrust |
| | Large joint fissure (stated) |
| | Large joint fissure (assumed) |
| | Small fissure |
| | Industrial site (ПП) |
| | Boundary of highly radioactively contaminated site of Mayak PA |

The crust is like veneer reached up to 20 – 25 m in thickness. It is an upper part of the whole tectonic zone, reached 100 m in thickness. The crust comprises of clayey zone of intermediate decomposition or detrital weathered rock zone. As found, a crust type called belik (a limestone and siltstone mixture) reached up to 14 m in thickness.

Cainozoic deposits are fairy widespread in the considered site. They are presented with a variety of sedimentary rocks of different origin. Marine sediments are widespread in the northeastern part of the site and presented with silt clays, diatomites with sand intercalations and unconsolidated sandstones.

In this site, Quaternary deposits are very widespread and presented with alluvial-talus formations, including loams and clays with gravel, rubble and grit. They provide a continuous cover for the valley slopes of Techa, Zyuzelga and Mishelyak Rivers. The rocks of the friable cover (Meso-Cainozoic geostructural layer) are either not or only very slightly dislocated. In Figure 2.2, one profile of the weathering crust is presented. Map signs are shown in Table 2.3.

The processes of weathering have played a significant role in affecting variations in the mineralisation and chemical compositions of the igneous /sedimentary rocks. In the relic weathering profile, one can recognize a number of zones (top to bottom), disintegration, incipient clay alteration (transitional) and clay alteration (subdivided into two groups of predominant mineralogy). The thickness of the weathered rock profile is mostly about 20 - 25 m but varies widely from 1 to 80 m. The thickness of the zone of clay alternation reaches 30 m. The production of secondary clay minerals has occurred to such a degree so as to increase the sorption and ion-exchange capacities downwards within the weathered profile.
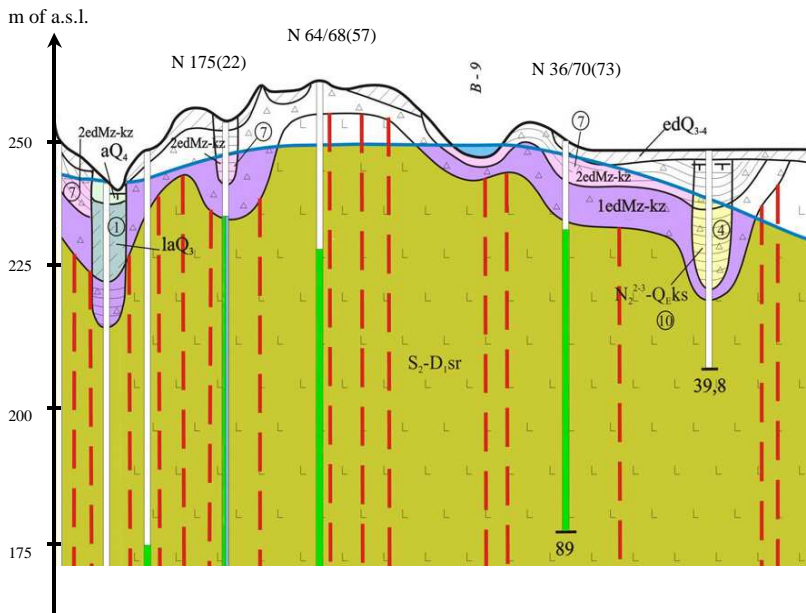
Figure 2.2 - Geological – hydrogeological vertical profile made along the line throughout boreholes with numbers 175(22), 64/68(57) and 36/70(73)

Table 2.3: Legends of stratigraphical, hydrological and lithological signs

| Map sign | Meaning of map sign |
|---|---|
| **Stratigraphical signs** | |
| $S_2-D_1 sr$ | Stratigraphical sign of Sergaidy sedimentary complex $S_2 -D_1$ sr |
| 1edMz-kz | Stratigraphical sign of nonsegmented Mesozoic – Cainozoic age. It corresponds to eluvial – deluvial formations of clayey weathering crust. |
| 2edMz-kz | Stratigraphical sign of nonsegmented Mesozoic – Cainozoic age. It corresponds to eluvial – deluvial formations of rubbly weathering crust. |
| 89 | Well with number of its depth. Color shows sulphate mineral waters in well |
| **Hydrological signs** | |
| 1 | Neo- Pleistocene- Holocene water-bearing horizon in alluvial, lake-alluvial, limnetic and limnetic -swampy depositions of sediments |
| 4 | Miocene and Pliocene- Pleistocene water-bearing horizon ($N_1^2$; $N_2^{2-3}$ - $Q_E$ks) |
| | Paleozoic zones of tectonic joint fissure |

| | Lithological composition of rocks | | | | |
|---|---|---|---|---|---|
| | Basalt, diabase, porphyry | △ △ △ △ △ | Gruss | ///// | Loams |

## 2.1.2    **Landscapes**

Geoecological and landscape investigations of PA Mayak site allowed for giving in detail its landscape and geochemical properties. These properties hint at the main directions of raionuclide transport in natural and built-up landscapes, help to separate contact areas of landscapes with contrasting geochemical barriers, working as potential geochemical barrier. Landscape of area is described with elementary (basic) landscapes that include defined type of relief, embedded from single rock or alluvium, and covered with vegetation.

Trans-Ural peneplain – slightly dismembered area characterized with spacious plateau (flattening) of watershed areas and piled lofted hills. In accordance with it, eluvial landscapes of considered plated areas are divided into two types with following different migration processes: eluvial-accumulative and trans-accumulative. First type is characterized in general with the dominant lateral flow and subordinate vertical migration. Accumulative processes take place only locally. The second type of landscapes, corresponding to lengthy gentle slopes with broad gully, is characterized with accumulative processes of solids as well as soluble compounds. These basic landscapes are bound or not to flood of rivers and lakes. Also, geochemical parameters of trans-accumulative landscape are generally defined with geochemical status of autonomous (e.g. local) landscape.

Trans-Ural peneplain is characterized with skin-deep groundwater. Therefore, a lot of shallow gully became super wet and swampy.

At the Mayak PA site, the landscape of flattening areas is in general eluvium with smectic- kaolin mineral on, and gentle slopes are covered with clayey mineral. Plenty of swampy kettles and lakes without outlets surrounded with reeds. Dominant vegetation includes birch and pine forest and grass meadows. This region soils comprise pale grey and grey soils with slightly acid and neutral reaction, and leached black earth. Landscape category and its soda-and-acid conditions are characterized with H+-Ca++, Mg++, neutral. Development of the landscape of considered site took place on andesite-basalt porphyrites and peach- sericitic stones. Superaquatic landscapes are characterized with two types of redox and oxidizing reactions that define species of chemical element migration and potential immobilization. The complex paleogeographical structure of paleogenetic Quaternary, development of wide ancient hydrographical system, ancient and current processes of salinization and desalinization of soil had formed mixed picture of chemism and degree of solids of open water system at the considered site. Among geochemical landscapes, the site is mainly characterized with the following eluvial and superaquatic landscapes: $Э_2$ and $CA_{OB}^2$ (Figure 2.3; Table 2.4). Hydrogeochemical properties of pedogenic rocks are presented on Table 17.

In accordance with Alvyorov et al. (2007), the main geochemical barriers at the considered site are as follows: sorption with sedimentation and organic-mineral to high level.
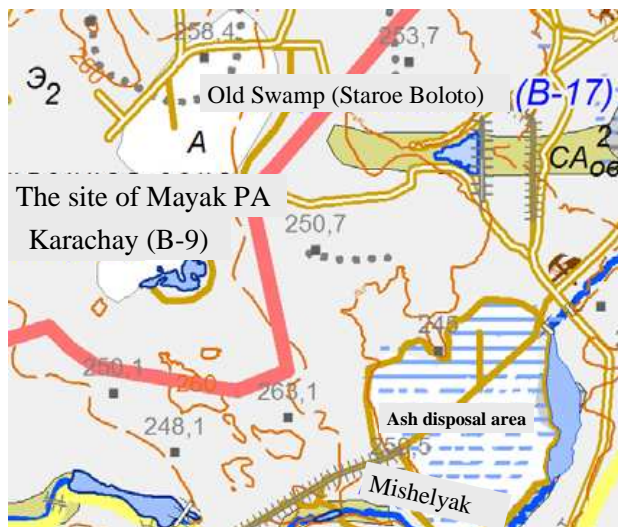


Figure 2.3 - Map of hydrochemical landscape of the Mayak PA site

Table 2.4: Description of geochemical landscapes presented

| Index | Map sign | Medium conditions | Particular development | Soils |
|---|---|---|---|---|
| *Eluvial geochemical landscapes* | | | | |
| $Э_2$ | | H+-Ca++, Mg++ Neutral rreaction | On the base of andesite-basalt porphyrites and peach-sericitic stones | Pale- grey and grey soils with birch–pine forest; grey and dark-grey soils with leached black earth; leached black earth with malt grey forestry soils |
| *Superaquatic landscape* | | | | |
| $CA_{OB}^2$ | | H-Ca\\|//H-Ca-Fe Change of ox-redox conditions | Depressions in the ground and shallow gully covered with deluvial loams | Alluvial meadow soils with developed wet vegetation and slough; grey and malt grey forestry soils with birch forest, wet motley grassy shrubbery meadows and shrubbery |

# 2.1.3 Granulometric composition of soils, lake sediments and suspended matter

The great influence on the radionuclide migration and immobilization is exerted by physical properties of soils and sediments of the site under consideration. Here, results of analyses of different experimental data of granulometric composition of soils, sediments and suspended matter of surface water. Data of the granulometric composition of soils, sediments and loams in industrial reservoirs and contaminated during accidents are shown on Table 18 and in Figure 19 (Grysin & Popova, 1962; Valizer et al., 1992, 1993; Kogotkov, ).
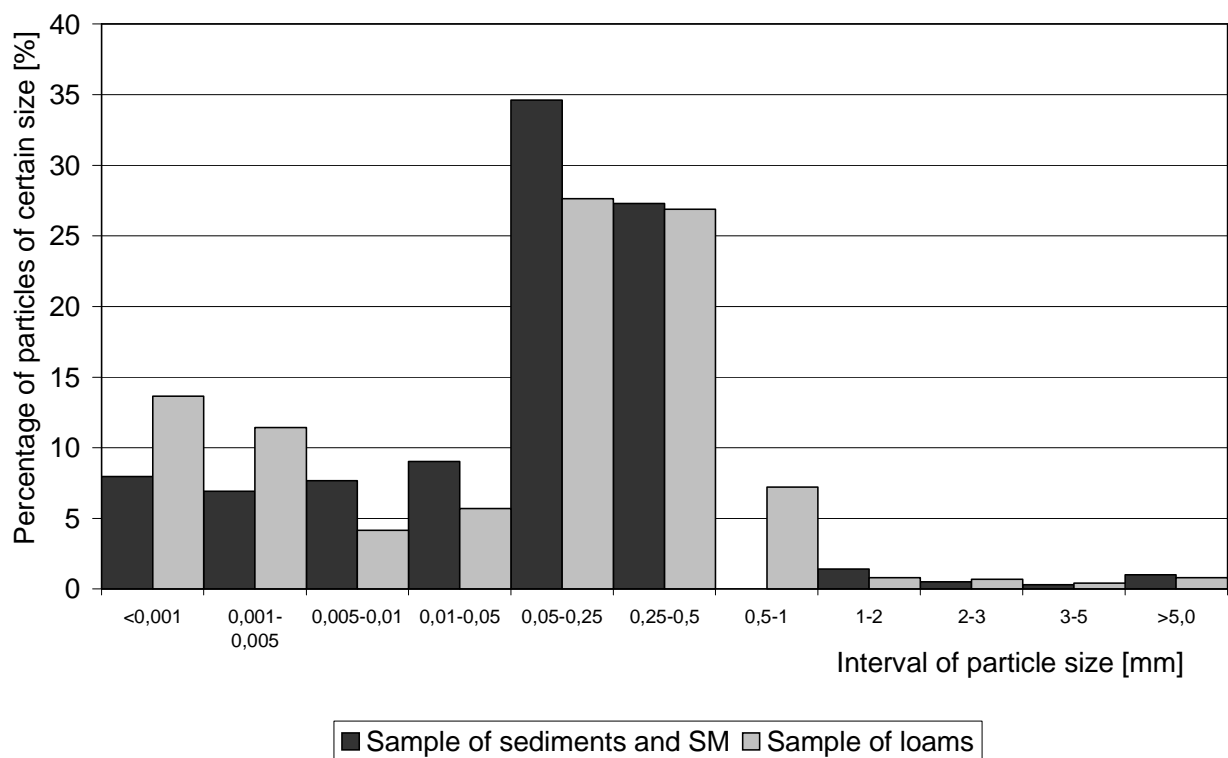


Figure 2.4 – Granulometric composition of sediments and loams at the site of Mayak PA (Karachay and Old swamp)

Table 2.5: The composition of SM and sediments (layer 0 –0.1 m) of lakes contaminated during
accidents

| | 1-0.25 mm | 0.25-0.05 mm | 0.05-0.01 mm | 0.01-0.005 mm | 0.005-0.001 mm | <0.001 mm | Organic matter |
|---|---|---|---|---|---|---|---|
| Lake | Portion of particles with certain size in sample [%] | | | | | | Portion in sample [%] |
| L. Igish | - | 22.8 | 50.5 | 9.0 | 9.64 | 7.96 | 83 |
| Tygish | 1.3 | 23.2 | 44 | 10.7 | 11.9 | 8.9 | 64 |
| Kuyanysh | 1.7 | 31.6 | 39.7 | 8.8 | 7.8 | 10.5 | 60 |
| S. Allaki | 2.2 | 77.6 | 1.04 | 6.6 | 5.3 | 7.3 | 5.4 |
| Alabuga | - | 28.3 | 38 | 14 | 15.6 | 7.1 | 23 |
| Kazhakul | 0.46 | 31.8 | 34.7 | 11.9 | 11.1 | 10 | 24 |
| Uruskul | - | 34.7 | 27.8 | 11.9 | 13.4 | 12.4 | 30 |

Humic substance part of soil particle affects significantly its physical and chemical properties. The
capacity of cationic exchange of HS reaches up to 300 – 930 mg-eq per 100 g of dry matter, and it
is 5-10 times more than the cationic exchange capacity of mineral colloids (Pinsky, 1975; Santos
Filho, 1985; Hornbeck & Federer, 1985; Prasad at al, 1987; Melnikov, 1990). Soil particle usually
comprises mostly mineral part, and 70.5% of the capacity of cationic exchange is defined by
mineral compound. However, decrease in the HS content of soil particle results in sharp increasing
of the capacity of cationic exchange (Drake & Motto, 1982). Other factor exerting influence on the
capacity of cationic exchange is dispersion of soil particles. In leached black earth, more than 86%
of the capacity of cationic exchange is defined by silt fraction with the particle diameter less than 1
μm (Nikolaeva, 1990). For lakes contaminated during accident, the fraction of particles with the
diameter <1 μm varies from 7.1 % to 12.4 %.

## 2.1.4    Climate

The considered region has a moderate continental climate, with a long moderate-to-severe winter
and a moderate-to-warm summer. The cold period begins in October and ends in May. The coldest
month is January, when the mean temperature is about $-14.7^0$ C, with an absolute minimum of $-50^0$
C observed in February 2006. The hottest month is July, when the mean temperature is $+18.7^0$C,

with an absolute maximal value of about $+40^0$C. The mean annual air temperature is $+2.6^0$C. The variation of daily temperature of air reaches 28 $^0$C in each season of the year.

The soil temperature of the superficial soil layer from 0 to 0.5 m generally follows the temperature of air. At a depth of 0.2 m, the highest mean monthly soil temperature reaches $+15.8^0$C, and the lowest $-4.2^0$C. The greatest depth of soil freezing is 1.8 – 2.0 m, and recorded in March.

The maximal atmospheric pressure is reached to 994 mbar in the winter, and falls in the summer. The lowest mean monthly atmospheric pressure is reached in July (983 mbar), coinciding with the maximal values of air temperatures.

The air humidity varies strongly during the day and the year, with it changing from minimal value of 56-68% in the coldest period to maximal value of 80 –83% in the hottest period. During the day, humidity falls from 70 – 80% in the morning to 40 –60%, and sometimes to 15 – 25%. The greatest number of dry days (i.e., relative humidity is less than 30%) is observed in May, reaching 10 – 12 days. The greatest number of wet days (i.e., relative humidity is of over 80% and more) is about 12 days a month, observed between December and January.

The considered region is located in an area of water deficiency. The mean annual atmospheric precipitate amounts to 429 mm. The first lying snow cover appears at the beginning of November. The number of days with snow cover varies from 150 to 170 days. In open places, the depth of snow can reach 30 –35 cm. The ice depth on lakes reaches 1 m. The snow usually begins to melt in late March. This region can experience fog, ice, thunderstorms, hail, snow and blizzards.
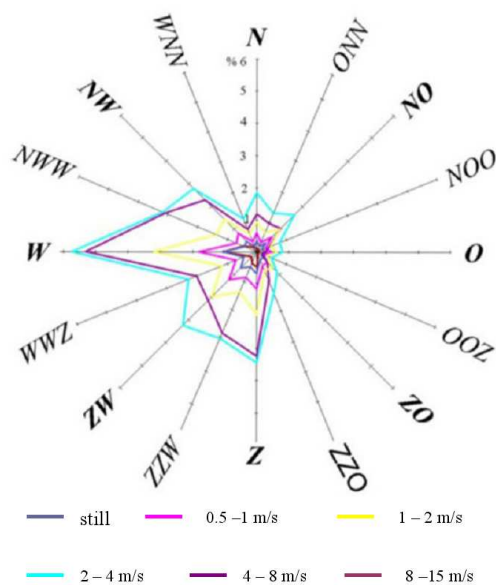


Figure 2.5 - Wind rose of the considered site of Mayak PA

Westerly winds (Figure 2.5) prevail throughout the year, which is favorable to the nearest inhabited settlements. The wind distribution in terms of directions and speeds shows a seasonal cycle. During the winter, the main influence on meteorological conditions in southern Ural is the western ridge of the Asiatic anticyclone. Thus, westerly winds with southerly components predominate (50-65%). In summer, the Azores

anticyclone causes a rise in atmospheric pressure towards the west of the Southern Urals, and winds with a westerly and northerly bearing prevail (50%). The mean speed of wind is 4.1 $m \cdot s^{-1}$. The maximal value of wind speed reaches 24 $m \cdot s^{-1}$. From 1889 to 1986, 6 hurricanes and 12 whirlwinds of varying degrees of intensity were registered. The dispersion of radioactive fine particles from Karachay in 1967 seems to be connected with one hurricane.

## 2.1.5      Hydrology of the site

Regional hydrographical system includes natural and artificial reservoirs, ponds and lakes, Techa, Suselga, Karabolka Rivers, Left shore and Right shore canals. The Techa River is part of the hydrographical system of the Ob River and is a tributary of the Iset River. The river system Techa-Iset-Tobol-Ob (Figure 2.6) discharges into the Kara Sea.
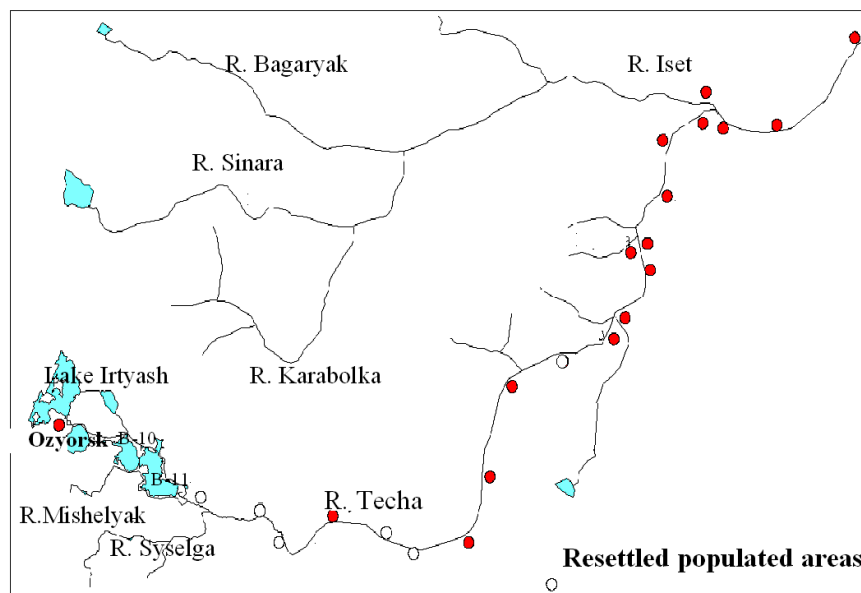


Figure 2.6 – Beginning of river system Techa – Iset – Tobol –Ob

The catchment basin of the Techa and Iset Rivers lies between the Urals Mountains and the Tobol River valley, within the Trans –Ural forest steppe. This is a flat, slightly raised plateau, falling

gently to the east and with an altitude between 130 and 230 m. These rivers have mixed sources, with snowmelt as dominating source (50 – 70 % of the annual run-off volume). Less than 20 – 30 % originates from rain. The contribution of ground waters is small.

The water type of River Techa changes along the river. Fist part of the river has hydrocarbonate type with $0.4\, g \cdot l^{-1}$, and a second part has sulphate hydrocarbonate and hydrocarbonate type with the same solids. Hydrochemical type of the river Mishelyak is formed dependent on anthropogenic genesis, and changes from hydrocarbonate to sulphate-hydrocarbonate. The water has changeable cation composition and solids of $0.4 – 0.7\, g \cdot l^{-1}$. The content of sulphate reaches 305 mg·l$^{-1}$, and the content of nitrate amounts to 5.6 – 29.0 mg·l$^{-1}$. The rightshore canal is a continuation of the river Mishelyak and is characterized with hydrocarbonate and sulfate hydrocarbonate and hydrocarbonate – sulpate type. The content of sulphate increases from 0.060 to 0.124 - $0.129\, g \cdot l^{-1}$. The solids' content is varied from 0.4 to $0.7\, g \cdot l^{-1}$. The solids' content of the left shore canal amounts to 0.3 – 0.5 $g \cdot l^{-1}$. The hydrochemical type of water is hydrocarbonate almost along the whole length with some variations to chloride –hydrocarbonate at the location of tectonic fracture.

Three small rivers as Karabolka, Sinara and Bagaryak flow throughout considered site (Figure 2.6). They discharge in the Iset River system. The most contaminated river is Karabolka. It is fed from the boggy area at the sufficiently contaminated part. Its width varies from 2 to 20 m. Average depth is about 1 m.  The averaged water discharge is about $1.1\, m^3 \cdot s^{-1}$. Flow rate is $0.6\, m \cdot s^{-1}$.

The southwestern part of the plateau forms the Kasli-Irtyash lake system. The eastern part is forest steppe with broad poorly drained and boggy interfluves and scattered with shallow lakes (2 –5 m of depth). The majority of lakes are characterized with hydrocarbonate-alkaline and hydricarbonate-magnesium type of water. Mostly, these are freshwater lakes with solids of $0.15 – 0.30\, g \cdot l^{-1}$. Some lakes formed in fractured zones have a high level of solids of $0.6 –1.7\, g \cdot l^{-1}$, and hydrochemical solution of chloride carbonate. The four most contaminated natural lakes as Lake Uruskul, Lake Berdenish, Lake Kazhakul have a water volume of 5 - $46 \cdot 10^6$ m$^3$, pH of 8.5 – 9.6, annual run-off of 25 mm, and annual evaporation of about 250 mm. Variations of hydrochemical parameters of lakes are presented on Table 2.6.

Table 2.6: Dynamic of hydrochemical composition of water (summer), mg $\cdot l^{-1}$

| Lake | год | H | $Ca^{2+}$ | $Mg^{2+}$ | $Na^{+}+K^{+}$ | $HCO_3^{2-}$ | $CO_3^{2-}$ | $SO_4^{2-}$ | $Cl^{-}$ |
|---|---|---|---|---|---|---|---|---|---|
| Berdenish | 1963 | 8.8 | 25 | 56 | 110[1] | 354 | 42 | 125 | 57 |
| | 1983 | 9.0 | 12 | 70 | 112 | 409 | - | 131 | 92 |
| | 1990 | 8.5 | 11 | 76 | 188 | 543 | | 134 | 91 |
| Uruskul | 1940 | - | | 156 | - | 1915 | | 173 | 1470 |
| | 1956[2] | 8.1 | 14 | 119 | 1340 | 2310 | | 168 | 1070 |
| | 1962 | 9.0 | | 117 | 1003 | 1990 | 206 | 94 | 866 |
| | 1983 | 9.0 | 11 | 124 | 338 | 1770 | - | 1350 | 1072 |
| | 1990 | 9.0 | 11 | 148 | 1165 | 1379 | 222 | 211 | 872 |
| Kazhakul | 1940 | 9.1 | 9 | 5 | 550 | 1270 | | 17 | 402 |
| | 1963 | 8.9 | | 86 | 472 | 1110 | 1 86 | 34 | 330 |
| | 1983 | 9.3 | 7 | 114 | 623 | 1237 | | 58 | 442 |
| | 1990 | 9.2 | 10 | 127 | 490 | 881 | 66 | 98 | 418 |

The content of solids in such industrial reservoirs as B-9 and B-17 accounts correspondingly 8.2 and 3.6 $g \cdot l^{-1}$. Reservoirs B-10 and B-11 contain sulfate water with 1.0 and 1.1 $g \cdot l^{-1}$. Water in B-3 and B-4 is sulphate –hydrocarbonate with 0.6 and 0.5 $g \cdot l^{-1}$. Water of B-2 and B-6 used for circulating water supply has chloride-sulphate-hydrocarbonate type with 0.9 and 0.1 $g \cdot l^{-1}$.

## 2.1.6 Radioactive contamination of surface water systems influenced by the activity of Mayak PA

The regional surface water systems radioactively contaminated are divided into three groups:

♦ Industrial reservoirs, rivers, and canals contaminated as a result of routine nuclear wastes disposal;

♦ Lakes and river contaminated as a result of accidents of 1957 and 1967 (Table 1.5);

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[1] Corresponds only to $Na^{+}$

[2] Measurements are carried out in April (lake is coved with ice)

♦ Lakes and rivers contaminated due to global radioactive fallout (for example, Lake Irtyash, Lake Ulagach, river Suselga).

The current contamination of the ***industrial reservoirs*** and rivers (Figure 2.7; Table 2.7 – 2.8) depends on radiochemical and reactor manufactures that is connected mostly with producing of radionuclides for civil use and reprocessing of the spent fuel from reactors and nuclear vessel power units.

As a result of routine work from the beginning of 50-ies years, about 550 Million Ci of summary nuclear wastes were discharged into industrial reservoir Lake Karachay[1] (B-9), and about 15 Million Ci of β-emitting radionuclides into the industrial reservoir Old Swamp (Staroe boloto, B-17). The industrial reservoirs B-9 and B-17 were used to deposit a rest of the most contaminated liquid nuclear waste of the plutonium and radiochemical nuclear production (correspondently) after the step of solidification and vitrification (Malyshev et al., 1997). First, the most contaminated waste was directed into Techa River (Mokrov, 2002).
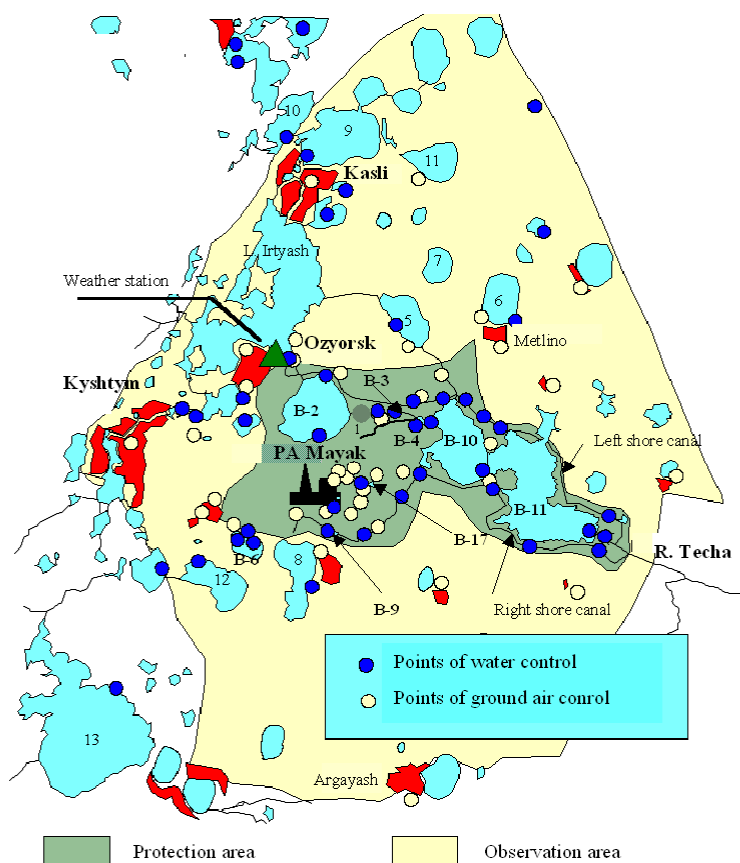


Figure 2.7 - Industrial reservoirs (B-2, B-3, B-4, B-6, B-9, B-17), Kisliy canal (1) and lakes of protection and observation areas: 5 – L.Berdenish; 6 – L Kazhakul; 7 – L. Uruskul; 8 – L. Ulagach; 9 – L. Large Kasli; 10 – L. Kirety; 11 – L. Alabuga; 12 – L. Akulya; 13 – L. Uvildy

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[1] This value is shown including short living radionuclides

The contamination of B-6, B-9, B-17 and river Techa with α – radionuclides is due to sum of uranium isotopes $^{233}U$, $^{234}U$, $^{235}U$, $^{236}U$ $^{238}U$, sum of plutonium isotopes $^{238}Pu$, $^{239}Pu$, $^{240}Pu$, and radionuclides $^{241}Am$, $^{244}Cm$, $^{226}Ra$, $^{91}Pa$, $^{237}Np$. The contamination of all industrial reservoirs and Kisliy canal with β-radionuclides is due mostly to $^{90}Sr$ and $^{137}Cs$, and, in parts, $^{134}Cs$, $^{144}Ce$, $^{106}Ru$, $^{154}Eu$, $^{155}Eu$, $^{125}Sb$, $^{60}Co$. The important part in β-contamination is due to tritium ($^{3}H_2O$).

Table 2.7 – Industrial reservoirs and their current characteristics

| Reservoir | 2 | 6 | 3 | 4 | 10 | 11 | 17 | 9[1] |
|---|---|---|---|---|---|---|---|---|
| Starting of operation | 1948 | 1948 | 1951 | 1949 | 1957 | 1964 | 1952-54 | 1951 |
| Total activity of β-emiting radionuclides, Bq | $1 \cdot 10^{15}$ | $5.9 \cdot 10^{11}$ | $2.8 \cdot 10^{14}$ | $5.6 \cdot 10^{14}$ | $3.9 \cdot 10^{15}$ | $1.6 \cdot 10^{15}$ | $4.4 \cdot 10^{16}$ | $9.4 \cdot 10^{17}$ |
| Total activity of α-emiting radionuclides, Bq | - | $1.8 \cdot 10^{12}$ | - | - | - | $8.0 \cdot 10^{11}$ | $1.1 \cdot 10^{15}$ | $4.4 \cdot 10^{16}$ |
| Content of solids, mg·l$^{-1}$ | 450-500 | 380-400 | 600-700 | 500-600 | 1100-1500 | 1100-1250 | 1900-2500 | 10000-20000 |
| Area of reservoir surface, km$^2$ | 18.6 | 3.6 | 0.8 | 1.3 | 18.3 | 47.0 | 0.13 | 0.11 |
| Reservoir volume, $10^6$ m$^3$ | 86.2 | 19.4 | 0.88 | 4.6 | 82.5 | 270 | 0.36 | 0.4 |

The contamination of canals and rivers such as Kisliy canal (Medvedev et al., 2008), Techa River (Mokrov, 2003), Mishelyak River, Karabolka River (Figure 2.6; Antonova et al., 1999; Antonova et al., 2007) took place during routine working with disposal of radioactive waste. Starting at the beginning of 1971, the Kisliy canal (Table 2.8; Figure 2.7) is an artificial facility used to direct the liquid nuclear waste to disposal areas (B-4). Recently, about $1.1 \cdot 10^{14}$ - $1.85 \cdot 10^{14}$ Bq of nuclear waste has passed through Kisliy canal per year (Medvedev et al., 2008). The canal sediments mostly have high contents of organic matter (from 40 to 100%). In recent time, significant desorption of radionuclides from the sediments took place. Sometimes, a part of radionuclides is exported out of

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[1] Data of activity are shown for unclosed part of reservoir B-9

the canal water and sediments to the surrounding floodplain. The contamination of the right shore canal water changes from 16.5 to 1200 Bq·l⁻¹. The contamination of water of the left shore canal changes from 8.4 – 9.8 to 1300 Bq·l⁻¹. As for the upper part of Techa River, the current contamination of water amounts to $10^4 \div 5 \cdot 10^4$ $Bq \cdot m^{-3}$ of $^{90}$Sr and ~ 0.5 $Bq \cdot m^{-3}$ of sum of plutonium isotopes $^{239}$Pu, $^{240}$Pu (Trapeznikov & Trapeznikova, 2006). The current contamination of water of Mishelyak River amounts to $10^3 \div 3 \cdot 10^3$ $Bq \cdot m^{-3}$ of $^{90}$Sr (Malyshev et al., 1997).

**Table 2.8 - List of parameters and units of Kisliy canal (Medvedev et al., 2008)**

| | Property of the Kisliy canal | Value | Units |
|---|---|---|---|
| 1 | Starting of operation | 1971 | - |
| 2 | Usage | It directs the liquid nuclear waste to disposal area | - |
| 3 | Length | 2891 | $m$ |
| 4 | Depth | From 1.5 to 3.0 | $m$ |
| 5 | Current activity passed through the canal | $1.1 \cdot 10^{14}$ - $1.85 \cdot 10^{14}$ | $Bq$ per year |
| 6 | Averaged thickness of sediments | 0.7 | $m$ |
| 7 | Content of organic matter in sediments | From 40 to 100 | % |
| 8 | Maximal specific β –activity of sediments | $2 \cdot 10^8$ | $Bq \cdot kg^{-1}$ d.m. |
| 9 | Total content of β –activity in sediments | $9.25 \cdot 10^{13}$ | $Bq$ |
| 10 | Maximal specific α –activity of sediments | $5 \cdot 10^7$ | $Bq \cdot kg^{-1}$ d.m. |
| 11 | Total content of α –activity in sediments | $1.85 \cdot 10^{13}$ | $Bq$ |
| 12 | External exposure of the canal shores | 0.78 | $mSv \cdot h^{-1}$ |

The significant contamination of some natural lakes took lace via accidents in 1957 (Table 2.9) and 1967. The contaminated in 1957 area is named the East Ural Radioactive Trace (EURT) (Figure

1.2). It included parts of the Chelyabinsk, Sverdlovsk and Tyumen Regions. The area covered about 15000 km$^2$ with the activity density of about and more than 0,2 Ci·km$^{-2}$. The central part contamination of $^{90}$Sr reached 4000 Ci·km$^{-2}$ (Malyshev et al., 1997). The lakes influenced by accidents in 1957 and 1967 are considered as the lakes of the second contaminated group.

Table 2.9 - Original composition of the release of radioactivity into atmosphere in 1957

| Radionuclides | Part of the activity in release | Units | Total content in release | Units |
|---|---|---|---|---|
| $^{90}$Sr and $^{90}$Y | 5.4 | % | 54 | kCi |
| $^{95}$Zr and $^{95}$Nb | 24.8 | % | 496 | kCi |
| $^{106}$Ru and $^{106}$Rh | 3.7 | % | 74 | kCi |
| $^{137}$Cs | 0.35 | % | 7.0 | kCi |
| $^{144}$Ce and $^{144}$Pr | 65.8 | % | 1316 | kCi |
| Sum of isotopes of Pu | 0.002 | % | 0.038 | kCi |

The original strong contamination of ***the second group of water systems via accidents*** is shown on Table 2.10. In accordance to radioactive decay and natural remediation, the radionuclide activity of water has decreased about 100 times but stays sufficiently high (Figure 2.8). The current contamination of water is due mostly to $^{90}$Sr. At the present time, Lake Uruskul is contaminated with ~ 50 Bq·l$^{-1}$, and Lake Berdenish with ~ 10 Bq·l$^{-1}$. The water contamination of little river Karabolka has diminished from 500 Bq l$^{-1}$ (1957) to 2-5 Bq l$^{-1}$ (2004) (Antonova et al., 2007).

Table 2.10 - The original activity of radionuclides in the reservoirs (Autumn, 1957), kCi

| Lake | Content of radionuclides in the lake [kCi] | | | | Total activity of the lake [kCi] |
|---|---|---|---|---|---|
| | Radionuclides | | | | |
| | $^{90}$Sr and $^{90}$Y | $^{144}$Ce and $^{144}$Pr | $^{106}$Ru and $^{106}$Rh | $^{137}$Cs | |
| Berdenish | 10.8 | 131 | 16.2 | 0.099 | 158 |
| Uruskul | 3.6 | 43.5 | 5.4 | 0.033 | 62.5 |
| Kazhakul | 0.02 | 0.242 | 0.03 | 0.00018 | 0.292 |
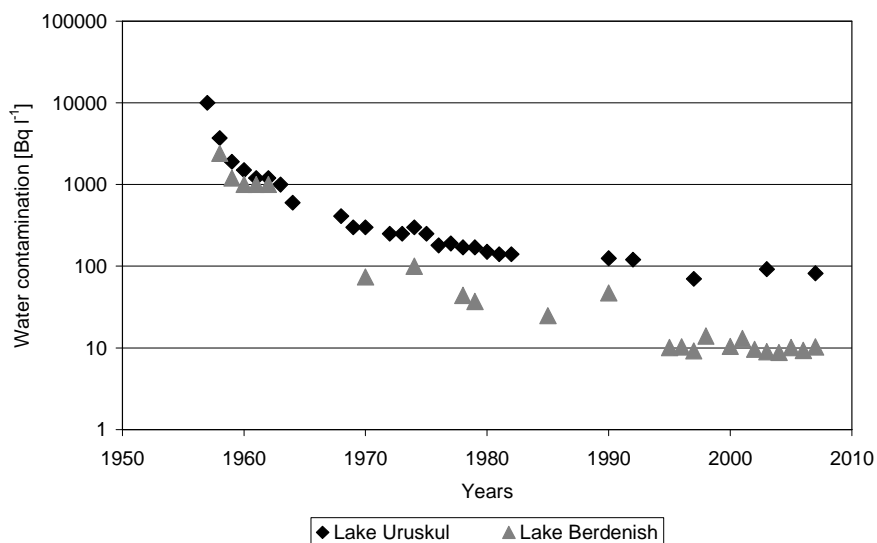
Figure 2.8 – Attenuation of total contamination of Lake Uruskul and Lake Berdenish

The contamination of **water reservoirs of the third group** of South Ural (for example, Lake Irtyash, Lake Ulagach, river Suselga, Figure 2.7) has place due to global radioactive fallout and runoff, and varies form 90 to 300 $Bq \cdot m^{-3}$ of $^{90}$Sr and $^{137}$Cs (Figure 2.9).
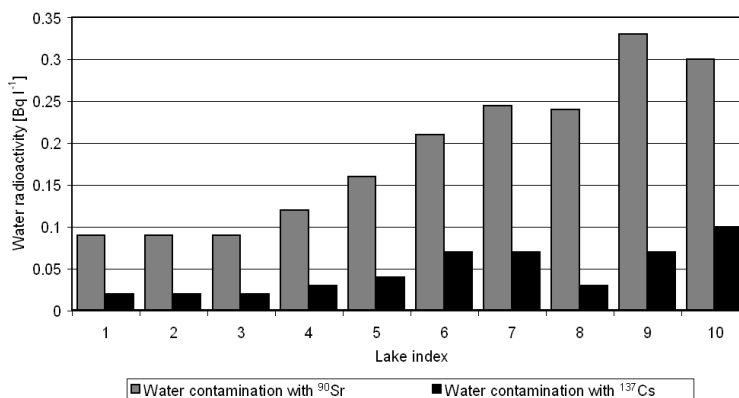


Figure 2.9 - Contamination of regional lakes with $^{90}$Sr and $^{137}$Cs: 1- Silach; 2- Sungul; 3- Kirety; 4- Large Kasli; 5- Irtyash; 6- Large Nanoga; 7- Small Nanoga; 8- Akakul; 9- Ulagach; 10-Kazhakul

## 2.2    Required experimental data

Required data are experimentally investigated at Mayak PA during ecological monitoring. These data used for interpretation of the remediation effect of HS include information on concentrations of microelements (sodium, potassium, calcium, magnesium, manganese, uranium), anions (carbonate, sulphate, chloride, bicarbonate, acetate), content of total organic matter, physico-chemical water parameters (hardness, bichromate oxidizability, permanganate oxidizability), content of solids, volumetric activities of dissolved and adsorbed radionuclides ($^{90}$Sr, $^{137}$Cs, $^{134}$Cs, $^{60}$Co, $^{106}$Ru, $^{154}$Eu, $^{241}$Am, $^{244}$Ci, sum of plutonium isotopes $^{239}$Pu and $^{240}$Pu, sum of uranium isotopes $^{235}$U and $^{238}$U), and granulometric and mineral composition of solids.

### 2.2.1    Peculiarity of current sampling of experimental data

Several monitoring programs were carried out to investigate the water body and the sediment of different reservoirs during the entire period of the past and present activities of PA Mayak. In these campaigns, physicochemical, sedimentary, and biotic parameters, such as contamination of different types of fresh water biota (benthos and fish), were measured in high spatial resolution. To calculate the spatial distribution of radionuclides in water systems, water and sediment samples were taken at some locations in the reservoirs at various depths, using the freeze core technique (Stukalov et al., 2007). The freeze core technique was applied to some industrial open water systems (Old swamp (B-17), Kisliy canal, Mishelyak River). The long cored pipes were submerged in water straight down to loam at several locations of reservoir, and frozen. The frozen cores were cut into smaller parts and subsequently analyzed for chemical and physical properties.

### 2.2.2    Required long-term originating experimental data

Regular ecological monitoring of all radioactively contaminated environments started in 1951. As shown by the first detailed investigations, the Mayak PA caused a large-scale contamination of the surrounding environment. A lot of radionuclides migrated into the environment and very dangerous for human health such as $^{90}$Sr, $^{137}$Cs, $^{131}$I, $^{60}$Co, $^{103}$Ru, $^{106}$Ru, and α-emitting nuclides were taken under control. Complex investigations were carried out in the case of industrial reservoirs, river and their biota. Besides Mayak PA, regular monitoring was carried out by such regional and state laboratories, institutes and universities as Goshydromet, Gossanepidnadzor, Biological Department of Moscow State University, Departments of Moscow Biophysical Institute. In 1957 at the head of

EURT, the Experimental Scientific Research Laboratory was organized to investigate results of dynamics of radioactive contamination of all environments, genetic mutations in vegetation, biota and animals after strong radioactive contamination of territory. The problem of rehabilitation of contaminated areas was examined by the State Agrophysical Institute, the State Institute of Zoology, the State Institute of Applied Geophysics, the Ural Department of Academy of Science, the Institute of Atomic Energy, and the State Institute of Geochemical Research. In 1985, the project Mirage was ended. This project included large-scale investigation of influence of the activity of Mayak PA and its accidents on surrounding environments stated in 1957 (Romanov et al., 1974; Fyodorov et al., 1972). The current ecological state of contaminated areas and water systems with complex investigation was accomplished by Hydrospezgeologia, the State Institute of Mineral Resources, the State Institute of Physical Chemistry, the laboratory of radiochemistry etc. Within international programs, Russian scientists work with expert from USA (DOE), Germany (GSF), Great Britain (BNFL), and Norway (Norwegian Radiation Protection Authority, NRPA) etc. In 2007, the Atlas of geoecological maps of the Mayak PA site was published (Alvyorov et al., 2007) that combined a lot of results obtained during the long-term monitoring of the contaminated region.

## 2.2.3    Sampling and sample preparation

### 2.2.3.1        Suspended matter, sediments, water

The water body samples were divided into two parts (solids and solution), using filter with $2 \cdot 10^{-6}$ m diameter porous. Solid and solution parts were analyzed separately. The solid parts were dried, heated to $100^0$ C and then to $600^0$ C. Physicochemical analyses were carried out at each step. We correlated the analytical results of the physicochemical parameters to the concentrations of radionuclides applying single regression analyses. Further characteristics of the samples were obtained applying radiographical, radiochemical, electron microscopic, and spectroscopic investigations of suspended matter, sediments and loam (Antonova et al., 1999; Bachur et al., 2005).

### 2.2.3.2        Biota

Sampling of fish was carried out once a year at the end of biological summer. An accumulation of 90Sr in the entire wet weight of the fish specie *Rutilus rutilus* was considered in the case of the sub-

group of reservoirs with sub-equal content of calcium. Concerning enlarged group of reservoirs, we considered the following fish species: *Rutilis rutilus*, *Perca*, *Tinca tinca*, *Cyprinus*, *Coregonus* and *Carassius*. The wet weight of each fish amounted to 3 – 5 kg. Fish was examined with the ichthyological method and subsequently dismembered into bones, muscles, and carcass. These three parts were dried at 1050C and burned up at 4500C. At each step, samples were analyzed for radionuclide contents in different tissues (Ternovskiy et al., 1985; Antonova et al., 1999; Trapeznikov & Trapeznikova, 2006; Antonova et al., 2007).

#### 2.2.3.3        *In situ* gamma measurements

At sites of sampling, in situ gamma measurements were carried out with a portable $3'' \times 3''$ NaI detector connected to a multichannel analyzer (Canberra Series 10+). At all sites the $^{137}$Cs peak was easily detected. At some places, it was not possible to use this equipment due to high counting rates.

### 2.2.4        Analytical techniques

#### 2.2.4.1        Gamma emitters

Measurements were carried out using a NaI (TI) high-sensitivity spectrometers (SGS-200). The NaI (TI) well-detector has a diameter of 60 mm and depth 100 mm. The detector efficiency is 25% and energy resolution is 10.5% at the energy of 662 keV. The detection limit is in the range 2 – 3 $Bq \cdot kg^{-1}$ with a counting error of less than 10%.

#### 2.2.4.2        Beta emitters ($^{90}$Sr)

For determination of $^{90}$Sr, different methods were used. For water and sequential extraction solutions, samples were subjected to liquid-liquid extraction of $^{90}$Y by toluene containing 5% HDHEP, and back extracted into 3 M $HNO_3$. The Cherenkov radiation from $^{90}$Y was determined by low-level liquid scintillation counter (Bjørnstad et al., 1990). Chemical yields were determined either by $^{89}$Sr spike and/or by complexometric titration of the Y-carrier with EDTA.

To determine the content of $^{90}$Sr in solids and tissues, the following technique was used. It is based on the oxalate-nitrate method. Stable strontium carrier was added to the samples and after a 12 hours contact time, incinerated at 600 $^0$C. The ash residue was treated three times with hot 6 – 7 M HNO$_3$. The solution was filtered, the ash residue reincinerated and treated once again with nitric acid. The filtrates were combined and the $^{90}$Sr concentration was measured. After hydroxide precipitation, the levels of radioactive and stable strontium were determined. The error due to the measurement was less than 8 %. The $^{90}$Sr activity falling in interval from 0.1 Bq to 10 Bq per sample was measured using a low background, end window Geiger-Mueller counter, containing a gas mixture of 90 % helium and 10 % ethyl alcohol vapor. The entry window had a diameter of 60 mm and a working area of 21 cm$^2$. The thickness of the aluminium foil was about $2\,mg\cdot cm^{-2}$. The background count rate was about 0.07 cps. The efficiency is 50 %, and the detection limit of $^{90}$Sr was approximately $1\,Bq\cdot kg^{-1}$, with a maximal error of 23 %. Chemical yields were determined by emission flame spectrophotometric analysis of stable Sr (UM-2 monochrometer). The averaged yield was about 70%.

### 2.2.4.3 Alfa emitters

Total activity of the alfa-emitting plutonium isotopes ($^{238}$Pu, $^{239}$Pu, $^{240}$Pu) was determined by radiochemical extraction of plutonium followed by total alpha measurements. The method was based on selective extraction of plutonium (IV) from acidified HNO$_3$ solution using a VP-IAP anion-exchange resin (grain size of 0.2 mm). This procedure separates uranium, thorium, americium, neptunium and other α-emitting radionuclides from plutonium. Incinerated samples (at 600 $^0$C) were dissolved in boiling 7.5 M HNO$_3$, and the solution eluated through the ion-exchange columns at a rate of 2 $ml\cdot min^{-1}\cdot cm^{-2}$. Then, thorium was eluated using a 9 M HCl solution, uranium was eluated at the next step, using a 7.5 M HNO$_3$ solution. The plutonium was eluated, using a 0.01 M hydrofluoric acid solution in 0.35 M HNO$_3$ at a rate of less than $1\,ml\cdot min^{-1}\cdot cm^{-2}$. The activity of the extract was measured by α-spectrometry with α-radiometer. The counting time was 300 seconds. Counting efficiency was 30 %, and the detection limit of activity amounted to $0.2\,Bq\cdot kg^{-1}$, with an error of less than 20 %. The chemical yield for plutonium was at least 70 %.

## 2.2.5      Intercomparison and quality control of data

For quality control purposes, some intercomparisons were carried out. One intercomparison was carried out within the Norwegian – Russian programme on Mayak PA that was initiated in 1993. Soil (from EURT) and sediment (from B-11) samples were analyzed for relevant radionulides by some laboratories in Russia and Norway. Results showed a good agreement between the different laboratories within a standard deviation less than 10% for $^{137}$Cs, 12 % for $^{90}$Sr, and less than 10 % for plutonium isotopes. Analyses of all samples showed that the correlation between Norwegian and Russian results was found to be equal to $r^2= 0.93$ for $^{137}$Cs and $r^2= 0.81$ for $^{90}$Sr (Malyshev et al., 1997).

# 2.3      Partition of radionuclides between solid and liquid phases in the water body of surface reservoirs

The key process in the radionuclide fate and transport poses the partition of radionuclide between solid and liquid phases in the water body. Application of the averaged values doesn't lead to correct results. Especially, it takes place in the case with the nuclear disposal. The research of environmental medium of considered water reservoirs allows for definition of spatial compartments of water reservoir that possess homogeneous chemical and physical properties in respect to accumulation of radionuclides. For each compartment considered lower, there are its own first order and second order mechanisms that influence on radionuclide immobilization or their further transport. Detailed investigation of radionuclide binding to solids in water solution allowed for stating a criterion how one needs to separate nepheloid layer and sediments at experiments. Studying of hydrodynamics results in definition of hydrodynamic status of the surface water reservoir as mixed or not mixed. These results were used at investigation of radionuclide accumulation in fish. For fish studying, well- mixed surface water reservoirs were taken.

## 2.3.1 Modelling of hydrodynamic compartments of the water body

Using the approach proposed by Håkanson (1981), the areas of erosion, transport, and sedimentation areas in the reservoir were calculated (Aleksandrova, 2006). Håkanson (1981) subdivided standing waters into three spatial compartments of net erosion, net deposition, and a transition zone of nearly zero changes in sediment depths, where lateral transport processes are assumed to be predominant.
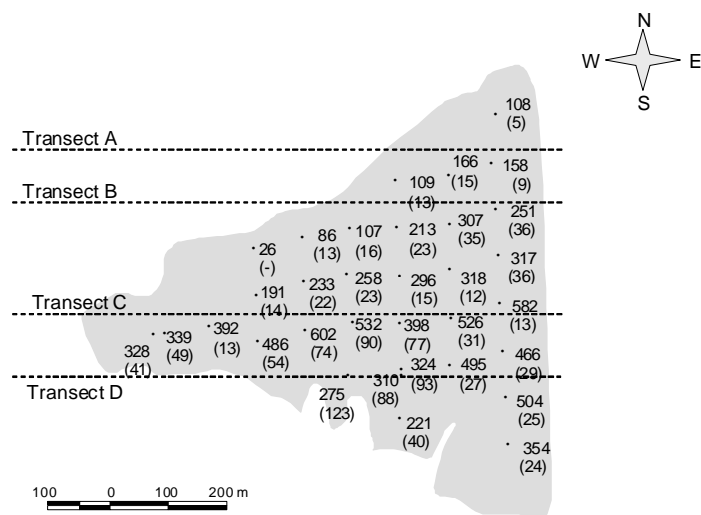


Figure 2.10 - Map of the Old Swamp reservoir (B-17) giving transects A, B, C, and D and sampling locations of the complex monitoring program with a) water depth, cm (upper number), and b) sediment depth, cm (lower number in brackets).

For some lakes and water reservoirs, the hydrodynamic compartments were defined to estimate influence of water solution stirring-up with wind and mixing processes on radionuclide interaction with solids. In the reservoir Old Swamp (Figure 2.6), the most part of the water body is located in the sedimentation area (Figure 2.7). It resulted in non-homogeneous distribution of hydrochemical parameters, solids, volumetric content of organic matter in the water body. Additional turbidity for different transects (Figure 2.6) was calculated. These results are related to a typical wind velocity of ~ 6 m·s$^{-1}$ and the dominant west wind direction. In summer, the calculated additional turbidity caused by wind-induced mixing mostly varied between 5·10$^{-4}$ and 3·10$^{-3}$ kg·m$^{-3}$, partly reaching 0.02 kg·m$^{-3}$ in line D. This additional turbidity increases the average volumetric mass of suspended matter (SM) that has a minimum value of 0.02 kg·m$^{-3}$ from November to April, when the reservoir is covered with ice. For Lake Uruskul, the most part is well mixed (Figure 2.8). It means that distribution of hydrochemical and physical parameters are homogeneous in the water body of Uruskul. According to these results, turbulent mixing caused by wind slightly influences on radionuclide transport and their partitioning between solid and liquid phases in the water body of Old swamp, and defines shown processes in the water body of Uruskul.

Distance from the western margin of reservoir along the profile C [m]
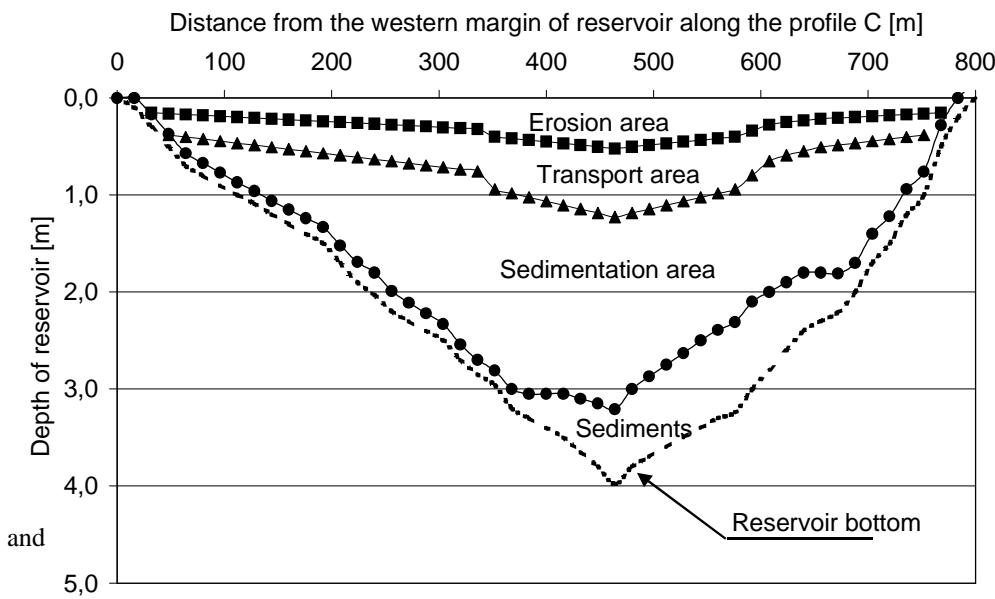
Figure 2.11 - Cross section from West to the East of the reservoir Old Swamp with areas of net sediment accumulation, transport, and erosion. The lines show boundaries between net sedimentation, transport, and net erosion

and

Figure 2.12 – Cross section from West to the East of the Lake Uruskul with areas of net sediment accumulation, transport, and erosion. The lines show boundaries between net sedimentation, transport, and net erosion

Distance from western point to the East [m]
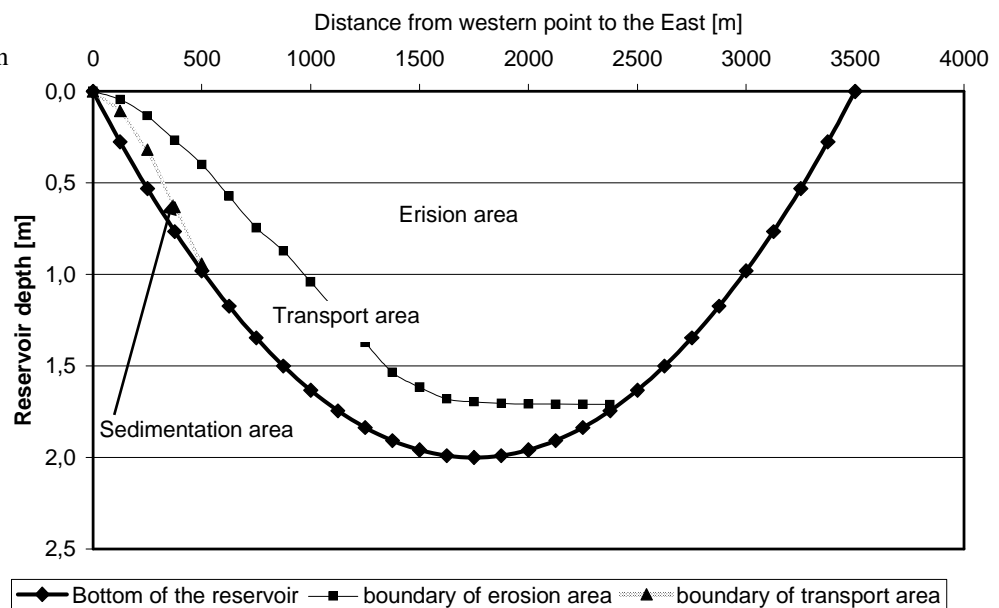
The lakes of second and third groups have such location of hydrodynamic compartments as in the case of Lake Uruskul. Among the industrial reservoirs, the reservoirs B-2, B-6, B-10, B-11 are described also this way. The reservoirs B-3, B-4, B-9, and B-17 have a thin mixed layer and almost the whole water body is not well mixed.

## 2.3.2 Peculiarities of the depth profiles of radionuclides and hydrological parameters

Based on the empirical research carried out in 2006 and our estimates of the influence of SM on physical and chemical processes in water and sediments, the reservoir Old Swamp was subdivided into three hydrological layers: open water with SM, nepheloid layer, and profundal sediment layer without turbulence diffusion. This approach allows for taking into account of peculiarities of radionuclide and microelement depth profiles (Figure 1.4, 1.6, 1.8) in the surface water reservoirs.
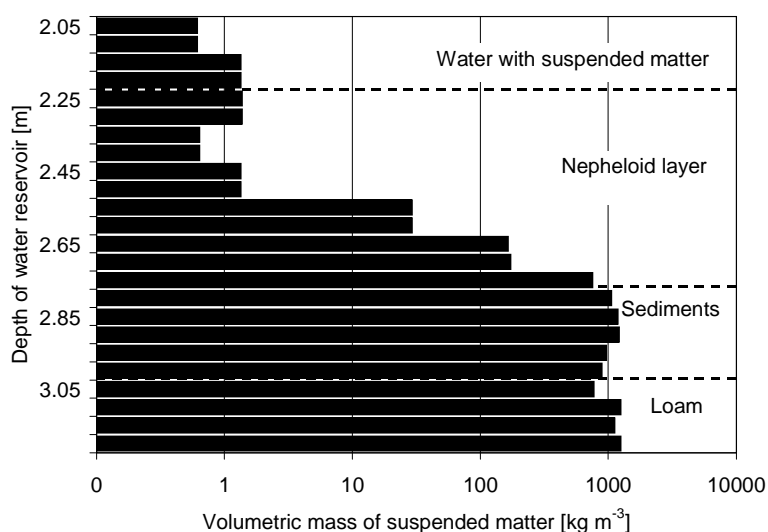
Figure 2.13 – Depth profile of the volumetric mass of solids in the pelagial region of the Reservoir Old Swamp measured in March 2006

Figure 2.14 – Depth profile of the volumetric activity of $^{137}$Cs in the pelagial region of the reservoir Old Swamp measured in March 2006
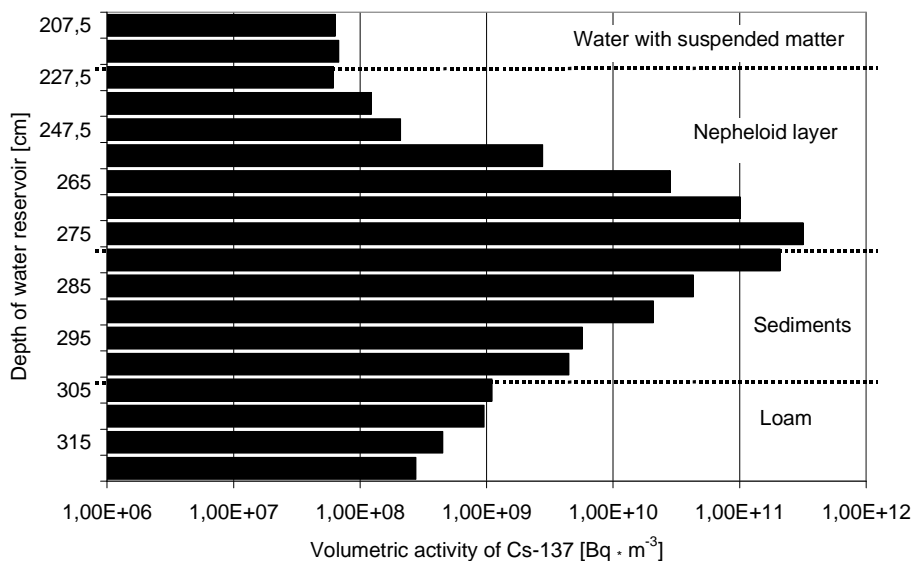
The term 'nepheloid layer' describes a layer easy to resuspend with physical characteristics (e. g. density) between those of profundal sediment and open water with SM.

The main criteria to define three compartments are based on: (1) the vertical change of the volume-weighted mass of suspended matter (related to dry weight; SM) with water depth presented in Figure 2.9 and (2) the distribution of the radioactive contamination of water in these layers. In the Figures 2.10, the typical depth distribution of $^{137}$Cs activity per volume in Old Swamp is presented. Both criteria, based on the profiles of the volumetric mass of SM and the volumetric activity of radionuclides, were considered for the classification of the layer system, because the processes described in our analytical solution depend on sedimentary characteristics and are characterized by the spatial distribution of radionuclides. So in the open water down to the defined water depth, SM does not exceed 1-2 kg·m$^{-3}$ (Figure 2.9). At the sampling location this depth amounts to 2.50 m. Below this layer till a water depth of 2.75 m, SM increases significantly from 1 to 1000 kg·m$^{-3}$. Again below down to a layer of loam, the volumetric mass of the solid residual barely varies around the latter value. The chemical properties of the open water and the nepheloid layer are significantly different from the sediments. The samples taken from sediments do not contain any filterable water. In these samples, water exists only in forms of porous and hydrated water. In other words, in this sediment layer the entire water is closely bound to the solid residual. Contrary to the two upper layers, there is no suspended matter in the sediment layer. In the two upper layers, suspended particles are present and defined as SM. This criterion helps to distinguish between sediments and the nepheloid layer, which represents a transition layer between the layers 1 (water with sediments) and 3 (sediments). The granulometric composition of both, SM and sediment, is characterized by high portions of feldspar (50 %) with an average size of $2 \cdot 10^{-6}$ - $3 \cdot 10^{-6}$ m, and quartz (40%) with an average size of $7 \cdot 10^{-6}$ m .

The second criterion to subdivide the reservoir into three compartments is connected with the different behavior of the volumetric activity of radionuclides changing with depth (Figure 2.10). These profiles illustrate that different processes play the dominant role in the layers. In the upper water layer, almost all parameters are averaged because of good mixture of water. In the nepheloid layer, a sharp increase of radionuclide activity is observed. However at the boundary of the nepheloid layer with sediments, the decrease of activity of such radionuclide as $^{235}$U, $^{238}$U, $^{239}$Pu, $^{240}$Pu, and $^{90}$Sr takes place. For the sediment layer, we observe mainly a decrease in the volumetric activity with depth. This requires that the dominant processes especially in the nepheloid layer should be more detailed studied.

## 2.3.3 Influence of the radionuclide partition on the general model of radionuclide behavior in surface water reservoirs

In accordance to received experimental data, the not mixed water body should be considered as a n-layers system. Correspondently, the mathematical setting of the vertical radionuclide transport can be written as follows (Monte et al., 2005; Nosov et al., 2006; Suhoruchkin, 1985; Fesenko, 1984; and Prohorov, 1981).

$$
\begin{cases}
\eta_1 \cdot \dfrac{\partial C_1}{\partial t} = div(D_1 \vec{\nabla} C_1) - \lambda \cdot C_1 + F_{12}(C_1, C_2) - F'_{filtr1} + F'_{surf} + R'_0 - E'_v \\[2mm]
\eta_2 \cdot \dfrac{\partial C_2}{\partial t} = div(D_2 \vec{\nabla} C_2) - \lambda \cdot C_2 + F_{21}(C_1, C_2) + F_{23}(C_2, C_3) - F'_{filtr\_2} \\[2mm]
\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots \\[2mm]
\quad \eta_n \cdot \dfrac{\partial C_n}{\partial t} = div\left(D_n \vec{\nabla} C_n\right) - \lambda \cdot C_n + F_{n,n-1}(C_{n-1}, C_n) - F'_{filtr\_n}
\end{cases}
\tag{1}
$$

where $C_i$ [Bq m$^{-3}$] is volume-weighted concentration of radionuclide *RN* in the layer $i$; $D_i$ is the diffusion coefficient in the corresponding layer ($i$) ($i$ =1, n); $\eta_i$ is a coefficient of medium porosity[1]; $\lambda$ is the radioactive decay constant. The term $F'_{surf}$ describes the increase of the contamination concentration in time via runoff. The value $R'_0$ corresponds to the increase of radionuclide concentration in time due to the original input of radionuclide ($i$) into the lake in the case of accident or via routine discharge. A part of radionuclides escapes from the water body with lateral surface and through the bottom into ground water and via evaporation. The velocity of loses are described with the following values correspondingly: $\sum\limits_{i=1}^{n} F'_{filtr\_i}$ and $E'_v$. The values $F_{i,i-1}(C_{i-1}, C_i)$ and $F_{i,i+1}(C_i, C_{i+1})$ characterize the interaction of layer ($i$) with layers ($i$-1) and ($i$+1), including diffusive mass exchange and output of particles from the layer ($i$) through the sedimentation of SM, and can be written as follows:

$$
F\left(C_{i-1}, C_i\right) = \frac{\beta_{i,i-1}}{h_i} \cdot \left(\alpha_{diss,\,i-1} C_{i-1} - \alpha_{diss,\,i} C_i\right) + \frac{U_{i,i-1}}{h_i}\left(\alpha_{SR,\,i-1} C_{i-1} - \frac{m_{i-1}}{m_i} \cdot \alpha_{SR,\,i} C_i\right)
\tag{2}
$$

---

[1] Porosity describes the relation of the volume of pores to the volume of the whole sample, with being calculated based on the values of sample density $\rho_s$ and density of solid phase $\rho_{s\_ph}$:    $\eta$ =1- $\rho_s/\rho_{s\_ph}$.

The values used here are given in Table 2.11.

Table 2.11 - List of parameters and units

| Parameter description | Parameter symbol | Parameter unit |
|---|---|---|
| Volume-weighted concentration of radionuclides in the layer i | $C_i$ | Bq m$^{-3}$ |
| Coefficient of diffusion exchange between layers $i$ and $(i-1)$ | $\beta_{i,i-1}$ | m s$^{-1}$ |
| Portion of dissolved radionuclide in the water layer $i$ | $\alpha_{diss\_i}$ | [-] |
| Partition coefficient | $K_{d(i)\_RN}$ | m$^3$ kg$^{-1}$ |
| Density of the solid matrix in layer $i$ | $m_i$ | kg m$^{-3}$ |
| Velocity of net motion of weighted particles bound with radionuclides in the layer $i$ water solution | $U_i$ | m s$^{-1}$ |
| Portion of radionuclide bound to solids in layer $i$ | $\alpha_{SR\_i}$ | [-] |
| The thickness of layer ($i$) | $h_i$ | [m] |

The terms on the right-hand side of equation (2) are from left to right:

• Loses and gains of radionuclides by diffusion exchange of dissolved radionuclides between the layers ($i$ -1) and $i$;

• Loses and gains of radionuclides by diffusion exchange of radionuclides adsorbed by solids (SR) between the layers ($i$ -1) and $i$.

• In equation (2), the particle motion according to Stoke's law with velocity U (m/s) is taking into account. The values $\alpha_{diss\_i}, \alpha_{SR\_i}$ characterize the portion of radionuclides in dissolved and bound to solids forms in the layer $i$, which are calculated as follows:

$$\alpha_{diss\_i} = \frac{1}{1 + m_i \cdot K_{d(i)\_RN}} \tag{3}$$

$$\alpha_{SR\_i} = \frac{m_i \cdot K_{d(i)\_RN}}{1 + m_i \cdot K_{d(i)\_RN}} \tag{4}$$

As shown by the general model of the radionuclide transport (equations 1-4), such values as the portions of bound to solids $\alpha_{SR\_i}$ and dissolved radionuclides $\alpha_{diss\_i}$ are defined by the local

partition processes, and in turn, by the local concentration of humic substances in water solution. Correct calculation of the partition coefficient $K_{d(i)\_RN}$ for each layer ($i$) allows for estimating of the portions of radionuclides that can be immobilized in water body and that will migrate into ground water and other environments. Thus, the first problem is development of the $K_{d\_RN}$ theory (Figure 2.15) based on the unique experimental data (Chapter 3) and the application of a new approach to this problem connected with the use of disperse system theory and quantum statistics. This approach is presented in Chapter 4.
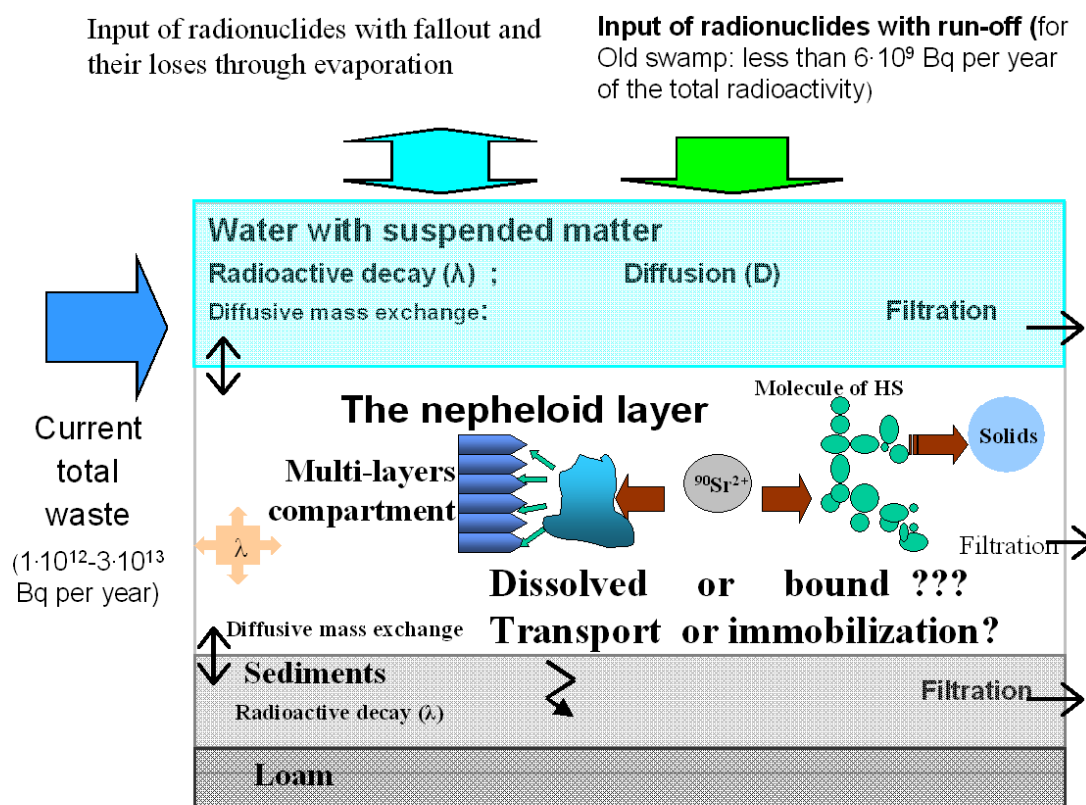


Figure 2.15 – Influence of radionuclide partition process on kinetic model of radionuclide fate and transport in the water body including three main compartments: (1) the water layer with suspended matter; (2) the multi-layers' nepheloid compartment; (3) the multi-layers' sediment.  The estimations correspond to the industrial reservoir B-17.

The system of differential equation (1) used to describe the behavior of radionuclides in the water reservoir first requires the coerrect values of water body parameters, including the $K_{d(i)\_RN}$ value. However, the partition coefficient is usually incorrect defiend, varying 100 times for one compartment that leads to incorrect solution of (1) and wrong understanding of radionuclide migration processes. Investigation of HS influence on RN provides the correct value to describe the partition process of radionuclide between solid and liquid phases. This value will be introduced as a modified partition coefficient and doesn't change from one location to another in the water body of one reservoir.

## 2.4 Environmental relevance of humic substances in surface water

The results of a systematical experimental survey of several water reservoirs in South Ural used as deposits of highly radioactive waste from nuclear production site "Mayak" (Figure 1.1) show that inorganic colloids, humic substance (HS) and their derivatives play an important role in retardation of radionuclide transport in natural and artificial surface waters (Polyakov et al., 2007; Sapozhnikov et al., 2005; Periminova et al., 2007). Furthermore, HS polymerize under special conditions. This polymerization partly leads to coagulation and precipitation of complexes of HS with radionuclides (Polyakov, 2007).

Macromolecules of HS consist of a hydrophobic aromatic backbone that is surrounded with functional groups, such as carboxyl groups and hydroxyl groups. The structural complexity inherent in HS creates opportunities for a broad range of chemical interactions as indicated in Figure 2.16:
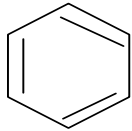
| Structural moiety | Type of related interaction |
|---|---|
| - COOH<br>- OH<br>>C=O<br><br>- CH$_n$ | ion-exchange, complexation<br>complexation, hydrogen bonding<br>reduction-oxidation<br>donor-acceptor interaction<br>(charge transfer complexes)<br><br>hydrophobic interaction |

Figure 2.16 – Diversity of structural moieties inherent in HS provides a broad range of chemical interactions they are able of.

The structure of HS (Figure 1.3) causes hydrophobic, and distinct redox, ion exchange, and chelating properties. The enriched fraction of oxygen donor groups within the humic molecule fosters the formation of stable complexes with actinides (Perminova et al., 2007). The chemical behavior of HS in the water reservoirs depends on the phase of water ingredients and the concentration of organic matter (OM). Beyond the critical concentration of micelle formation (MCC), HS exhibit properties of an electrolyte consisting of long-chained macromolecules. HS may

act as a polyfunctional complexing ligand or as a cation exchange system of super-dispersed particles (Polyakov, 2007). In the state of MCC, the properties of HS become complex.

## 2.4.1 Behavior of depth profiles of radionuclide adsorbed activity, solids and humic substances in different compartments of the water reservoir

The depth profiles of adsorbed activities (AA) of several radionuclides, adsorbed microelement concentrations, and the volumetric contents of solids (SR) and humic substances (HS) demonstrate a strong interdependence between AA of radionuclides and HS in the nepheloid layer and the layer with suspended matter (Figures 1.4 - 1.5). In the water layer with suspended matter, the volumetric content of AA, SR and HS almost don't change, except the upper part of this layer that contains about 90 – 99% of gas dissolved in water. The nepheloid layer is characterized by a steep increase in the volumetric content of AA, SR and HS. However at the boundary with sediments, the AA, SR and HS concentrations decrease slightly. In sediments and loam, this correlation is not so high. Basing on the similar change of AA, SR and HS in the water layer with suspended matter and nepheloid layer, the close interdependence was assumed and investigated.

## 2.4.2 Mediating effect of humic substances

Mediating effects of humic substances on toxicity and bioaccumulation by aquatic biota of heavy metals, polyaromatic and polychlorinated hydrocarbons, pesticides and low molecular weight organics are summarized by Perminova et al. (2006), studying their relation to the type of test organism and source of model humic compound. It was shown that the results of laboratory studies depend greatly on the source of humic substances, and the molecular weight distribution is among the first priority factors determining the kind of effect exposed by humic substances on the biological activity of different ecotoxicants. According to the studies of Khristeva (1953), Prát and Pospišil (1959), Prát (1963), Rypáček (1968), Vaughan (1974), Vaughan and MacDonald (1976), Ziechman (1980), Batalkin et al. (1982), Vakhmistrov et al. (1987), Mazhul et al. (1993), Perminova et al. (2006), HS can permeate or modify cellular membranes. It was shown also, that FA are to be taken up to a larger degree than HA, and lower molecular weight HS (< 2500 Da) to a greater extent than the higher molecular weight material (Prat, 1963; Führ and Sauerbeck, 1965;

Führ, 1969). Perminova et al. (2006) concluded that the mentioned above membranotrophic fraction of HS can facilitate penetration into the cell of bound to it low molecular weight compounds. Among such compounds can be ions of heavy metals as well as molecules of pesticides or other toxic chemicals (Figure 2.17).

Figure 2.17 - Stable complexes of HS with shown elements and compounds
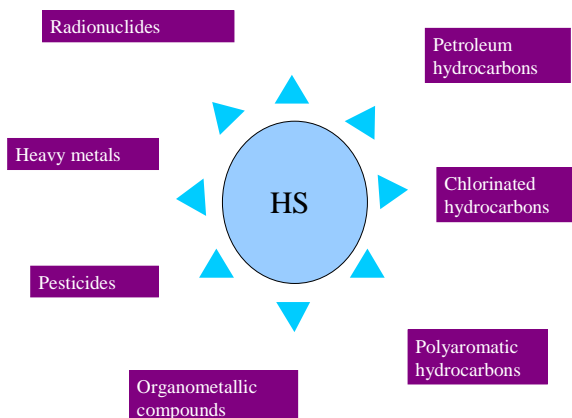
It is the enhanced translocation of the toxic chemicals across biological membranes which seems to



be responsible for the discussed increase in toxicity of the certain contaminants in the presence of HS with a predominance of the low molecular weight compartment. As shown by Orlov et al. (2005), Perminova et al. (2006), the mediating effects of HS can be proposed as follows: (1) Contaminants (Cont) are bound to HS chemically with formation of the non-toxic and non-bioavailable species of contaminants in water solution; (2) HS are bound to the cell and modify its permeability for contaminants; (3) The species of contaminants bound to HS modify biochemical processes. To estimate the contribution of the chemical binding in mediating effect of HS, they wrote the interaction between HS and Cont as follows:

$$HS + Cont \overset{K_{OC}}{\Longleftrightarrow} HS - Cont \tag{5}$$

The equilibrium sorption constant $K_{OC}$ was described with following equation:

$$K_{OC} = \frac{1-\alpha}{\alpha} \times \frac{1}{C_{HS}} \tag{6}$$

where α is the portion of the freely dissolved Cont in the presence of HS, $\alpha = [Cont]/C_{Cont}$; the value $C_{Cont}$ is the total mass concentration of contaminant; $C_{HS}$ is the total mass concentration of HS normalized to the content of organic carbon (OC), $kg\ C \cdot l^{-1}$, and $C_{HS} >> C_{Cont}$.

As shown by (Perminova et al., 2006), the immobilization of hydrophobic organic contaminants (HOC) was several orders of magnitude higher for humics immobilized on sediments compared to those dissolved in water, and that the sorption capacity for HOC was proportional to soil/ sediment

organic carbon mass fraction (Perminova et al., 2006), and the partitioning coefficient $K_{d\_Cont}$ depends on the soil/ sediments organic carbon mass fraction ( $f_{OC}$ ): $K_d = K_{OC} \cdot f_{OC}$ .

The reduction in toxicity of contaminants is provided exclusively by its binding to HS. And response of living organism to contaminants in the presence of contaminants is due two effects: (1) the sequestration of toxicity caused by a reduction in the concentration of freely dissolved contaminants and (2) the stimulation effect of HS on living organism. This effect is described with the bioconcentration factor ( $K_{acc}$ ):

$$K_{acc} = \frac{concentration \text{ of Cont in test - organism}}{\text{concentration of Cont in test solution}} = \frac{C_{living}}{[Cont]}, \tag{7}$$

with $C_{living}$ being defined only by freely dissolved contaminant.

# 2.4.3 Remediation Action of Humic Substances in Contaminated Water

Behavior of radionucldes, their precipitation, sorption and migration in the surface water system depend on a lot of factors. However, significant factors are as follows:

♦ hydrochemical, microbiological and physical properties of the water solution;

♦ chemical species of radionuclides in the water solution.

In natural water with pH≤5, cations of calcium and strontium are sufficiently mobile and not mobile in alkalescent solution where in its turn U(V) and U(VI) well migrate. Species with uranium U(III) and U(IV) are not so mobile in surface water as species with U(V) and U(VI).

These factors are significantly influenced by organic matter and products of its destruction as HS that appear in the surface water with sanitary sewage. HS provide reduction of penta – and hexavalent actinides (for example, U(VI) and U(V); Pu(VI) and Pu(V) etc) to three-valence and tetravalent state (correspondingly, U(VI) and U(III), Pu(III) and Pu(IV)). HS form strong complexes with actinyls and cations of metals. Under alkaline conditions, some complexes of HS with radionuclides tend to adsorb or precipitate. According to experimental data (Marey, 1976), the partition coefficient of radionuclide $K_{d\_RN}$ changed from 22 - 65 $l \cdot kg^{-1}$ to 148 - 1110 $l \cdot kg^{-1}$ for ^{90}Sr and from 583 – 660 to 1840 to 4730 for ^{137}Cs at the investigation of samples taken first from sand and loams, and second from soils enriched in organic matter as sapropel, peat and etc (Table 2.12).

Table 2.12 - Radionuclide partitioning coefficient for different types of soils sampled from Ural lakes L. Miasovo and L. Tatkul

| Soils | Partitioning coefficient $K_{d\_RN}$ $[l \cdot kg^{-1}]$ | |
|---|---|---|
| | For $^{90}$Sr | For $^{137}$Cs |
| Siliceous sapropel | 218 | 2503 |
| Mixed sapropel | 1110 | 1840 |
| Peat soils | 244 | 3850 |
| Calcareous soils | 25 | 660 |
| Uliginous solis | 148 | 4730 |
| Sandy soils | 22 | 583 |
| Clay loam | 65 | 647 |

A comparison of partitioning coefficients of $^{90}$Sr and $^{137}$Cs presented for different kinds of the solid phase (Table 2.12) shows that sapropel and uliginous soils provide strong increasing of radionuclide immobilization. So, sapropel and uliginous solis are good sources of HS in surface water reservoirs. The investigation of experimental data sampled by Kogotkov (1976) shows that an increasing of the organic matter part in solid phase causes more strong increase in the volumetric content of radioactivity (Figure 2.18).
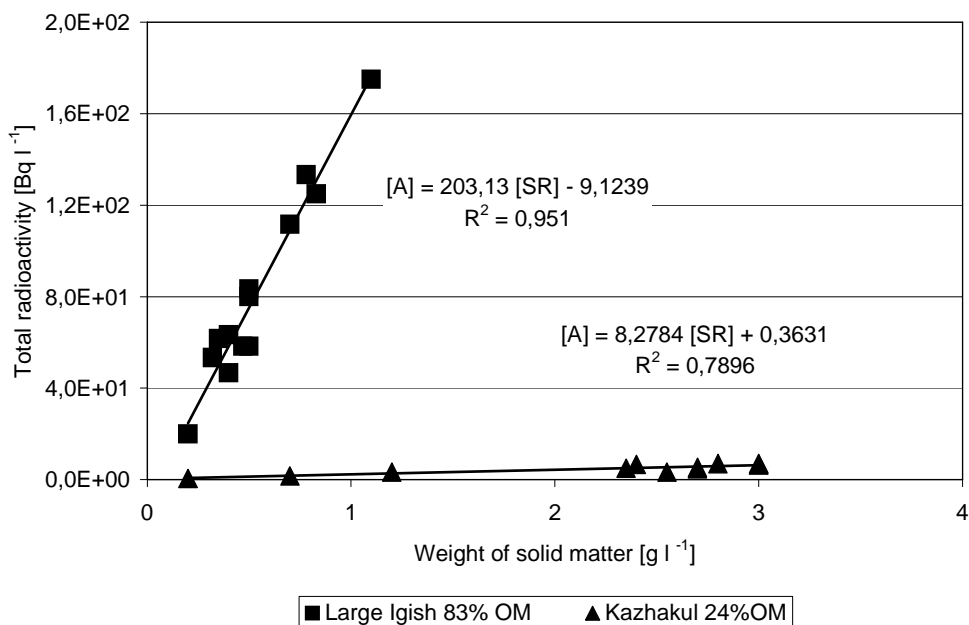


Figure 2.18 – Scatter plot of total radioactivity per volume in dependence on weight of solid phase in lake Large Igish (83% of SR is OM) and Kazhakul (24% of SR is OM)

As usually in the natural surface water, HS provide acidic state, and a lot of factors significantly affect radionuclide behavior. In the case of nuclear waste deposits, alkalescent solution is kept to avoid transport of several heavy metals and radionuclides into the environment. As shown in this thesis under these conditions, HS form different complexes of HS with radionuclides and mineral solids are formed, and provide immobilization of radionuclides by solid phase.

Also, one needs to take into account a change of sorption properties in the case of highly dispersed mineral solid particles. So in foamy solution of silts, sediments or mica-minerals in the presence of HS, the concentration of adsorbed radionuclides increases 1000 – 2000 times (Marey, 1976).

HS can be transformed from dissolved to colloidal state. Being in colloidal state, HS and their complexes with radionuclides and microelement cations are not enough investigated. As shown by many authors, HS in colloidal state can't diffuse through permeable membranes of living organisms.

The influence of the organic matter content on decreasing of radionuclide bioavailability was described in 50-ties years by Kogotkov (1967). In the eutrophic water system, the content of organic matter in water reservoir is more than in the oligotrophic water system. In surface water, organic matter (OM) provides a growth of vegetation. This vegetation adsorbs radionuclides from water solution in summer, and in autumn these radionuclides return into water. The season variations of radionuclide concentration in water presented in Figure 2.19 are strongly dependent on the OM content.
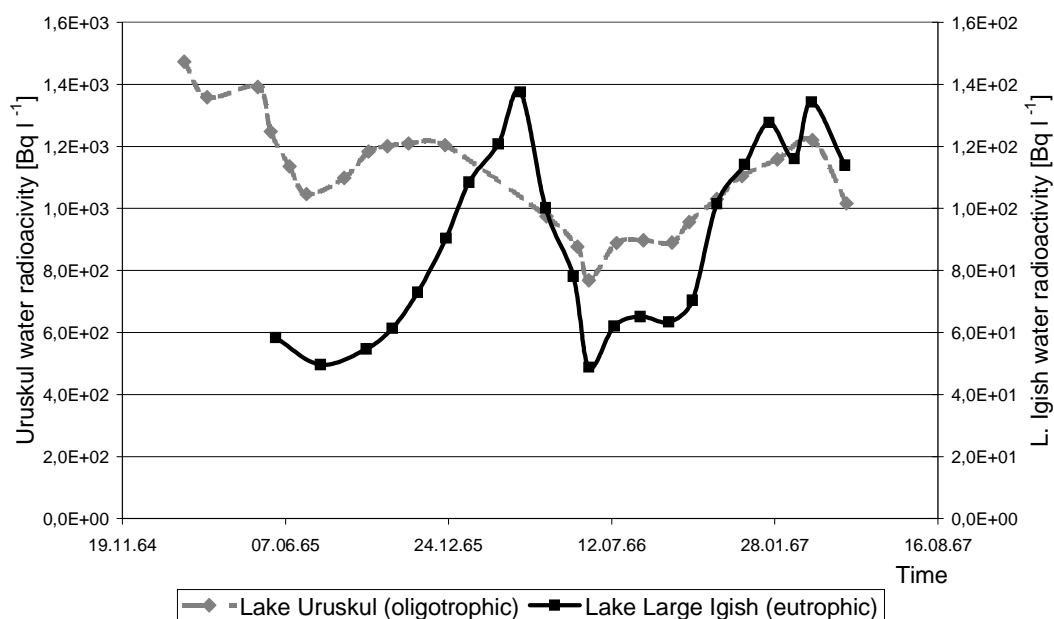


Figure 2.19 - Influence of the lake type on season variation of radioactive contamination of water

Organic matter was shown to contain mostly HS. The comparison of the radionuclide accumulation in fish shows that in eutrophic lakes, fish is less contaminated than in oligotrophic lakes (Table 2.13). High content of OM results in enrichment of water system in HS.

Table 2.13 - Dependence of bioconcentration factor on content of organic matter in water system

| Group of lakes | Type of lakes | Water hardness | Organic matter | BCF (Bioconcentration factor) | |
|---|---|---|---|---|---|
| | | | | Skeleton $\left[l \cdot kg^{-1} d.m.\right]$ | Muscle $\left[l \cdot kg^{-1} w.m.\right]$ |
| 1. Berdenish, Uruskul, Kazhakul | Oligotrophic | $14 - 18$ $mg - eq \times l^{-1}$ | sapropel | $1.1 \cdot 10^4$ $(8.9 \cdot 10^3 - 1.2 \cdot 10^4)$ | 70 (25-120) |
| 2. Chervyanoe, Travyanoe | Partly swampy | $5 - 28$ $mg - eq \times l^{-1}$ | mixed | $2.1 \cdot 10^3$ $(1.9 \cdot 10^3 - 2.2 \cdot 10^3)$ | 51 (29-73) |
| 3. Large Sungul, Tygish, Alabuga, Large Igish | Eutrophic | $2.5 - 5.3$ $mg - eq \times l^{-1}$ | sapropel | $8.6 \cdot 10^2$ $(7.0 \cdot 10^2 - 1.0 \cdot 10^3)$ | 19 (6.5-37) |

All these data hint at a significant influence of organic matter and especially HS on the processes of radionuclide accumulation by solids and in fish. The next chapter is devoted to mathematical analyses of wide experimental data sampled for the purpose to understand and quantify the remediation effect of HS.

# Chapter 3

# Results and Discussions[1]

## 3.1 Results of analyses of experimental data of radionuclide distribution in Old swamp

In contaminated water reservoirs, the sorption and binding of radionuclides to solids (SR) determines their bioavailability and transport and thus human and ecosystem exposure. The influence of organic matter (OM) on binding of the radionuclides $^{90}$Sr, $^{137}$Cs, sum of $^{235}$U, $^{238}$U, and sum of $^{239}$Pu, $^{240}$Pu to solids are investigated, using experimental data derived from ecological monitoring of radioactive waste deposits in South Ural (Russia). Industrial reservoir Old swamp B-17 (Staroe Boloto) is one of the most radioactively contaminated water reservoirs used as a deposit of radioactive waste (Aleksahin et al., 1997). At present, the total contamination with β– nuclides (mostly $^{90}$Sr, $^{137}$Cs) amounts to $4.4 \cdot 10^{16}$ Bq, and the total contamination with α – nuclides amounts to $1.1 \cdot 10^{15}$ Bq (Stukalov and Simkina, 2003; Stukalov et al., 2007). During the entire working period, approximately $3.9 \cdot 10^{17}$ Bq of β–nuclides were deposited in Old swamp. OM in the water reservoir mainly consists of humic substance (HS) that forms humates and fulvates with radionuclides and binds to solids via different mechanisms, such as coordinating bound or covalent bound. These processes are strongly dependent on the phase state of HS, which can be colloidal or soluble high-molecular compounds. As shown in the experimental investigation, relation of the humic acid (HA) concentration to the concentration of fulvic acids (FA) amounts to 10 to 1 in Old swamp. Thus in binding processes of radionuclides to solids, HA play the significant role.

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[1] This chapter is partially published in Aleksandrova et al. (2008a, b) and Aleksandrova et al. (2009).

## 3.1.1 Correlations of the local contents of adsorbed radionuclides, minerals, and organic matter in Old swamp

The depth profiles of adsorbed activities (AA) of several radionuclides, adsorbed microelement concentrations, and the volumetric contents of SR and OM demonstrate a strong interdependence between AA of radionuclides and OM (Figure 1.4), and between the volumetric content of microelements and SR, respectively (Figure 1.6). Correlation analyses was assumed to apply to these data, and obtained significant correlations. Table 3.1 exemplifies some results of correlation analyses. These results point at strong correlations of the depth profiles of adsorbed radionuclides activities (AA) with the volumetric content of SR ($r_{SR\_Old\ swamp} > 0.71$, n = 20, p < 0.05) and OM ($r_{OM\_Old\ swamp} > 0.67$, n = 20, p < 0.05).

**Table 3.1: Correlation coefficients between the depth profiles of adsorbed activities of considered radionuclides and the volumetric mass of solids SR, organic matter (OM), cations, anions and dissolved activities of the same radionuclides in the water body of Old swamp**

| Coefficients (r) of correlation between depth profiles of bound radionuclides and the value: | Volumetric content of radionuclides bound to SR | | | |
|---|---|---|---|---|
| | $^{90}$Sr | $^{137}$Cs | Sum of $^{239}$Pu, $^{240}$Pu | Sum of $^{235}$U, $^{238}$U |
| Volumetric content of SR | 0.85 | 0.71 | 0.77 | 0.79 |
| Volumetric content of OM | 0.82 | 0.67 | 0.74 | 0.76 |
| Volumetric content of cations bound to SR | | | | |
| Na | 0.87 | 0.96 | 0.91 | 0.92 |
| Mg | 0.86 | 0.95 | 0.90 | 0.91 |
| Ca | 0.75 | 0.87 | 0.80 | 0.82 |
| Fe | 0.87 | 0.96 | 0.91 | 0.92 |
| Volumetric content of cations dissolved in water | | | | |
| Mg | 0.35 | 0.38 | 0.36 | 0.37 |
| Ca | 0.46 | 0.58 | 0.51 | 0.53 |
| Na | 0.38 | 0.48 | 0.42 | 0.44 |
| Volumetric content of anions in water | | | | |

| Coefficients (r) of correlation between depth profiles of bound radionuclides and the value: | Volumetric content of radionuclides bound to SR | | | |
|---|---|---|---|---|
| | $^{90}$Sr | $^{137}$Cs | Sum of $^{239}$Pu, $^{240}$Pu | Sum of $^{235}$U, $^{238}$U |
| Chloride | 0.61 | 0.69 | 0.64 | 0.65 |
| Nitrate | 0.51 | 0.60 | 0.54 | 0.56 |
| Sulfate | 0.51 | 0.61 | 0.55 | 0.57 |
| Bicarbonate | 0.44 | 0.56 | 0.48 | 0.50 |
| Volumetric content of dissolved in water radionuclides | | | | |
| $^{90}$Sr | 0.96 | 0.98 | 0.97 | 0.98 |
| $^{137}$Cs | 0.11 | 0.18 | 0.13 | 0.15 |
| Sum of $^{239}$Pu, $^{240}$Pu | 0.37 | 0.34 | 0.35 | 0.36 |
| Sum of $^{235}$U, $^{238}$U | 0.21 | 0.17 | 0.19 | 0.19 |

In a next step, a particularity of depth profiles of radionuclides AA was taken into account (Figure 1.4): Depth profiles of AA revealed a partial release of AA at the boundary between nepheloid layer and sediments. The nepheloid layer is characterized by a steep increase in the volumetric content of SR, and therefore, in the AA of radionuclides. However at the boundary with sediments, AA of radionuclides starts to decrease. All data were separated into two groups: (1) data from the layer of water with suspended matter and nepheloid layer, and (2) data from profundal sediments and loams. The first data group was subdued to nonlinear regression analyses (Figure 3.1 – 3.2) with the model parameters a and b:

$$[A_{RN\_sorb}] = a_1 \cdot [m_{SR}]^{b_1} \tag{8}$$

where $A_{RN\_sorb}$ is the volumetric activity adsorbed by solids [Bq·m$^{-3}$], and $m_{SR}$ is the volumetric content of SR in the water body [kg·m$^{-3}$]. Also, the nonlinear regression $[A_{RN\_sorb}] = a_2 \cdot [m_{OM}]^{b_2}$ was calculated where $m_{OM}$ is the volumetric content of OM in the water body [kg·m$^{-3}$]. The results of regression analyses applying equation (8) are given in Figure 3.1 and 3.2 and in Table 3.2. The results of regression analyses applied to the first group demonstrate significant correlations between radionuclide AA and the volumetric content of SR and OM: $r_1(^{90}$Sr, $^{137}$Cs) > 0.98 for SR and $r_2(^{90}$Sr, $^{137}$Cs) > 0.99 for OM at n = 9, p < 0.05 in the case of correlation of $^{90}$Sr and $^{137}$Cs with SR and OM. In the case of isotopes of uranium and plutonium, $r_1$(U, Pu) > 0.96, n = 7, p < 0.05 for their correlation with SR, and $r_2$(U, Pu) > 0.97, n = 7, p < 0.05 for their correlation with OM. It

hints at an important impact of SR and OM, mostly consisting of HS, on radionuclide adsorption in the two upper layers. Data of the second group presented in Figure 3.1 and 3.2 illustrate the release of some part of adsorbed radionuclides at the boundary of the nepheloid layer with sediments.
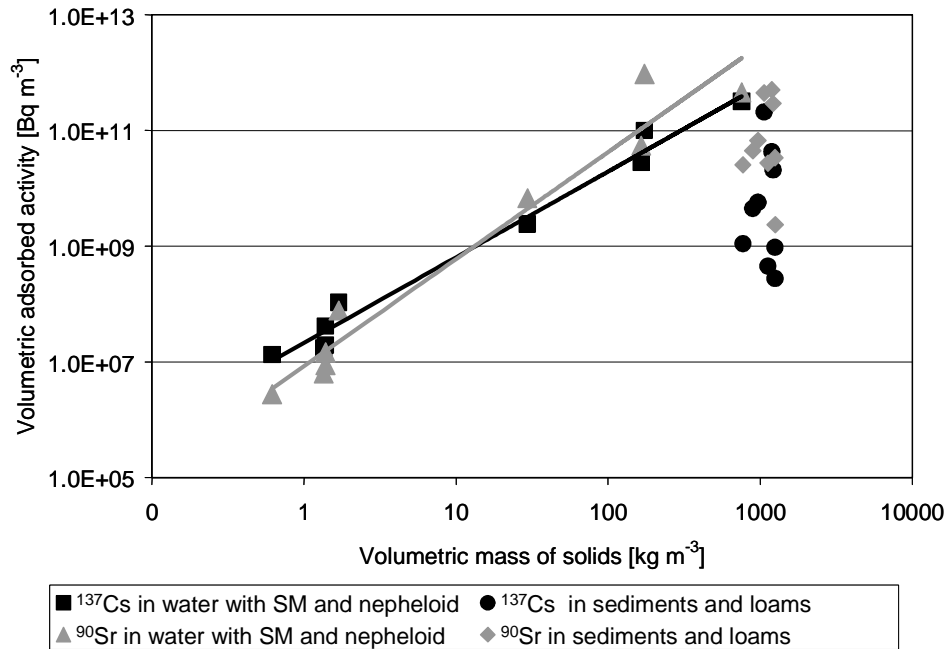


Figure 3.1 – Non-linear regression of the volumetric adsorbed activities (AA) of radionuclides $^{90}$Sr and $^{137}$Cs on the volumetric content of solids (SR)
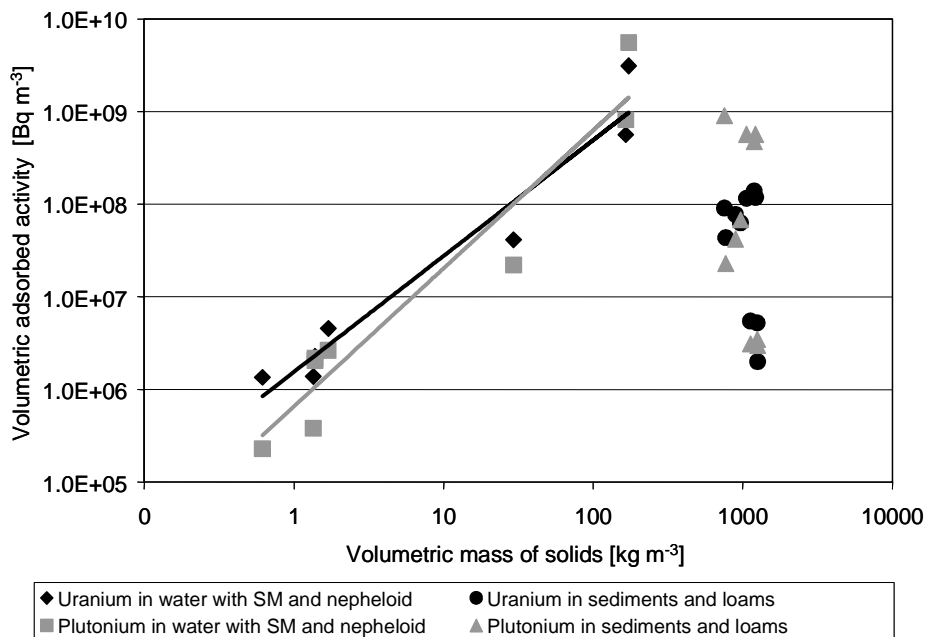


Figure 3.2 – Non-linear regression of the volumetric adsorbed activity (AA) of sum of uranium isotopes $^{235}$U, $^{238}$U, and sum of plutonium isotopes $^{239}$Pu, $^{240}$Pu on the volumetric content of solids (SR)

Table 3.2: Parameters of nonlinear regressions of the volumetric activities of $A_{RN\_sorb}$, [Bq m$^{-3}$] on the volumetric content of solids $m_{SR}$, [kg·m$^{-3}$] and OM $m_{OM}$, [kg·m$^{-3}$] in the water layer with suspended matter and nepheloid layer

| Parameters of nonlinear regression | Considered radionuclides and isotope sums | | | |
|---|---|---|---|---|
| | $^{90}$Sr | $^{137}$Cs | Sum of uranium isotopes$^{235}$U, $^{238}$U | Sum of plutonium isotopes$^{239}$Pu, $^{240}$Pu |
| Regression $[A_{RN\_sorb}] = a_1 \cdot [m_{SR}]^{b_1}$ | | | | |
| $a_1$ | 8.0·10$^6$ | 2.0·10$^7$ | 2.0·10$^6$ | 6.58·10$^5$ |
| Interval estimation[1] of $a_1$ at p < 0.05, n=9 | (2.4·10$^6$; 29.8·10$^6$) | (1.13·10$^7$; 4.05·10$^7$) | (0.7·10$^6$; 3.4·10$^6$) | (2.02·10$^5$; 21.5·10$^5$) |
| $b_1$ | 1.85 | 1,45 | 1,25 | 1,49 |
| Interval estimation[1] of $b_1$ at p < 0.05, n=9 | (1.48: 2.21) | (1.29; 1.66) | (0.84; 1.66) | (1.08; 1.90) |
| Correlation coefficients, r$_1$ | 0.98 | 0.99 | 0.97 | 0.96 |
| Regression $[A_{RN\_sorb}] = a_2 \cdot [m_{OM}]^{b_2}$ | | | | |
| $a_2$ | 5.0•10$^8$ | 6.0 •10$^8$ | 2.0•10$^7$ | 1.0•10$^7$ |
| Interval estimation[1] of $a_2$ at p < 0.05, n=9 | (2.4•10$^8$; 10.7•10$^8$) | (3.1•10$^8$; 10.5•10$^8$) | (1.1 •10$^7$; 4.3•10$^7$) | (0.5 •10$^7$; 3.8•10$^7$) |
| $b_2$ | 1.68 | 1.33 | 0.88 | 1.06 |
| Interval estimation[1] of $b_2$ at p < 0.05, n=9 | (1.41; 1.94) | (1.11; 1.54) | (0.76; 1.29) | (0.87; 1.60) |
| Correlation coefficients, r$_2$ | 0.99 | 0.99 | 0.98 | 0.97 |

Generalizing regression results, we assume that in the water and nepheloid layer, radionuclides are bound to mineral SR via formation of radionuclide complexes with humates. This way, we determine HA as a key chemical agent in radionuclide sorption. We rely on the polyelectrolyte

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[1] To estimate the influence of the uncertainty of the initial data on the calculated results, a statistical analysis using T-statistics was carried out.

theory of HA (Orlov et al., 2005) and apply it to the considered water systems. Below, we introduce two key parameters to describe binding processes: the adsorbing area of mineral surface per volume and a modified partitioning coefficient.

## 3.1.2 Modelling of influence of the mineral surface area on radionuclide sorption

We studied the interdependence between AA of radionuclides and adsorbing surface area of volume-weighted SR ($S_{sorb}/V$) for the considered radionuclides in the two water reservoir. In our model, SR in the water body were assumed to be round granules of alumosilicate with defined porosity and an average size of approximately 4 µm. This assumption was made for the water layer with suspended matter and the upper part of nepheloid layer. However, compression and consolidation of SR ($m_{SR} > 700$ kg·m$^{-3}$; with 77% of particles $> 10$ µm diameter) in the lower nepheloid layer and sediments lead to a considerable decrease in adsorbing surface area. According to the granulometric structure and moisture of profundal layers, we calculated the surface area of SR per volume ($S_{sorb}/V$) in sediments and loams, and applied nonlinear regression analyses with AA of radionuclides as dependent and the adsorbing surface area of SR ($S_{sorb}/V$) as independent variables for the entire water reservoir:

$$\left[A_{RN\_sorb}\right] = a_3 \cdot \left[S_{sorb}/V\right]^{b_3} \tag{9}$$

The results of these regressions are presented in Figure 3.3 and Table 3.3.
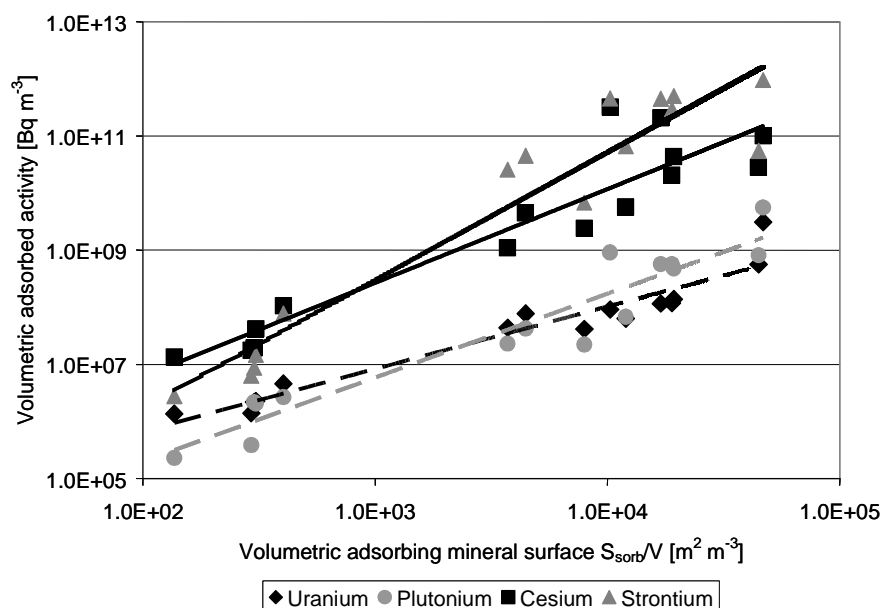


Figure 3.3 – Non-linear regression of the volumetric adsorbed activity of radionuclides $^{90}$Sr and $^{137}$Cs, sum of uranium isotopes $^{235}$U, $^{238}$U, and sum of plutonium isotopes $^{239}$Pu, $^{240}$Pu on the volumetric adsorbing surface area

Table 3.3 - Parameters of nonlinear regression of the activities of adsorbed radionuclides $A_{RN\_sorb}$, [Bq m$^{-3}$] and partitioning coefficient $K_{d\_RN}$ [m$^3$·kg$^{-1}$] on the volumetric content of adsorbing surface of SR $S_{sorb}/V$, [m$^2$·m$^{-3}$]

| Parameters of nonlinear regressions | Considered radionuclides and isotope sums | | | |
|---|---|---|---|---|
| | $^{90}$Sr | $^{137}$Cs | Sum of isotopes of | |
| | | | $^{235}$U, $^{238}$U | $^{239}$Pu, $^{240}$Pu |
| Regressions $\left[A_{RN\_sorb}\right] = a_3 \cdot \left[S_{sorb}/V\right]^{b_3}$ | | | | |
| $a_3$ | 58.0 | 3.145·10$^3$ | 4.346·10$^3$ | 229 |
| Interval estimation[1] of $a_3$ at p < 0.05, n=16 | (1.7; 1921.8) | (134.0; 73264.9) | (901.5; 21076.6) | (22.6; 2301.5) |
| $b_3$ | 2.24 | 1.64 | 1.09 | 1.47 |
| Interval estimation[1] of $b_3$ at p < 0.05, n=16 | (1.82; 2.65) | (1.26; 2.01) | (0.90; 1.27) | (1.19; 1.74) |
| Correlation coefficient, $r_3$ | 0.96 | 0.94 | 0.96 | 0.96 |
| Regressions $\left[K_{d\_RN}\right] = a_4 \cdot \left[S_{sorb}/V\right]^{b_4}$ | | | | |
| $a_4$ [2] | 0.018 | 0.085 | 4.088 | 0.001 |
| $b_4$ [2] | 0.241 | 0.274 | 0.076 | 8.51 |
| Correlation coefficient, $r_4$ | 0.62 | 0.62 | 0.32 | 0.58 |

It was found good and significant correlations between AA and the adsorbing surface area per volume for all radionuclides considered ($r_3 > 0.94$, n = 16, p < 0.05). These results indicate that the value s=$S_{sorb}$/V of mineral surface could be considered as significant parameter to describe radionuclide adsorption.

The influences of SR consolidation processes are well-mirrored in the shape of the modified sorption isotherms. As shown in Figure 1.7, both sorption isotherms for $^{90}$Sr and a sum of plutonium isotopes $^{239}$Pu, $^{240}$Pu are due to a steep increase in radionuclide AA, which again points

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[1] To estimate the influence of the uncertainty of the initial data on the calculated results, a statistical analysis using T-statistics was carried out.

[2] The statistical analysis showed that for all considered radionuclides an interval estimation at p <0.05 covers $b_4$=0 that reflects the hypothesis of regression dependence.

at a steep increase in adsorbing surface area of mineral solids with increasing SR. However, considering only the upper two layers without this boundary, sorption processes follow the S-type. In contrary, consideration of the partitioning coefficient $K_d$ value as a function of the adsorbed surface area gave weak non-significant correlations. The results of nonlinear regression analyses, applied to $K_d$ values and the adsorbing surface area per volume, are given in Table 3.4. Correlation coefficients amounted to 0.62, 0.62, 0.32, and 0.58 for the radionuclides ^{90}Sr, ^{137}Cs, sum of [235]U, [238]U, and sum of [239]Pu, [240]Pu, respectively.

### 3.1.3 Modelling of the mediating role of humic acids to bind radionuclides to solids

HA form stable heteropolar complexes with radionuclides via chemical reaction.

For the interaction of HA with bivalent metal cations, such as $Sr^{2+}$ and $UO_2^{2+}$, we formulate:

$$HA-(COOH)_2 + Me^{2+} \xrightarrow{K_1} HA-(COO^-)_2(Me)^{2+} + 2H^+, \tag{10}$$
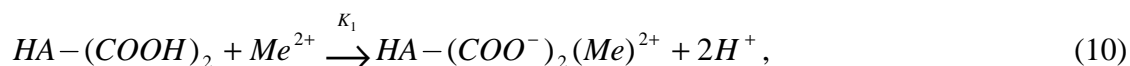
where $[HA-(COOH^-)_2(Me)^{2+}]$, $[H^+]$, $[HA-(COOH)_2]$, and $[Me^{2+}]$ are equilibrium

concentrations of the reaction products (humates, protons) and equilibrium concentrations of educts (HA with carboxyl groups and bivalent cations of radionuclides).

In the case of thermodynamic equilibrium for each depth h, we write the definition of the reaction rate constant $K_1$ as

$$K_1 = \frac{[HA-(COOH^-)_2(Me)^{2+}] \cdot [H^+]^2}{[HA-(COOH)_2] \cdot [Me^{2+}]} \tag{11}$$

Considering the relation between the volumetric content of humates ($HA-(COOH^-)_2(Me)^{2+}$),

bound to SR, to the volumetric content of dissolved radionuclides (RN) as the partitioning coefficient $K_{d\_RN}$, we can rewrite equation (11), taking into account that pH is kept constant in the entire reservoir, as follows:

$$\frac{K_{d\_RN}}{m_{HA}} = K_1 / [H^+]^2 \qquad (12)$$

Equation (12) gave a hint that the value $\dfrac{K_{d\_RN}}{m_{HA}}$ can be considered as a parameter describing the influence of HA on radionuclide binding to SR. The volumetric content of HA ($m_{HA}$) changes with depth h, and therefore, the ratio between soluble and bound compounds ($K_{d\_RN}$) also changes with depth.

The nonlinear regression analysis was applied to the value $\dfrac{K_{d\_RN}}{m_{HA}/m_{HA(0)}}$ on adsorbing surface area of mineral SR ($S_{sorb}/V$). Here, $m_{HA}$ is the volumetric content of SR at the depth h of the water layer with suspended matter and of the nepheloid layer; $m_{HA(0)}$ is the volumetric content of SR in the upper layers of water liable to turbulent mixture. Their relation of $m_{HA}/m_{HA(0)}$ corresponds to an increase in HA with increasing depth. The results of these analyses are presented in Figure 3.4. For all radionuclides considered, the correlation coefficients $r_5$ were $> 0.92$ ($n = 9$, $p < 0.05$; Table 3.4).
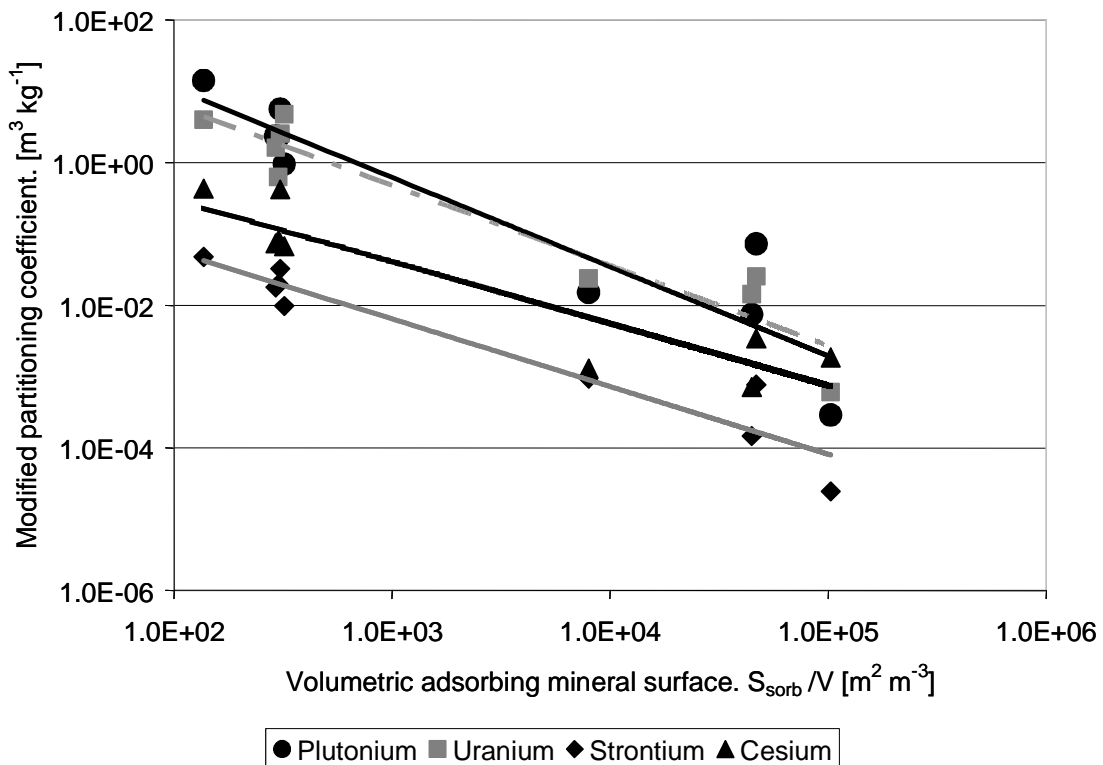


Figure 3.4 - Non-linear regression of the modified partitioning coefficient $K_{d\_mod(RN)} = \dfrac{K_{d\_RN}}{m_{HA}/m_{HA(0)}}$ on the volumetric adsorbing surface area for radionuclides ^{90}Sr, ^{137}Cs, the sum of uranium isotopes [235]U and [238]U, and plutonium isotopes [239]Pu and [240]Pu

Table 3.4: Parameters of nonlinear regression $K_{d\_mod(RN)} = \dfrac{K_{d\_RN}}{m_{HA}/m_{HA(0)}} = a_5 \cdot [S_{sorb}/V]^{b_5}$

| Parameters of nonlinear regression | Considered radionuclides and isotope sums | | | |
|---|---|---|---|---|
| | $^{90}$Sr | $^{137}$Cs | Sum of uranium isotopes $^{235}$U, $^{238}$U | Sum of plutonium isotopes $^{239}$Pu, $^{240}$Pu |
| $a_5$ | 4.546 | 16.61 | 1112.2 | 3530.9 |
| Interval estimation[1] of $a_5$ at p < 0.05, n=9 | (0.588; 35.516) | (1.11; 247.85) | (85.2; 15749.9) | (92.4; 59874.1) |
| $b_5$ | -0.92 | -0.85 | -1.12 | -1.25 |
| Interval estimation[1] of $b_5$ at p < 0.05, n=9 | (- 1.20; - 0.69) | (-1.21; - 0.53) | (- 1.44; - 0.79) | (- 1.69; - 0. 80) |
| Correlation coefficient, $r_5$ | 0.96 | 0.92 | 0.95 | 0.93 |

We rewrite the calculated nonlinear regression, applying a Taylor approximation, as follows:

$$a_5 \cdot [S_{sorb}/V]^{b_5} = a_5 \cdot [S_{sorb}/V]^{-1+\alpha_{RN}} = a_5 \cdot [S_{sorb}/V]^{-1} \cdot \sum_{n=0}^{\infty}\left(\frac{(\alpha_{RN} \cdot \ln(S_{sorb}/V))^n}{n!}\right) \qquad (13)$$

Here, we define the parameter $b_5$ as follows: $b_5 = -1.00 + \alpha_{RN}$, because $b_5$ is changing from -0.85 to -1.25 for considered radionuclides (Table 3.5). Therefore, $\alpha_{Sr}$=0.08, $\alpha_{Cs}$=0.15, $\alpha_{U}$=-0.12, $\alpha_{Pu}$=-0.25.

For the surface area of SR ($S_{sorb}/V$) < $10^2$ m$^2$·m$^{-3}$, we can use only the main part of the Taylor approximation:

$$\frac{K_{d\_RN}}{m_{HA}/m_{HA(0)}} = a_5 \cdot (S_{sorb}/V)^{-1} \qquad (14)$$

In a general case, we must write for the entire reservoir as follows:

$$K_{d\_RN} \cdot \frac{m_{HA(0)}/s_{(0)}^{1-\alpha_{RN}}}{m_{HA}/s^{1-\alpha_{RN}}} = const, \qquad (15)$$

where $s_{(0)} = (S_{sorb}/V)_0$ is the volumetric content of adsorbing surface area in the upper layers of water liable to turbulent mixture; $s = S_{sorb}/V$ is the adsorbing surface area in the volume unit; and the value ($m_{HA}/s$) in equation (14) characterizes the allocation of HA to the surface of SR. $\alpha_{Me}$

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[1] To estimate the influence of the uncertainty of the initial data on the calculated results, a statistical analysis using T-statistics was carried out.

characterizes the peculiarity of each radionuclide and is defined by the regression parameter $b_5$ as:

$\alpha_{RN} = b_5 + 1$.

As it results from equation 15, a dependence of radionuclide AA on the activity of dissolved radionuclides is described as follows:

$$A_{RN\_sorb} = const \cdot \frac{m_{HA} / s^{1-\alpha_{RN}}}{m_{HA(0)} / s_{(0)}^{1-\alpha_{RN}}} \cdot A_{RN\_diss} \quad (16).$$

Keeping the volumetric content of HA and adsorbing area of mineral surface constant, we obtain Henry's sorption. However, increasing $m_{HA}$ and s results in a modification of Henry's sorption in waste deposits.

Therefore, equation 16 can be considered as a quantitative estimation to describe the binding of radionuclides to the solid phase via: (1) chemical interaction of radionuclides with HA via formation of heteropolar complexes (humates); and (2) sorption interaction of humates with mineral SR, causing allocation of humates with radionuclide onto the surface of SR.

# 3.1.4 Modelling of the influence of humic substances on partitioning coefficient of radionuclides between liquid and solid phases in the water reservoir

According to the assumed radionuclide binding mechanism, we quantified the partitioning processes of radionuclides introducing $inv(K_{d\_RN})$, instead of the usual $K_d$ value for the water reservoirs used as radioactive waste deposits. The value $inv(K_{d\_RN})$ is kept constant in the entire

reservoir and equal to $K_{d\_RN} \cdot \frac{m_{HA(0)} / s_{(0)}^{1-\alpha_{RN}}}{m_{HA} / s^{1-\alpha_{RN}}}$. This results in linear increases in the partitioning

coefficient $K_{d\_RN}$ with increasing volumetric content of HA and decreasing adsorbing surface of mineral solids per volume. In the case of constant mass of HA and adsorbing surface of SR, we become Henry's sorption. Equation (16) points at a strong influence of HA and SR on Henry's sorption in the water reservoirs used as waste deposits. The calculated dependencies of radionuclide AA on the activity of dissolved radionuclides (Figure 1.6) confirm a steep increase in the number of sorption sites in the upper two layers of the water body. Our new approach provides a quantification of radionuclide partitioning in contaminated water, introducing an invariant value of modified $K_{d\_mod(RN)}$:

$$K_{d\_\mathrm{mod}(RN)} = K_{d\_RN} \cdot \frac{m_{HA(0)} / s_{(0)}^{1-\alpha_{RN}}}{m_{HA} / s^{1-\alpha_{RN}}} \tag{17}$$

Peculiarities in the different radionuclide binding processes are well described by the parameter $\alpha_{RN}$.

# 3.2 Interpretation of experimental data of the vertical distribution of adsorbed radionuclides in Kisliy canal

Starting at the beginning of 1971, the Kisliy canal is an artificial facility used to direct the liquid nuclear waste to disposal areas (B-4). Recently, about $1.1 \cdot 10^{14}$ - $1.85 \cdot 10^{14}$ Bq of nuclear waste has passed through Kisliy canal per year (Medvedev et al., 2008). The canal sediments mostly have high contents of organic matter (from 40 to 100%). In recent time, significant desorption of radionuclides from the sediments took place. Sometimes, a part of radionuclides is exported out of the canal water and sediments to the surrounding floodplain.

## 3.2.1 Correlations of local contents of adsorbed radionuclides, minerals and humic substances in Kisliy canal

Based on the results of our investigations carried out and described by Aleksandrova et al. (2008), regression analyses were applied to the contaminated Kisliy canal. It was examined the vertical profiles of the volumetric content of organic matter (OM) and solids (SR) and the volumetric activities of adsorbed radionuclides (AA): $^{90}$Sr, $^{137}$Cs, sum of uranium ($^{235}$U, $^{238}$U) isotopes, and sum of plutonium ($^{239}$Pu, $^{240}$Pu) isotopes (Figure 1.8). The vertical profiles of radionuclides and OM look similar. In Kisliy canal, correlation coefficients $r_{OM\_Kisliy}$ between OM, mostly consisting of HA, and AA of radionuclides account to 24,1% for $^{90}$Sr, 34,4% for $^{137}$Cs, 66% for sum of uranium isotopes, and 84% for sum of plutonium isotopes at n=18, p<0.05 in each case. The values of $r_{OM\_Kisliy}$ are not as high as in Old swamp for all investigated radionuclides: $r_{OM\_Old\,swamp} \geq 0.67$ (Aleksandrova et al., 2008).

### 3.2.2 Modelling of mediating role of humic substances in binding of radionuclides to solids in the river water

The regression dependence of the normalized partition coefficient $K_{d\_RN}^{*} = \dfrac{K_{d\_RN}}{m_{HA\_sorb}^{*}}$ on the accessible adsorbing mineral surface area $s = S_{sorb}/V$ gave correlation coefficients $r_7 \sim 99\%$ for all considered radionuclides (Figure 3.5). Parameters of the power regression $K_{d\_RN}^{*} = a_7 \cdot [S_{sorb}/V]^{b_7}$ are given in Table 3.5. Thus, regression analyses show that not only for Old swamp but also for Kisliy canal, the key parameter of radionuclide binding to solids via HA is $K_{d\_RN}^{*} = \dfrac{K_{d\_RN}}{m_{HA\_sorb}^{*}}$, stressing the mediating effect of HA in the contaminated surface water reservoirs.
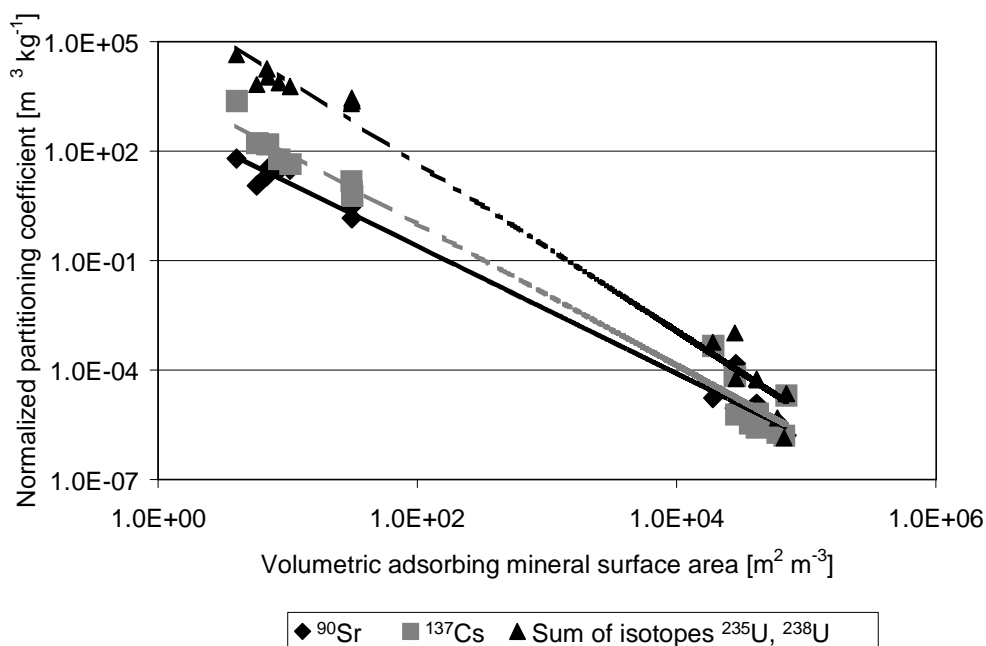


Figure 3.5 - Dependence of the normalized partitioning coefficient of radionuclide $RN$ $\dfrac{K_{d\_RN}}{m_{HA}^{*}} = \dfrac{K_{d\_RN}}{m_{HA}/m_{HA(0)}}$ on the volumetric content of adsorbing mineral surface area $s = S_{sorb}/V$ in Kisliy canal for a) $^{90}$Sr and $^{137}$Cs, b) sum of uranium isotopes uranium ($^{235}$U, $^{238}$U).

Table 3.5 - Parameters of nonlinear regression $K_{d\_RN}^{*} = \dfrac{K_{d\_RN}}{m_{HA}/m_{HA(0)}} = a_7 \cdot [S_{sorb}/V]^{b_7}$

| Parameters of nonlinear regression | Considered radionuclides and isotope sums | | |
|---|---|---|---|
| | $^{90}$Sr | $^{137}$Cs | Sum of uranium isotopes $^{235}$U, $^{238}$U |
| $a_7$ | 766.32 | 7070.8 | $2 \cdot 10^6$ |
| Interval estimation[1] of $a_7$ at $p < 0.05$, n=18 | (317.73; 1508,35) | (2440.6; 20332.9) | $(0.3 \cdot 10^6; 9.3 \cdot 10^6)$ |
| $b_7$ | -1.7442 | -1.9287 | -2.2865 |
| Interval estimation[1] of $b_7$ at $p < 0.05$, n=18 | (- 1.8516; - 1.6483) | (- 2.0684; - 1.7915) | (- 2.4436; - 2.1364) |
| Correlation coefficient, $r_7$ | 0.99 | 0.99 | 0.99 |

### 3.2.3 Modelling of the influence of humic substances on the partitioning coefficient of radionuclides between liquid and solid phases in the river water

Results of regression analyses lead to equation $\dfrac{K_{d\_RN}}{m_{HA}^{*}/s^{b_7^{*}}} = a_7 = const$  $(b_7^{*} = -b_7 > 0)$, with constant

$a_7$ describing any local point of the reservoir under consideration. The value $a_7$ is an invariant value for one considered reservoir, but different for different reservoirs. For one reservoir, one can define the influence of HA on the processes of radionuclide partitioning between solid and liquid phases of water body can be written as follows:

$$A_{RN\_sorb} = a_7 \cdot (m_{HA}^{*}/s^{b_7^{*}}) \cdot A_{RN\_diss} \tag{18}$$

Increasing the content of HA related to the power $b_7^{*}$ of the accessible adsorbing mineral surface area *s* causes an increase in the adsorbed radionuclide amount, and therefore, immobilization of radionuclides. This in turn results in attenuation of dissolved radioactivity in the water of the nuclear deposit without simple dilution. Summarizing these results, a new formula for the

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[1] To estimate the influence of the uncertainty of the initial data on the calculated results, a statistical analysis using T-statistics was carried out.

partitioning coefficient $K_{d\_RN}$ should be introduced taking into account the influence of HA on radionuclide binding to solids. As in the case with Old swamp, the partitioning process can be described with the value of modified partitioning coefficient (eq. 17):

$$K_{d\_mod(RN)} = K_{d\_RN} \cdot \frac{m_{HA(0)} / s_{(0)}^{1-\alpha_{RN}}}{m_{HA} / s^{1-\alpha_{RN}}} \cdot$$

## 3.3 Interpretation of experimental data of $^{90}$Sr and $^{137}$Cs accumulation in fish in surface water systems

We investigated bioaccumulation, applying correlation analyses to experimental data of $^{90}$Sr activity in reservoir solution and accumulation of $^{90}$Sr in fish sampling from the same reservoir. Results calculated for the sub-group of reservoirs with sub-equal content of calcium are presented in Figure 1.9. The correlation coefficient between the volumetric content of $^{90}$Sr in water solution and the accumulated content of $^{90}$Sr in fish is equal to 0.423. Correlation analyses hint at complex relations between the contamination of water and contaminant accumulation in fish.

Taking into account the mitigating effect of HA and calcium (Bakunov & Makeev, 2004) on the fish contamination with $^{90}$Sr in aqueous solution, we calculated a regression of $K_{RN\_acc} = \dfrac{A_{RN\_fish}}{A_{RN\_diss}}$ on the value $m_{HA\_diss} \cdot m_{Ca}^*$, where the value $A_{RN\_fish}$ [$Bq \cdot kg^{-1}$ w.m.] is the accumulated activity of $^{90}$Sr in fish, $K_{RN\_acc}$ is the coefficient of accumulation of $^{90}$Sr in fish. The value of dissolved calcium $m_{Ca}^*$ is taken relative to the dissolved calcium content in Lake Irtyash $m_{Ca}^* = \dfrac{m_{Ca\_diss}}{m_{Ca\_diss\_Irtyash}}$. The use of the value $m_{Ca}^*$ allowed for considering a competing mechanism between calcium and strontium. The value $m_{Ca}^*$ of the enlarged group varied between 0.2 and 6.3. The high values of $m_{Ca}^*$ correspond to industrial reservoirs. The value $m_{HA\_diss}$ described the averaged content of HA in the water reservoir, and varied from 0.0038 to 0.0225 $kg \cdot m^{-3}$ for the considered enlarged group of reservoirs. The results of the calculated power regression (see Figure 3.6):

$$K_{RN\_acc} = a_8 \cdot (m_{HA\_diss} \cdot m_{Ca}^*)^{b_8} \tag{19}$$

has a high correlation coefficient ($r_8 = 0.85$, n = 18, p < 0.05), where the values $a_8$ and $b_8$ are defined as regression parameters: $a_8 = 0.0007$; $b_8 = -0.9819$.
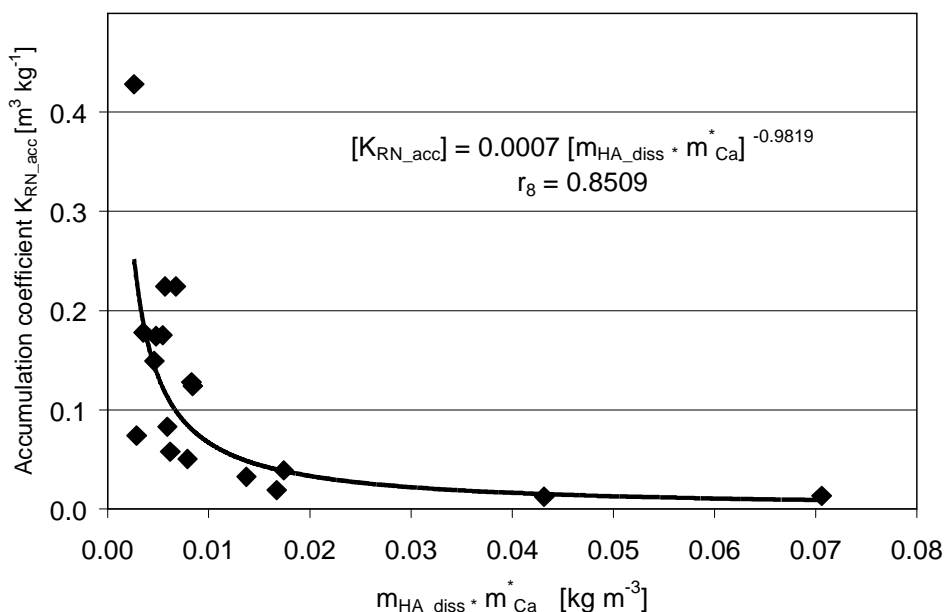
Figure 3.6 - Scatter plot of the ^{90}Sr accumulation coefficient in fish on the product of the content of dissolved HA and relative content of calcium per volume.

As shown in Equation (19), the accumulated activity of ^{90}Sr in fish varies in inverse proportion to the product of the volumetric contents of HA and calcium. An increase in the product of $m_{HA\_diss}$ and $m_{Ca}^*$ causes a decrease of accumulation of contaminant in fish.

To analyze the influence of HA on decreasing in the radionuclide bioavailability, we considered aromaticity of dissolved HS and introduced the aromaticity index (AI) that provides structural information on HS and characterizes the content of aromatic carbon in HS (Perminova et al., 1999; Koch & Dittmar, 2006). In Figure 3.7, the result of regression analyses of $K_{RN\_acc} = \dfrac{A_{RN\_fish}}{A_{RN\_diss}}$ on the value AI is presented. The correlation coefficient $r_9$ is equal to 0.7 at n = 18, p < 0.05. This result hints at significance of the aromaticity of HS in water solution in decreasing in radionuclide bioavailability for fish.

Figure 3.7 - Scatter plot of the $^{90}$Sr accumulation coefficient in fish on the value of the aromaticity index (AI).

Results of an investigation of the influence of HA on accumulation of $^{137}$Cs in fish for the same lakes are presented in Figure 3.8.
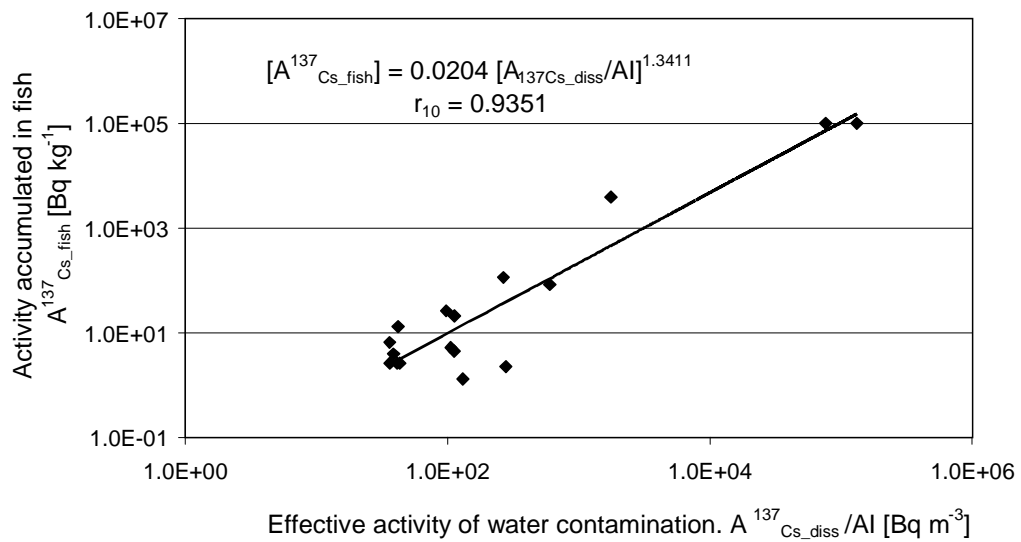


Figure 3.8 – Mitigating effect of HA in the process of radionuclide accumulation

As shown in Figure 3.8, accumulation of $^{137}$Cs in fish depends on the value $\dfrac{A_{^{137}Cs\_diss}}{AI}$. It means that

the effect of the influence of contaminated water on fish is attenuated in AI times, and this process

can be described with the same descriptor $\dfrac{K^{-1}_{^{137}Cs\_acc}}{m_{HA\_diss}}$.

To estimate the influence of the uncertainty of the initial data on the calculated results (Figures 3.6
– 3.8), a statistical analysis using T-statistics was carried out. At the significance level $p < 0.05$, the
confidential intervals of regression parameters $a_8 = 0.0007$ and $b_8 = -0.9819$ ($n_8 = 18$) correspond to
(0.00013; 0.0033) and (-1.3581; -0.6658); $a_9 = 14.884$ and $b_9 = -4.763$ ($n_9 = 18$) correspond to
(5.095; 44.330) and (-7.580; -1.960), and $a_{10} = 0.0204$ and $b_{10} = 1.341$ ($n_{10} = 17$) correspond to
(0.0040; 0.1100) and (1.060; 1.620).

# 3.4 Modelling of the key factors of remediation effect of humic substances

## 3.4.1 Aromaticity index as a key factor of remediation effect of humic substances in the contaminated water reservoir

To analyze the influence of HA on decreasing in the radionuclide bioavailability, we considered
aromaticity of dissolved HS and introduced the aromaticity index (AI) that provides structural
information on HS and characterizes the content of aromatic carbon in HS (Perminova et al., 1999;

Koch & Dittmar, 2006). In Figure 3.7, the result of regression analyses of $K_{RN\_acc} = \dfrac{A_{RN\_fish}}{A_{RN\_diss}}$ on the

value AI is presented. The correlation coefficient $r_9$ is equal to 0.7 at $n = 18$, $p < 0.05$. This result
hints at significance of the aromaticity of HS in water solution in decreasing in radionuclide
bioavailability for fish.

## 3.4.2 Attenuation of water contamination influenced by humic substances

Our attempt to estimate a remediation effect of HA is based on investigation of mediating action of HA in both processes of radionuclide accumulation by solid phase and in fish. Both processes are examined only for $^{90}$Sr. The accumulation of radionuclides by solids are calculated for $^{90}$Sr, $^{137}$Cs, sum of uranium isotopes $^{235}$U, $^{238}$U and sum of plutonium isotopes $^{239}$Pu, $^{240}$Pu. Developing our results obtained in (Aleksandrova e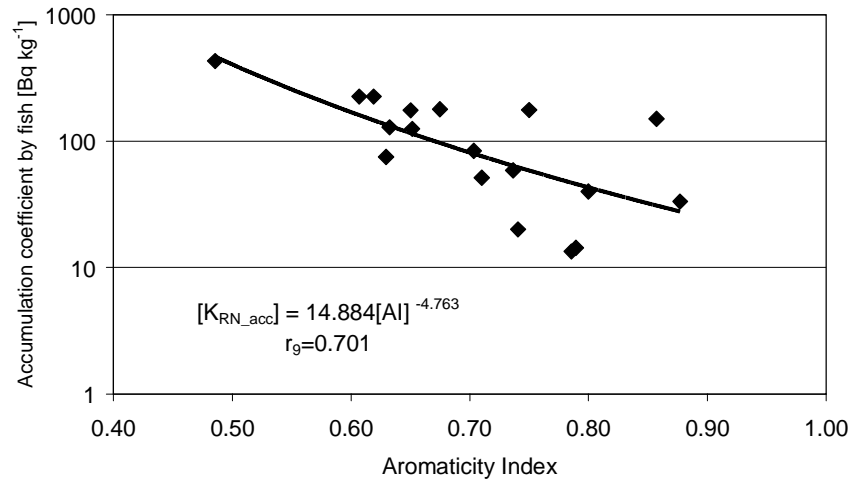t al., 2008) for Old swamp, we proved in the case of Kisliy canal that the operating factor of radionuclide binding to solid phase in surface water reservoirs is the

value $\dfrac{K_{d\_RN}}{m^{*}_{HA\_tot}}$, where $m^{*}_{HA\_sorb} = \alpha_{HA\_sorb} \cdot m^{*}_{HA\_tot}$; $m^{*}_{HA\_tot}$ is the total (adsorbed and dissolved)

volumetric content of HA taken relative to the upper mixed water layer as taken for $m^{*}_{HA\_sorb}$;

$\alpha_{HA\_sorb}$ is the partition coefficient of HA in water solution. Thus, the partitioning of radionuclides

is influenced by the volumetric content of HA at any location of water reservoir. Increasing of

$m^{*}_{HA\_tot}$ results in decrease of contamination of water. Therefore, the remediation effect of the

contaminated water reservoir can be estimated with the following attenuation factor:

$$\theta_{water} = \frac{A_{RN\_tot}}{A_{RN\_diss}} = a_j \cdot m^{*}_{HA\_sorb} / s^{b^{*}_j} + 1, \ \ j = 5; 7 \tag{20}$$

The factor $\theta_{water}$ shows a degree of water remediation. Decreasing $\theta_{water}$ means an increase of contamination of water.

## 3.4.3 Decreasing in radionuclide bioavailability influenced by humic substances

The estimation of protective action of HA in respect to fish in the contaminated water reservoir concludes from equation (19):

$$\frac{K_{RN\_acc}^{-1}}{m_{HA\_diss}} \cong \frac{m_{Ca}^*}{a_8}, \, a_8 > 0, \, b_8 = -0.9819 \cong -1. \tag{21}$$

In equation (21), the inverse of the coefficient of radionuclide accumulation in fish the value $K_{RN\_acc}^{-1}$ $[m^{-3} \cdot kg^1]$ normalized to the value $m_{HA\_diss}$ $[kg \cdot m^{-3}]$ might be hold constant for reservoirs with the same volumetric content of calcium. Thus, the value $\dfrac{K_{RN\_acc}^{-1}}{m_{HA\_diss}}$ can be considered as a significant factor (descriptor) of protective function of HA. It shows that increasing of $m_{HA\_diss}$ results in a decrease in fish contamination.

## 3.4.4 Modelling of remediation effect of humic substances

This natural remediation influenced by HA includes physical, chemical and biological phenomena, and is due to the wide spectrum of properties of HA. The regression analyses allowed for defining descriptors of both considered processes: $\dfrac{K_{d\_RN}}{m_{HA\_sorb}^*}$ and $\dfrac{K_{RN\_acc}^{-1}}{m_{HA\_diss}}$. The descriptor described radionuclide accumulation by solids was also supposed by Perminova & Hatfield (2005) and Perminova et al. (2006). In our study of Kisliy canal, the attenuation factor of water contamination of $^{90}$Sr was proportional to $m_{HA\_sorb}^*$ (see equation 20), and the mitigation factor of accumulation of $^{90}$Sr in fish was proportional to $\sim m_{HA\_diss}^{0.9819}$ times (see equation 19). As shown by our recent investigation in accordance to $^{137}$Cs for the same lakes, the $^{137}$Cs accumulation in fish is also defined by the descriptor $\dfrac{K_{^{137}Cs\_acc}^{-1}}{m_{HA\_diss}}$. In the case with $^{137}$Cs, we calculated the effective value of the water contamination activity: $\dfrac{A_{^{137}Cs\_diss}}{AI}$, and found that accumulation of $^{137}$Cs in fish $A_{^{137}Cs\_fish}$ depends proportionally on the value of $\dfrac{A_{^{137}Cs\_diss}}{AI}$. However to understand these effects, we need to concern the influence of aromatic carbon of HA on the considered processes, and point at high significance of the interaction between HA and water as solvent. The content of aromatic carbon is an important property of HA in the processes of radionuclide binding to solids and decreasing of bioavailability in water solution. The aromaticity index (AI) of HA in water solution of the considered reservoirs is about 0.49 – 0.88 that points at a more condensed aromatic structure of HA. At high level of the value AI, the degree of hydrophobic interaction between HA and water as

solvent is significant to push out complexes with HA to heterogeneous surfaces, to other hydrophobic organic molecules or to promote further combining of HA complexes. On the one hand, significant hydrophobic interaction provides binding of radionuclides to solids in water solution. On the other hand under condition of increasing of the volumetric content of HA in aqueous solution, these complexes reached the critical value of mass, and are converted into colloidal form. Possibly, this conversion is connected with degeneration of the portion of free protons ($H^+$) in solution and can be described and calculated with the quantum-statistical distribution of Fermi-Dirac applied to protons. Being colloidal particles, they become non-bioavailable for fish contamination through gills at its breathing in water solution. There are several pathways of accumulation of strontium in fish: gills at breathing in water solution, adsorption by scales, and via the gastrointestinal tract through swallowing water with dissolved radionuclides and contaminated plankton. The investigation by Ilyenko (1980) showed that for fish the main pathway of strontium intake is through gills into the blood system, and then through the blood system, the accumulation of radionuclide in different tissues takes place. Possibly, this non-bioavailability is connected with a change in electrical status of the complex from multi-pole molecule complex to charged micelle. As shown by Fridrichsberg (1984), proteins of the membrane of gill cells lose $H^+$ via dissociation of the carboxyl functionalities $RCOO^-$ - $H^+$, prevailing at pH > 4.7, and protein molecules become charged negatively. Thus, negatively charged micelles are influenced by the electrostatic repulsion from the membrane. Our assumption of an influence of aromaticity of HA on strontium accumulation in fish is based on investigations of Perminova et al. (1999), Perminova et al. (2005), Giesy et al. (1983), Hongve et al. (1980).

In the industrial reservoirs, the protective function of HA in respect to ichthyofauna is restricted by the content of nitrate and sulphate anions in water solution that accounts to 10.5 $kg \cdot m^{-3}$ in Karachay and 1.8 $kg \cdot m^{-3}$ in Old swamp (Aleksandrova et al., 2008), and exceeds a lethal dose for fish.

## 3.5 Discussions

The remediation effect of HS in several surface water reservoirs presented in this thesis was investigated and quantified. As shown in Chapter 3, the attenuation of the contamination of water and contaminant accumulation in fish deals with the volumetric content of HA $m^*_{HA\_tot}$ in the surface water reservoir. This natural remediation influenced by HS includes physical, chemical and biological phenomena, and is due to the wide spectrum of properties of HS. The regression analyses

allowed for defining descriptors of both considered processes: $\dfrac{K_{d\_RN}}{m^{*}_{HA\_sorb}}$ and $\dfrac{K^{-1}_{RN\_acc}}{m_{HA\_diss}}$. The factor

$\dfrac{K_{d\_RN}}{m^{*}_{HA\_sorb}}$ was also suggested by Perminova & Hatfield (2005) and Perminova et al. (2006). In our

study of Kisliy canal, the attenuation factor of water contamination of $^{90}$Sr was proportional to

$m^{*}_{HA\_sorb}$ (see equation 20), and the mitigation factor of accumulation of $^{90}$Sr in fish was

proportional to $\sim m^{0.9819}_{HA\_diss}$ times (see equation 19). As shown by the investigation in accordance to

$^{137}$Cs for the same lakes, the $^{137}$Cs accumulation in fish is also defined by the descriptor $\dfrac{K^{-1}_{^{137}Cs\_acc}}{m_{HA\_diss}}$ .

In this case, the effective value of the water contamination activity is calculated as

follows: $\dfrac{A_{^{137}Cs\_diss}}{AI}$ . It shows that accumulation of $^{137}$Cs in fish $A_{^{137}Cs\_fish}$ depends proportionally on

the value $\dfrac{A_{^{137}Cs\_diss}}{AI}$ . Therefore, increasing of the part of aromatic carbon in HS molecules leads to

increase in AI, and in turn, results in decreasing of the effective value of dissolved contamination.

However to understand these effects, one needs to concern the influence of aromatic carbon of HS

on the considered processes, and point at high significance of the interaction between HS and water

as solvent. The content of aromatic carbon is an important property of HS in the processes of

radionuclide binding to solids and decreasing of their bioavailability in water solution. In the

considered reservoirs, the aromaticity index (AI) of HS in water solution varies from 0.49 to 0.88

that point at a more condensed aromatic structure of HS. At high level of the value AI, the degree of

hydrophobic interaction between HS and water as solvent is significant to push out complexes with

HS to heterogeneous surfaces, to other hydrophobic organic molecules or to promote further

combining of HS complexes. On the one hand, it results in the significant hydrophobic interaction

that provides binding of radionuclides to solids in water solution. On the other hand under condition

of increasing of the volumetric content of HS in aqueous solution, these complexes reached the

critical value of molecular mass are converted into micelle form. Being colloidal particles,

complexes of HS with radionuclides are likely to become non-bioavailable for fish contamination

Possibly, this non-bioavailability is connected with a change in electrical status of the complex from

multi-pole molecule complex to charged micelle. Negatively charged micelles are influenced by the

electrostatic repulsion from the membrane. At higher value of AI, the transformation of multi-pole

molecules is likely to start for the less molecular mass of HS. This assumption of an influence of

aromaticity of HS on $^{90}$Sr and $^{137}$Cs accumulation in fish is based on investigations of Perminova et

al. (1999), Perminova et al. (2006), Giesy et al. (1983), Hongve et al. (1980). The theoretical interpretation of these results will be presented in Chapter 4.

In the industrial reservoirs, the protective function of HS in respect to ichthyofauna is usually restricted by the content of nitrate and sulphate anions in water solution that accounts to 10.5 $kg \cdot m^{-3}$ in Karachay and 1.8 $kg \cdot m^{-3}$ in Old swamp (Aleksandrova et al., 2008), and exceeds a lethal dose for fish.

The quantitative estimation of natural remediation of water via HA and decreasing of the radionuclide accumulation in fish can be used to develop the concept "designer-humics" and production humic materials that remediate a water medium with higher degree. This concept is well developed in respect to polycyclic aromatic hydrocarbons (PAH). The fate of PAH released into the environment is affected by HS, and it is connected significantly with diverse reactivity and aromaticity of HS.

The remediation effect of HS revealed in respect to heavy metals, pesticides, organometallic components, petroleum hydrocarbons, chlorinated hydrocarbons and polyaromatic hydrocarbons (Perminova & Kulikova, 2008) is described mostly qualitatively. This thesis presents the calculated quantitative estimations of the remediation effect and protective function of HA that could constitute a scientific basis to calculate risk to fresh water biota in contaminated surface water reservoirs, and lead to a better understanding of the biospherical circle of radionuclides in the environment and the role of HS in this process.

# Chapter 4

# Summary and Conclusions

This thesis is based on originating experimental data measured during long-term ecological monitoring of radioactively contaminated surface water reservoirs in South Ural. The contaminated area with contaminated surface waters covers a significant part of South Ural and West Siberia and significantly influences on all compartments of the environment. To understand the processes that govern radionuclide transport, their accumulation by solids, and contaminant accumulation in fresh water biota in reservoirs used as nuclear waste, the present investigations and analyses were carried out, and the descriptors of considered processes were calculated. Using quantitative estimations of humic substance influence on radionuclide fate and transport allows for developing the principles of natural remediation of numerous surface water reservoirs radioactively contaminated.

## 4.1  General interpretation of research results

Summarizing all results of correlation, regression analyses and modeling of remediation effect of humic substances in respect to radionuclide contaminated surface water systems, the following interpretation of considered processes is supposed to be stated. The suggested in the presented thesis approach assumes to take into account quantum statistical effects of interaction of humic substance molecules with other particles.

1.      In surface water systems, the macroscopic effect of interaction between HS and radionuclides is revealed. The local increasing of the HS concentration results in an increase of the

local adsorbed activity of radionuclides. As shown by presented thesis, this phenomenon should be quantified by the modified Henry's sorption law calculated at this work (see equation 16):

$$A_{RN\_sorb} = const \cdot \frac{m_{HA} / s^{1-\alpha_{RN}}}{m_{HA(0)} / s_{(0)}^{1-\alpha_{RN}}} \cdot A_{RN\_diss}$$

Keeping the volumetric content of HA and adsorbing area of mineral surface per volume constant, we obtain the Henry's sorption law in water solution. However, increasing of $m_{HA}$ and *s* with depth increasing is described only with a modification of Henry's sorption law in waste deposits (*e.g.* Equation 16).

2.      In surface water reservoirs, a binding of radionuclides and their compounds to solids is defined first by interaction with HS molecules. HS molecules interact with radionuclides, forming radionuclide humates, and, in turn, are bound to solids. However, HS molecule binds radionuclides and their compounds not only via chemical interaction but also can accumulate them by adsorption layer of micelle granule when it is converted into micelle. Intensive phase transformation of multipolar molecules into micelles with increasing of the HS concentration provides a sharp increase in the bound radioactivity with depth increasing.

3.      Physicochemical properties of HS are defined by the value of hydrophobic interaction between HS molecules and water as solvent. Its strength can be characterized with the aromaticity index (AI) that in fact shows a part of aromatic carbon in HS molecules, and reflects a dual nature of HS with a relation of aromatic to aliphatic carbon. Thus, a solution of HA in water can be considered as unstable dynamic equilibrium. The dynamic equilibrium of FA molecules in water solution is mostly stable. An increasing of HA concentration results in increasing of hydrophobic interaction strength, shifts equilibrium state, and causes development of hydrodynamic instability of a system of HA associates dissolved in water solution. As for the Taylor' hydrodynamic instability, any fluctuation causes a coupling of some HS molecules to minimize their surface. Being too nearly, HS molecules can chemically interact among themselves, forming new HS associates, or bearing out to mineral solid surface. In the case of HS interaction, it leads to increasing of length and mass of some HS molecules. The effect of multipolar molecule phase transformation into micelle takes place in the water solution when $m_{HS}$ reaches and exceeds the defined critical value $m_{HS\_critical}$ of HS concentration.

4.      Phase transformation of multi-pole molecule of HS into a charged micelle and an additional capture of radionuclides by its adsorption layer is assumed in this work to be explained, considering each molecule of HS as a quantum object and protons (H$^+$) as a "gas", following the Fermi – Dirac statistics. At the critical value $m_{HS\_critical}$, a quantum statistical effect of HS molecules takes place.

An enlargement of similar molecule chains corresponds to effect of decreasing in temperature that, in turn, influences on the statistical Fermi-Dirac distribution of protons ($H^+$) (Figure 4.1). A part of the protons ($H^+$) degenerates. Now, these protons are located in the adsorption layer of HS micelle. Not degenerated protons are shifted into the diffusive layer of micelle. The spatial separation of protons results in formation of a double electrical layer. The increasing of HS concentration with increase of reservoir depth leads to an extensive conversion of multi-pole HS molecules into micelles with capture by the micelle adsorption layer of not only degenerated protons but also radionuclides and their compounds that can be described as fermions.
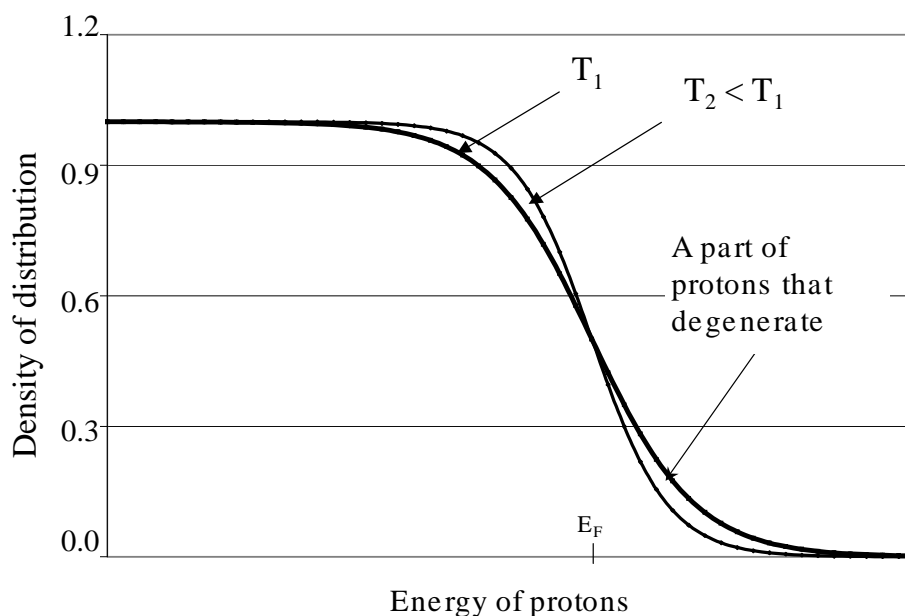


Figure 4.1 - A change of statistical Fermi-Dirac distribution of protons ($H^+$) with increasing of HS concentration in the water solution

Described process occurs extensively in the nepheloid layer. These micelles are fostered to bind to mineral solids in the water solution. Partially, it is connected with hydrophobic interaction between HS molecules and water as a solvent, and partially, with an effect of the curvature of the mineral particles surface. As a result, a significant increase of adsorbed radionuclides with increasing depth in the nepheloid layer is observed. At the boundary between the nepheloid layer and consolidated

sediments, coagulation starts. Micelles lose their adsorption layers containing radionuclides, and are converted into coagulants. It corresponds to a decrease in the adsorbed radioactivity in the lower part of the nepheloid layer.

5.      One should to mark that the observed phenomenon is defined by the behavior of the single ensemble of HS associates, micelles, and coagulants and can be quantified as follows. The distribution of HS particles having a different microphase state can be described, using Gibbs' statistics for a molecule and associate ensemble. Introducing a distribution function $f(m_{HS})$ of masses $m_{HS}$ of HS molecules and associates, and fixing the critical values of mass $m_{HS\_critical\_micelle}$ for phase transformation of HS molecules into micelle and $m_{HS\_critical\_coagulant}$ for conversion of micelle into coagulant, the portions of multi-pole molecules, micelles and coagulated particles are calculated according to the following equations (Figure 4.2):

$$N_{multi-pole} = \int_{0}^{m_{HS\_critical\_micelle}} f(m_{HS})dm_{HS} \tag{15}$$

$$N_{micelle} = \int_{m_{HS\_critical\_micelle}}^{m_{HS\_critical\_coagulant}} f(m_{HS})dm_{HS} ; \tag{16}$$

$$N_{coagulant} = \int_{m_{HS\_critical\_coagulant}}^{M_{HS}} f(m_{HS})dm_{HS} . \tag{17}$$

**Distribution function f(m$_{HS}$)**
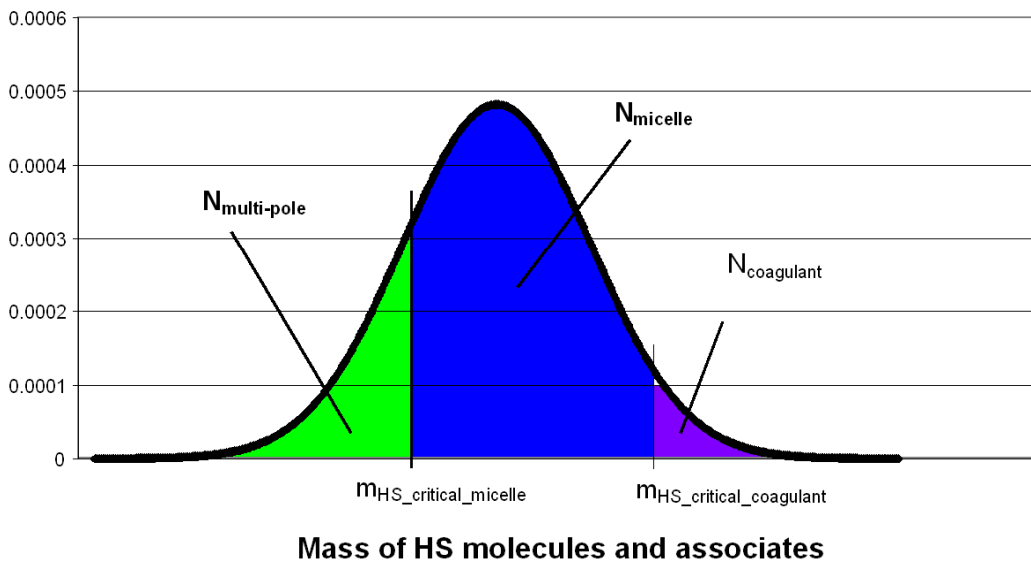


Figure 4.2 – Statistical distribution of an ensemble of HS molecules and associates

Increasing of the concentration of HS in the solution results in change of distribution (*e.g.* distribution shifts to the right), with the portion of multi-pole molecules of HS being decreased

from $\displaystyle\int_0^{m_{HS\_critical\_micelle}} f_{original}(m_{HS})dm_{HS}$ to $\displaystyle\int_0^{m_{HS\_critical\_micelle}} f_{after}(m_{HS})dm_{HS}$ that geometrical corresponds to change

from marked areas A $\cup$ B to marked area B (Figure 4.3).

### Distribution function f(m$_{HS}$)
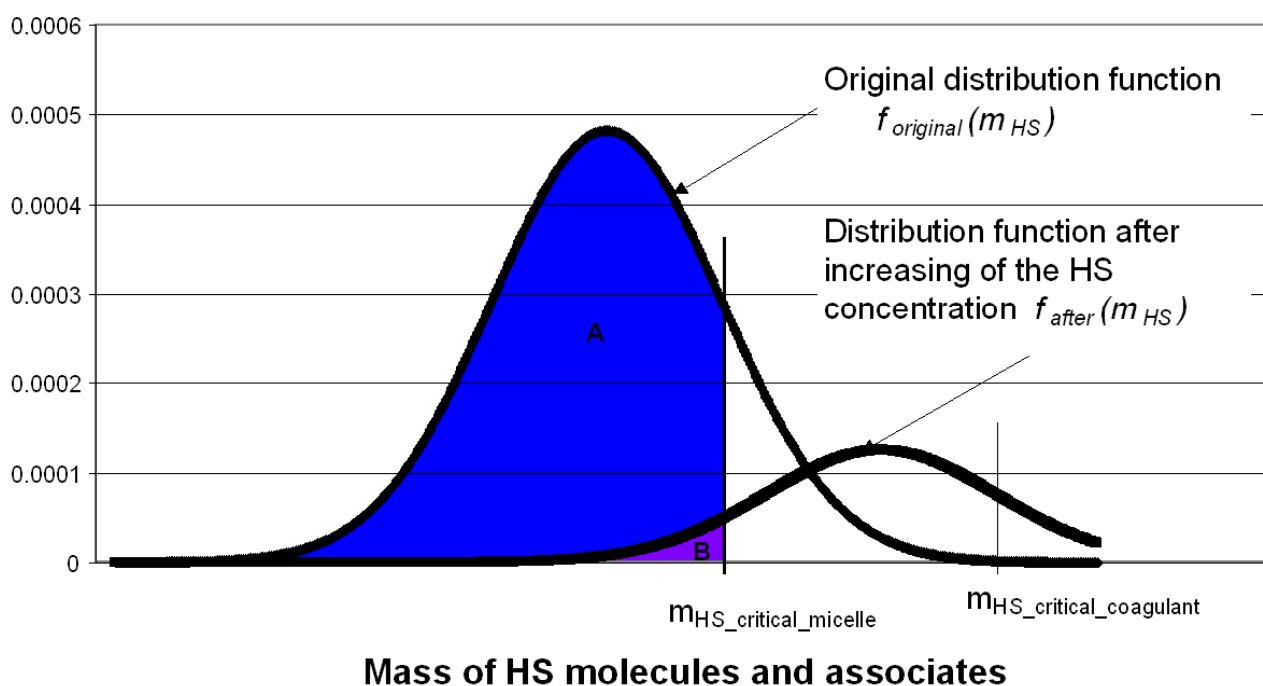


Figure 4.3 - Change of the distribution function as result of increasing of the HS concentration in water solution with increasing depth

Thus, the phase transformation of the significant portion of multi-pole molecules of HS into micelles containing radionuclides as bound chemically and captured by adsorption layer of micelle granule provides a sharp increase of adsorbed radionuclides in the nepheloid layer of the water reservoir with increasing depth.

6.      Interpretation of decrease in radionuclide bioavailability with increasing HS concentration is based on understanding of the main pathway of radionuclide intake and the membrane structure of fish gills. One should mark that described below process takes place under certain conditions in

surface water reservoirs with pH>5. The main pathway of $^{90}$Sr and $^{137}$Cs intake is through gills of fish at its breathing in water solution. The membrane of gill cells includes lipids and proteins. Surface activity of protein depends on the value pH of solution medium. At pH>4.7 mostly, carboxyl functionalities $RCOO^- - H^+$ dissociate. H$^+$ is separated off protein molecule, and protein molecule is charged negatively. Micelles are mostly charged negatively too. Thus, HS micelles containing radionuclides and their compounds are influenced by electrostatic repulsion from membrane. As a result, radionuclides bound to HS micelles become non bioavailable for fish.

A concept of remediation action of HS in surface water systems used as deposits of nuclear waste or contaminated during accidents was further developed, investigated. The concept defines an attenuation of water contamination of radionuclides and the HS mitigating activity in the system "fresh water biota – radioactively contaminated surface water". The first process leads to radionulide immobilization, restricted by the presence of accessible adsorbing sites on the mineral surface. The second action promotes decreasing of radionuclide bioavailability for fish. This behavior of HS can be considered as protective function, and is due to, first, a very diverse reactivity of HS and different nature of their molecules, and, second, the formation of a single ensemble of multi-pole HS molecules, micelles of HS, and HS coagulants. The remediation effect was quantified produced by HS with the attenuation factor, and provided the significant factors (descriptors) $\dfrac{K_{d\_RN}}{m^*_{HS\_sorb}}$ for radionuclide accumulation by solids and $\dfrac{K^{-1}_{RN\_acc}}{m_{HS\_diss}}$ in fish.

## 4.2   Conclusions and outlook

Ecosystems are dynamic and possess innate, yet finite, abilities to adapt to environmental conditions and changes. For many environmental contaminants, the potential risks they pose to ecosystems decrease over time because of changes in physical, chemical and biological properties and the natural assimilative abilities of the environment. The natural remediation characterizes a complex of processes, such natural attenuation, passive remediation, intrinsic remediation, bioattenuation. Specifically, natural remediation is defined as a sum of the nanoanthropogenic physical, chemical and biological processes that reduce potential risk to the ecosystems by altering, the concentration, mobility, toxicity, and /or bioavailability of contaminants. In addition, biological and ecological responses to contamination may alter the potential impact of contaminants, and thus

also contribute to the natural remediation phenomenon. Radionuclides are unique among environmental contaminants. Some radionuclides have a long decay time, and will dangerous in thousand years, being in the environment. Chemical transformation does't change this effect. Their natural spontaneous decay is accompanied by release of energy proportional to the mass of the particles released. This energy is in the form of ionizing radiation. Ionizing radiation has enough energy to change the atomic balance of substances (e.g., tissues) through which it moves. These changes are manifested in different ways and can cause several types of damage at all biological levels. Scientific inquiry into the biological impacts of radionuclides has focused primarily on human receptors, with much less attenuation paid to ecological effect. Those environmental studies usually that have been conducted generally fall into 2 categories: those that monitor the concentrations of radionuclides in environmental media and those that investigate the chemistry of radionuclides with respect to their fate and transport in the environment. This thesis extents methods and tools of correlation and regression analyses on measured data. In this thesis, not only the mechanism of radionuclide partitioning between solid and liquid phases are studied also but the quantum-statistical approach is applied to describe observes phenomena and calculated results. A description of a set of HS associates as unique statistical ensemble was supposed, and applied to understand macroscopic effect of interaction of humic substances, radionuclides $^{90}Sr$, $^{137}Cs$, isotopes of uranium $^{235}U$, $^{238}U$ and plutonium $^{239}Pu$, $^{240}Pu$, and solids in water solution. This approach demonstrates that the aromaticity index reflects the strength of hydrophobic interaction of HS associates with water, with an increase of HS concentration in the water solution resulting in increase its strength and enlargement of HS molecules, and HS multi-pole conversion into micelles. Being as a micelle, HS particle keeps radionuclides not only via chemical bonds but also by adsorption layer of micelle granule. First, these effects are provided by basic properties of HS molecules to possess high dispersity and high functionality. Second in this work, a collective effect of interaction between microparticles and nanoparticles was taken into account.

In this thesis, the key processes of interaction of HS with radionuclides and solids were considered. The quantitative estimation of attenuation effect of humic substances in respect to radionuclides in the waste disposal can help to find himics (e.g., "humic-designers") with optimal properties to immobilize radionuclide in sediments, and provide the chemical conditions to prevent a further radionuclide transport into environmental. The developed models help further consider the kinetic of sorption processes by mineral solids in water solution to define the key parameters of mineral surface that must well keep radionuclides, radionuclide humates, and their compounds. Application of quantum approach to problems of colloidal chemistry allows for understanding a lot of mechanisms of interactions between nano-particles. Use of methods of dispersion systems is

expected to help to solve a lot of problems connected with the contaminants sorption and transport not only in the aquatic environment also but in the porous medium modeled the porous medium as dispersion system.

Presented physicochemical modelling is accomplished for the first time, and poses only the first conclusions of new theory 'An extension of theory of aggregative states on condensed media" that is currently developed.

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