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STUDY OF TRITIUM MIGRATION AND RETENTION MECHANISMS IN THE GEOLOGICAL ENVIRONMENT (BY THE EXAMPLE OF THE KYIV RADIOACTIVE WASTE STORAGE FACILITY)

Radioactive waste storage facilities (RWSF) are a potential source of tritium in the biosphere. Engineered concrete constructions are not sufficiently reliable forasmuch as water leaks contaminated with tritium from the storage facilities into the geological environment has been detected. The barrier properties of the natural environment at the storage sites are determined by the ability to absorb and retain heavy isotopes of hydrogen during a considerable period of time and thus exclude its circulation in the biosphere. Various elements of the natural ecosystem take part in the absorption of tritium – the geological environment, soil organic matter, annual and perennial vegetation, micro- and macrobiota. A certain part of tritium in the gaseous and aerosol form is released into the air. The highest concentrations of tritium are recorded in the area close to the concrete radioactive waste (RW) storage facilities, where the vapor-gas emanation plume is least dispersed. With distance from the storage facilities, the tritium concentration in the soil humus layer significantly decreases due to the spatial dispersion of the tritium in the atmospheric plume. Tritium from the air enters the soil with the atmospheric precipitation and is partially retained in the humified layer of the soil. Most of the tritium from the atmospheric precipitation is transported by the vertical infiltration flow through the sedimentary layers represented by loess sandy loams and loams, where it is finally retained. In the area close to RWSFs, the concentration of heavy hydrogen isotope in pore, interstitial and film water (1 fraction) is up to 87 % of its total content in an elementary block. In the more tightly bound forms (2 and 3 fractions), it is 9 % and 4 %, respectively. Farther from the RW storage facilities in the predominant air flow direction, the tritium concentration in free water decreases to 75 %. In this area, more intensive redistribution of tritium between the structural sites is observed. At the more distant monitoring points (wells), from 25 % to 37 % of the total tritium amount in the soils is retained in more tightly bound forms in the structure of rock-forming, mainly clay minerals.

Key words: radioactive waste, tritium, clay minerals, natural barriers, hydrogen.

Safe storage of radioactive waste (RW), ionizing radiation sources and biological materials which contain significant amounts of tritium is an important task to prevent tritium circulation in natural and technogenic biogeosystems. To solve this problem, radioactive waste storage facilities (RWSF) for high-, intermediate- and low-level waste have been constructed.

Such objects are a powerful potential source of tritium in the biosphere. In RW storage facilities, significant amount of radioactive waste of various origin with high tritium content is deposited. Today in the world, the storage facilities for low- and intermediate-level radioactive waste (LLW and ILW) range from the surface facilities to engineered geological repositories. During the operation of the RW storage facilities, the countries that use various options for radioactive waste disposal faced significant problems. It turned out that the concrete engineered constructions are not sufficiently reliable, forasmuch as tritium contaminated water leaks from the storage facilities into the geological environment has been detected. To solve the problem of tritium extraction from

the hydrogeochemical migration cycle, it is necessary to have sufficient initial data on the mechanisms of tritium migration from the surface RW storage facilities and to take into account the properties of the geological media as the last barrier on the way of possible hydrogeofiltration release of radionuclides outside the engineered barrier structures.

The retaining properties of the natural environment at the locations of the tritium-containing radioactive waste storage facilities are determined by the ability to absorb and retain this heavy hydrogen isotope during a considerable time period and thus prevent its circulation in the biosphere. Taking into account the relatively short half-life of tritium, long-term deposition in the environment results in the decrease in its absolute concentration. Various elements of the natural ecosystem take part in the absorption of tritium – the geological environment, soil organic matter, annual and perennial vegetation, micro- and macrobiota. A certain amount of tritium in the gaseous and aerosol form is released into the air. Thus, the comprehensive assessment of the barrier

properties of the natural environment requires using a differential approach, taking into account the fact that the nature and capacity of tritium absorption and retention in various elements of the environment are different.

The aim of the work is to determine the mechanisms of migration and retention of tritium in the geological environment as the last barrier for tritium hydrogeofiltration release into the environment from the radioactive waste storage facilities.

Materials and methods.

To assess the protective barrier properties of the top layer of a soil profile in the area influenced by the Kyiv RWSF (KRWSF), soil samples were taken from pits (T. 1

– T. 20) at the depth of 1.2-1.5 m, located in 3 profiles within the sanitary protection zone (SPZ), starting from the KRWSF fence to the bottom of the slope (Fig. 1). Samples were taken from soil sections (pits) at intervals of 0-25 cm (layer 1, humified podzolized sandy loam and loam); 25-60 cm (layer 2, sandy loam and loam of the upper part of the sections); 60-120 and 120-150 cm (layers 3 and 4, sandy loam and loam of the lower parts of the sections). To assess the possible release of the hydrogeofiltration release of tritium into the aquifer discharge zone (sands of the Novopetrivsk Formation), soil samples were taken at monitoring points OC 1 ÷ OC 8 (Fig. 2.1), located along the bottom of the slope (contour profile) composed of Kyiv marl suite.

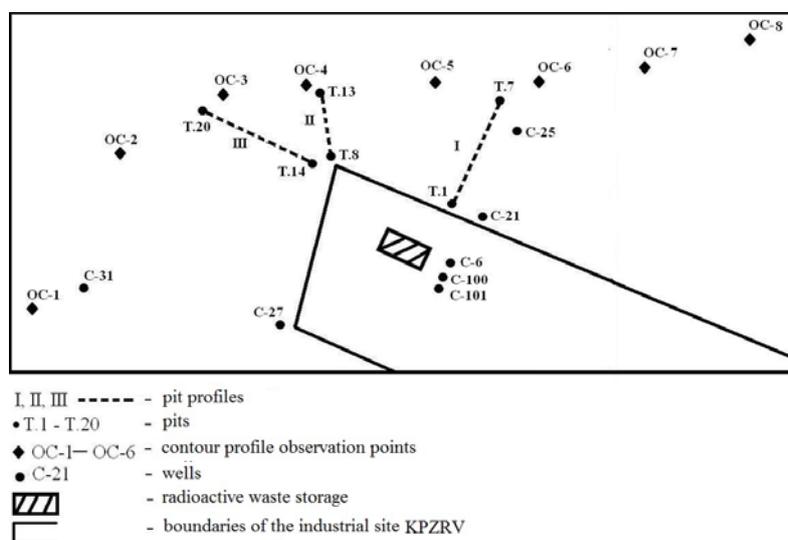


Рис. 1 Схема відбору проб ґрунтів в СЗЗ КПЗРВ.

Fig. 1 Scheme of soil sampling in SPZ KRWSF

In addition to monitoring of the tritium distribution in the soil surface layers, tritium deposition was studied in the deeper layers of the sedimentary strata (down to the depth of 4 m from the surface) using wells. The wells were drilled along the northeastern (C-21, C-25) and northwestern (C-27, C-31) hydrogeomigration tritium flows (Fig. 1). The wells C-21 and C-27 crossed the upper parts of the sedimentary strata, which supplemented data for the assessment of the barrier properties of the humus layer obtained from the pits, and allowed to determine the retaining properties of the loess sandy loam and loam directly underlying this layer. The wells C-25 and C-31 were drilled to obtain material to determine the tritium content in the aquifer at the interface with the impermeable Kyiv marl suite [2].

From the soil samples, water extracts corresponding to pore and surface adsorbed water (fraction 1; extraction temperature 16-120 °C), hydrated water and interlayer water of clay minerals (fraction 2; 120-300 °C) and structural OH groups of clay minerals (fraction 3; 450-750 °C) were prepared. After purification from organic

impurities (oxidation with an anhydrous oxidizing agent) and distillation, the water extracts were mixed with a Hi Sife 3 Wallac scintillator in a ratio of 8:12. The tritium content in the emulsions was determined by a liquid low-background scintillation β -spectrometer Quantulus 1220 (LKW Wallac).

Assessment of the barrier properties of the upper layer of the soil profile.

The results of determining the tritium content in the water extracts from these samples at 16-120 °C are given in Tables 1 and 2.

Dependence of the tritium content on the spatial location of soil samples is shown in Fig. 2.2 and 2.3. Tritium from the steam-gas releases outside the RW storage facilities according to the physicochemical processes occurring in the air entered the soil surface with atmospheric precipitation. The higher humus saturation of the surface soil section (spacing 0-25 cm) provided more efficient immobilization of tritium (Fig. 2).

Таблиця 1. Питома активність тритію у ґрунтових перегінах шурфів, Бк×дм⁻³ [2].
Table 1. Specific activity of tritium in soil sections of pits, Bq·dm⁻³ [2].

Profile N	Pit N	Layers and intervals of soil sections (cm)			
		1 (0 – 25)	2 (25 – 60)	3 (60 – 120)	4 (120 – 150)
1	1	19194	7920	9290	
1	2	8200	4750	4000	
1	3	3430	2850	345	
1	4	122	147	178	
1	5	136	345	1490	
1	6	845	1570	700	
1	7	644	810	164	
2	8	1940	146	130	
2	9	690	1100	138	
2	10	530	615	162	
2	11	460	560	137	107
2	12	74	75	106	79
2	13	306	367	457	373
3	14	1300	2378	1300	
3	15	917	2230	1260	
3	16	930	1470	1300	
3	17	1160	1450	753	
3	18	450	722	574	
3	19	1286	868	520	
3	20	570	870	500	

The highest concentrations of tritium are recorded in the area close to the concrete radioactive waste storage facilities, where the vapor-gas emanation plume is least dispersed (Fig. 2.1, pits 1, 2 of profile 1 and pits 8, 9 of profile 2). Further along the slope, the tritium concentration in the soil humus layer decreases significantly (Fig. 2.2, A, B) due to the spatial dispersion of tritium in the atmospheric plume.

The loess sand and loam layers that lie under the humus-rich soils (layers 2, 3, 4; Table 2.1) are the main geological barrier for the surface hydrogeofiltration flows of tritium. Thus, the layers 3 and 4 almost completely block the vertical migration of tritium in soil sections (Fig. 2, A, B). A decrease in the accumulation of the organic matter in the upper soil layer can probably be explained by the convex shape of the surface relief

(profile 3; Fig. 2, B), compared with the concave shape (profiles 1 and 2). Nonetheless, the tritium from the atmospheric precipitations is efficiently retained in loess sands and loams that occur directly under the humus layer.

Increased concentrations of tritium caused by the hydrogeofiltration flows coming from the unsealed RW storage facilities have been detected along the base of the stream valley slope in the sands of the Novopetrivsk Formation and marls of the Kyiv Formation (Table 2, Fig. 2).

These data indicate that the surface soils at the base of the stream valley slope also partially retained tritium coming from the atmospheric precipitation and hydrogeofiltration flows from radioactive waste storage facilities.

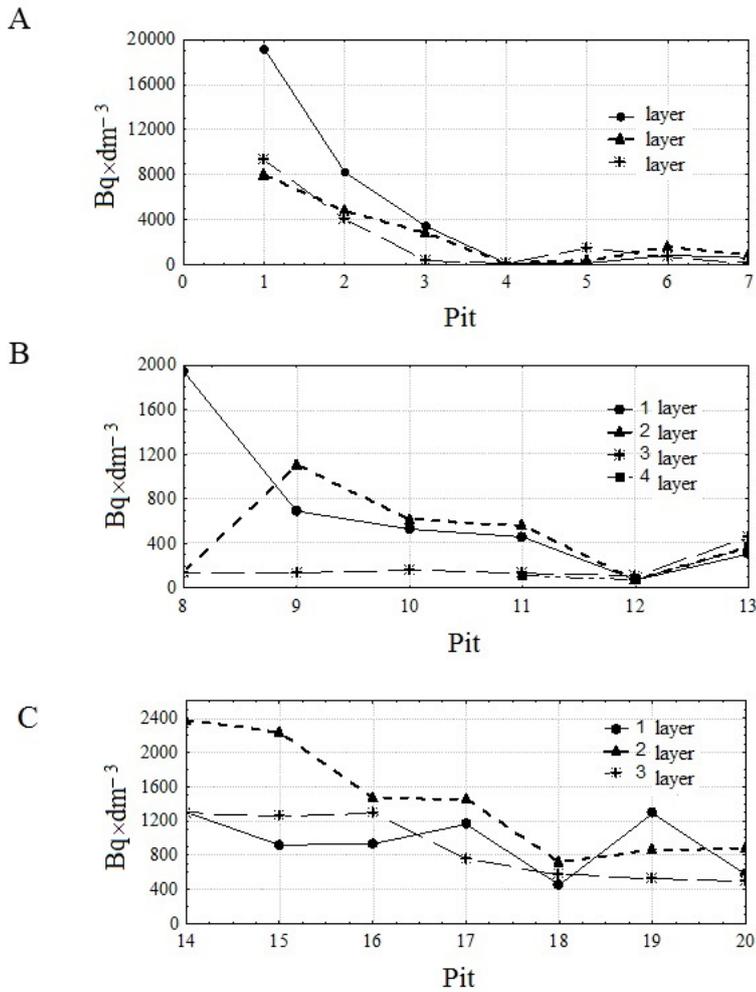


Рис. 2. Депонування тритію в поверхневих шарах ґрунту санітарно-захисної зони КПЗРВ. А - профіль 1, Б - профіль 2, В - профіль 3 (розташування профілів див. рис. 1).

Fig. 2. Deposition of tritium in the soil surface layers in the KRWSF sanitary protection zone. A - profile 1, B - profile 2, C - profile 3 (location of profiles see Fig.1).

Таблиця 2. Питова активність тритію в гумусованих ґрунтах контурного профілю С33 КПЗРВ.

Table 2. Specific activity of tritium in humus-rich soils of the SPZ KRWSF contour profile.

М.р.	10С	20С	30С	40С	50С	60С	70С	80С
$Bq \cdot dm^{-3}$	710	92	520	330	1980	200	593	287

Примітка: Т.с. – точки спостережень.

Note: M.p. – monitoring point

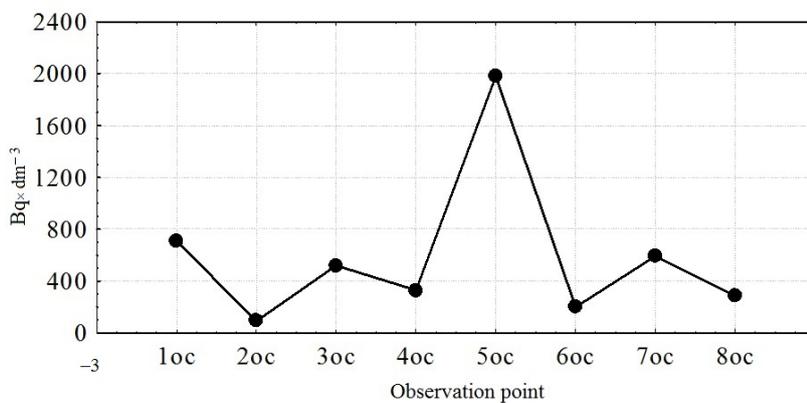


Рис. 3. Питова активність тритію в ґрунтах контурного профілю вздовж підосви схилу С33 КПЗРВ.

Fig. 3. Specific activity of tritium in the soils of the contour profile along the base of slope near SPZ KRWSF

Таблиця 3. Вміст тритію у ґрунтах вертикальних перетинів свердловин.

Table 3. The content of tritium in soils in the vertical sections of wells

Type of soil	Sampling depth, cm	Sample number	Water extract volumes, ml			Tritium specific activity in soil moisture fractions, Bq·dm ⁻³		
			1 fraction	2 fraction	3 fraction	1 fraction	2 fraction	3 fraction
Well 21								
Humus Soil	5	21/1	15.4	6.75	2.12	849	563	575
Humus Soil	25	21/2	7.97	4.1	1.3	283	251	185
Sandy loam	50	21/3	8.43	1.94	0.91	351	180	121
Clay sand	80	21/4a	18.43	2.3	1.4	468	283	343
Loam	160	21/5a	15.05	0.81	1.55	810	753	484
Sand loam	200	21/6a	7.1	1.45	1.41	591	185	105
Clay sand	230	21/7	6.85	2.87	1.53	968	621	262
Clay sand	280	21/8	9.59	2.1	0.82	1003	610	415
Loess loam	330	21/9	13.78	1.55	1.4	1044	474	300
Loess loam	400	21/10	13.03	3.4	1.98	776	329	247
Well 25								
Humus soil	5	25/1	29.35	5.3	1.39	230	245	72
Humus slide rock	25	25/2	14.02	9.54	1.46	130	138	158
Loam	50	25/3	16.8	8.7	1.5	173	96	60
Variegated loam	100	25/4	19.3	8.47	1.5	216	139	60
Silt loam	150	25/5	15.6	8.4	1.0	428	435	420
Wet sandy loam	200	25/6	28.3	11.8	1.4	774	808	432
Damp sandy loam	255	25/7	28.94	13.25	0.85	906	946	506
Sand	300	25/8	6.9	0.78	2.09	445	205	139
Damp mergel	350	25/9	23.76	9.44	1.67	64	46	6
Damp mergel	400	25/10	47.74	10.42	3.51	45	39	14
Well 27								
Humus Soil	5	27/1	28.05	5.8	2.05	458	249	366
Humus sand loam	25	27/2	6.6	0.24	1.97	452	450	363
Humus sand loam	50	27/3	9.08	2.04	1.06	264	370	250
Clay sand	100	27/4	10.27	2.18	1.57	308	327	272
Clay sand	150	27/5	9.24	2.6	1.44	215	197	184
Damp clay sand	200	27/6	13.49	5.47	1.64	268	217	419
Damp clay sand	250	27/7	19.73	7.2	1.8	277	224	326
Damp clay sand	300	27/8	16.31			174		
Loess clayey sand	350	27/9	9.35	3.95	1.7	93	148	283
Loess clayey sand	400	27/10	8.53	6.35	1.72	130	130	65
Well 31								
Humus Soil	5	31/1	14.3	5.6	2.04	175	141	382
Humus Soil	25	31/2	9.76	0.71	0.89	131	605	471
Sand loam	50	31/3	3.86			214		
Silt loam	100	31/4	8	1.4	0.42	179	329	147
Damp sand loam	150	31/5	22.18	7.14	2.94	136	123	146
Damp sand loam	200	31/6	21.33	7.4	2.83	106	83	137
Damp sand loam	250	31/7	31.9	5.81	0.99	106	221	134
Carbonate gley	300	31/8	15.38	8.41	3.84	22	80	117
Carbonate ferruginized gley	350	31/9	27.97	15.25	5.54	73	88	96
Carbonate ferruginized gley	400	31/10	28.5	9.34	5.6	73	88	96

Estimation of barrier properties of the sedimentary stratum in the SPZ KRWSF geological environment.

The distribution of tritium specific activity in vertical sections up to the depth of 4 m is presented in Table 3 and Figure 4 [2].

As it was found in the field studies, tritium extracted from the air comes on the soil surface with atmospheric precipitation and is partially retained in the soil humus layer (Fig. 4, A).

Most of the tritium from the atmospheric precipitation is transported with a vertical infiltration flow through the sedimentary layers represented by loess clayey sands and loams, where it is finally retained. This significantly reduces the specific activity of tritium. A part of the heavy hydrogen isotope infiltrates into the aquifer. While in the vicinity of the radioactive waste storage facility the

specific activity of tritium in the hydrogeofiltration flow reaches $n \times 10^7 \text{ Bq} \cdot \text{m}^{-3}$, in the area of aquifer discharge in the local stream valley slope, it is about $900 \text{ Bq} \cdot \text{m}^{-3}$ (Table 3, well 25, spacing 200-300 cm). Thus, the specific activity of tritium decreases by 4 orders of magnitude during tritium migration with the infiltration flows from the storage facility through the geological environment at KRWSF site.

A slight increase in the tritium concentration to $64 \text{ Bq} \cdot \text{dm}^{-3}$ is observed in the upper part of the local impermeable layer due to water exchange between wet sand loams and wet upper marl layers (Table 3). So, the local impermeable horizon represented by marls and gleys is an efficient barrier for the vertical migration of tritium (Table 3).

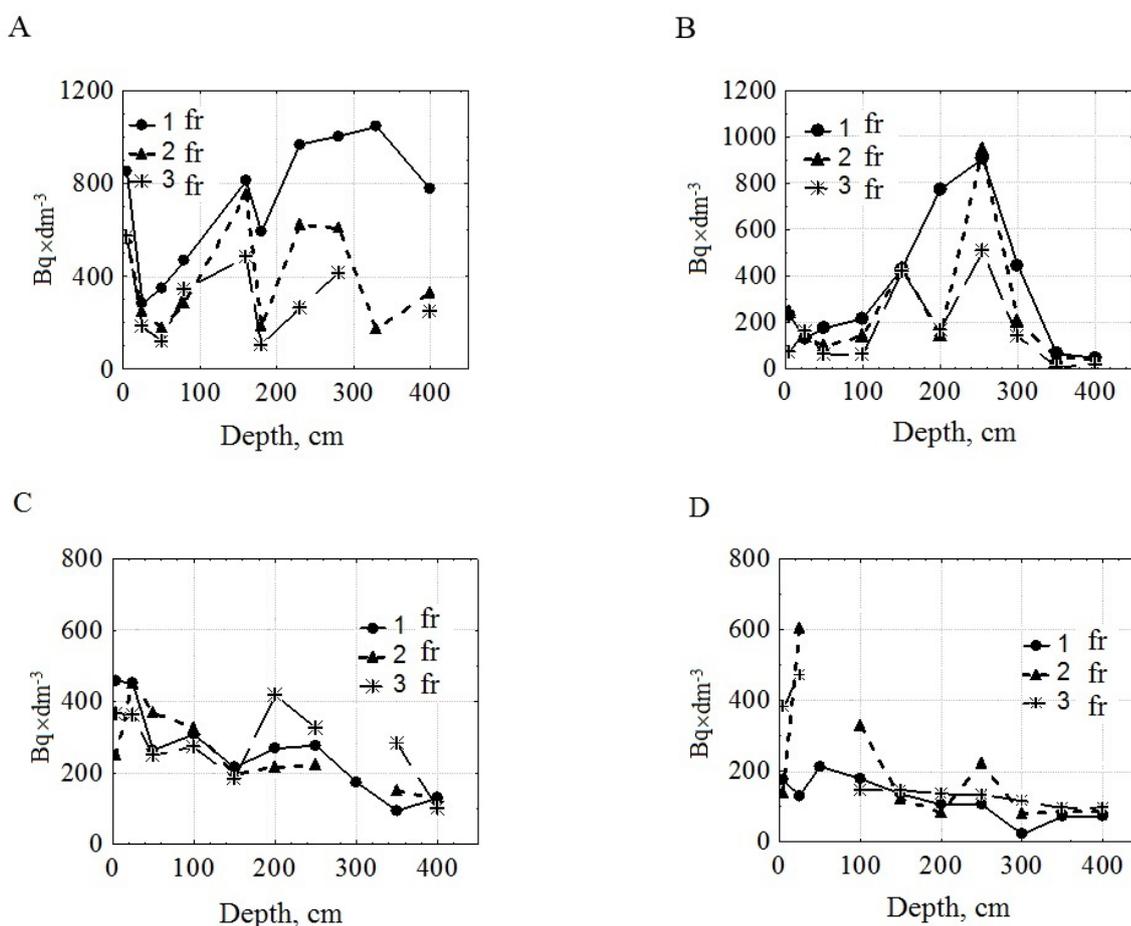


Рис. 4. Розподіл питомої активності тритію у вертикальних перетинах ґрунтів. Свердловини 21 (А); 25 (Б); 27 (В); 31 (Г). Санітарно-захисна зона КПЗРВ.

Fig. 4. Tritium specific activity distribution in vertical soil sections. Wells 21 (A); 25 (B); 27 (B); 31 (D). Sanitary protection zone of KRWSF.

Estimation of the degree of tritium retention in the geological environment.

A more adequate assessment of the geological environment retention properties is the indicator of the specific tritium reserve in unit mass ($\text{Bq} \cdot \text{kg}^{-1}$) or volume

($\text{Bq} \cdot \text{dm}^{-3}$) in soil section components. This approach is based on the methodological recommendations developed by B.A. Polynov and M.A. Glazovskaya for study of the chemical element redistribution processes from the landscape geochemistry standpoint [3, 5]. Indicative

parameters of the geological environment retention properties were calculated within the elementary blocks typical for some parts of the forest landscape at the Kyiv SPZ RWSF. The blocks with the surface area of $0.5 \times 0.5 \text{ m}^2$ and the depth of 4 m (the total volume 1 m^3) were studied. Specific tritium amount was determined separately for each layer of the soil section from the aeration zone, aquifer and impermeable horizons. The water extractions (fractions) corresponding to different structural positions in the mineral sample were examined at different temperatures (Table 4). The tritium amount in each block was calculated from expressions (1) (for 1 kg of soil in each layer) and (2) (for the block as a whole):

$$Q_i^m = A_i \times V_{i,j} \times m_i^{-1} \quad (1)$$

where: Q_i^m – tritium reserve in the mass of the i^{th} layer of the soil section, $\text{Bq} \cdot \text{kg}^{-1}$; A_i – specific tritium activity in the i^{th} layer of the soil section, $\text{Bq} \cdot \text{dm}^{-3}$; $V_{i,j}$ – volume of the j^{th} water extract from the sample of the i^{th} layer of the soil section, dm^{-3} ; m_i – mass of the sample from the i^{th} layer of the soil section, kg.

$$Q_{total} = \sum Q_i^m \times h_i \times S \times \delta \quad (2)$$

where: Q_{total} – total tritium reserve in the elementary block, Bq; h_i – thickness of the i^{th} layer of the soil section, m; S – cross-sectional area of the elementary block, m^2 ; δ – soil density, $\text{kg} \cdot \text{m}^{-3}$.

In the natural-technogenic biogeosystem consisting of the acceptor part of the system and the donor element that as a result of releases from RW storage facilities forms atmospheric and hydrogeofiltration tritium transfer plums, the geological environment is a high capacity heavy hydrogen isotope retention medium. In the area close to the radioactive waste storage facility where the air plume is least dispersed, the atmospheric precipitation contains the highest tritium amount (elementary block C-21; Tables 4 and 5) resulting in higher heavy hydrogen isotope contents in free water – pore, interstitial and film water (1st fraction) – up to 87 % of its total content in the block.

In more strongly bound forms (2 and 3 fractions), 9 % and 4 % are fixed, respectively. Farther from the radioactive waste storage facilities in the predominant direction of air flow, the concentration of tritium in free water decreases to 75 % (block C-25; table 5). The less powerful plume of tritium air transport from RW storage facilities in the north-western direction caused less

concentrated fallouts from the atmosphere to soil (wells C-27 and C-31; table 4). Far from RW storage facilities, a more intensive redistribution of tritium between structural positions is observed. Thus, in remoter wells C-25 and C-31 from 25% to 37% of the total tritium amount in the soil sections is included in more strongly bound forms in the structure of rock-forming, mainly clay minerals (table 5).

The surface humus layer is the first element in the landscape in the path of vertical migration of tritium which entered the soil surface with precipitation. From 1.6 % (C-25) to 3.4 % (C-31) of tritium is retained in this layer (Table 6).

During further infiltration of the precipitation through the sedimentary layer, tritium is most efficiently retained by clay sands and loams. They retain respectively 15 % and 25 % of the total content of tritium in the elementary block of the landscape (table 2.6). It should be noted that the main part of the tritium reserve in the elementary blocks of the SPZ KRWSF landscapes is in loosely bound pore and film water – from almost 87 % in C-21 block to 63 % in C-31 block (Table 2.6). The content of tritium in other structural positions of sand and loam minerals varies depending on the content in the sections of the clay component, as the main component that provides the binding of the heavy isotope in more firmly fixed positions.

Within the local aquifer, two water flows of tritium are probably combined – the infiltration from atmospheric precipitations and hydrogeofiltration ones, which form releases from unsealed RW storages. Thus, in all structural positions of wet sandy loams, a significant increase in the specific tritium activity was found (Table 2.4), which is due to the presence of up to 50-70 % of the total tritium amount in the landscape elementary blocks C - 31 and C - 25 in this horizon (Table 2.5). The clay component in the upper part of the impermeable horizon (carbonate ferruginized gley of Kyiv suite P2kv) facilitates absorption of tritium (in general, in the carbonate ferruginized gley layer of block C - 31 – up to 37 %). While in solid mergels the amount of tritium is up to 9 % over the layer (block C – 25; table 2.4).

In the process of hydrogeomigration, tritiated water filtered through the sedimentary layer can fill intergranular pores (gravitational and capillary water), form adsorption films around mineral particles (film and hygroscopic water), and interact with rock-forming minerals (Fig. 2.5).

Таблиця 4. Питомі запаси тритію в елементарних блоках геологічного середовища СЗЗ ПЗРВ Київського ДМСК [2].

Table 4. Specific tritium reserve in the elementary blocks of the geological environment at the Kyiv SPZ RWSF [2].

Type of soil	Layer volume, m ³	Tritium reserve in soil moisture fractions, Bq·kg ⁻¹ of soil			Layer-by-layer tritium reserve in soil moisture fractions, Bq		
		1 fraction	2 fraction	3 fraction	1 fraction	2 fraction	3 fraction
Well 21							
Humus soil	0.013	42.2	12.3	3.9	516	150	48
Humus soil	0.050	7.3	3.3	0.8	437	206	48
Sandy loam	0.063	10.0	1.1	0.4	1074	127	40
Clay sand	0.075	28.0	2.1	1.5	3756	283	209
Loam	0.200	35.0	1.7	2.1	12600	612	756
Sand loam	0.050	14.0	0.9	0.5	1260	81	45
Clay sand	0.125	19.0	5.1	1.1	4275	1148	248
Clay sand	0.125	27.0	3.7	1.0	6075	833	225
Loess loam	0.125	41.1	2.1	1.2	9248	472	270
Loess loam	0.175	28.9	3.2	1.4	9100	1007	440
Total (Q_{total})					48341	4918	2329
Well 25							
Humus soil	0.013	19.0	3.7	0.3	285	56	5
Humus slide rock	0.050	5.0	3.8	0.7	300	228	42
Loam	0.063	8.0	2.4	0.3	900	270	34
Variegated loam	0.125	10.0	2.9	0.2	2250	653	45
Silt loam	0.125	17.0	9.1	1.1	3825	2048	248
Damp sandy loam	0.125	55.0	4.2	0.6	12375	945	135
Damp sandy loam	0.138	66.0	31.0	1.1	16335	7673	272
Sand	0.113	8.0	0.4	0.7	1620	81	142
Damp mergel	0.125	4.0	1.1	0.0	950	261	7
Damp mergel	0.125	6.0	1.1	0.1	1425	261	24
Total (Q_{total})					40265	12475	953
Well 27							
Humus soil	0.013	32.1	3.6	1.9	482	54	28
Humus sand loam	0.050	7.5	0.3	1.8	447	16	107
Humus sand loam	0.063	6.0	1.9	0.7	449	142	50
Clay sand	0.125	7.9	1.8	1.1	1779	401	240
Clay sand	0.125	5.0	1.3	0.7	1117	288	149
Damp clay sand	0.125	9.0	3.0	1.7	2034	668	387
Damp clay sand	0.125	13.7	4.0	1.5	3074	907	330
Damp clay sand	0.125	7.1			1596		
Loess clayey sand	0.125	2.2	1.5	1.2	489	329	271
Loess clayey sand	0.125	2.8	2.1	0.3	624	464	63
Total (Q_{total})					12092	3269	1624
Well 31							
Humus soil	0.013	6.3	2.0	1.9	94	30	29
Humus soil	0.050	3.2	1.1	1.0	192	64	63
Sand loam	0.063	2.1			232		
Silt loam	0.125	3.6	1.2	0.2	806	259	35
Damp sand loam	0.125	7.5	2.2	1.1	1697	494	241
Damp sand loam	0.125	5.7	1.5	1.0	1272	345	218
Damp sand loam	0.125	8.5	3.2	0.3	1902	722	75
Carbonate ferruginized gley	0.125	0.8	1.7	1.1	190	378	253
Carbonate ferruginized gley	0.125	5.1	3.4	1.3	1212	797	316
Carbonate ferruginized gley	0.125	5.2	2.1	1.3	1235	488	319
Total (Q_{total})					8832	3578	1549

Таблиця 5. Узагальнений запас тритію у фракціях вологи з ґрунтів та їх співвідношення в елементарних блоках лісового ландшафту СЗЗ КПЗРВ.

Table 5. General tritium amount in soil moisture fractions and their ratio in the elementary blocks of the forest landscape near SPZ KRWSF.

Elementary block	Tritium amount in landscape elementary block, Bq				Ratio of general tritium amount in soil moisture fractions		
	1 fraction	2 fraction	3 fraction	Q_{total}	Kr^*	Kr^{**}	Kr^{***}
C 21	48341	4918	2329	55588	0.87	0.09	0.04
C 25	40265	12475	953	53692	0.75	0.23	0.02
C 27	12092	3269	1624	16986	0.71	0.19	0.10
C 31	8832	3578	1549	13959	0.63	0.26	0.11

Note: Q_{total} – General tritium amount in elementary blocks, Bq; Kr^* , Kr^{**} , Kr^{***} Ratio of general tritium amount in soil moisture fractions in 1st (1fr./ Q_{total}), 2nd (2 fr./ Q_{total}) and 3rd (3 fr./ Q_{total}) fractions, respectively.

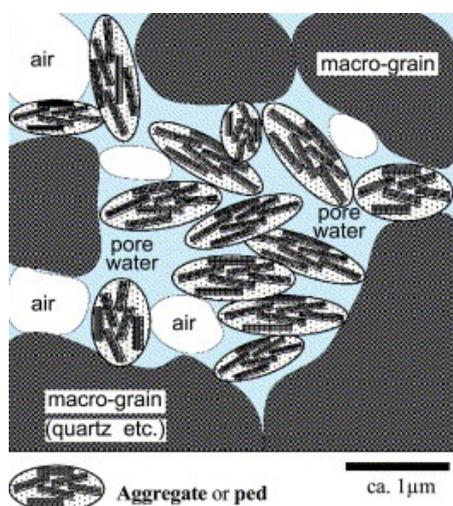


Рис. 5. Структура глинистих порід. Агрегат – глиниста частинка, що складається з сукупності елементарних структурних пакетів [18].

Fig. 5. Clay rock structure. Aggregate is a clay particle consisting of a set of elementary structural packages [18].

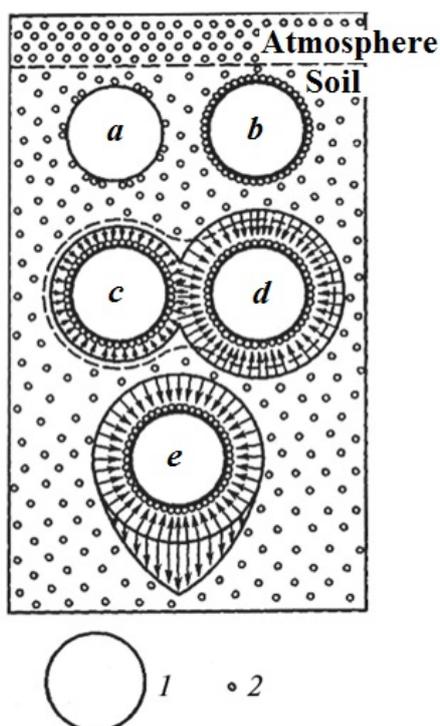


Рис. 6. Розташування молекул води в межах дифузійного шару твердої частинки породи. 1 - частинки породи; 2 - краплі води у вигляді пари; а - частинки з неповною гігроскопічністю; б - частинки з максимальною гігроскопічністю; в і г - частинки з плівковою водою (вода рухається від частинки г до частинки в, оточеній більш тонкою плівкою); д - частинки з гравітаційною водою [1].

Fig. 6. The location of water molecules within the solid rock particle diffusion layer. 1 - rock particles; 2 - water drops in the steam form; a - particles with incomplete hygroscopicity; b - particles with maximum hygroscopicity; c and d - particles with film water (water moves from particle g to particle c, surrounded by a thinner film); e - particles with gravitational water [1].

Таблиця 6. Пошарова частка запасу тритію у фракціях ґрунтової вологи від загального запасу в елементарних блоках лісового ландшафту СЗЗ КПЗРВ (%).

Table 6. Layer-by-layer percentage of tritium amount in soil moisture fractions in the elementary blocks of the forest landscape in SPZ KRWSF (%).

Type of soil in elementary blocks	Layer volume, m ³	Percentage of tritium amount in soil moisture fractions, %			
		1 fr./Q _{total}	2 fr./Q _{total}	3 fr./Q _{total}	Total
C 21					
Humus soil	0.013	0.93	0.27	0.09	1.28
Humus soil	0.050	0.79	0.37	0.09	1.24
Sand loam	0.063	1.93	0.23	0.07	2.23
Clay sand	0.075	6.76	0.51	0.38	7.64
Loam	0.200	22.67	1.10	1.36	25.13
Sand loam	0.050	2.27	0.15	0.08	2.49
Clay sand	0.125	7.69	2.06	0.45	10.20
Clay sand	0.125	10.93	1.50	0.40	12.83
Loess loam	0.125	16.64	0.85	0.49	17.97
Loess loam	0.175	16.37	1.81	0.79	18.97
Total (Q_{total})		86.96	8.85	4.19	100.0
C 25					
Humus soil	0.013	0.53	0.10	0.01	0.64
Humus slide rock	0.050	0.56	0.42	0.08	1.06
Loam	0.063	1.68	0.50	0.06	2.24
Variegated loam	0.125	4.19	1.22	0.08	5.49
Silt loam	0.125	7.12	3.81	0.46	11.40
Damp sandy loam	0.125	23.05	1.76	0.25	25.06
Damp sandy loam	0.138	30.42	14.29	0.51	45.22
Sand	0.113	3.02	0.15	0.26	3.43
Wet mergel	0.125	1.77	0.49	0.01	2.27
Wet mergel	0.125	2.65	0.49	0.04	3.18
Total (Q_{total})		74.99	23.23	1.77	100.0
C 27					
Humus soil	0.013	2.84	0.32	0.17	3.32
Sand loam	0.050	2.63	0.10	0.63	3.36
Sand loam	0.063	2.65	0.83	0.29	3.77
Clay sand	0.125	10.47	2.36	1.41	14.25
Clay sand	0.125	6.58	1.70	0.88	9.15
Loam	0.125	11.97	3.93	2.28	18.18
Loam	0.125	18.10	5.34	1.94	25.38
Clay sand	0.125	9.40			9.40
Loess clayey sand	0.125	2.88	1.94	1.59	6.41
Loess clayey sand	0.125	3.67	2.73	0.37	6.78
Total (Q_{total})		71.19	19.25	9.56	100.0
C 31					
Humus soil	0.013	0.67	0.21	0.21	1.09
Humus soil	0.050	1.37	0.46	0.45	2.29
Sand loam	0.063	1.66			1.66
Clay sand	0.125	5.77	1.86	0.25	7.88
Damp sandy loam	0.125	12.16	3.54	1.73	17.42
Damp sandy loam	0.125	9.11	2.48	1.56	13.15
Damp sandy loam	0.125	13.63	5.17	0.53	19.33
Carbonate ferruginized gley	0.125	1.36	2.71	1.81	5.89
Carbonate ferruginized gley	0.125	8.68	5.71	2.26	16.66
Carbonate ferruginized gley	0.125	8.85	3.50	2.29	14.63
Total (Q_{total})		63.27	25.63	11.09	100.0

Structural and physicochemical features of quartz and feldspar, the most common minerals among the clastogenic part of loess rocks, determine the possibility of formation of adsorption films and condensed hygroscopic water on the grain surface (Fig. 6) with HTO molecules not being a part of their structure. Hygroscopic water covers the surface of mineral grains and structural aggregates of the soil with a very thin film.

Hygroscopic water is formed by water vapor deposition from the air. This water is firmly held on the surface of the particles by molecular and electrical forces and can be removed only at a temperature of 105-110 °C. Quantitatively, the process of physical monomolecular adsorption is described by Langmuir's equation (3) [4].

$$\theta = \frac{\alpha \cdot P}{1 + \alpha \cdot P} \quad (3)$$

where: θ – adsorbent particle surface area fraction occupied by the adsorbate, α – Langmuir adsorption coefficient, P – adsorptive concentration

The adsorption equilibrium state can be expressed like (4)

$$K = \frac{\theta}{(1 - \theta)P} \quad (4)$$

Hygroscopic water movement is possible only after transition into the vapor state. Depending on the amount of hygroscopic water retained on the rock particles, incomplete (Fig. 6, a) and maximum hygroscopicity (Fig. 6, b) are distinguished. The maximum hygroscopicity of fine-grained and clay rocks can reach 18 %, in more coarse-grained rocks it drops to 1 % by dry matter weight.

Film water is formed on rock particles at a humidity level exceeding the maximum hygroscopicity. The surface of the particles is enveloped by a water film which is several molecular layers thick and covers the hygroscopic moisture (Fig. 6, c, d). The film water is retained on the rock particles by molecular adhesion forces. The thinnest layer of water immediately adjacent to the particle is most strongly bound. As the film thickness increases, the action of the retention forces markedly decreases up to insignificant level on the surface of the film. The moisture content in the rocks that corresponds to the maximum film thickness, corresponds to the maximum molecular moisture content.

The film water is able to move as a liquid from thicker films to thinner ones. The maximum content of the film water (maximum molecular moisture content) is (%): sands – 1-7, sand loams – 9-13, loams – 15-23 and clays – 25-45. When the thickness of the film increases to the size that does not ensure retention of its outer layers, the film water becomes free, which under the gravity effect will flow from the rock particles, and thus is a source of gravitational groundwater resupply (Fig. 6, d).

The gravitational water fills the pores in sedimentary rocks and can move freely through the pore space in unsaturated (aeration zone) and saturated filtration areas. This type of water is weakly held by the mineral phase, and though being partially imbibed in the mineral mass, it can move through the sediments.

When migrating through the hydrogeofiltration flow sediments, the tritium concentration in different types of water in the pore space changes due to diffusion processes according to Fick's 2nd law (5)

$$\frac{dc}{dt} = D \frac{d^2c}{dx^2} \quad (5)$$

At a low filtration rate through the loess and sandy loam layers ($5.6 \times 10^{-7} - 2.6 \times 10^{-6}$) m·s⁻¹, this may further tritium retention in the sedimentary layer.

The main adsorbent component in these rocks, as shown by our study of the landscape-geochemical system of the KRWSF site, are clay minerals [6-17], the presence of which in the sedimentary deposits underlying the RW storage facilities reduces the specific tritium activity in the geofiltration flow by several orders of magnitude.

Conclusions

In the natural-technogenic biogeosystem consisting of the acceptor part of the system and the donor element which as a result of releases from radioactive waste storage facilities forms atmospheric and hydrogeofiltration tritium transfer plumes, the geological environment is a high capacity reservoir of heavy hydrogen isotope.

The surface humus layer is the first element in the landscape in the path of vertical migration of tritium which entered the soil surface with atmospheric precipitation. Up to 3.5 % of tritium precipitated on the soil surface is retained in this layer. Most of the tritium from the precipitation is transferred by a vertical infiltration flow through the sediment layer, where it is almost completely retained. The adsorption capacity of 1 m³ of soil may exceed 55,000 Bq.

The main part of the tritium reserve in the elementary blocks of the SPZ KRWSF landscape is in loosely bound pore and film water. In the area close to the RW storage facilities, where the air plume is least dispersed and the atmospheric precipitation containing the highest tritium amount enters the soil surface, most of the heavy hydrogen isotope – up to 87% of its total content in the elementary block of the geological environment is accumulated in such form, and only up to 13 % is in more firmly fixed forms.

Father from the RW storage facilities along with decrease in the tritium concentration in the atmospheric migration flow in the free water, its content decreases to

65-75 %, with more intensive redistribution of tritium between structural positions, where from 25 % to 37 % of the total tritium amount in soils is retained in the structure of rock-forming, mainly clay minerals.

The amount of tritium in the more firmly fixed positions in sands and loams depends on the clay content

in them. The presence of clay as the main component in the sediments underlying the radioactive waste storage reduces the specific activity of tritium in the geofiltration flow by several orders of magnitude and provides more reliable immobilization of the heavy isotope in the mineral structure.

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ВИЗНАЧЕННЯ МЕХАНІЗМІВ МІГРАЦІЇ ТА ДЕПОНУВАННЯ ТРИТІО В ГЕОЛОГІЧНОМУ СЕРЕДОВИЩІ (НА ПРИКЛАДІ КИЇВСЬКОГО ПУНКТУ ЗБЕРЕЖЕННЯ РАДІОАКТИВНИХ ВІДХОДІВ)

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Пункти збереження радіоактивних відходів (ПЗРВ) є потужним потенційним джерелом тритію у біосфері. Інженерні споруди з використанням бетонних конструкцій не є достатньо надійними, оскільки на подібних об'єктах виявлено протікання зі сховищ в геологічне середовище забрудненої тритієм води. Бар'єрні властивості природного середовища в місцях розміщення сховищ визначаються здатністю поглинати та утримувати значний час цієї важкої ізотоп водню і таким чином виключати його з кругообігу у біосфері. У поглинанні тритію приймають участь різні ланки природної екосистеми – геологічне середовище, ґрунтова органіка, однорічна та багаторічна рослинність, мікро- та макробіота. Певна частина тритію у вигляді газу та аерозолей надходить у повітряний басейн. Найбільші концентрації тритію фіксуються в зоні, наближеній до бетонних сховищ радіоактивних відходів (РАВ), де шлейф паро-газових еманцій найменш диспергований. З віддаленням від сховищ концентрації тритію в гумусованому шарі ґрунту суттєво зменшуються внаслідок просторової дисперсії концентрації тритію в атмосферному шлейфі. Тритій, що вилучається з повітря потрапляє на поверхню ґрунту з атмосферними опадами і частково затримується у гумусованому шарі ґрунтового перетину. Більша частина тритію з атмосферних опадів переноситься з вертикальним інфільтраційним потоком крізь товщу осадових відкладів, представлених лесовидними супісками та суглинками де остаточно депонується. У наближеній до сховищ РАВ зоні - більш високий вміст важкого ізотопу водню у вільній – поровій, інтерстиційній та плівковій воді (1 фракція) - до 87% від його загального вмісту в елементарному блоці. У більш міцно зв'язаних формах (2 і 3 фракції) закріплюються відповідно 9% і 4 %. З віддаленням від сховищ РАВ в переважному напрямку дії атмоімграційного потоку концентрація тритію у вільній воді зменшується до 75% . З віддаленням від сховищ РАВ спостерігається більш інтенсивний перерозподіл тритію між структурними позиціями. У більш віддалених точках спостережень (свердловинах) від 25% до 37% загального запасу тритію в ґрунтах перетинів затримується у більш міцно зв'язаних формах в структурі породотвірних, головним чином глинистих мінералів.

Ключові слова: радіоактивні відходи, тритій, глинисті мінерали, природні бар'єри, водень