Processes of chemical element dispersion and redistribution in the environment with wastewater sludge used for recultivation of woodcutting areas

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Possibilities to use the wastewater sludge of Panevėžys polluted by technogenous elements and unsuitable to agriculture for recultivation of woodcutting areas have been investigated. It has been determined that in the course of sludge mineralisation the content of organic matter and Ca decreases, while the concentrations of other elements increase and their soluble forms transfer to mineral forms. Trace elements can be washed into deeper horizons of the ground together with particles of sludge, but their mobile forms are completely stabilised by soil (especially peaty) and by geochemical barriers (Fe–Mn hydroxide, carbonate–alkaline and other) forming in deeper horizons, therefore there is no danger of groundwater contamination. Such a way of polluted wastewater sludge utilisation is most rational under suitable geological-geochemical conditions.

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Keywords: wastewater sludge, trace elements, geochemical associations, geochemical barriers, soluble forms, background value

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INTRODUCTION

In towns with developed industry the problem of wastewater sludge utilisation is complicated, because great contents of heavy metals always accumulate in it, thus limiting the possibility of its usage in agriculture, which is regulated now by the LAND 20–2001 standard "Requirements for wastewater sludge utilisation for fertilising" (Valstybės žinios, 2001).

Wastewater sludge of Panevėžys, especially the previously accumulated one, contains perhaps the highest metal concentrations in Lithuania (including Ce, Bi, Cd which are rarely found elsewhere) accumulated due to specific technologies used in "Ekranas", "Tikslioji mechanika" and other plants.

At present, with the production volume decreased, the content of most technogenous metals in sludge has also diminished 2–2.5 times, but still it is too high for the sludge to be used as a fertiliser in agriculture. Though elevated amounts of calcium, magnesium, phosphorus and biophilic minor elements (Zn, Cu, B, Mo, Co, Mn) in sludge are useful or can be tolerated, the increased contents of lead (up to 1500 mg/kg), nickel (up to 550 mg/kg), chromium (up to 400 mg/kg) and cadmium (up to 20 mg/kg in dry sludge) are unallowable, can poison the soil and make it unsuitable for agriculture, because according to heavy metal concentrations it would belong to the third category. Depositing of sludge in sites and reservoirs requires great capital investments, while other way of its utilisation (incineration) also poses many problems due to a low content of organic matter (up to 50%) and greatly toxic products of burning.

In search of the ways to solve this problem, based on experience and data of foreign countries (Gal, 1984; Grant, Olesen, 1984) and the Institute of Geology (Diliūnas et al., 1998), as well as on the initiative of Ecological Department of Panevėžys City Municipality and JSC "Aukštaitijos vandenys", with the approval of Ministry of Environment and administration of Panevėžys district forests, experimental and industrial investigations of wastewater sludge utilisation for fertilising of replanted woodcutting areas in Gilėnai forest of Taruškos forestry were done in 1996–2001, aiming to determine the scale of hazardous chemical element dispersion in the environment (ground, groundwater and vegetation) (Fig. 1). The following principles must be followed when choosing the woodcutting areas: a) the site must be located in the area with as small run-off as possible, b) its geological structure must be suitable for forming the geochemical barriers (Fe–Mn, carbonate-alkaline and other), c) the site must have a sufficiently thick layer of peat and forest litter which best of all can stabilise the mobile element forms, d) the waterproof loamy horizon must be not deeper than 2–3 m, e) the forest in the chosen areas must be not used for gathering berries, mushrooms and medicine raw material.

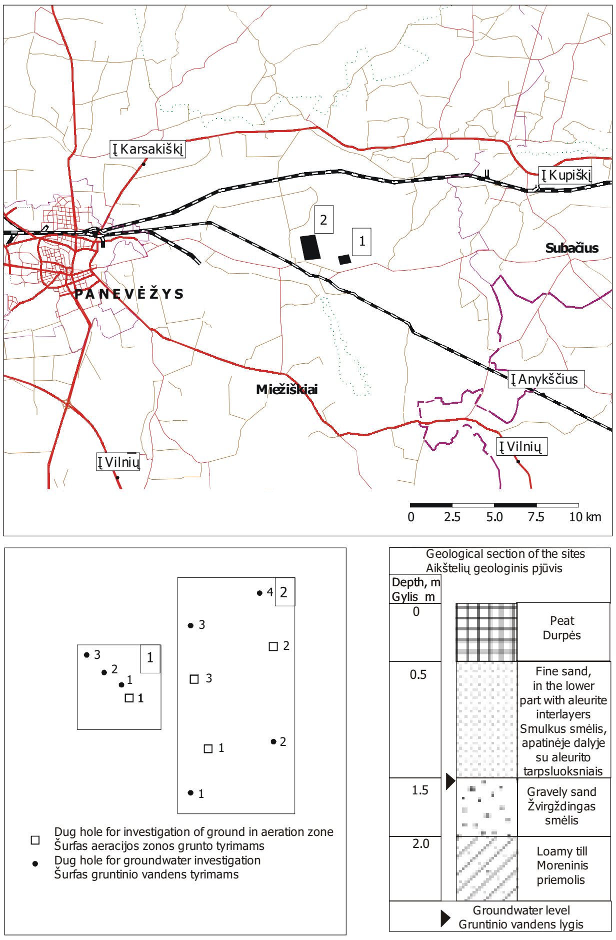

Fig. 1. Location scheme of sites for Panevėžys wastewater sludge utilisation and observation points there. 1 – experimental site, *2* – industrial site

1 pav. Panevėžio miesto vandenvalos dumblo utilizavimo aikštelių ir stebėjimo taškų jose išsidėstymo schema. *1* – eksperimentinė aikštelė, *2* – gamybinė aikštelė

ORGANISATION AND METHODS OF INVESTIGATION

The site (400 m^2) was chosen for experimental investigations in 1995–97. On an undisturbed forest soil layer 25 t of sludge was spread. Dispersion of chemical elements in soil, ground (one stationary dug hole until the waterproof loamy horizon was made), groundwater, surface water and vegetation was investigated. On obtaining positive results the woodcutting site 2 ha in area was chosen for industrial investigations in 1998; 300 t/ha sludge was spread on it. When the technical problems of sludge spreading arose, the stumps of the trees were uprooted and buried in trenches, thus the forest soil and partly also the natural ground (subsoil) were disturbed. Four stationary dug holes up to groundwater level (1.5 m) were arranged.

When the total contents of trace elements in the sludge spread on the chosen sites, as well as the amount of water-soluble (mobile) element forms in it, natural (background) element content in soil, subsoil and water of woodcutting areas had been determined, the following indices were investigated twice a year (in spring and autumn): a) variation of trace element total content and their mobile forms in sludge, main technogenous elements (Zn, Cu, Cr, Ni, Pb, Cd) in particular, b) migration of elements in inert and mobile forms from sludge to soil, subsoil, groundwater in constantly equipped observation points, c) variation of trace element content in vegetation (fir-tree seedlings, deciduous trees, bushes, grass, etc.) in the sites and in control areas.

Laboratory investigations of the samples were done in the spectral and hydrochemical certified laboratories of the Institute of Geology according to the standard methods of geochemical investigations (Radzevičius et al., 1997). The average values of element total content in sludge (Table 1) were calculated after elimination of sandy samples from the set of results, as due to a low content of elements these samples make the set inhomogeneous. The total contents of elements in the ground of the industrial site (Table 2) were the average values in the corresponding layers of four observation points; they characterise the whole investigated area more gene-

Table 1. **Variability of chemical element median values in wastewater sludge, ppm**
1 lentelė. **Cheminių elementų medianinio kiekio kaita vandenvalos dumble ppm**

Year / Metai	LOI/KN	pH	Ca	P	Ag	Cr	Cu	Ni	Pb	Zn	Ce	Bi	Cd
1998 09	68.5	8.2	8.2	21507	17.6	295	291	92	1456	4296	715	6.2	5.3
1999 05	46.2	7.8	6.3	21917	15.4	280	362	221	1075	1422	1081	5.6	14.3
1999 09	27.2	7.5	4.3	5580	14.4	407	581	425	1065	1072	1649	4.9	18.7
2000 05	23.9	7.1	2.9	17288	13.1	494	313	76	754	690	357	5.5	8.1
2000 09	47.6	7.1	2.3	3242	11.2	304	212	44	699	360	180	3.6	7.5
2001 05	67.9	6.8	1.9	21764	14.2	205	295	43	544	3394	726	2.3	3.1

LOI – loss on ignition, %

Table 2. **Variability of chemical element average contents in industrial site ground, ppm**
2 lentelė. **Cheminių elementų vidurkinio kiekio kaita gamybinės aikštelės grunte ppm**

Depth, m Gylis m	LOI KN	pH	Al*	Ca	Fe	Mn	P	Sr	Ag	Cr	Cu	Ni	Pb	Zn	Ce	Bi	Cd
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Background / Fonas																	
0.2	25.7	5.6	2.9	0.1	0.1	215	490	13	0.074	25.3	3.1	4.9	11.9	16.3			
0.4	0.6	6.2	3.4	0.1	0.1	225	497	16	0.056	32.8	2.2	6.4	8.7	2.2			
0.8	2.2	6.4	4.5	0.1	0.2	198	359	21	0.057	28.4	2.9	9.3	9.6	5.6			
1.2	0.8	6.6	5.2	0.1	0.6	574	296	32	0.065	26.4	2.5	11.5	9.1	4.3			
1.5	0.4	6.8	4.6	0.4	0.9	659	273	51	0.076	25.3	9.9	29.6	14.3	21.8			
1998 09																	
0.2	9.3	7.9	4.3	0.8	0.6	390	1312	53	0.125	62.1	8.9	6.1	15.1	16.3	89	6.6	5.9
0.4	2.7	5.8	4.2	0.2	0.5	436	482	31	0.117	20.5	5.8	4.9	9.7	1.6	21	2.9	2.1
0.8	6.9	6.8	5.1	0.2	0.4	348	327	52	0.097	19.5	5.8	6.8	9.4	2.5	9	2.8	0.9
1.2	1.9	6.8	4.9	0.1	0.5	229	332	42	0.078	20.4	3.4	8.8	8.3	2.2	9	2.8	0.9
1.5	1.2	7.6	4.1	0.4	0.9	664	390	67	0.054	24.7	4.1	8.3	11.9	19.8	10	2.9	1.1
1999 05																	
0.2	6.3	8.2	2.3	0.8	0.6	326	1177	103	0.16	59.3	9.6	44.1	45.3	49.5	168	8.7	6.3
0.4	3.7	7.1	2.4	0.4	0.6	250	555	106	0.06	26.2	3.9	8.3	13.4	9.2	39	2.7	1.8
0.8	6.5	6.2	3.3	0.4	0.5	278	742	65	0.05	17.4	3.2	6.8	13.2	9.6	28	2.2	0.7
1.2	5.3	6.7	2.5	0.3	0.6	289	289	66	0.06	20.6	2.4	5.2	11.6	10.3	12	2.2	0.8
1.5	2.4	8.8	2.6	0.4	0.8	716	372	98	0.07	20.9	1.6	5.6	10.2	10.8	9	2.4	1.4
1999 09																	
0.2	16.3	7.8	3.2	0.8	0.7	422	1450	328	0.59	43.3	11.2	38.5	47.6	48.3	287	7.5	7.1
0.4	3.2	7.1	2.4	0.4	0.2	285	487	145	0.09	18.5	4.2	12.7	14.2	22.2	28	2.8	0.9
0.8	8.4	7	2.2	0.2	0.4	246	432	162	0.07	28.2	4.3	8.3	7.6	10.5	28	2.8	0.9
1.2	5.1	6.5	2.1	0.2	0.7	263	432	157	0.11	20.6	2.1	3.1	8.2	10.6	29	2.9	0.7
1.5	1.8	8.4	2.6	0.5	0.9	746	559	145	0.06	10.8	3.2	7.9	7.1	9.1	29	2.9	0.4
2000 05																	
0.2	6.6	7.6	2.9	2.1	2.0	382	1027	115	0.51	32.5	9.9	25.3	39.3	27.3	264	9.2	4.6
0.4	24.7	7.5	1.5	1.6	0.9	163	678	134	0.05	26.3	6.1	9.2	18.1	14.1	22	2.1	0.4
0.8	22.8	7.8	1.6	0.9	0.7	178	464	99	0.04	25.2	5.2	9.2	7.2	14.6	19	2.0	0.5
1.2	4.8	7.6	1.3	0.5	1.9	189	336	109	0.06	26.4	6.3	12.5	7.5	8.1	19	1.3	0.3
1.5	1.6	7.4	1.5	0.8	3.4	338	886	94	0.09	37.8	2.2	7.6	10.3	8.2	24	2.5	0.3
2000 09																	
0.2	7.4	7.4	2.4	2.3	2.1	415	689	1597	7.19	96.3	71.9	16.3	280	687	194	9.6	3.9
0.4	20.1	7.4	2.7	1.2	1.1	252	677	194	0.08	26.1	4.8	5.9	15.2	19.6	18	2.3	0.2

Table 2 (continued)
2 lentelė (tęsinys)

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
0.8	7.4	7.2	2.9	0.8	1.2	275	688	147	0.12	35.3	5.9	5.7	11.3	20.2	14	2.1	0.4
1.2	5.1	7.2	2.1	1.3	0.6	205	585	156	0.06	33.2	6.2	7.3	9.6	15.5	17	1.7	0.4
1.5	2.5	7.4	1.7	0.2	3.6	513	829	98	0.06	23.6	4.9	3.8	8.4	10.7	21	2.1	0.3
2001 05																	
0.2	19.5	8.2	2.1	4.9	6.6	596	7400	459	6.44	427	563.5	233.5	2013	725	129	4.4	24.2
0.4	4.2	7.4	2.8	1.4	1.3	260	883	97	0.59	41.2	0.9	14.9	35.2	29.2	16	2.2	1.2
0.8	12.3	6.8	3.1	0.5	1.0	147	654	51	0.06	35.7	1.9	6.1	14.1	7.4	12	1.4	0.5
1.2	1.1	7.4	3.3	0.5	1.1	201	575	63	0.07	34.9	2.1	6.5	13.3	8.3	12	1.2	0.4
1.5	3.8	7.4	2.2	0.6	2.4	469	888	60	0.05	23.6	3.2	5.3	8.6	6.7	18	2.0	0.2

* Al, Ca, Fe – %

Table 3. **Variability of the contents of trace element mobile and potentially mobile forms in wastewater sludge in industrial site ground, ppm**
3 lentelė. **Tirpių ir potencialiai tirpių mikroelementų formų kiekio kaita vandenvalos dumble ir gamybinės aikštelės grunte ppm**

Year / Metai	Zn			Cu			Pb			Ni			Cr			Cd		
	B.k.*	F.k.**	%	B.k.	F.k.	%	B.k.	F.k.	%	B.k.	F.k.	%	B.k.	F.k.	%	B.k.	F.k.	%
Deponed wastewater sludge / Kauptuvų dumblas																		
1996	4296	465	10.8	291	44.5	15.3	1456	62.7	4.3	92	53.8	58.9	295	37.9	12.8	6.2	2.2	37.3
Introduced wastewater sludge / Paskleistas dumblas																		
1998 09	994	308	31.0	104	92.7	89.1	958	52.6	5.5	107	34.2	31.9	93	16.8	18.1	3.6	0.8	21.7
1999 05	1442	398	27.6	362	16.4	4.5	675	36.2	5.4	221	18.5	8.4	280	9.3	3.3	14.3	1.0	6.9
1999 09	1072	370	34.5	581	5.6	1.0	1065	48.3	4.5	425	17.8	4.2	407	4.2	1.0	18.7	1.6	8.3
2000 05	1163	240	20.6	145	19.9	13.7	1091	44.6	4.1	116	37.1	31.9	124	10.2	8.2	11.6	0.6	5.5
2000 09	1125	149	39.5	142	2.9	6.9	1161	10.5	6.5	125	5.2	20.8	143	3.2	7.4	1.8	0.2	8.9
2001 05	3394	153	4.5	295	7.9	2.7	1077	4.3	0.4	43	2.6	6.1	205	1.2	0.6	3.1	0	0
Ground / Gruntas																		

Depth, m Gylis m	Year Metai	Zn			Cu			Pb			Ni			Cr			Cd		
		B.k.	F.k.	%	B.k.	F.k.	%	B.k.	F.k.	%	B.k.	F.k.	%	B.k.	F.k.	%	B.k.	F.k.	%
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
0.2	1998 09	263	7.7	2.9	6.4	0.40	6.3	15	4.7	32.3	9.5	0.5	5.5	29.1	0.8	2.8	2.2	0.19	8.7
0.4		181	4.3	2.4	2.8	0.09	3.2	29	8.2	28.7	8.3	0.6	7.5	29.4	0.8	2.6	1.9	0.14	7.3
0.8		42	5.4	12.9	3.1	0.31	10.0	10	1.3	13.0	7.1	1.0	13.9	22.9	0.7	2.9	0.6	0.05	7.8
1.2		45	4.9	10.9	2.0	0.23	11.5	8	1.8	22.3	5.2	0.9	18.8	13.9	0.5	3.9	0.9	0.10	11.8
1.5		87	4.3	4.9	2.0	0.32	16.0	8	1.4	16.2	5.6	1.3	22.7	14.1	0.5	3.4	0.7	0.08	10.8
0.2	1999 05	49	5.6	11.4	9.2	0.56	6.2	45	6.4	14.2	44	1.5	3.4	43	0.5	1.1	7.1	0.23	3.2
0.4		9	2.4	26.4	3.1	0.21	7.0	13	1.9	14.2	8	1.2	15.1	18	0.2	1.2	0.9	0.13	14.4
0.8		9	3.6	39.4	3.0	0.22	7.3	13	1.5	11.5	6	1.0	16.3	28	0.5	1.7	0.9	0.02	2.2
1.2		10	3.1	30.2	2.2	0.31	15.5	11	1.2	11.1	5	0.5	10.2	20	0.1	0.7	1.0	0.01	1.0
1.5		10	4.1	41.2	1.8	0.18	18.0	10	0.9	9.9	5	0.6	11.0	20	0.05	0.3	1.0	0.01	1.0
0.2	1999 09	39	3.5	9.1	7.2	0.63	9	50	1.8	3.6	35	1.22	3.5	50	0.36	0.7	4.7	0.16	3.4
0.4		10	2.7	26.6	3.1	0.45	15.3	12	0.7	5.9	5	0.93	18.6	22	0.24	1.1	1	0.01	1.0
0.8		10	4.3	42.8	3.3	0.26	8.7	7	0.12	1.7	6	0.84	14.1	24	0.21	0.9	1	0	0
1.2		10	1.9	19.4	2.4	0.09	4.5	8	0.11	1.4	3	0.26	8.7	18	0.13	0.7	1	0	0
1.5		10	2.9	29.0	3.0	0.74	24.7	7	0.1	1.4	7	0.99	14.4	21	0.08	0.4	1	0	0
0.2	2000 05	17	4.4	25.9	9.3	4.28	46.0	19	1.92	10.1	7.0	4.04	57.7	18.7	7.68	41.1	3.9	0.44	11.3
0.4		23	2.5	10.9	6.1	3.48	58.0	18	0.12	0.7	9.0	0.57	6.3	30.1	0.45	1.5	1	0.04	4.3
0.8		20	2.8	14.1	5.4	3.85	71.3	13	0.06	0.5	9.3	0.86	9.4	26.3	0.29	1.1	1	0	0
1.2		20	3.1	15.4	5.9	1.64	27.8	13	0.05	0.4	11.7	0.01	0.1	30.2	0.22	0.7	1	0	0
1.5		29	1.1	3.6	1.9	0.08	4.2	11	0	0	10.5	0	0	39.9	0.16	0.4	1	0	0
0.2	2000 09	10	2.6	25.6	6.7	1.49	22.2	16	0.83	5.2	4.4	0.14	3.2	21.1	6.14	29.2	4.5	0.05	5.1

Table 2 (continued)
2 lentelė (tęsinys)

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
0.4		17	1.9	11.1	5.6	1.35	24.1	12	0	0	5.9	0.21	3.6	25.9	0.38	1.5	1	0.07	7.4
0.8		11	2.7	24.7	2.8	1.17	41.8	9	0.24	2.7	5.7	0.09	1.6	35.2	0.84	2.4	1	0.003	0.3
1.2		10	2.7	26.8	2.8	0.31	11.1	9	0.05	0.5	7.1	0	0	33.2	0.86	2.6	1	0	0
1.5		10	0.9	9.3	4.8	0.07	1.5	11	0	0	3.8	0	0	22.9	0.22	1.0	1	0	0
0.2	2001 05	493	69.5	14.1	180.9	23.20	12.8	510	5.9	1.2	74.0	1.8	2.5	123.0	12.1	9.8	2.2	0.01	0.5
0.4		7	1.3	18.6	2.6	0.06	2.3	6	0	0	4.2	0	0.0	18.0	0.06	0.3	1	0	0
0.8		8	0.6	7.5	3.0	0.03	1.0	7	0	0	4.3	0	0	19.1	0.02	0.1	1	0	0
1.2		7	0.8	11.4	0.9	0.01	1.1	7	0	0	4.9	0	0	23.2	0	0	1	0	0
1.5		8	0.5	6.3	1.9	0.02	1.1	7	0	0	7.5	0	0	24.1	0	0	1	0	0

* Total content, ppm / bendras kiekis ppm.
** Content of mobile and potentially mobile forms, ppm / judrių ir potencialiai judrių formų kiekis ppm.

rally, while mobile plus potentially mobile element forms determined using 1N ammonium acetate solution at pH 7 and 4.8 respectively characterise concrete samples (Table 3).

RESULTS

Geological structure of the sites. The chosen woodcutting areas were situated at the edge of a small local limnoglacial basin. The surface was plane, with a small run-off, mainly bogged up, in some places drifted, with fragments of continental dunes. The waterproof horizon consisting of loamy till of Baltic formation was 8–14 m thick, the depth of its occurrence was 1.5–2.5 m. The overlying cover consisted of: a) a 0.2–0.5 m thick layer of peat and forest litter (it is disturbed in industrial site), b) a 0.8–1 m thick fine sand layer with small interlayers of aleurite in the lower part (in industrial site sometimes also with introduced pieces of peat), c) a 0.3–0.5 m thick gravely sand, in experimental site with pebble, while in the industrial one in some places cemented with iron hydroxides ("ortstein") at the groundwater level. The amount of carbonates was also considerably increased there. The obvious geochemical barriers were two – the upper one related to the peat layer and the lower one to Fe–Mn hydroxides. They play the main role in the stabilisation of chemical element mobile forms in sludge.

Variability of trace element content in sewage sludge. Sewage sludge spread in woodcutting areas is quickly mineralised, the content of organic matter and calcium in it decreases (from 75–42% to 32–22% and from 8.2 to 1.9%, respectively), while the amount of other trace elements, especially of Pb, Ce, Cr, Ni, Cu, Bi, Cd, increases. This is most clearly reflected in data on the experimental site (Fig. 2). The maximum concentrations in the industrial site sludge were observed after a year, later they slightly decreased. The content of silver and of the elements related to the mineral part of sludge was constant, while the content of phosphorus was increasing in spring seasons. The concentration of zinc was most variable, its content was especially high in the last (fourth) year of investigation. It is noteworthy that when the content of Ca in sludge decreased and pH was reduced, its concentration in ground increased. During the second year, when new soil was forming, the content of organic matter and trace elements in sludge increased again and later remained almost stable. This variation (partly depending on the inhomogeneity of a sample set) probably reflects the processes of element rotation in the system "soil–vegetation–soil", because an especially great increase of the content in sludge was observed for organic matter and the elements having the greatest concentration in grass vegetation and deciduous trees.

At the initial stage of mineralisation, the content of mobile and potentially mobile forms of chemical elements in sludge reached the following values (per cent from total content of the element): Cu – 89, Ni – 32, Zn – 31, Cd – 22, Cr – 18, Pb – 5.5. The content of element mobile forms in sludge was decreasing constantly (Table 3), they must have been gradually replaced by potentially mobile, until stable (immobile) forms were finally left.

Factor analysis results indicated the absence of stable associations in sewage sludge (wet). The loading coefficients of the first factor are formed by the following variables: Cr–Mo–Co–LOI–Ca–Cd–Y–Ce–Ni–Yb–Pb–Fe–Cu–Mn and Sn (where LOI is weight loss on ignition), *i.e.* technogenous elements related to the organic, carbonate and Fe–Mn hydroxide part of sludge. The second association consists of Li–Zr–Ti–As–Bi and part of Y, La, Ba, Sr. This is a mixed association of weathering-resistant minerals and carbonates. Mg–Sr–Ba and part of Ca, Ce and La are associated with alkaline medium (high pH). The fourth association is natural, it is related to allothigenous minerals of sludge (Al–Ga–Nb–B). An obvious relation of Al with Zn and Bi and the absence of Ag and Rb in associations must be due to the specificity of their forms.

After spreading of sludge and change of the medium conditions (reducing anaerobic conditions changed to oxidising), with organic matter decay, these unstable associations quickly disintegrated. First of all, the relationship of technogenous elements with organic matter disappeared and they started to group themselves according to the sorbing medium. Within the first three years a constant relationship of technogenous elements with carbonate-sulphate, Fe–Mn hydroxide, phosphate material and weaker bonds with clayey part were formed in sludge, *i.e.* inert compounds of a corresponding composition appeared. The first association consisted of Pb–Zn–**Fe**–Cr–Cu–Bi–Cd–Sn and part of V, the second one of Mn–**Ca**–Ag–Mo–Ni–**Mg–Sr.** The third association (Li–Al–Ga–Zr–Yb–Ti–Nb–Ce–La) is related to main and accessory minerals in sludge, its antagonists are Ba, V, P and LOI which have no significant relationships with other elements and form their own separate associations with a lower percentage of variance. These results show that regular processes of chemical element redistribution are going on during disintegration of sewage sludge, they are leading to formation of stable, mostly mineral forms. They are inert in nature and have no significant negative influence on the environment. The process lasts 2–3 years. Analogous processes are going on in municipal solid waste landfills (Katinas, 1993).

Migration of elements in ground. Similar redistribution processes of chemical elements are going on also in the ground of woodcutting areas where the element contents correspond to the background values of sandy soil in Panevėžys region (Kadūnas et al., 1999). Peaty soils contain more Ca, Cu, Mn, P, Pb and Sc, while sandy ones – Ti, Zr, Nb, Ag, Al, B, Ba, Sn and Zn. In soil the elements form two main associations: a) **Al–Ga–Ti–Co–Cr–Li–Sc–**Ni–La–Sn–Ba–B–Nb–V–Ag–Zr–Mo–Yb–**Fe–Mn–P** with a small part of Y, Pb, Cu; their antagonists are LOI and Ca; b) **Ca–pH–Mg–Sr**–Y–Pb–Cu with part of P, Yb and LOI. These associations are natural, the first one reflects the relationship of the elements with main allothigenous minerals of sand, aleurite and clay fractions and Fe–Mn hydroxides, while the second one – with small amount of carbonates (the elements of deponing medium are indicated in bold).

After spreading of sludge in the experimental site the content of technogenous elements increased only in the surfice part of the peat layer (Fig. 2). Only small part of them in soluble form reached the ferriferous sand layer and was sorbed there (Katinas, 1999, Katinas, Radzevičius, 1999). The content of elements in ground layers of the industrial site was changing unevenly. It depended greatly not only on redistribution processes of elements, their migration forms and formation of geochemical barriers, but also on ground mixing level during arrangement of the site. After disturbance of soil no protective layers of forest litter and peat remained which could sorb the mobile forms of most elements. When inclusions of organic matter appeared in permeable sandy ground, the barriers reducing (or enhancing) the mobility of separate elements were formed. This predetermined the uneven concentration of elements both in separate layers of ground and in the area. Within the first year most of the elements in sludge (Pb, P, Fe, Ca, Ag, Cr, Ni, Cu, Ce, Cd, Bi and other) were accumulating in the surface layer of the site (due to mechanical washing-in of sludge particles), while their mobile forms reached the ferriferous sand horizon to a depth of 0.8–1.2 m and were

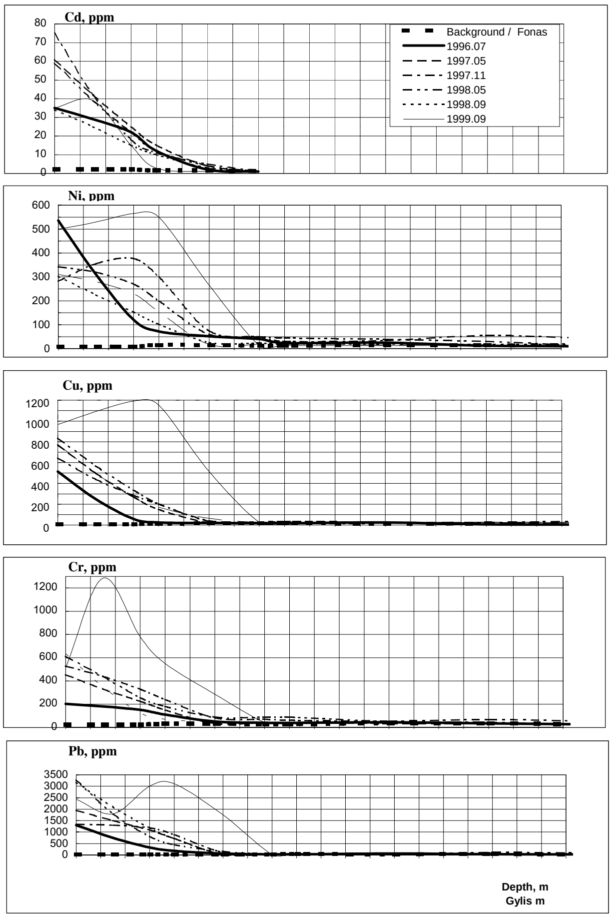

Fig. 2. Variation of trace element concentrations in the ground of experimental site, ppm
2 pav. Mikroelementų koncentracijos kaita eksperimentinės aikštelės grunte ppm

sorbed there. Later a rather intensive accumulation of Fe, Mn, P, Ca, Sr, Cr occurred there. Migration of biophilic Zn was very uneven, the variability of its total concentration and content of mobile forms was probably controlled by biogenic factors (Table 2). In deeper horizons no significant concentration of technogenous elements from sludge was found.

The extremely variable at that time element associations in ground can also illustrate the course of this process. In 1998–99 the first association was formed by immobile elements of main allothigenous minerals and technogenous elements (Yb, Y, Ce, La, Al, V, Mn, Ga, Fe, Nb, Li) and the second one by technogenous elements of unknown deponing medium (Ag, Zn, Pb, As, P, Rb, Mo, Bi, Cd, Sn with part of Ce and La). At the end of investigation the first two stable associations were formed only by technogenous elements from sludge (Sn–Ag–Cr–Ni–V–**Mn–Fe–P**–Co–Pb–Bi–Cd and Zn–Mo–Yb–La–Ce–Cu–Ba–**Sr–Ca–LOI–Mg**), their antagonists were Ga, Zr, Ti, Nb, while the elements of main and accessory minerals were found only in the third–fifth associations. The elements of the first two associations are well differentiated also according to the deponing media (Fe–Mn hydroxides – phosphates and carbonates – organic matter). Unlike in sludge, technogenous elements in ground are little associated with organic matter, and their relationships with clay fraction elements are negative.

The stability of relationships of these elements in ground can also be proved by the composition of secondary associations which reflect natural bonds of elements in clay (Li–Al–Mn–Ga), carbonate (pH–Ca–Sr–Mg) and accessory (Nb–Ti–Zr) minerals.

Variation of chemical element mobile forms. Within the study period the content of mobile forms of main technogenous elements (except Zn) in sludge was decreasing, though not always evenly (Table 3). Only the content of mobile forms of Zn and Cu in the ground of both sites constantly but slowly increased, especially in the lower horizon, while the concentration of Cd, Pb, Cr and Ni was elevated only in spring of 1998. After that it decreased again. The level of ground pollution is best of all reflected not by the amount of mobile and potentially mobile forms, but by their percentage from the total content of elements in a sample. It can be seen from the data presented in Table 3 that only in 1999 slightly more copper reached the deeper horizons, while in 2000 the content of mobile (mostly potentially mobile) forms of all the elements was insignificant. During the second year of investigation the mobile forms both in sludge and in ground were replaced by potentially mobile ones, depending on the acidity-alkalinity level of the medium. The latter one is everywhere alkaline (Table 2), unfavourable for element migration.

In 2001, in the surface layer of industrial site ground only traces of mobile forms of Zn, Cu and Pb were found, while the content of potentially mobile forms of Zn and Cu decreased 2 times, Cr – 3, Pb – 5 and of Cd even 10 times. In deeper layers only a small amount of potentially mobile forms of Zn, traces of Cu and Cr were found, and no mobile forms of Pb, Ni and Cd were left (Table 3). The increased mobility of Zn and Cu probably depends on their biophility, while of Cr – on the type of its compounds or its valency.

The soluble forms of technogenous elements which are washed out of the sludge are extremely intensively sorbed by the organic matter of soil, especially by peat (Klimantavičiūtė, 1997), therefore these elements are accumulating only in the surface (20–60 cm) layer of peat or forest soil (Fig. 2). It also holds up sludge particles which are mechanically washed out by water. Only an insignificant part of Ni, Cr, Cu, Zn mobile forms penetrates deeper where it is sorbed by ground carbonates and especially by Fe–Mn hydroxides. Thus, only insignificant amounts of the polluting technogenous elements studied can get into groundwater. When the soil is disturbed, the mechanical washing-in of trace elements with sludge particles into sandy ground is going on and the mobile forms are migrating slightly deeper, however, they do not reach the groundwater, either, because they are bound in the ferriferous sand layer. In this layer the content of technogenous elements significantly increases.

In surface water and groundwater, in the surroundings of both sites no elevated content of hazardous elements washed out from sludge was found during the investigations; only rather high iron and manganese concentrations (0.42–0.67 and 0.02–0.06 mg/l, respectively), however, this is a specific feature of the whole region of Panevėžys. Only the content of Pb, Ni and Cr in surface water slightly exceeded the regional background during the first year (Table 4).

No success was achieved in determination of variation regularities of trace element content in vegetation; the concentration of hazardous elements in control samples was often higher than in samples taken from the sites. Technogenous elements from sewage sludge had probably a secondary influence on vegetation. It depended much more on the individual properties of a plant, period of vegetation, atmospheric pollution, climatic and other factors. Seedlings and one-year-old sprouts of fir-trees and birches, raspberries, absinthium, cereal grass (roots and overground part) and mushrooms have been investigated. Technogenous elements (Zn, P, Cr, Cu, Pb)

Table 4. **Average contens of trace element in groundwater, mg/l**
4 lentelė. **Mikroelementų vidurkinis kiekis gruntiniame vandenyje mg/l**

Year Metai	Fe	Mn	Zn	Cu	Pb	Ni	Cr	Co	Cd
1998 09	0.645	0.021	0.0054	0.0026	0.0052	0.0027	0.0021	0.0004	0.00031
1999 05	0.663	0.032	0.0074	0.0031	0.0019	0.0031	0.0012	0.0003	0.00024
1999 09			0.0029	0.0057	0.0016	0.0041	0.0007		0.00022
2000 05	0.626	0.028	0.0011	0.0029	0.0013	0.0035	0.0009	0.0003	0.00018
2000 09	0.665	0.034	0.0023	0.0062	0.0013	0.0036	0.0008	0.0002	0.00015
2001 05	0.673	0.036	0.0018	0.0034	0.0017	0.0028	0.0008		0.00012
Fonas	0.344	0.011	0.013	0.0151	0.0024	0.0049	0.0015	0.0005	0.008

accumulated slightly more in mature tissues and at the end of vegetation, while in grass plants they prevailed in roots. Mushrooms accumulated rather much Mn, P, Pb, Zn, Cu, Ag, Ni. The sludge had an obvious positive influence on seedlings (especially on their growth rate) but during the first year the excess of toxic elements and their mobile forms depressed their rooting and uptake of some biophilic trace elements. Besides, the sludge was extremely polluted by weeds (mostly by absinthium) which depressed the seedlings.

CONCLUSIONS AND RECOMMENDATIONS

During mineralisation of wastewater sludge the content of technogenous elements increases with a decrease of organic matter and calcium amount. The redistribution of chemical elements in sludge and ground is going on, their stable associations are forming, related with Fe–Mn hydroxides, carbonates-sulphates, phosphates, in some cases with organic matter. Migration of the technogenous elements studied and their mobile forms to groundwater is insignificant, because it is restricted by geochemical barriers (peat, carbonates, Fe–Mn hydroxides). The resulting stable, inert element compounds are not hazardous to the environment.

The data obtained indicate that wastewater sludge contaminated with technogenous elements can be successfully applied for recultivation of peaty woodcutting areas and fertilisation of newly planted forest areas when the soil structure is undisturbed. This way of utilisation of wastewater sludge extremely polluted by hazardous chemical elements is at present most rational, because: a) it does not pose noticeable danger to the environment, b) it is cheaper than deponing in special depositories, c) it is more safe and cheap than utilisation by incineration.

It is recommended: a) to use wastewater sludge for fertilising the replanted woodcutting areas or territories that are newly planted with forest and have undisturbed peaty soil; b) after spreading the sludge to destroy the sprouted weeds during the first year and only then to plant the seedlings. In this way the negative influence of the excess of soluble forms of hazardous elements on rooting and growing of the seedlings will be avoided.

Applying this way of wastewater sludge utilisation in any region, it is not enough to base on these general regularities or similarity of the geological structure, because their geochemical conditions and processes, depending on may factors, can differ greatly. In each case it is recommended: a) to determine natural (background) geochemical parameters of the area; b) to know element content in sludge; c) to accomplish a 2–3-year course of investigations of element migration.

The optimal norm of wastewater sludge in replanted woodcutting areas of peaty forests in Panevėžys region is 300 t/ha. It can be increased to 400 t/ha and more in the cases when: a) the content of hazardous chemical elements (especially their soluble forms) in sludge is correspondingly lower, b) the thickness of undisturbed peaty forest soil layer is greater than 0.5 m.

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CHEMINIŲ ELEMENTŲ SKLAIDOS IR PERSISKIRSTYMO APLINKOJE GEOCHEMINIAI PROCESAI, PANAUDOJANT VANDENVALOS DUMBLĄ MIŠKO KIRTAVIEČIŲ REKULTIVACIJAI

Santrauka

Pramoniniuose miestuose visada iškyla vandenvalos dumblo, itin užteršto kenksmingais metalais, utilizavimo problema, nes jis netinka žemės ūkio reikmėms. Atlikti tyrimai parodė, kad toks dumblas gali būti panaudotas durpingų miško kirtaviečių rekultivacijai, tik svarbu parinkti mažai nuotakius, durpingus plotus su negiliai slūgsančiu vandensparos horizontu. Dumblui mineralizuojantis, mažėja organinės medžiagos ir kalcio, atitinkamai daugėja likusių elementų. Į gilesnius grunto sluoksnius jie patenka daugiausia su dumblo dalelėmis. Giliau migruoja Ca ir vandenyje tirpios formos (pH 7), kurias palaipsniui keičia potencialiai tirpios (pH 4,8), be to, judrias formas intensyviai sorbuoja dirvožemio organinė medžiaga, o jų likutį stabilizuoja giliau esantys geocheminiai barjerai (Fe ir Mn hidroksidų, karbonatinis ir kt.). Formuojasi naujos mikroelementų asociacijos, susijusios su deponuojančios terpės (hidroksidinės, karbonatinės-sulfatinės, organomineralinės ir kt.) mikroelementais. Nauji elementų junginiai yra inertiški, nesklinda aplinkoje, todėl nekelia pavojaus. Tinkamomis geologinėmis-geocheminėmis sąlygomis užterštas dumblas gali būti naudojamas kirtaviečių rekultivacijai – tai racionaliausias jo utilizavimo būdas. Optimali įterpimo norma priklauso nuo dumblo užterštumo laipsnio (tirtame objekte ji sudaro 300 t/ha). Medžių sodinukams dumblas turi ryškų teigiamą poveikį.

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ПРОЦЕССЫ МИГРАЦИИ И ПЕРЕРАСПРЕДЕЛЕНИЯ ХИМИЧЕСКИХ ЭЛЕМЕНТОВ В ПОЧВЕ ПРИ ИСПОЛЬЗОВАНИИ ОСАДКОВ СТОЧНЫХ ВОД ДЛЯ РЕКУЛЬТИВАЦИИ ЛЕСНЫХ ВЫРУБОК

Резюме

В промышленных городах часто возникают проблемы утилизации сильно загрязненных токсичными химическими элементами осадков сточных вод, непригодных для сельского хозяйства. Исследования показали, что такой ил пригоден для рекультивации вырубок торфянистых лесов. Важно выбрать слабосточные участки с мелкозалегающим водоупорным горизонтом. При минерализации ила содержание органического вещества и кальция понижается, но соответственно повышается содержание остальных элементов. В грунт они проникают с частицами ила. Глубже проникают кальций и водорастворимые формы (pH = 7) элементов, но они скоро замещаются потенциально растворимыми (pH = 4,8). Подвижные формы хорошо сорбируются органическим веществом почвы, а их остатки стабилизируются геохимическими барьерами грунта (гидроокисным, карбонатным и др.). При этом образуются новые ассоциации микроэлементов, связанные с элементами депонирующих сред. Новые соединения элементов малоподвижны и влияния на среду не оказывают. Поэтому загрязненный ил при соблюдении соответствующих геологических условий вполне пригоден для рекультивации лесных вырубок, а этот способ его утилизации является наиболее рациональным и рентабельным. Норма внедрения зависит от степени загрязнения ила; в исследованном объекте она составила 300 т /га.