169 OIL SHALE 1991, vol. 8, No. 2
ГОРЮЧИЕ СЛАНЦЫ 1991, том 8, № 2

https://doi.org/10.3176/oil.1991.2.09

UDC [550.42 : 546 : 552.57] : 502.76(474.2)

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HEAVY METALS IN THE ENVIRONMENT OF THE KOHTLA-JÄRVE AREA, ESTONIA

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ТЯЖЕЛЫЕ МЕТАЛЛЫ В ОКРУЖАЮЩЕЙ СРЕДЕ РАЙОНА г. КОХТЛА-ЯРВЕ (ЭСТОНИЯ)

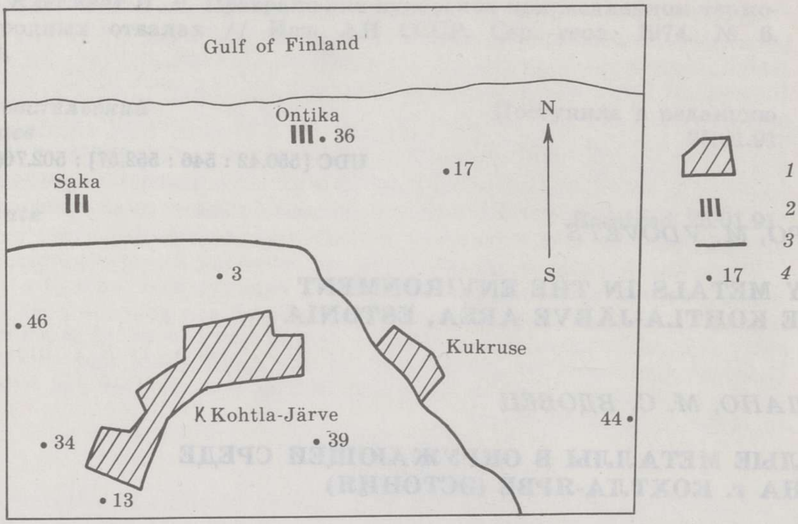
As is generally known, the ever growing oil shale production and processing results in substantial environmental pollution [1—3], phenol being the major polluting component in the regions, where oil shale processing plants are concentrated. Pollution by dust particles derived from oil shale, enclosing rocks and volatile ash as well as by various hydrocarbons, hydrogen sulphide, sulphur oxides, carbon and nitrogen, ammonia and other toxic compounds also takes place.

The effect of oil shale production and processing on the concentration of heavy metals in environment has been inadequatly studied so far [4]. As for NE Estonia, which is the region of intensive development of oil shale industry with its centre in Kohtla-Järve, only suggestions have been made on this occasion [1, 2], though data on the heavy metal contents in kukersite processing products are available (Table 1). Lead and cadmium contents in the blood and hair of inhabitants of the region differ significantly from their background values [7].

Table 1. **Heavy metal contents (g/t) in wastes of kukersite production and processing in Estonia according to L. Pets et al. [5, 6]**

Таблица 1. **Концентрация тяжелых металлов (г/т) в отходах сланцедобывающей и сланцеперерабатывающей промышленности в Эстонии (прив. по Л. И. Пец и др. [5, 6])**

Study material	1st class of hazard			2nd class of hazard			
	Pb	Zn	Hg	Cu	Ni	Co	Sb
Kukersite	23.5	48.7	0.08	17.0	21.0	2.9	0.47
Slag	13.0	81.5	data are	24.5	29.0	4.1	0.41
Ash from steam heaters	39.5	72.0	lacking	23.0	30.0	4.8	0.47
Ash from cyclones	56.5	61.0	0.01	23.0	28.5	4.9	0.48
Ash from electric precipitators:							
I	42.0	70.7	0.02	13.0	35.0	5.2	0.62
II	97.5	116.0	0.05	19.0	38.0	5.8	1.31
III	113.5	135,3	0.01	16.0	38.0	6.1	1.42
IV	121.5	140.3	0.21	18.0	41.0	6.3	1.76
Ash from chimneys	163.5	183.6	0.68	33.0	53.0	6.4	1.63



Scheme of the territory under study demonstrating the sites with the most polluted soils. Legend: *1* — regions of the town of Kohtla-Järve; *2* — settlements; *3* — Leningrad-Tallinn highway; *4* — site numbers

Схема изученной территории с указанием точек с наибольшим загрязнением почв. Условные обозначения: *1* — районы г. Кохтла-Ярве; *2* — поселки; *3* — шоссе Ленинград—Таллинн; *4* — номера точек

The present investigation attempts to solve problems related with the heavy metals input sources and their distribution in the components of environment in the Estonia's oil-shale mining and processing area. The investigation was carried out at Kohtla-Järve and in the adjacent territory. The area of 110 sq. km under study, represents a core of urbanic agglomeration with a territory adjacent in the north, bounded by the Gulf of Finland (Figure). Isolated parts of the Kohtla-Järve agglomeration, i. e. Kohtla-Järve proper (Sotsgorod), Kukruse and Käva, are situated in the southern part of the territory under study. Technogenic landscapes with waste heaps of the Slantsekhim Production Association and Kohtla-Järve Thermoelectric Power Plant, former *Kukruse* and *Käva* mines, and agricultural lands occupy most of the territory. The sampling was carried out at 60 sites, situated, as a rule, in a standard network 2 × 2 km, with detailization of some areas.

The territory of Lahemaa National Park (Estonia) and the area around Dolgoye Lake (south-east of Leningrad District) were used as background territories where the level of pollution was at its lowest for the given region.

About 450 samples of various components in the environment of Kohtla-Järve and the background territories were investigated.

The subdivision of heavy metals according to classes of hazard was performed according to the generally accepted All-Union State Standard 17.4.1.02-83 [8].

During the investigation, precision methods of heavy metal contents determination were used: X-ray spectral method [9] for Pb, and atomic absorption spectrophotometry (AAS) for Hg (in cold vapours), Zn (in flame), Cu, Ni, Co, Cd and Sb (in tubular graphite sprayer) [10, 11]. Semiquantitative spectral analysis (SQSA) [12] predominated at preliminary stages of the investigation and for routine study of samples of plants and fungi. The results obtained were processed on ES-1033 computer.

Wastes of oil shale producing and processing plants, situated both in the area under study (Slantsekhim Production Association, Kohtla-Järve Thermoelectric Power Plant) and in its vicinity (*October* open-pit, *Estonia* and *Ahtme* mines) were analysed as potential sources of environmental pollution by heavy metals. The results obtained are given in Table 2 (in all cases, Cd contents were below detection limit, 1 g/t).

The concentrations of heavy metals in the wastes of oil shale production industry, are, for the most part rather low, as is seen from Table 2 and previously obtained results. So, in all cases Cd, Hg, Ni and Co contents were lower than the clarke of lithosphere, Pb and Cu contents were higher only in one case out of three (enrichment factor 1.5—1.7). Nevertheless, Zn and Sb contents in oil shale production wastes exceeded the clarke (enrichment factors 1.8—2.2 and 9.4—24.8, respectively). These data demonstrate that in oil shale production wastes Sb and, to a lesser extent Zn create a major source of environmental pollution.

The study of oil shale-processing wastes composition (Table 2) showed that Pb and Hg (enrichment factor up to 3.4 and 7.2, respectively), but also Sb (enrichment factor up to 15.6) may cause considerable ecological damage. Earlier investigations of the kind, carried out by D. Yegorov [4] and L. Pets with co-authors [5, 6], demonstrated that kukersite

Table 2. **Heavy metal contents (g/t) and their enrichment factor in wastes of oil-shale industry plants at Kohtla-Järve* (on a few samples)**

Таблица 2. **Содержание тяжелых металлов (г/т — в числителе) и их коэффициенты концентрации (в знаменателе) в отходах предприятий сланцевой промышленности района г. Кохтла-Ярве (по единичным образцам)**

Industrial plants	Kind of waste	1st class of hazard			2nd class of hazard			
		Pb	Zn	Hg	Cu	Ni	Co	Sb
O i l - s h a l e p r o d u c t i o n								
October open-pit	Concentrated plant wastes	9 / 0.5	153 / 1.8	0,015 / 0.2	7 / 0.1	22 / 0.4	4 / 0.2	4,7 / 9.4
Estonia mine	Idem	11 / 0.7	180 / 2.2	0.068 / 0.8	70 / 1.5	38 / 0.7	6 / 0.3	not deter
Ahtme mine	Idem	27 / 1.7	160 / 1.9	0.037 / 0.5	10 / 0.2	36 / 0.6	5 / 0.3	12,4 / 24.8
O i l s h a l e p r o c e s s i n g								
"Slantsekhim" Production Association	Coke of furnace	45 / 2.8	50 / 0.6	0.12 / 1.5	30 / 0.6	44 / 0.8	3 / 0.2	3.52 / 7.0
Idem	Ash of the 3rd gasgeneration station	23 / 1.4	60 / 0.7	0.60 / 7.2	10 / 0.2	40 / 0.7	3 / 0.2	7.81 / 15.6
Kohtla-Järve Thermoelectric Power Plant	Ash-slag mixture from *Reley-Stoker* boilers	54 / 3.4	60 / 0.7	—	40 / 0.9	44 / 0.8	5 / 0.3	2.34 / 4.7

* Numerator is element content according to data of precision methods of analysis; denominator is enrichment factor in respect to lithosphere clarkes [13].

combustion products can also be a source of environmental pollution by Zn, Ni, Co and V.

The accumulation of heavy metals was studied in soil (the humus horizon), forest litter, 30 species of terrestrial higher plants and also in fruiting bodies of pileate fungi. Average contents of heavy metals in these environmental components are given in Table 3. Cd and Sb contents were as a rule below the limit of detection of these elements by SQSA method. According to AAS data, an average Hg content in soil was 0.08 g/t, Cd content in soil was less than 1 g/t and in litter 4 g/t, Sb content in soil was 1.5 g/t and in litter 3.7 g/t.

The degree of pollution of environmental components by heavy metals in the territory under study was determined by comparing the data presented in Table 3 with those for background areas, and in case of soils, also with their clarkes [from 15, 16].

Table 3. **Average heavy metal contents* (g/t, for ash mass) in environmental components at Kohtla-Järve and its vicinity**

Таблица 3. **Среднее содержание тяжелых металлов (г/т, на зольную массу) в компонентах окружающей среды изученной территории района г. Кохтла-Ярве (данные полуколичественного анализа)**

Environmental components	Number of samples	1st class of hazard		2nd class of hazard			Total	
		Pb	Zn	Cu	Ni	Co	1st class	2nd class
Soil (the humus horizon)	47	40	40	40	26	6	80	72
Forest litter	14	60	140	35	21	6	200	62
Terrestrial higher plants	358	10	40	15	6	4	50	25
Fruiting bodies of pileate fungi	51	7	170	190	3	<3	177	195

* Semiquantitative spectral analysis data.

The average enrichment factors of heavy metals in the Kohtla-Järve District were as follows: for soils — Co 5.0, Pb 4.7, Ni 2.9, Zn 1.3 (Cu concentrations were almost equal to those for the study area and the background territory); for plants — Pb and Zn 1.8, Co 1.7 (Ni concentration were approximately equal). The average enrichment factor values of heavy metals in the soils of Kohtla-Järve (with respect to corresponding clarkes) were as follows: Hg 8.0, Pb 3.0, Sb 1.5; average contents of other heavy metals were lower than clarkes (enrichment factor below 1).

Judging by these data, it can be concluded that environmental components in Kohtla-Järve are mainly polluted by Hg, Pb and Sb. The pollution by Zn, Ni, Co and Cu is more problematic, as the concentrations of the first three elements in soils of the territory under study are higher than their corresponding background values, but lower than those of clarkes; differences in the Cu content were mainly established in plants.

Environmental pollution of the territory under study by Hg, Pb and Sb is primarily due to oil shale processing plants.

The distribution of heavy metals was compared in different environmental components of the territory under study.

The concentration of Pb and Zn, heavy metals of the first class of hazard, proved higher in forest litter than in soils (Table 3); the contents of heavy metals of the second class of hazard (and their sums) were approximately equal in both components. According to AAS data (see above), Cd and Sb contents are also higher in the forest litter than in soil. All heavy metal contents are lower in the ash of the terrestrial plants than in soil and forest litter (excluding Zn, whose content in ash is similar to that in soil). Pb, Ni and Co concentrations are low in pileate fungi, whereas those of Zn and Cu are high.

Thus, in the area under consideration heavy metals accumulate primarily in the humus horizon of soils and in forest litter. Fruiting bodies of pileate fungi are active accumulators of Zn and Cu, but due to low biomass, they, accumulate only insignificant part of toxic elements distributed in the environment.

Heavy metal concentration in plants is not high on average, and it depends both on plant species and heavy metal contents in the environment. But it should be noted that heavy metal contents in the plants aren't only indicative of the environmental pollution level but serve also as a criterion of the part of technogenic pollution that enters the biogeochemical cycle and is therefore most dangerous for inhabitants' health. In view of this, phytogeochemical method of indication is very important for investigation of environmental pollution with heavy metals [17—19].

Table 4. **Heavy metal contents* in samples of the most polluted soils at Kohtla-Järve and its vicinity in comparison with their average contents and maximum permissible concentration (MPC) of soils**

Таблица 4. **Содержание тяжелых металлов в пробах наиболее загрязненных почв района г. Кохтла-Ярве в сопоставлении со средними их содержаниями и ПДК почв**

Locality No.**	Position	Sample No.	A^d, %	1st class of hazard			2nd class of hazard			
				Pb	Zn	Cd	Cu	Ni	Co	Sb
3	2 km east of Kolga	K-21g	26	38	29	<0,8	7	11	26	0,7
13	1.5 km west of Kohtla	K-187g	86	116	52	0,9	60	32	53	Not determined
17	Near Valaste	K-241g	82	197	353	2	21	34	7	1,5
34	3 km north of Kohtla	K-651g	82	92	131	Not determined	44	43	7	Not determined
36	Near Ontika	K-618g	82	18	213	Idem	189	24	7	Idem
39	1 km north of Peery	K-592g	92	24	71	„	222	18	6	„
44	1.5 km north-west of Kotinuka	K-546g	82	203	197	„	44	19	2	„
46	2.5 km south-west of Saka	K-640g	96	17	71	..	144	28	6	„
	Average content in soils		82	49	114	<1	35	26	8	1,5
	MPC of soils		—	20—400	50—400	3—8	35—125	45—100	25—50	5—10

* According to data of precision methods of analysis per dry matter.
** See the Figure.

Maximum permissible concentrations (MPC) of toxic elements in soil are an important index of environmental situation. MPC values, which are very different in literature [16, 20, 21], are given in Table 4 in comparison with average and maximum heavy metal contents in soils of the given territory. Judging by these data, even average contents of Pb (49 g/t), and Zn (114 g/t) in soils are higher than minimum MPC values of these elements (20 and 50 g/t, respectively), but their contents in the most polluted soils do not exceed maximum MPC values (400 g/t in both cases). Average Cu content in soils of the territory (35 g/t) coincides with minimum MPC values; its content in the most polluted soils (144—222 g/t) even exceeds maximum MPC value. In all cases the contents of other heavy metals given in Table 4 (Cd, Ni, Co and Sb) and Hg in soil are lower than minimum MPC values (except for Co at the sites 3 and 13).

Distribution of localities with the largest pollution of soil with heavy metals (Table 4; see Figure) cannot be explained unambiguously yet. According to available material, the most polluted soils are situated at some distance from sources of pollution (oil shale processing plants), but not in their vicinity. It is apparently connected with considerable scattering of oil shale processing wastes, volatile ash in particular. Considerable soil pollution by Pb, Zn and Cu at site 44 can be caused by close disposition of town dump of Jõhvi.

Thus, on the basis of these investigations, it can be concluded that intensive development of oil shale industry at Kohtla-Järve and in its vicinity results in environmental pollution of the adjacent territory not only by organic compounds (as was previously known) but also by some heavy metals, namely by Hg, Pb and Sb and to a lesser degree by Zn and Cu.

Accumulation of Pb and Zn takes mainly place in the humus horizon of soils and in forest litter. Selective accumulation of heavy metals takes place in biota (higher plants and pileate fungi).

РЕЗЮМЕ

Изучен район с интенсивным развитием сланцевой промышленности — часть г. Кохтла-Ярве и прилегающая территория (рисунок). В качестве потенциальных источников загрязнения тяжелыми металлами были исследованы отходы сланцедобывающей и сланцеперерабатывающей промышленности, а в качестве сред, депонирующих это загрязнение, — почвы (гумусовый горизонт), лесная подстилка, 30 видов наземных высших растений и плодовые тела шляпочных грибов (таблицы 1—4).

Сделан вывод, что интенсивное развитие сланцевой промышленности на изученной территории приводит к загрязнению окружающей среды тяжелыми металлами, в первую очередь ртутью, свинцом и сурьмой, в меньшей степени цинком и медью. Масштабы этого загрязнения по сравнению с загрязнением в районах сосредоточения крупных предприятий металлургии относительно невелики.

Распределение точек с наибольшим загрязнением почвы тяжелыми металлами не поддается однозначному объяснению. Характерно, однако, что наиболее загрязненные почвы расположены не в непосредственной близости от предприятий сланцеперерабатывающей промышленности, а на некотором удалении от них. Это, по-видимому, связано со значительным разносом летучей золы.

Накопление свинца и цинка происходит главным образом в гумусовом горизонте почв и лесной подстилке. Биота — высшие растения и грибы — накапливают тяжелые металлы избирательно.

REFERENCES

1. *Луйга П. О., Паальме Г. П.* Охрана окружающей среды при добыче и использовании эстонских горючих сланцев // Горючие сланцы. 1985. Т. 2, № 2. С. 206—213.
2. *Jegorov D., Trapido M., Rajur K., Loosaar J.* Põlevkivienergeetika ja keskkond // Kaasaegse ökoloogia probleemid. Ökoloogia ja ühiskond. Vabariikliku IV ökoloogiakonverentsi teesid, Tartu, 23.—25. märts 1988. Tartu, 1988. Lk. 38—40.
3. *Пихлак А.* Проблемы современной экологии и горючие сланцы // Горючие сланцы. 1988. Т. 5, № 3. С. 328—329.
4. *Егоров Д., Трапидо М., Раюр К. и др.* Воздействие сланцевой промышленности северо-восточной части Эстонской ССР на состояние Чудского озера // Изв. АН ЭССР. Биол. 1989. Т 38, № 2. С. 131—136.
5. *Пец Л. И., Отт Р. Э.* Ртуть в минеральной части продуктов сжигания и переработки сланца-кукерсита // Горючие сланцы. 1989. Т. 6, № 3. С. 287—290.
6. *Пец Л. И., Ваганов П. А., Кнот И. и др.* Микроэлементы в золах сланца-кукерсита Прибалтийской ГРЭС // Там же. 1985. Т. 2, № 4. С. 379—390.
7. *Viitak A., Kahn H., Vilkis A., Hödrejärv H.* Pb ja Cd sisaldus Eesti NSV tööstuspiirkondade elanike veres ja juustes // Kaasaegse ökoloogia probleemid. Lk. 163—166.
8. ГОСТ 17.4.1.02-83. Охрана природы. Почвы. Классификация химических веществ для контроля загрязнения / Издательство стандартов, 1985.
9. *Сериков И. В., Цимошенко Б. А.* Рентгеноспектральный флуоресцентный анализ // Тр. ВСЕГЕИ. 1986. Т. 338. С. 83—125.
10. *Столярова И. А., Филатова М. П.* Атомно-абсорбционная спектрометрия при анализе минерального сырья. — Л., 1981.
11. *Пятова В. Н., Крошкина А. Б., Константинова М. Г., Сидорук Е. И.* Атомно-абсорбционное определение сурьмы с использованием графитового трубчатого атомизатора // Атомно-абсорбционные методы анализа минерального сырья : Сб. науч. тр. ВИМС. М., 1982. С. 51—60.
12. *Борин Ю. Н., Тарновская А. Н.* Полуколичественный (приближенно-количественный) эмиссионный спектральный анализ // Тр. ВСЕГЕИ. 1986. Т. 338. С. 137—145.
13. *Войткевич Г. В., Кокин А. В., Мирошников А. Е., Прохоров В. Г.* Справочник по геохимии. — М., 1990.
14. *Вдовец М. С., Лапо А. В.* Вызывают ли загрязнение окружающей среды отходы ПО «Эстонсланец» // Сланцевая промышленность. Информационная серия 1. 1987. № 6. С. 1—3.
15. *Ковальский В. В., Андрианова Г. А.* Микроэлементы в почвах СССР. — М., 1970.
16. *Kabata-Pendias A., Pendias H.* Trace elements in soils and plants // Boca Raton (Florida), CRC Press, 1985. (Рус. перевод: Кабата-Пендиас А., Пендиас Х. Микроэлементы в почвах и растениях. — М., 1989.)
17. Биогеохимическая индикация окружающей среды : Тез. докл. Всесоюз. сем. посв. 125-летию со дня рожд. В. И. Вернадского, Ленинград, 30 марта 1988 г. — Л., 1988.
18. *Lapo A. V.* Rational complex of phytogeochemical indicators of environmental pollution by toxic microelements // 9th Int. Symp. on Environm. Biogeochemistry : Abstr. Moscow, 1989. P. 199.
19. *Lapo A. V., Vdovets M. S.* A phytogeochemical method for studying heavy metal contaminations on the technosphere // Int. Symp. of Geochem. Prospecting : Extended Abstr. Prague, Geological Survey, 1990. P. 19.

20. *Вертинская Г. К., Малахов С. Г., Махонько Э. П.* Метод оценки приоритетности веществ, подлежащих контролю в почвах // Тр. Ин-та экспериментальной метеорологии. Сер. Загрязнение природных сред. 1988. Вып. 16 (133). С. 117—120.
21. *Димитриев М. Т., Казнина Н. И., Пинигина И. А.* Санитарно-химический анализ загрязняющих веществ в окружающей среде : Справочник. — М., 1989.

Presented by A. Raukas
Received
19.06.90

A. P. Karpinsky Geological Research Institute Leningrad

Представил А. В. Раукас
Поступила в редакцию
19.06.90

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