

Chapter 6

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Transfer of Contaminants from the Area of Pesticide Dump into the Surrounding Ecosystems

For many years the method to get rid of the unwanted wastes was to dig it underground. During the XXth century this procedure has been widely applied to substantial amounts of hazardous materials including industrial refuses, communal wastes, and unwanted pesticides. Residual compounds emerged from the badly secured dumps and were transported by the ground waters, absorbed by plants and built into the food chain creating hazard to living organisms of the ecosystem. With time many cases from all over the world proved the hazard of the not properly protected wastes left in the environment and generated actions to clear out the wastes, e.g. the project of liquidating of pesticide dumps in Poland (see Chapter 2).

May be, all the known dumps will be excavated with time and their contents will be taken away to be burn or properly protected. The question remains how to find the forgotten ones, that slowly release hazardous residues to the environment. This was the reason to carry over the project on the influence of a pesticide dump on the surrounding ecosystems – the study area has been described in Chapter 5, and Chapters 7-10 are devoted to the results of experiments using plants and animals of the study area. Of course, an attempt has been also made to determine the residues of the contaminants in soils of the surrounding environment.

The selected for study dump was founded with the beginning of 1970's (fig. 1 in Chapter 5) and taken away in 2004. It worked for over 30 years collecting banned DDT pesticide formulations, old chemicals, drugs etc., so, for chemical analysis of soil DDT but also lead and cadmium have been chosen. Samples of soil from the area of the dump (zone I), from the gravel-ground (zone II), bog at the bottom of the dump hill (zone III) and wood (zone IV) were collected in 2002, 2003 and 2006 after excavating of the wastes. Samples of bottom sediment of the drainage ditch draining off waters from the study area to the lake (S) and of bottom sand from its

estuary to the lake (J) were also collected. Anticipation on routs of rain-fall water flow down served to choose the points of sampling.

The samples of soil were air-dried and sieved. For DDT analysis 50 g subsamples were extracted 3 times with 50 cm³ of a mixture of petroleum and ethyl ethers (1:1). The combined extracts were evaporated, then dissolved in 1 cm³ of n-hexane and injected onto a column $\phi=10$ mm filled with 2 g of florasil and 2 g of anhydrous sodium sulphate. The pesticides were eluted with 20 cm³ of 6% ethyl ether in petroleum ether. The eluate was evaporated, dissolved in n-hexane and analysed using gas chromatograph with electron capture detection.

Soils were examined for the contents of free fractions of Pb and Cd in a filtrate of 1M HCl, and for the total contents of the metals analysed after dissolving the sample in aqua regia. Concentrations of lead and cadmium in the extracts obtained were assayed with flame atomic absorption spectrometry. A variation analysis of the results was completed with the unpaired t test with Welch's correction.

Contamination with DDT

Concentrations of DDT and its metabolites in samples collected in 2002 are presented in table 1. This time the soil samples in zone I were collected near the wall of visible wells at the depth of 50 cm. No residues of DDT were detected in one case, comparatively low levels were determined in 3 cases and extremely high concentration (almost 27 mg kg⁻¹) was found in one case. Some concentration was determined in the soil from zone II, from the place with traces of rain-water fall down. In the zone III the sampling points were set beginning from the bottom of the dump hill in the direction towards the lake and the concentrations (except the first sampling point) decreases with increase of the distance to the hill. Not much DDT residues were determined in the soil of the wood (zone IV) and some residues were found in the bottom sandy sediments of the lake .

More soil and sediment samples were analyzed in 2003. In zone I soil samples were collected from areas adjoining the 3 wells, which were selected during a preliminary examination in 2002. Three bore-holes were drilled around each well and soil samples were collected at depths of 0 - 30 cm, 30 - 60 cm, and 70 - 100 cm. The samples collected at the same depth around the well were combined and treated as one.

Table 1

DDT and its metabolites [mg kg⁻¹] in soil and lake sediments (Skibniewska et al 2003)

Zone	N	DDE	DDD	DDT	Σ DDT
I	7	n.d. – 2.147	n.d – 3.200	n.d. – 21.333	n.d. – 26.680
II	1	0.051	0.047	0.098	0.196
III	7	n.d. – 0.225	n.d.	n.d. – 0.300	0.033 – 0.300
IV	4	n.d. 0.098	n.d.	n.d. – 0.030	n.d. 0.099
lake	6	n.d. 0.800	n.d. – 0.733	n.d.	n.d. – 1.533

Zone II covered a disused gravel pit from the south to the dump hill and soil samples were taken from bore-holes made along hollows of the area, which indicated the direction of rainfall discharge. South-east of the dump, facing the lake, a strip of ground was spreading out whose flora (i.e. reed) implied another route of waterfall discharge (zone III). Sample III₁ was collected at the foot of the pesticide dump, and then every 5 m. Zone IV covered a strip of forest between the dump and the pond. The first sample was collected at the height of the dump, and then every 50 m. In zones II – IV, soil samples were collected from an area size of ca. 1 m², at 3 depths (0 - 30 cm, 30 - 60 cm, and 70 - 100 cm). The soil samples collected at the same depth were merged, and a mean sample was obtained.

The results of the 2003 samples are presented in table 2. Though the soil samples were collected by these wells, around which the highest DDT concentrations were determined in the previous year, no result exceeded 1 mg kg⁻¹. The highest concentrations of the compounds were determined at the area of a pesticide dump, but no clear pattern was observed concerning transfer of DDT down the ground: the highest concentrations were detected at the top layer of the soil round well I₁, 0.5 m down the well I₃ and 1 m down the well I₂. Some amounts of DDT were washed down to the gravel pit in the southern direction and to the bog (zone III) in the northern direction.

Table 2

DDT and its metabolites [mg kg⁻¹] in soil collected in 2003

Station	Layer 0-30 cm		Layer 30-60 cm		Layer 60-100 cm	
	DDE	ΣDDT	DDE	ΣDDT	DDE	ΣDDT
I ₁	0.0020	0.0405	0.0022	0.0055	n.d.	0.0243
I ₂	0.0583	0.3632	0.0579	0.3200	0.0391	0.5548
I ₃	0.0109	0.1228	0.0084	0.1624	0.0060	0.0803
II ₁	0.0075	0.0399	0.0062	0.0480	-	-
II ₂	0.0046	0.0396	0.0030	0.0232	0.0028	0.0431
II ₃	0.0009	0.0053	0.0018	0.0114	n.d.	0.0100
III ₁	n.d.	0.0106	0.0145	0.1377	-	-
III ₂	0.0014	0.0297	0.0017	0.0116	-	-
III ₃	0.0025	0.0186	0.0037	0.0434	-	-
III ₄	0.0043	0.0450	n.d.	0.0053	0.0041	0.0203
III ₅	0.0022	0.0808	0.0028	0.0091	-	-
III ₆	0.0016	0.0081	n.d.	0.0022	n.d.	0.0024
III ₇	0.0011	0.0059	0.0015	0.0246	n.d.	0.0097
IV ₁	n.d.	0.0046	0.0047	0.1641	n.d.	0.0096
IV ₂	0.0110.	0.1492	0.0098	0.3473	0.0031	0.0674

Results for this zone confirmed the supposition that rain-water rinse the contaminants out of the pesticide dump wells out into the environment: concentrations of DDT decreased with increase of the distance to the dump. Again, no clear pattern of DDT concentrations in the layers at the sampling points were observed.

The transfer of contaminants in the western direction, through the wood to the reclamation ditch, has been also proved (zone IV). Sediments of the ditch (samples S) contained surprisingly low DDT levels because sediments were rich in organic matter of high absorbance capacity (table 3). DDT concentrations in the sandy bottom of the lake were not very high and also decreased with increase of the distance to the shore (samples J).

Statistical analysis (table 4) proved clearly the that the hazardous wastes were protected insufficiently and were washed out with the rain-water. The highest concentrations were detected in the sampling points at the area of the pesticide dump. Considerable high DDT concentrations in soil of the wood separating the dump and the reclamation ditch might be the result of the soil type (Chapter 5).

Table 3

DDT and its metabolites [mg kg^{-1}] in bottom sediments of the lake and the reclamation ditch

Station	DDE	Σ DDT
J₁	n.d.	0.0195
J₂	0.0013	0.0418
J₃	0.0015	0.0255
J₄	n.d.	0.0168
J₅	0.0032	0.0580
J₆	0.0073	0.0255
J₇	0.0013	0.0154
J₈	0.0024	0.0460
J₉	n.d.	0.0130
S₁	0.0012	0.0142
S₂	n.d.	0.0131
S₃	0.0019	0.0249

Table 4

Statistical parameters of DDT and its metabolites [mg kg^{-1}] content in soils and sediments

Station	Mean \pm SEM	Variation coeff. [%]	Significance
I	0,186 \pm 0,1874	100,77	I versus I**
II	0,025 \pm 0,0184	75,20	I versus III**
III	0,022 \pm 0,0331	149,48	I versus J**
IV	0,124 \pm 0,1286	103,94	I versus S**
J	0,029 \pm 0,0158	54,40	
S	0,017 \pm 0,0065	37,46	

* - $p < 0.05$, ** - $p < 0.01$

For the last time the soil samples were collected in 2006, two years after liquidation of the dump i.e. taking away the wastes and also soil from the area of the dump (table 5). Traces only were determined in the soil samples from the area of the dump and small concentrations were found in the soil from gravel pit. It should be emphasized that no residues of the maternal compound DDT were determined. Some residues, both of the DDT and its metabolites, were still present in the bog soil samples (zone III), probably because of higher organic matter content in these soils. Sediments of the reclamation ditch (zone S), though rich in organic matter, contained much less of the maternal DDT though similar concentrations of DDE. Relatively high concentration of residues, especially maternal DDT. in samples of bottom lake sediments (J) proved again that the compounds rinsed out of the dump were transferred to the lake with ground water.

Table 5

DDT and its metabolites [mg kg^{-1}] in soil collected in 2006

Zone	N	DDE	DDD	DDT	Σ DDT
I Average	5	n.d. – 0.0002 0.0001	n.d.	n.d.	n.d. – 0.0002 0.0001
II	2	n.d. – 0.0011	n.d.	n.d.	n.d. – 0.0011
III Average	7	n.d. – 0.0053 0.0007	n.d – 0.0094 0.0008	n.d. – 0.1152 0.0144	n.d. – 0.1218 0.0158
S	2	0.0010 – 0.0011	n.d.	0.0005 – 0.0006	0.0016
J	7	0.0001 – 0.0041	n.d. – 0.0009	n.d. – 0.0991	0.0001 – 0.1097

Contamination with heavy metals

A hypothesis was advanced that the deposited materials contained also Pb and/or Cd pollutants able to migrate with rainfall. There was the question at the beginning of the study how to evaluate the contamination of the ecosystem with heavy metals – there were no information on the heavy metals content in the soil before founding the dump. Determination of the fraction soluble in 1M HCl has been chosen assuming that the elements flowing out of the wastes had to be in a soluble form.

In 2002 soil samples were collected in October, at the depth of 50 cm (table 6). Increased content of the soluble in 1M HCl fraction proved leakage of the contaminants out of some wells. Also, increased levels were determined in some sampling points proving the anticipations of routes of rain-fall-water flowing down the hill towards the lake; part of the flow went down the zone III and part went under the wood towards the reclamation ditch, and along the ditch to the lake.

Table 6

Content of lead and cadmium soluble in 1M HCl [mg kg^{-1}] in soils and sediments (2002)

Zone	N	lead	cadmium
I	7	1.764 – 14.025	0.028 – 0.652
II	1	1.110	0.063
III	7	1.632 – 7.003	0.048 – 0.363.
IV	4	3.028 – 3.991	0.108 – 0.168
J	6	1.084 – 2.936	0.067 – 0.245

In July 2003 lead and cadmium soluble in 1 M HCl content was determined at three depths (table 7). Samples of two of the stations examined contained Pb and Cd in amounts several times higher than the other concentrations: the sample from station I₂, collected next to one of the damaged wells, and the sample from station III₁, collected at the rainfall discharge from the dump and constituting the material deposited on the impermeable layer; these samples were excluded from the pool of results subjected to a statistical analysis. Higher heavy metals content was determined in samples of reclamation ditch sediments than of the lake ones (table 8), which was likely to result from the higher sorption capacity of the peat-muck soils occurring therein.

Zones of the investigated area were not differentiated in terms of the cadmium soluble in 1 M HCl content, yet highly significant differences were found in respect to the content of free lead fraction, which proved the course of rainfall discharge from along the forest to the reclamation ditch and then down to the lake (tab. 9). A substantially higher content of organic matter in the ditch resulted in the

accumulation of this element in ditch sediment. Due to the sandy bottom, however, elevated concentrations of that element were not reported in the lake.

Table 7

Concentration of metals soluble in 1 M HCl [mg kg^{-1}] in soil at particular stations and depths

Station	Layer 0-30 cm		Layer 30-60 cm		Layer 60-100 cm	
	Pb	Cd	Pb	Cd	Pb	Cd
I₁	2.945	0.175	2.079	0.140	2.887	0.155
I₂	26.304*	1.433*	4.523	0.398	1.998	0.141
I₃	3.467	0.103	2.667	0.044	1.041	0.037
II₁	3.966	0.250	2.739	0.178	3.009	0.263
II₂	1.532	0.048	1.426	0.048	1.303	0.052
II₃	1.701	0.053	2.091	0.051	2.990	0.356
III₁	5.401	0.364	24.922*	1.142*	-	-
III₂	4.013	0.257	3.847	0.343	-	-
III₃	5.402	0.265	6.995	0.258	-	-
III₄	3.777	0.141	4.744	0.388	4.881	0.502
III₅	3.843	0.093	1.249	0.045	-	-
III₆	2.166	0.060	1.029	0.028	1.255	0.038
III₇	6.656	0.122	3.648	0.082	4.524	0.093
IV₁	4.340	0.067	3.063	0.056	1.074	0.035
IV₂	5.969	0.238	4.165	0.104	2.321	0.154

* value excluded from the mean

Table 8

Concentration of metals soluble in 1 M HCl [mg kg^{-1}] in bottom sediments of the lake and the reclamation ditch

Station	Pb	Cd
J₁	1.312	0.086
J₂	2.402	0.196
J₃	1.117	0.074
J₄	2.619	0.237
J₅	1.735	0.143
J₆	1.299	0.083
J₇	1.178	0.087
J₈	1.883	0.154
J₉	2.525	0.218
S₁	6.707	0.311
S₂	8.343	0.399
S₃	6.224	0.172

Table 9

Statistical parameters of the concentration of free lead fraction [mg kg^{-1}] in soils and sediments

Station	Mean \pm SEM	Variation coeff. [%]	Significance
I	2.701 \pm 0.3693	38.68	I versus III * I versus S** II versus III** II versus S* III versus J*** III versus S* IV versus S** IV versus J*
II	2.306 \pm 0.3050	39.67	
III	3.964 \pm 0.4521	45.62	
IV	3.489 \pm 0.7002	49.16	
J	1.786 \pm 0.2011	33.78	
S	7.091 \pm 0.6412	15.66	

* - $p < 0.05$, ** - $p < 0.01$, *** - $p < 0.001$

In 2003 content of total elements have been also determined. The concentrations of total lead and cadmium determined in the mean samples of the soils and sediments examined (table 10) should be acknowledged as natural values estimated for light soils, since Kabata-Pendias and Sadurski (2004) reported the following mean and maximum values of background ranges: 22 and 70 mg kg^{-1} for lead, and 0.37 and 2.7 mg kg^{-1} for cadmium. On the other hand, according to Terelak et al. (2001), Pb and Cd concentrations in the surface horizon (0 - 20 cm) of soils of the agricultural acreage of the Warmia and Mazury Province account for 12.2 and 0.15 mg kg^{-1} , respectively. All soils demonstrate a sorption capacity towards cations, thus with a high content of organic matter and granulometric loamy fraction, display the capability for firm binding of trace elements and their retention in surface horizons.

Table 10

Total lead and cadmium [mg kg^{-1}] in soils and sediments

Zone	Layer 0 - 30 cm		Layer 30 - 60 cm		Layer 60 -100 cm	
	Pb	Cd	Pb	Cd	Pb	Cd
I (without I ₂)	6.842	0.215	5.134	0.189	3.642	0.194
II	5.433	0.237	4.989	0.202	6.200	0.364
III (without III ₁)	9.121	0.401	4.658	0.311	7.651	0.323
IV	9.772	0.209	6.137	0.187	3.956	0.206
Ditch	12.329	0.518	-	-	-	-
Lake	3.216	0.236	-	-	-	-

These soils also include calciferous soils as well as neutral and alkaline ones. Sandy soils with a low sorption capacity and usually acid pH poorly absorb trace elements. In general, most heavy metals are leached out from these types of soils and penetrate into underground waters.

Soil and sediment samples were collected again in 2006, two years after removing the dump out. 54 tons of wastes were taken away to be burn in an express combustion plant. Soil samples collected from the area of the previously located wells contained small amounts of heavy metals (table 11). Smaller amounts of the metals were detected in all sampling points what was the evidence that this area was contaminated with them.

Table 11

Heavy metals soluble in 1 M HCl content [mg kg^{-1}] in soil collected in 2006

Zone	N	Pb	Cd
I Average	5	1.764 – 14.025	0.028 – 0.652
II	2	1.110	0.063
III Average	7	1.632 – 7.003	0.048 – 0.363
S	2	3.028 – 3.991	0.108 – 0.168
J Average	7	0.837 – 2.165 0.117	0.003 – 0.132 0.057

Summing up the results obtained, it should be emphasized that the analyses were carried out around a marked pesticide dump, in a hydrologically examined area. Samples were collected at sites where elevated concentrations of contaminants were expected due to the routes of rainfall discharge from the pesticide dump area. The statistical analysis confirmed highly significant differences between the concentrations of contaminants in individual zones. While searching for lost waste dumps in the area characterised by light soils, thus demonstrating a low sorption capacity, a chemical analysis may yield misleading results.

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