DETERMINATION OF DDT AND ITS METABOLITES IN SOIL, TREE BARK AND EARTHWORM SAMPLES NEAR THE BUDAPEST CHEMICAL WORKS

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Abstract

An abandoned industrial site of the former Budapest Chemical Works (BVM) company has been found to contain 2000-3000 tonnes of leaking industrial waste and dangerous chemicals in corroded barrels on bare ground. The waste lot includes general industrial reagents and intermediates, some 100-200 tonnes of sulphuric acid, several hundred tonnes of 1.2 dichlorobenzene and isopropanol, and numerous other substances falling into toxicity categories from toxic to very toxic or carcinogenic, such as dinitrobenzoic acid, as well as chemical wastes from the pesticide production of the company. BVM used to manufacture numerous pesticide active ingredients, including chlorinated hydrocarbons. Thus, it produced the insecticide DDT in large quantities until the ban of the compound in 1968 and derogated approval for sales until 1974.

The premises of the company has been reported previously to be contaminated, therefore, in the scope of our pesticide residue monitoring surveys between 2015 and 2019, we carried out sampling in its immediate vicinity. In our study, soil (8 samples), surface water (2 samples), tree bark (*Robinia pseudoacacia*, *Sambucus nigra*, *Populus nigra*) and common reed (*Phragmites australis*, (6 samples), as well as earthworms (*Lumbricus terrestris*; 1 sample) sampled next to BVM were analyzed for DDT and metabolite (~DDT) levels. Exceedingly high ~DDT levels above the accepted limit (0.1 mg/kg) were detected in soil samples: nearly 1.5 mg/kg in one sample and 0.11-0.484 mg/kg in other 5 cases. Among the biological samples (tree bark, common reed and earthworm) 0.184 and 0.190 mg/kg concentrations of ~DDT were determined in a black poplar and in an earthworm sample. These findings indicate that the well-known persistency problem related to chlorinated hydrocarbon insecticides, particularly to DDT remains actual to our days.

Introduction

The chemical work premises of BVM (Budapesti Vegyiművek) were constructed in the 19th century, in the outskirts of Budapest at that time. Upon a rugged business history, in 1948 the legal predecessor of BVM [1] began manufacturing the two leading chlorinated hydrocarbon insecticides of the time, 1,1'-(2,2,2-trichloroethane-1,1-diyl)bis(4-chlorobenzene) or by its outdated chemical name dichloro-diphenyl-trichloroethane (from which it earned its acronym DDT) and hexachlorocyclohexane (HCH). A comprehensive study published in 2003 on persistent organic pollutant (POP) compounds manufactured and sold between 1950-2000 by the Hungarian pesticide industry, detailed information is available on the production of BVM as well [2]. Being unaware of the hormonal and other detrimental effects of DDT and particularly its metabolites (~DDT) on warm-blooded organisms, discovered only a decade later, the compound was listed as non-hazardous [3]. This, along with the outstanding economy of the chemical technology resulted in a boost in the production and sales. In turn, driven by the precautionary warning by Hungarian toxicologists, Hungary was the first country banning DDT in 1968. Turnover statistics [2] clearly indicate the above: sales of DDT showed an

increase from 1950 to 1970 with a total of 39 476 tons of the active ingredient sold in two decades (Figure 1).

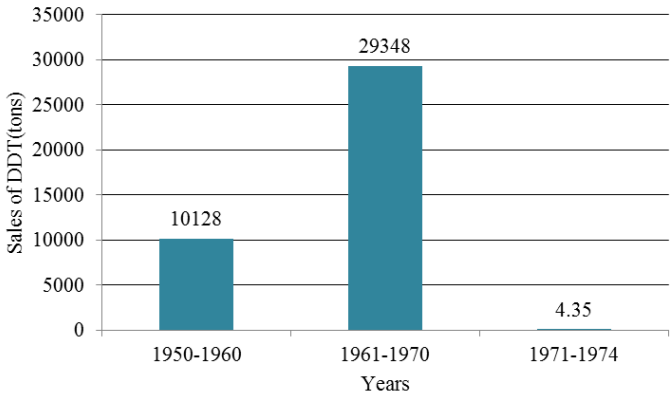

Figure 1. Sales of DDT by Hungary between 1950 and 1974 [2].

The production process, however, doesn't end at the finished product. Waste management is also a fundamental issue in any technology, particularly in the case of substances of high persistence. In addition, in spite of the 6-year derogation period after the ban of DDT, substantial lots of DDT remained on BVM premises, stored mostly in steel drums with expected lifespans of 13-30 years. Long-term storage of obsolete pesticides is a worldwide problem [4] that in sustained time often leads to occupational and environmental risks. Leaching of chemicals from corroded, ballooned or otherwise severely damaged steel drums has occurred also at BVM. Soil contamination by chlorinated hydrocarbons has been detected in the vicinity of the BVM premises quite soon after the bankruptcy of the corporation in 2007. Certain levels of non-systematic contamination is legally tolerated, but residue levels above the maximum residue limit (MRL), defined as the highest overall concentration of a compound and its metabolites officially permitted, call for subsequent legal measures.

In 2011, ELGOSCAR-2000 Kft. started a remediation project by groundwater purification, in a seemingly useless exercise as the cracked barrels causing the pollution have not been removed from the spot. Remediation greatly reduced contaminant levels in groundwater, but recontamination has risen to baseline levels within 2-3 years. 2011 measurements prior to remediation indicated concentrations of benzene and chlorobenzene in groundwater at peak levels of 100 mg/l at some points, which in case of benzene is 100 000 times of the permissible limit [5-7]. The scope of the ELGOSCAR project did not include DDT. A study by WESSLING Hungary Ltd. in 2015, which already focused on chlorinated hydrocarbon insecticides among industrial chemical pollutants, indicated that groundwater pollution had already escaped from the premises of the former BVM [8]. High ~DDT levels (0.16 and 0.22 mg/kg) were detected in two soil samples [9], exceeding the 0.1 mg/kg MRL. Another survey by Greenpeace monitoring ~DDT in house dust and in the eggs of household-raised chicken (*Gallus gallus domesticus*) in the region showed that ~DDT contaminants appeared in nearby homes. Chemical analysis revealed an extremely high level of ~DDT concentration of 1.69 mg/kg in egg [10].

Experimental

The aim of our study was to determine residue levels of DDT (~DDT) in samples collected nearby the former BVM. The sampling regime study included soil (8 samples) and surface water from Illatos ditch (2 samples), as well as biological samples, tree bark (*Robinia pseudoacacia*, *Sambucus nigra*, *Populus nigra*) and common reed (*Phragmites australis*, 6 samples), as well as earthworms (*Lumbricus terrestris*; 1 sample) near or within a 2 km vicinity of the BVM premises.

Preparation of solid samples was carried out by solvent extraction [11], while surface water samples were processed by solid phase extraction [12]. The concentrations of DDT and metabolites in the sample extracts were determined by instrumental analysis, gas chromatography coupled with electron capture detection (GC-ECD).

Results and discussion

Levels of ~DDT were measured in all these samples, as shown along with sample information in Table 1.

Table 1. Sampling points with code, GPS coordinate, type, and place of sampling and the results of the ~DDT measurement

Sample code	GPS coordinate (latitude, longitude)		Type of sample	Place of sampling	DDT content (mg/kg)
BVM1	47.45322	19.10800	soil (10 cm depth)	BVM	1.43
BVM2	47.45321	19.10760			0.345
BVM3	47.45311	19.10727			0.416
BVM4	47.45320	19.10667			0.484
BVM5	47.45323	19.10732	earthworm		0.190
BVM6	47.45455	19.11147	tree bark (*Robinia pseudoacacia*)		0.0109
BVM7	47.45474	19.11167	tree bark (*Populus nigra*)		< LOD*
BVM8	47.45469	19.11137	soil (10 cm depth)		0.0745
BVM9	47.45469	19.11137	soil (60 cm depth)		0.110
BVM10	47.45469	19.11137	soil (30-40 cm depth)		0.0963
BVM11	47.45451	19.11059	tree bark (*Sambucus nigra*)		0.0591
BVM12	47.45365	19.11129	tree bark (*Populus nigra*)		0.184
BVM13	47.45365	19.11129	tree bark, wood chips (*Populus nigra*)		0.0169
BVM14	47.45560	19.10558	surface water (Illatos ditch I.)		< LOD*
BVM15	47.45560	19.10558	surface water (Illatos ditch II.)		< LOD*
BVM16	47.45560	19.10558	common reed (Illatos ditch)		0.0488
BVM17	47.44576	19.12961	soil (10 cm depth)	164. Kisfaludy St.	0.144
BVM18	47.44571	19.12961	tree bark (*Salix* sp.)		0.0440
BVM19	47.44571	19.12955	tree bark (*Tilia* sp.)		0.0206

* below the limit of detection (LOD) of the analytical method, 0.01 mg/l.

An exceedingly high (nearly 1.50 mg/kg) ~DDT level was measured in a soil sample collected near the fence of the BVM premises along the rail cargo tracks, and high concentrations were determined in 5 cases (0.110-0.484 mg/kg) (Figure 2). The ~DDT concentration in 2 soil samples remained below the MRL for ~DDT is soil, 0.1 mg/kg. This indicates MRL violation if 75% of the soil samples, on one occasion by 15 times.

The concentration of ~DDT remained below the LOD of the GC-ECD instrumental analytical method applied, 0.01 mg/l, in both surface water samples collected, [13] however, substantial amounts of metolachlor was detected. Metolachlor (it was officially used until 2003 in

Hungary) is a chloroacetanilide-type herbicide active ingredient with a high potential for runoff into surface water [14], also manufactured by BVM. Exceedingly high levels (0.750-1.279 µg/l) of metolachlor were detected in these samples, quite atypical in the winter period.

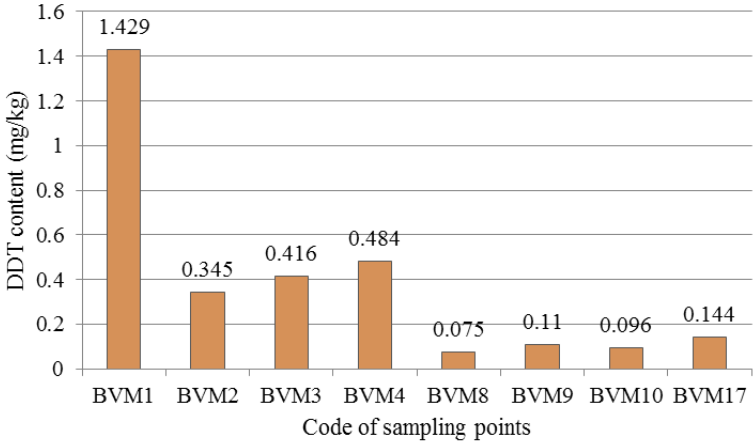

Figure 2. ~DDT content in soil samples.

Among the tree bark and common reed samples, high concentration (0.1837 mg/kg) of ~DDT was measured in a black poplar sample (Figure 3). A similarly high level of ~DDT (0.19 mg/kg) was determined in the earthworm sample studied (Figure 3), indicating substantial soil-borne exposure.

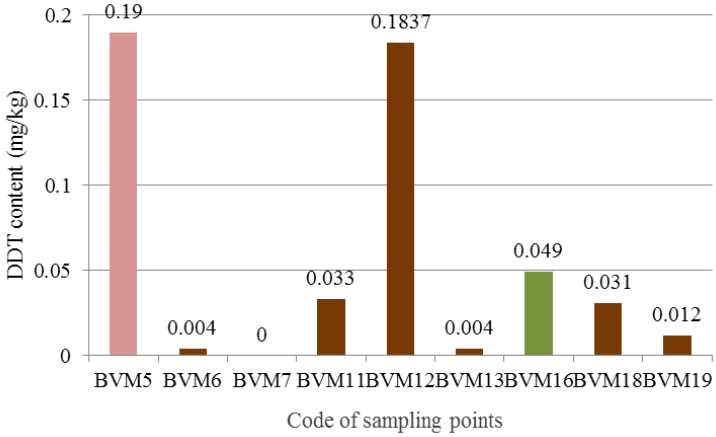

Figure 3. ~DDT content in tree bark (brown), common reed (green) and earthworms (pink) samples.

Conclusion

Along with several former studies, our survey also demonstrated that ~DDT residues remain to be an actual problem nearby Illatos road in Budapest close to residential areas. Almost 2,500 tons of extremely hazardous materials were stored in appalling conditions. Heavily eroded barrels were lying on bare ground, with often unidentifiable chemicals leaching into the soil and groundwater. Upon pressure by Greenpeace, finally all of the 2,493 tons of toxic waste has been removed from the area, and reassessment, including a detailed analysis of the soil and groundwater, are planned with remediation plans to follow [15], although the removal of the hazardous waste barrels ceased the ongoing pollution of the area, natural dissipation for these persistent pollutants is very slow, and the alleged remediation has not started to this date.

Acknowledgements

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References

[1] Ferencváros Önkormányzata (2009) Integrált Városfejlesztési Stratégia. *http://www.ferencvaros.hu/doks/FOE_FoepiteszIroda/IVS_1_5_fej_20091216.pdf*

[2] Á. Pethő, Z. Ocskó (2003) POP hatóanyagot tartalmazó növényvédőszerek hazai felhasználása 1950-2000, In: A környezetben tartósan megmaradó szerves szennyező anyagok (POP) országos leltára a Stockholmi Egyezményben előírt intézkedési terv készítéséhez- GEF/UNIDO projekt száma: GF/HUN/01/005 (Lotz T, Tátrai I.szerk.) Környezetgazdálkodási Intézet, Budapest.

[3] B. Darvas, (2000) Egy Nobel-díjas: a DDT. pp. 131-135. In *Virágot Oikosnak*. l'Harmattan http://mek.oszk.hu/09800/09886/

[4] FAO (1996) Disposal of bulk quantities of obsolete pesticides in developing countries. *http://www.fao.org/fileadmin/user_upload/obsolete_pesticides/docs/w1604e.pdf*

[5] ELGOSCAR-2000 Környezettechnológiai és Vízgazdálkodási Kft. (2011) Vizsgálati jegyzőkönyv, Talaj- és talajvíz-tisztítás, kármentesítés a Bp. Illatos úti telephelyen. *http://kimittud.atlatszo.hu/request/4413/response/7394/attach/4/30%20130%202015%203mell%20klet.pdf*, *http://www.fava.hu/siofok2010/eloadasok/2nap/1215_illesnesa_magyarb.pdf*

[6] G. Simon(2015). V. Ökotoxikológiai Konferencia (Darvas B. szerk.) 5, 34-35. http://www.ecotox.hu/ecotox2/download/konf/2015/motkonf2015.pdf

[7] Nemzeti Élelmiszerlánc-biztonsági Hivatal (Nébih) (2015) Összefoglaló értekezés a Budapest Illatos árok és Ráckevei Dunaág növényvédőszeres szennyezettségével kapcsolatos panaszbejelentéséről. Ikt: 04,2/6297-1/2015.

[8] Wessling Hungary Kft. (2015) Szakértői vélemény, Budapest IX. kerület Talaj-, talajvíz, felszíni víz vizsgálat.

[9] KvVM-EÜM-FVM (2009) A földtani közeg és a felszín alatti víz szennyezéssel szembeni védelméhez szükséges határértékekről és a szennyezések méréséről, 6/2009 (IV.14.) KvVM-EÜM-FVM együttes rendelet.

[10] Greenpeace (2020) Mérgezett örökségünk. *https://hu.greenpeace.org/mergezett-oroksegunk/bvm*

[11] S. Sporring, S. Bøwadt, B. Svensmark,, E. Björklund (2005) *J. Chromatogr. A*, 1090, 1-9.

[12] E. Maloschik, A. Ernst , G. Hegedűs, B. Darvas, A. Székács, (2007) *Microchem. J.* 85, 88-97.

[13] Vidékfejlesztési Minisztérium (2010) a felszíni víz vízszennyezettségi határértékeiről és azok alkalmazásának szabályairól, 10/2010 (VIII.18.) VM rendelet

[14] Y.-J. Lin,, M. Karuppiah,, A. Shaw,, G. Gupta, (1999) *Ecotox. Environ. Saf.* 43 (1), 35-37.

[15] Pest Megyei Kormányhivatal (2016) Folytatódik az Illatos út rendbetétele. http://www.kormanyhivatal.hu/hu/pest/hirek/folytatodik-az-illatos-ut-rendbetetele