PESTICIDES AND RESIDUES IN DIFFERENT MEDIA WITH ESPECIAL REGARD TO WATERS IN HUNGARY

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Abstract. Agriculture practices using chemicals endanger soils and drinking water supplies worldwide. But, without chemicals, most agricultural systems cannot meet the requirements of our modern world. In soils, pesticide residues accumulate due to soil water retaining capacity. But after a time, pesticides eventually appear in surface waters and groundwater. (Solymosi, 2006) Regular water quality monitoring and the reduction of pesticide use are recommended in river catchment areas, and especially in the catchment of those surface and subsurface waters, which are used as source water for drinking water supplies. Low level contamination of drinking water sources may occur, especially in intensive agricultural areas, even though there is regular water quality monitoring, and occasionally it can contaminate the finished drinking water as well. (Várvölgyi, 2011) Our aim was to give a comprehensive picture on the average yearly occurrence of pesticides and pesticide degradation products in Hungarian drinking water supplies. Data of 3 years were analyzed, using the Hungarian Drinking Water Quality Database of National Institute of Environmental Health (NIEH). In 2008-2010, up to 2% of all drinking water samples analyzed for pesticides per year were above the limit values. The main limitation of the monitoring and data interpretation is the low number of pesticides measurements, a large proportion (about 89%) of the water supply zones were not analyzed for pesticides in this period.

Keywords: drinking water, pesticides, database

L.Simeonov, F. Macaev and B. Simeonova (eds.), *Environmental Security Assessment and Management of Obsolete Pesticides in Southeast Europe,*

1. Introduction

Pesticides are substances or mixture of substances intended for preventing, destroying, repelling or mitigating any pest (Bordás, 2006). 'Pesticides' include: organic insecticides, organic herbicides, organic fungicides, organic nematocides, organic acaricides, organic algicides, organic rodenticides, organic slimicides, related products (*inter alia*, growth regulators) (Government Decree No. 201/2001.)

Agriculture practices using chemicals endanger soils and drinking water supplies worldwide. But most agricultural systems cannot meet the current requirements on the volume and stability of yield without the use of chemicals. So there are two important aspects of agriculture, which need to be balanced: the amount of the chemicals used should meet the amount what is necessary to raise the crop and maintain its health, but should not exceed it. To calculate the trade-off, regional and nationwide water quality measurements, mass transport studies, simulation models and applied mathematical methods are needed. (Solymosi, 2006).

The currently applied pest control methods do not restrict the effect of the pesticides to the place of application, or the desire action range. Even the most carefully designed treatments have some side effects, i.e. environmental pollution of soil, surface water and groundwater.

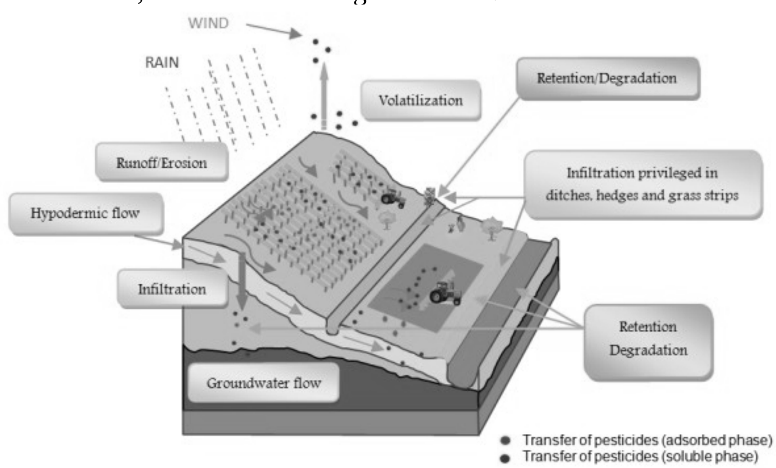

Figure 1. Main pesticides transfers at the catchement area scale.

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In soils, pesticide residues accumulate for a time due to the soil's water retaining capacity. But pesticides are eventually transported through various transportation pathways and make their appearance in surface water and groundwater (Figure 1).

Pesticide pollutions can originate from various sources. First, there are the negative effects of intentional pesticide usage (e.g. spraying against aquatic insects or weeds). Agricultural pesticides can contaminate waters through leaching or run-off. Furthermore, there are the direct or indirect pollution of industrial sewage or discarded liquid agents. Havaria incident during pesticide production, packaging, storage or transport can also contribute to environmental pollution. Surface water and groundwater pollution should be prevented to the greatest possible extent, because its implications on human health and aquatic ecosystems, both directly (via water toxicity) and indirectly (via the food chain). Some pesticides (and/or the pesticide degradation products) generate taste and odour changes in the water, even at very low concentration. These changes can make the polluted water unacceptable for drinking. Furthermore, some pesticides (and/or the pesticides' degradation products) are toxic to non-target organisms, like phytoplankton and other aquatic invertebrates. (Varga, 2010)

Potential carcinogenic and mutagenic effects, and the impacts on fetal development and on the immune and hormonal system of certain pesticides are becoming more precisely understood. Pesticides are known to reduce biodiversity, thus degrading the quality of soils. Nitrogen fixation and the decomposition of organic materials are getting slower as a consequence. Through the food chain (consumption of polluted produce or drinking water) – directly or indirectly –humans are also affected. Since the human population is exposed to pesticide residues through the above pathways, to protect human health, optimal microbial degradation of pesticides in the soil should be ensured. With the help of pesticides degrading microorganisms in the soil ecosystem, soils can in time be cleared from pesticide residues and even ecological (or organic) cultivation can be possible. (Varga, 2010)

To prevent the above detailed negative health or environmental outcomes, regular water quality monitoring and the reduction of pesticide usage are recommended in river catchment areas, especially in the catchment of those surface and subsurface waters, which are used as a source of drinking water supply. Low level contamination of drinking water sources may occur in heavily used agricultural areas despite the regular water quality monitoring. (Várvölgyi, 2011) Occasionally pollution can affect the finished drinking water as well. Aim of the present study was to assess the prevalence of pesticide pollution in the drinking water supplies of Hungary by data mining of the National Drinking Water Quality Database.

2. Health Effects of Some in Hungary Typical Occurring Pesticide Agents.

Table 1 shows the hazard information and the main properties of the most frequently measured agents.

Aldrin and dieldrin are chlorinated pesticides that were used against soil-dwelling pests and for wood protection. Dieldrin was used against insects of public health importance. The use of dieldrin is restricted or banned in many countries since the early 1970s. Aldrin transforms rapidly to dieldrin in the environment and in the body. Dieldrin is a persistent and has low mobility in soil. Aldrin and dieldrin are listed as Persistent Organic Pollutants. They have multiple toxic mechanisms, both are toxic to experimental animals, there is evidence on human healths effects from case studies. The target organs are the nervous system and the liver. Aldrin and dieldrin have been classified to Group 3 by IARC. Guideline value in drinking water is 0.03 μg/l (WHO, 2011).

Atrazine is used as a selective systemic herbicide to control annual weeds. According to current classification, it is unlikely that atrazine has genotoxic or carcinogenic risk to humans. It has reproductive toxicity in experimental animals. Atrazine was observed to attenuate the luteinizing hormone surge and disrupt the estrous cycle; teratogenic effect was not detected Its chloro-*s*-triazine metabolites have the same toxicity profile. The main effect of hydroxyatrazine was kidney toxicity; there was not evidence for carcinogenicity, neuroendocrine-disruption, or genotoxicity of these metabolites. The WHO guide values in drinking water are 100 μg/l for atrazine and its chloro-s-triazine metaboiltes, 200 μg/l for hydroxyatrazine metabolites (WHO, 2011).

Carbaryl is a broad-spectrum carbamante insecticide. Its primary mode of toxicity is the inhibitation of brain cholinesterase. In experimental animals (male mice) it caused vascular tumors. The health-based guide value is 50 μg/l (WHO, 2011).

Metolachlor is a selective pre-emergence herbicide. It is fairly mobile in soil, so under certain conditions it can contaminate groundwater. In animal experiments, the effects were decreasing kidney weight, body weight and survival in female mice, additionally increasing of liver tumors in female mice and a few nasal tumors in male mice. There is no evidence for carcinogenicity and genotoxicity. The WHO guideline value is 10 μg/l (WHO, 2011).

TABLE 1: The main hazard information about the most frequently measured pesticides

Agent	Hazard information**	Properties
atrazine	unclear	Triazin herbicide. Prohibited in most of EU members is prohibited, carcinogen. In Hungary there is “essential consent for use” for this agent.***
propachlor	Slightly hazardous	It obstructs the protein synthesis, the growth of root will be damaged.
metolachlor	Slightly hazardous	It obstructs the protein synthesis, the growth of root will be damaged.
trichlorfon	Slightly hazardous	Organic phosphoric acid ester. It is used for exterminate house flies, tick. It dissolves rapidly in water.
carbaryl	Moderately hazardous	It is used for worm extermination and plant thinning.

**Classification of pesticides based on their hazard *(LD50 (mg/kg) of rats)*

I. a. Extremely hazardous III. Slightly hazardous

I. b. Highly hazardous IV. Unlikely to present acute hazard hazardous

*** If there is not alternative, less harmful agent against a pest, the carcinogen, hormone-disrupting agent can be resrticted allowed in a resticted way.

3. Regulation of Pesticides in Water in Hungary

1) Directive 2000/60/EC (Water Framework Directive): extends to all of human activity that have negatively affected the status of waters, obstruct to approach or save them. 33 chemicals including 13 agents of pesticides to be monitored are listed in this directive that are particular hazard to the status of the waters. (Directive 2000/60/EC)

2) Government Decree No. 220/2004. (VII.21.) on protection of surface water quality standards: this decree regulates the quality of surface water, the list of indicative water pollutants and the hazard substances for the surface water quality, including a few pesticide agents and their decomposition products. In Annex 1 part C are required the agents their emission is illicit: hexachloro cyclohexane (HCH), aldrin, dieldrin, endrin, isodrin, DDT, pentachlorophenol. (Government Decree No. 220/2004.)

3) Ministry Decree No. 21/2002. (IV. 25.) on operation of water utilities: this decree requires the list of measured parameters in water wells. The measured pesticide agents: acetochlor, propachlor, 2,4-D, atrazine, lindane, malation, MCPA, metil-paration, simazine, 2,4,5-T, DDT/DDD/DDE, dezetil-atrazin, diazinon, hexaklórbenzol, dezipropil atrazine*, endrin*, phorat*, hexazinone*,

chlorpiriphos*, metribuzin*, prometrin*, propazin*, terbutilazin*, terbutrin* (*= based on local pesticide using and the list of Public Health Office). (Ministry Decree No. 21/2002.)

4) 98/83/EC of 3 November 1998 (Drinking Water Directive) on the quality of water intended for human consumption: this directive regulates the limit values, the monitoring and reporting systems of the drinking water quality for the members of European Union. (98/83/EC)

5) Government Decree No. 201/2001. (X.25.) on the quality standards and monitoring of drinking waters. This Decree implements the Drinking Water Directive in Hungarian legislation. The Decree regulates the limit values of pesticides in drinking water. The limit value applied to each individual pesticide concentration is 0.1 µg/l, and to total pesticides concentration is 0.5 µg/l. More strict limit value applies to aldrin, dieldrin, heptachlor and heptachlor epoxide (0.03 µg/l). (Government Decree No. 201/2001.)

4. Methods

Data mining in the Hungarian Drinking Water Quality Database was used to analyze the presence of pesticides in Hungarian drinking water. The Database compiles the results of drinking water compliance monitoring (including physical, microbiological, biological, organic and inorganic chemical parameters) in Hungary based on reports of local public health services and waterworks. Microsoft Office Excel 2003 and Microsoft Office Access 2003 programs were used during the analysis.

5. Results and Discussion

According to the Hungarian Drinking Water Quality Database, in 2008 there were 531 pesticide measurement in drinking water, 7 samples were above the limit value, so the non-compliance was 1.32%. In 2009 were 396 samples were analyzed for pesticides, none of them was above the limit value. Nine of the 414 pesticide measurements in drinking water in 2010 exceeded the limit value, which is 2.17% non-compliance (Table 2). All samples were taken at point of use.

TABLE 2: Total pesticides content in tap water samples and percentage of non-compliance with requirements (2008-2010) based on database of NIEH

	2008	2009	2010
Total amount of samples	531	396	414
Amount of non-compliance	7 (1.32 %)	0	9 (2.17 %)
The most frequently detected of pesticides in drinking water	atrazine propachlor metolachlor endosulfan		metolachlor propachlor carbaryl propanil trichlorfon

The total number of measurements was geographically very variable in the different Hungarian counties and the capital. Number of measurements was above average in Pest and Szabolcs-Szatmár-Bereg counties, and very low in Bács-Kiskun, Győr-Moson-Sopron and Vas counties in the analyzed three years (Figure 2). There is not sampling and measurement of drinking water for pesticides content in the most of water supply zones (87% in 2008, 90% in 2009 and 92% in 2010, 79% none of these years).

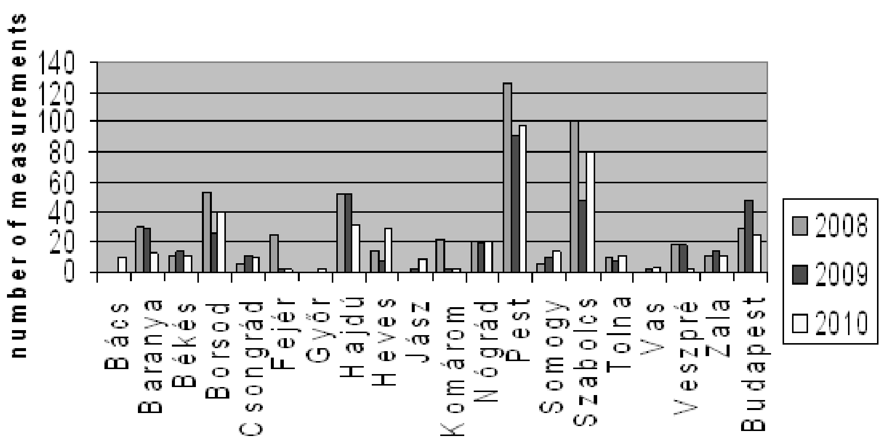

Figure 2. Geographical distribution of pesticide measurements in drinking water by counties and the capital (2008-2010).

The scope of pesticide measurements in drinking water samples depends on the local pesticides usage. The list of examined pesticides is defined annually by the Public Health Office, based on local information from environmental inspectorates, public health services and plant protection stations (Government Decree No. 201/2001. (X.25.)).

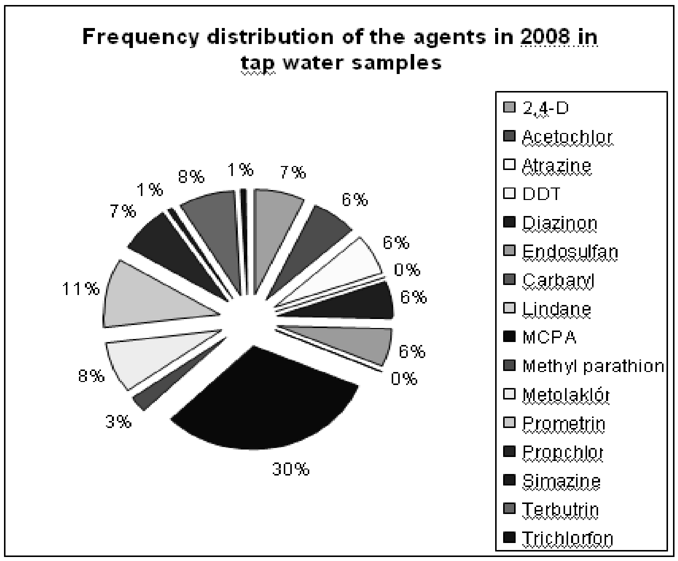

Figure 3. Frequency of pesticide measurements in drinking water in 2008.

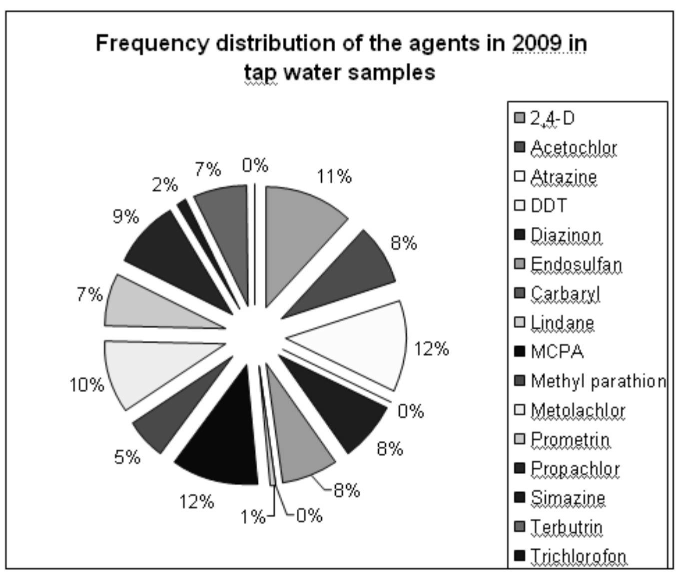

Figure 4. Frequency of pesticide measurements in drinking water in 2009.

Figures 3-5 present the frequency of measurements for the various pesticides in drinking water in 2008, 2009 and 2010.

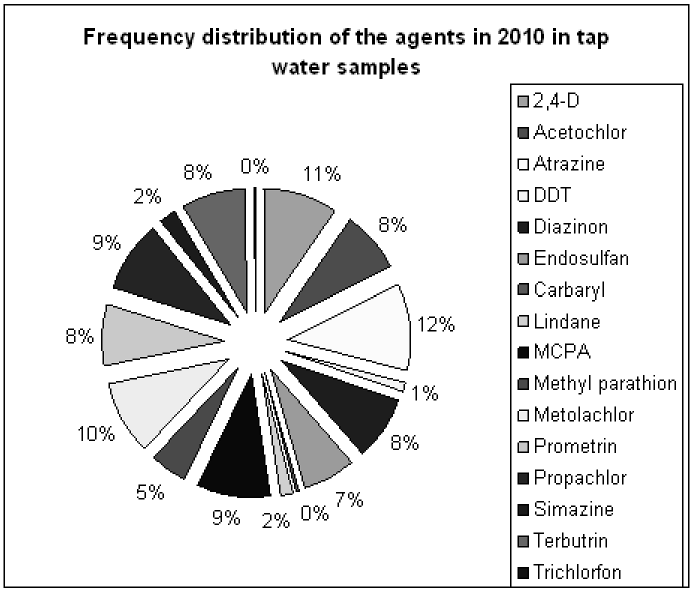

Figure 5. Frequency of pesticide measurements in drinking water in 2010.

6. Discussion

The presence of pesticides Hungarian drinking water supplies was observed in the 2008-2010 period, though the frequency was low. The non-compliance was 1.32% and 2.17% in 2008 and 2010, respectively; there was no non-compliance in 2009. Overall non-compliance for 2008-2010 is 1.16%. The total number of results is low, does not meet the required number of samples, and there is not sampling and measurement of drinking water for pesticides content in the most of water supply zones (about 89%). The maximum concentration of the most frequently detected pesticide in drinking water in the three year period was 10-16 times higher than the limit value (Table 3). Only carbaryl exceeded the health-based limit value of WHO (2011), but it can still pose a health risk to the consumers.

TABLE 3: The maximum values of the most frequently measured pesticides' agents in drinking water period in 2008-2010

Agent	Limit value	Maximum value
atrazine	0.10 μg/l	1.3 μg/l
propachlor	0.10 μg/l	1.4 μg/l
metolachlor	0.10 μg/l	1.6 μg/l
trichlorfon	0.10 μg/l	1.1 μg/l
carbaryl	0.10 μg/l	0.18 μg/l

7. Conclusion

The inappropriate use of pesticides can cause both environmental and human health risks. According to current monitoring results, pesticides are detected in drinking water samples in Hungary. In 2008-2010, up to 2% of all drinking water samples analyzed for pesticides per year were above the limit values based on Hungarian Drinking Water Quality Database. There is not detected not-allowed agent examined the occurring agents. There is statistical data on the amount of purchased pesticides, but there is no compiled data on their application (dosing, application area etc.). Pesticides are often used in unreasonably high quantity, or not in the appropriate period. To conclude, more attention needs to be paid to the health effect of these chemicals and to the updating of unpermitted agents. Also, targeted detection methods need to be applied to pesticides and their degradation products. The monitoring system of pesticides content in drinking water need to be developed, minimum annual measurement is necessary in all of water supply zones.

ACKNOWLEDGEMENTS

The authors acknowledge Attila Vecsey for the management of the Hungarian Drinking Water Quality Database.

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