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ORGANOCHLORINE INSECTICIDES IN DRINKING WATER IN THE CITY OF KRALJEVO

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Abstract. *Organochlorine insecticides (OCI) belong to the group of chlorinated hydrocarbons with wide, but often uncontrolled, application in agricultural production. The consequence of this is that OCI and their residues are found in numerous examples in the ecosphere. Contamination of aquatic environments has been particularly emphasized. Although OCI are toxic substances for wildlife, especially for humans, a large part of the population is daily exposed to their activities in small quantities. OCI presence in drinking water is generally below the maximum allowable concentrations, whereas repeated doses can cause chronic toxic effects. For these reasons, it is necessary to continuously monitor the concentration of OCI in drinking water and perform its purification in order to obtain water with the lowest possible concentration. This work included the analysis of individual OCI concentration in drinking water in the city of Kraljevo. Individual concentrations of seven OCI have been measured: alpha-hexachlorocyclohexane (α-HCH), gamma-hexachlorocyclohexane (lindane), heptachlor, aldrin, dieldrin, endrin, dichloro-diphenyl-trichloroethane (DDT). OCI have been treated according to the appropriate EPA-608 methods, and then detected by gas chromatography method with the appropriate columns. The measured concentrations for individual OCI show significant increase in heptachlor, which is almost four times higher, and the concentration of aldrin, which is two times higher compared to the threshold limit values defined by the Regulation on Maximum Allowable Concentrations (MAC). Measured concentration of dieldrin is at the upper limit value of the MAC. Measured concentrations of endrin could not be discussed about because they are not regulated by the Regulation on MAC.Cumulative concentration of OCI in water from pumping station is 0.294 μg/l, which is in line with the maximum allowed concentration of 0.5 μg/l defined by the Regulation on the hygienic quality of drinking water. Given that only seven organochlorine insecticides have been analyzed in this paper, it is not surprising that the value of their overall concentration is unexpectedly high (over 50%). Total concentration of OCI presented in drinking water, especially measured increased concentrations of aldrin and heptachlor, indicate the processes of chemical contamination. For these reasons, it is*

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necessary to continuously check the concentration of total and individual OCI in drinking water and take effective measures of water purification.

Key words: *organochlorine insecticides, drinking water, heptachlor, aldrin, contamination of water*

1. INTRODUCTION

Modern agricultural production cannot be imagined without the use of chemical agents to protect plants such as pesticides. Today, the world produces more than a million types of pesticides. The consequence of the technological development in agricultural production is intensive environmental pollution and the use of pesticides, particularly organochlorine insecticides (OCI). Nowadays, organochlorine insecticides pose a significant environmental problem.

Organochlorine insecticides are chemically chlorinated hydrocarbons. They are almost insoluble in water, but well soluble in organic solvents and fat. They have a high degree of resistance against physical, chemical, microbiological agents, and therefore remain in the environment for years. For this reason they could accumulate in soil, spread over vast expanses of air and water, thus continuously contaminating plants, animals and people. An extensive and uncontrolled use of, as well as perennial production of OCI, have led to their residues be found in a large number of samples in the ecosphere [1]. In particular, a higher amount of OCI in water leads to contamination of the aquatic environments.

Studies have shown that all foods contain residues of organochlorine insecticides and their derivatives. It is believed that people who are not occupationally exposed to OCI intake about 90% of these insecticides by food. Due to the presence of aromatic structure and large number of chlorine atoms, biotransformation would take pace slowly and it would be difficult to eliminate them from the body [2]. The risk of acute and sub acute toxicity is low. However, there is a risk of various toxic effects because OCI can accumulate in the body [2]. The solubility of organochlorine insecticides in fats leads to their accumulation in adipose tissue and organs: brain, liver, kidneys, where they get it is deposited. The amounts of accumulated organochlorine insecticides in adipose tissue are very different and depend on daily food intake. Although organochlorine insecticides have lower acute toxicity, due to the ability of accumulation in fatty tissues, they pose constant risk to humans. The mode of action is still not well known, but OCI are thought to inhibit an important enzyme system in the central nervous system. Also, mutagenic and carcinogenic effects have been shown in experimental animals.

The presence of OCI in drinking water is generally below the limit of maximum allowable concentrations, but repeated doses can cause chronic toxic effects [3]. For these reasons, the primary purpose of water purification (treatment) is to obtain water with lower OCI concentration. Water protection is a complex area of scientific and multidisciplinary character. Thus, the problem of water protection is an integral part of the overall problem of protection, promotion and preservation of the environment [4].

Standard methods of water purification do not remove pesticides; therefore, it is necessary to introduce some additional treatments by coagulation, oxidation and adsorption agents [5, 6]. The research is focused on treating the water with activated charcoal, which, for now, has been considered the most effective substance in the process of purifying water contaminated with chlorinated insecticides. However, this procedure is still being developed [7].

2. METHODOLOGY

The aim of the study was to perform qualitative and quantitative analysis of certain organochlorine insecticides in the drinking water of the City of Kraljevo [5].

The existing water supply system of the City of Kraljevo relies on four groundwater sources from the Ibar alluvium. One of them is the source Konarevo, with a total exploitation amount of about 60 l/s.

For testing, we used the samples of drinking water as follows:

I - chlorinated water taken from the tap at the Institute of Public Health in Kraljevo

II - based non-chlorinated water sampled from the pumping station in Konarevo (Water tank B-6), which is drinking water supply system of the City of Kraljevo.

Drinking water must match the quality standards provided by the Regulation on the hygienic quality of drinking water (Official Gazzette of FRY, No.42/98 and 44/99), which accepts the recommendations and standards of the World Health Organization and the European Union laboratory diagnosis relying on the application of ISO standards. The chemical quality of drinking water is extremely important in the assessment of hygienic quality.

All chemical analyzes in this research were performed in the laboratories in the Institute of Public Health in Kraljevo. Laboratory Institute holds accreditation of ISO / IEC 17025: 2006 by the Accreditation Body of Serbia.

In the samples of drinking water, by the following parameters were determined: pH value, the quantitative determination of organic matter ($KMnO_4$ consumption), chemical oxygen demand (COD), biochemical oxygen demand (BOD), suspended solids, total organic carbon (TOC), surface active substances (PAM), the content of nitrate and ammonium, calcium, magnesium and iron. The research was carried by applying the following accredited physicochemical methods: volumetric, electrochemical and spectrophotometric. For spectrophotometric determination, Lambda 2 spectrophotometer (Perkin Elmer) and Pastel-UV (Secoman Analyzer) were used.

A quantitative analysis involved certain organochlorine insecticides as prescribed by the Regulations on the hygienic quality of drinking water (Official Gazzette of FRY, No. 42/98 and 44/99): alpha-hexachlorocyclohexane (α-HCH), gamma-hexachlorocyclohexane (lindane), heptachlor, aldrin, dieldrin, endrin, dichloro-diphenyl-trichloroethane (DDT). Liquid-liquid extraction of organochlorine insecticides based on the allocation of active substances between two solvent different polarities wad carried out. Water samples for the determination of OCI were prepared by appropriate EPA-608 method liquid liquid extraction. The mentioned method can be used in water samples at the same time to qualitatively and quantitatively prove the presence of 87 pesticide compounds: 42 organochlorine compounds, organophosphorus compounds 38 and 7 carbamate compounds.

Tested organochlorine insecticides were detected by gas chromatography with gas chromatograp developed by Perkin Elmer - 8500 ECD electron capture detector, adhering to the appropriate standards.

The results of physicochemical parameters and investigated organochlorine insecticides in drinking water were compared with the values given in the Regulations on Hygienic Quality of Drinking Water, which accepts the recommendations and standards of the World Health Organization and the European Union.

3. RESULTS AND DISCUSSION

The results obtained by qualitative and quantitative analysis of physicochemical parameters in water samples from the pumping station Konarevo and the tap water of Department of Public Health Kraljevo are shown in Table 1.

Table 1 The values of physicochemical parameters in water sample

Physicochemical parameters	Sample of tap water-Department of Public Health	Sample of water from a pumping station Konarevo	MAC
pH value	7.78	8.05	6.80-8.50
Nitrate, NO_3 [mg/l]	13.40	12.90	50
Ammonia, NH_3 [mg/l]	0.058	0.050	0.1
Consumption of $KMnO_4$ [mg/l]	5.37	6,00	8
COD [mg/l]			/
BOD [mg/l]			/
Suspended solids [mg/l]			/
Calcium [mg/l]	40.08	44.08	200
Magnesium [mg/l]	0.60	0.60	50
Iron [mg/l]	0.061	0.052	0.3
TOC [mg/l]			/
PAM [mg/l]			/

Based on the obtained values of the analyzed basic physicochemical parameters of samples of drinking water from the tap in the Department of Public Health and the pumping station Konarevo, it can be concluded that the sampled water meets the standards prescribed by the Regulations on the hygienic quality of drinking water (Official Gazette of the FRY, No. 42/98 and 44/99) and, from this aspect it is safe for use.

These results are expected, because the Department of Public Health constantly checks the quality of any possible change in water quality and responds effectively.

Table 2 shows the values of the concentration of some tested OCI obtained by quantitative analysis of water samples and their total concentration, which is calculated as the sum of the examined OCI concentrations.

Table 2 The concentration of total and individual OCI examined in drinking water samples

OCI [μg/l]	Sample of tap water-Department of Public Health	Sample of water from a pumping station Konarevo	MAC [μg/l]
1. α-HCH	0.000	0.000	-
2. Lindane	0.043	0.057	0.2
3. Heptachlor	0.093	0.113	0.03
4. Aldrin	0.053	0.060	0.03
5. Dieldrin	0.028	0.000	0.03
6. Endrin	0.040	0.064	-
7. DDT	0.000	0.000	0.1
Total	0.257	0.294	0.5

The obtained values for the concentration of the tested OCI are very different. Concentration of certain OCI increased several times, and some are very low so that the methods described can not be determined.

In the samples of drinking water, using EPA-608 method, the concentrations of organochlorine insecticide alpha-hexachlorocyclohexane (α-HCH) have not been detected. The reason may be low concentrations of α-HCH and insufficient sensitivity of the method for the determination of low concentrations or the fact that insecticide has not been found in the water samples. For these reasons, it is necessary to carry out further tests in order to find the adequate analytical methods which could detect low levels of concentration α-HCH. Also, the Regulation on the hygienic quality of drinking water of the Republic of Serbia has not defined yet the threshold values of the maximum allowable concentration for α-HCH.

The measured concentrations of the insecticide lindane in the analyzed samples of drinking water are significantly lower than the amount prescribed by the Regulations.

In the analyzed samples of drinking water, there have been significantly increased concentrations of organochlorine insecticide heptachlor in relation to the maximum allowable value (0.03 μg/l) according to the Regulations. In a sample of water from the tap in the Department of Public Health the measured concentrations of heptachlor (0.093 μg/l) were three times higher , and in the sample of pumping station Konarevo almost 3.8 times higher (0.113 μg/l) in relation to the maximum allowable concentration (MAC) defined by the Regulations. These are important values, so it is necessary to carry out a detailed analysis with the aim to find the causes of increasing insecticide concentrations in the drinking water of the city of Kraljevo and implement the appropriate treatment accordingly. Drinking water with such a high concentration of heptachlor cannot be considered safe to human health.

The MAC value for aldrin, according to the Regulations on the hygienic quality of drinking water, is 0.03 μg/l. However, the increased concentrations of this substance have been measured in both sample locations: tap water from Department of Public Health - 0.053 μg/l - which is 1.8 times higher than the MAC values, and a sample from the pumping station Konarevo - 0.06 μg/l - which is two times higher than the MAC value. For these reasons it is necessary to perform waste water treatment in which aldrin would be removed and water would be safe to drink.

The measured value of the concentration of organochlorine insecticide dieldrin in drinking water samples were within the maximum permitted levels. In a sample of tap water from the Department of Public Health, dieldrin concentration was 0.028 μg/l, as compared to the MAC upper limit value (0.03 μg/l). However, in a sample of water from the pumping station Konarevo this insecticide was not detected. It is necessary to carry out further tests to be able to say that there is a possible contamination.

A regulation on Hygienic Quality of Drinking Water has not provided maximum allowable concentration of endrin. In a sample of tap water from Department of Public Health, the measured concentration was 0.040 μg/l, and in the pumping station Konarevo it was 0.064 μg/l. The comparison between the obtained values of endrin concentrations with the values of other tested OCI reveals a relatively high concentration of endrin; however, there is no limit value of MAC defined by the Regulations so it is rather difficult to claim this with certainty. For these reasons, it is essential to define the MAC for the endrin in the Regulations on Hygienic Quality of Drinking Water.

The concentrations of organochlorine insecticide DDT could not be detected in the samples of drinking water. This is expected considering that DDT has not been allowed for use in recent years.

The total OCI concentration in samples of drinking water was 0.257 μg/l, i.e. 0.294 μg/l, which is consistent with the values of the maximum permissible concentration of total pesticide insecticides according to the Regulations on Hygienic Quality of Drinking Water, Official Gazette of the FRY, 42/98, 44/99, in which the total allowed content of pesticide is 0.5 μg/l.

However, this study examined only seven OCI, which is a small fraction of the total number of OCI given in the Regulations. The results show that the total concentrations of the seven examined OCI in drinking water samples represent more than half (50%) of the MAC values given in the Regulations. On this basis, it can be expected that the total concentration of all pesticides defined by the Regulation were significantly higher than the maximum permissible concentration, and that the inhabitants of the test areas consume a considerable amount of organochlorine insecticides.

The results of total concentration of OCI in drinking water indicate their increased concentration which requires constant monitoring. It is known that insecticides are often found in increased quantities in food products, especially in fruits and vegetables. Insecticides in drinking water increase the amount of pesticide that enters the human body in numerous ways. Given that the OCI compounds in the human body can accumulate, causing a variety of toxic effects, it is necessary to take all measures to reduce the intake of contaminated food and water. For these reasons, drinking water should contain the smallest possible amount of pesticides [8]. It is also necessary to introduce the adequate methods for purification of drinking water that contains organochlorine insecticides.

4. CONCLUSION

On the basis of the obtained research results, we can draw the following conclusions:

In the samples of drinking water in the city of Kraljevo which were collected to examine certain organochlorine insecticides, there was a significant increase in the concentration of insecticides heptachlor, aldrin, and dieldrin concentration compared to the upper value MAC regulated by the Regulations on the hygienic quality of drinking water (Official Gazette of the FRY, No. 42/98 and 44/99).

Also, the aforementioned Regulations did not define the MAC values for all prescribed insecticides, and this needs to be done and harmonized with EU directives and the guidelines of the WHO. This is especially important for the insecticide endrin, whose measured concentrations are significant but not further discussed due to the lack of regulation.

The cumulative concentrations of these organochlorine insecticides in drinking water indicate that the water meets the requirements set by the Regulations for hygienic quality of drinking water. However, it should be noted that the cumulative concentration (0.257 μg/l, or 0.294 μg/l) was calculated for the seven examined OCI and represents more than 50% of the MAC (0.5 μg/l) for pesticides under the Regulations for hygienic quality of drinking water.

This study investigated the concentration of a limited number of insecticides in water. If we had determined the concentrations of all pesticides defined by the Regulation on the

hygienic quality of drinking water, total value would have probably been above the MAC values. From the data presented in this paper, we can conclude that drinking water in the City of Kraljevo is rather contaminated with insecticides.

All this indicates that it is vital to continuously check the concentration of total and individual OCI in drinking water and take effective measures of water purification.

Also, further research would be helpful to develop analytical methods for the determination of very low concentrations of certain organochlorine insecticides, considering that the methods recommended by the EPA are not precise enough when detecting small concentrations (such as 0.01 μg/l).

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ORGANOHLORNI INSEKTICIDI U VODI ZA PIĆE GRADA KRALJEVA

Organohlorni insekticidi (OHI) pripadaju grupi hlorovanih ugljovodonika, koji u poljoprivrednoj proizvodnji imaju široku, ali često i nekontrolisanu primenu. Posledica toga je da se OHI i njihove rezidue mogu naći u brojnim uzorcima ekosfere. Posebno je izražena kontaminacija vodenih sredina. Iako su OHI toksične supstance za živi svet a posebno za čoveka, veliki deo stanovništva je svakodnevno izložen njihovom delovanju u malim količinama. Prisustvo OHI u vodi za piće je uglavnom ispod granicae maksimalno dozvoljenih koncentracija, ali ponovljene doze mogu prouzrokovati hronične toksične efekte. Iz tih razloga je potrebno kontinualno praćenje koncentracije OHI u vodi za piće kao i njeno prečišćavanje u cilju dobijanja vode sa što manjom koncentracijom OHI. Ovim radom obuhvaćena je analiza koncentracija ukupnih i pojedinačnih organohlorni insekticida u vodi za piće gradu Kraljeva. OHI su tretirani prema odgovarajućoj EPA-608 metoda, ekstrakcije tečnog-tečnost, a zatim detektovani metodom gasne hromatografije sa odgovarajućim kolonama.

Ukupna koncentracija OHI u vodi sa crpne stanice je 0,294 μg/l, što je u skladu sa maksimalno dozvoljenom koncentracijom (MDK) od 0,5 μg/l prema Pravilniku o higijenskoj ispravnosti voda za piće. S obzirom da je ovim radom analizirano samo sedam organohlornih insekticida to je vrednost za njihovu ukupnu koncentraciju neočekivano velika (preko 50%). Određene su i pojedinačne koncentracije za sedam OHI: alfa-heksahlorcikloheksan (α-HCH), gama-heksahlorocikloheksan (lindan), heptahlor, aldrin, dieldrin, endrin, dihloro difenil trihloroetan (DDT). Od izmerenih koncentracija za pojedine OHI, značajno je povećanje za heptahlor, koje je skoro četiri puta, i

aldrina, dva puta veća, u odnosu na vrednost MDK pomenutog Pravilnika. Izmerena koncentracija dieldrina je na gornjoj granici vrednosti MDK. O izmerenoj koncentraciji endrina se ne može diskutovati jer Pravilnikom nije regulisana vrednost MDK. Vrednosti za ukupnu koncentraciju OHI, a posebno izmerene povećane koncentracije heptahlora i aldrina u vodi za piće ukazuju na procese hemijske kontaminacije. Iz tih razloga je neophodno vršiti stalnu proveru koncentracija ukupnih i pojedinih OHI u vodi za piće i preduzeti efikasne mere prečišćavanja

Ključne reči: *organohlorni insekticidi, voda za piće, heptahlor, aldrin, kontaminacija voda.*