DOI: 10.47743/achi-2021-2-0012 *ACTA CHEMICA IASI*, **29_2**, 166-182 (2021)

OCCURRENCE OF SELECTED ANTHROPOGENIC ORGANIC CONTAMINANTS IN DRINKING WATER FROM RURAL AREAS OF EASTERN ROMANIA

Daniela Dirtu[a*], Manuela Pancu[b], Luminita Minea[b]

[a]*Department of Chemistry, Alexandru Ioan Cuza University of Iasi, Carol I Blvd. No. 11, 700506, Iasi, Romania*

[b]*Regional Centre of Public Health Iasi, Victor Babes Street, No. 14, 700465, Iasi, Romania*

Abstract: The purpose of this study was to evaluate the trend of organochlorine pesticides (OCPs), trihalomethanes (THMs) and polycyclic aromatic hydrocarbons (PAHs) levels in drinking water sampled from rural areas located in Eastern Romania. After chemical analyses and data processing, 86% of the collected samples were found to be compliant with the Romanian and EU regulations. The set limits for measured contaminants in accordance with the Directive 98/83/EC were exceeded in the cases of THMs and benzo(a)pyrene. A diagnostic ratio method was applied in order to determine possible PAH sources in collected samples (petrogenic or pyrolitic). Our results evidenced a high percentage contribution of low molecular weight PAHs (96%) combined with high ratio for low/high molecular weight (31.4) suggesting that the contamination of the drinking water can be attributed to petrogenic pollution of the water sources rather than due its' storage and transport.

***Keywords*:** Drinking water; Organochlorine pesticides; Trihalomethanes; Polycyclic aromatic hydrocarbons; Human health.

Introduction

The monitoring of the drinking water quality in the public distribution networks is of particular interest due to the direct link between

[*] Daniela Dirtu, *e-mail: daniela.dirtu@uaic.ro*

water quality parameters and their potential effect on human health. In Romania, national monitoring programs concerning the drinking water quality are implemented on routine basis combined with compliance evaluation with the European Commission (EC) DIRECTIVE 98/83/EC[1] and national normative - Law no. 458/2002 regarding the drinking water quality, revised by Law 182/2011.[2] Previous studies on the evaluation of the Romanian drinking water quality[3,4] reported that, occasionally, drinking water exceeds the maximum law allowed concentrations suggesting that ongoing monitoring programs in this respect should be performed on routine basis.

Due to their bioaccumulation potential, persistence and toxicity, including immunotoxicity, reproductive effects or carcinogenicity, the determination of organochlorine pesticides (OCPs) in various environmental samples is commonly reported in scientific literature.[5,6] Previous studies on the presence of the chlorinated pesticides in samples collected from Eastern Romania evidenced relatively high levels of these contaminants in both environmental, food and human samples.[7-9]

Trichloromethane (chloroform), bromodichloromethane, dibromo-chloromethane and tribromomethane (bromoform) are currently considered as the trihalomethanes (THMs) of public health concern in drinking water. Their presence in drinking water is generally linked to their formation in the treatment plants and water supply systems, while these processes are influenced by multiple factors including the type and dose of disinfectant, precursor's characteristics and concentration, temperature and pH of the water, contact time. There are three major routes of human exposure to THMs: ingestion of chlorinated water by drinking or eating foods prepared with contaminated water, inhalation and dermal contact during personal

hygiene (showering, general cleaning and washing clothing)[10]. Several research groups warn about the negative impact on humans' health, various pathologies being associated with THMs exposure such as carcinogenicity (colon, bladder or rectum), damage to various organs (stomach, brain, pancreas or liver) and reproductive (low birth weight, intrauterine developmental delay, birth defects and miscarriage).[11-13]

Previous reports on Romanian water THM levels didn't report any exceeding of the maximum allowed concentrations recommended by the national and international legislation for drinking water. However, relatively high THMs' concentrations[3,4] are generally measured in drinking water samples and therefore, given the high toxicity acknowledged for these contaminants, their monitoring on a continuous basis has become necessary.

The presence of polycyclic aromatic hydrocarbons (PAHs) in different environmental compartments has been also widely investigated.[14,15] They are ubiquitous pollutants that can be emitted during anthropogenic activities: the incomplete combustion of organic substances is the main source of pollution along with natural phenomena such as forest fires and volcanic eruptions. The occurrence of adverse health effects due to human PAH exposure has been discussed in a number of studies and the carcinogenic and mutagenic effects are the most commonly associated to their presence.[16] So far, there are no available data in the literature concerning the presence of PAHs in drinking water samples from Romania.

In this context, the present study, initiated by the National Institute of Public Health in the frame of a monitoring program, aims to investigate the occurrence and distribution of several organic pollutants including organochlorine pesticides (OCPs), trihalomethanes (THMs) and polycyclic aromatic hydrocarbons (PAHs) in water samples, in order to determine the

quality of drinking water in the rural areas sampled from Eastern Romania (Moldavian Region).

Experimental

Sampling area and samples description

Water samples were collected during 2014–2016 from the northern, central and eastern area of the Moldavian Region. A standardized protocol, SR EN ISO 5667-3:2013: Water quality – Sampling – Part 3: Guidance on the preservation and handling of water samples was used. A total number of 47 tap water samples were collected from private homes and public buildings, including schools, city halls or hospital facilities.

Analytical measurement

Several OCPs and THMs were determined by gas chromatography (GC) using a Shimadzu GC 2010 equipped with ^{63}Ni selective Electron Capture Detector while polycyclic aromatic hydrocarbons (PAHs) were separated using HP Agilent 1100 with DAD and FLD detectors on the column Nucleosil 100-5, C18-PAH, 250x4.6 mm (Macherey-Nagel, Germany).

For OCPs determination, including α-HCH, β-HCH, δ-HCH, γ-HCH, p,p'-DDD, p,p'-DDE, p,p'-DDT, Endosulfan I, Endosulfan II, Endrin, Aldrin, Dieldrin, Heptachlor and Heptachlor epoxyd, international reference standard method was used (SR EN ISO 6468:2000: Determination of certain organochlorine insecticides, polychlorinated biphenyls and chlorobenzenes. Gas chromatographic method after liquid-liquid extraction). Calibration curves were plotted at six different concentrations ranging from 20 to 120 μg/L, using the subsequent dilution method of a standard mix solution SUPELCO CLP Organochlorine Pesticides Mix,

1x1 mL, Toluene: Hexane (50-50, *v/v*) at 200 μg/mL (regression coefficient higher than 0.997). Quantification limits, were ranging between 0.001 and 0.003 μg /L depending on the targeted analyte. Specific quantification limits for each compound are given in Table 1. Estimated recoveries for targeted OCPs ranged between 89-106%.

The four THMs (chloroform, bromodichloromethane, dibromochloromethane and bromoform) were determined using SR EN ISO 10301:2003 method (Determination of highly volatile halogenated hydrocarbons - Gas-chromatographic methods). THMs calibration mix solution of 200 μg/mL of each component in methanol, from SUPELCO was used and the calibration curves were plotted in the range of 20 – 100 μg/L (regression coefficient higher than 0.998). Estimated recoveries ranged between 91-105% while quantification limits were between 0.54 and 1.56 μg /L depending on the targeted THM. Specific quantification limits for each compound are given in Table 1.

We also determined fifteen PAHs including those considered priority pollutants by the US EPA Clear Water Act: naphthalene (NaP), acenaphthene (Ace), fluorine (Fl), phenanthrene (Phe), anthracene (Ant), fluoranthene (Flu), pyrene (Pyr), benzo[a]anthracene (BaA), chrysene (Chr), benzo[a]pyrene (BaP), benzo[b]fluoranthene (BbF), Benzo[k]fluoranthene (BkF), dibenzo[a,h]anthracene (DahA), benzo[g,h,i]perylene (BghiP) and indeno[1,2,3-cd]pyrene (IcdP)[14]. For PAHs analysis, in order to achieve better detection limits, a modified version of SR EN ISO 17993:2004 (Water quality - Determination of 15 polycyclic aromatic hydrocarbons (PAH) in water by HPLC with fluorescence detection after liquid-liquid extraction) was used by replacing liquid-liquid with solid-phase extraction.[17] Before extraction, the Chromabond C_{18}, (6 mL, 500 mg) SPE

cartridges purchased from Macherey-Nagel, Germany, were activated by washing three times with 5 mL dichloromethane, three times with 5 mL methanol, followed twice by 5 mL deionized water. Then, 300 mL water sample was passed through the cartridge at a flow rate of 2-3 mL/min under vacuum. Following extraction, the cartridges were dried for 30 min, and then eluted three times with 4 mL of dichloromethane. Finally, the extracts were concentrated under a gentle nitrogen stream and re-dissolved in 100 μL of acetonitrile and further injected into the HPLC system.

Analytical PAH 15 standard solution in acetonitrile, 10 ng/μL from Sigma-Aldrich was used to prepare the calibration curve in the 5 – 35 μg /L range (regression coefficient higher than 0.995). Estimated recoveries ranged between 68-104%, the lower recovery was for naphthalene while the highest recovery was obtained for phenanthrene. The quantification limits were ranging between 0.15 and 0.3 ng /L depending on the targeted PAH. Specific quantification limits for each compound are given in Table 1.

The quality assurance/quality control procedures included also regular analyses of blank and spiked samples with known amounts of certified standards of OCPs, THMs and PAHs.

Results and Discussion

Table 1 shows the main descriptive statistics for chemical contaminants measured in collected drinking water samples. Also, it presents the limits (MAC) stipulated by European Council Directive and Romanian regulation, along with their measured detection frequencies.

Table 1. Descriptive statistics for chemical contaminants measured in drinking water samples from Romania.

Compound	LOQs	Min	Max	Median	DF%	MAC
Benzo[a]pyrene (ng/L)	0.150	<LOQ	**21.78**	2.26	87	10
∑PAHs (ng/L)	-	5.79	96.31	28.53	-	100
$CHCl_3$ (µg/L)	1.56	<LOQ	**117.37**	23.40	82.6	-
$CHBrCl_2$ (µg/L)	1.38	<LOQ	55.79	11.34	91.3	-
$CHClBr_2$ (µg/L)	0.540	0.540	21.01	2.84	97.8	-
$CHBr_3$ (µg/L)	1.03	<LOQ	3.42	0.134	13	-
∑THMs (µg/L)	-	3.20	**197.3**	38.94	-	100
pp'-DDD (µg/L)	0.001	<LOQ	0.02	0.001	46.8	0.1
pp'-DDE (µg/L)	0.001	<LOQ	0.09	<LOQ	44.46	0.1
pp'-DDT (µg/L)	0.001	<LOQ	0.063	0.001	44.46	0.1
∑DDTs (µg/L)	-	0.001	0.160	0.003	-	-
α-HCH (µg/L)	0.001	<LOQ	0.002	<LOQ	34	0.1
β-HCH (µg/L)	0.002	<LOQ	0.012	<LOQ	25.5	0.1
δ-HCH (µg/L)	0.002	<LOQ	0.004	<LOQ	25.5	0.1
γ-HCH (µg/L)	0.001	<LOQ	0.015	<LOQ	38.2	0.1
∑HCHs (µg/L)	-	0.001	0.019	0.002	-	-
Aldrin (µg/L)	0.001	<LOQ	0.013	0.001	46.8	0.03
Dieldrin (µg/L)	0.003	<LOQ	0.005	<LOQ	17	0.03
Endrin (µg/L)	0.001	<LOQ	0.020	<LOQ	38.2	0.1
Hept. Epox. (µg/L)	0.002	<LOQ	0.013	<LOQ	34	0.03
Heptachlor (µg/L)	0.001	<LOQ	0.020	0.001	61	0.03
Endosulfan I (µg/L)	0.001	<LOQ	0.002	<LOQ	17	0.1
Endosulfan II (µg/L)	0.002	<LOQ	0.004	<LOQ	46.8	0.1
∑OCPs (µg/L)	-	0.005	0.191	0.016	-	0.5

LOQ – limit of quantification
DF - Detection frequency
MAC - Maximum admissible concentration

After chemical analysis and data processing, 86% among samples were found to be compliant with the Romanian and EU regulations. In one of the analyzed sample the level of benzo(a)pyrene exceeded the maximum admissible concentration while 12% of the samples presented levels above the regulation limits for THMs.

A comparison between the results of the present study and previously reported results for similar contaminants in water samples in European countries is presented in Table 2 which illustrates the concentration ranges and means values of PAHs, THMs and OCPs. The total PAH levels determined in this study ranged from 6.18 to 96.2 ng/L with a mean value of 53.5 ng/L. The PAHs levels reported in our study were found to be comparable with those reported in other countries like Iceland,[18] Spain[19] or lower when compared to those reported for Turkey[20] or Greece.[21] The highest concentrations of PAHs in drinking water samples were reported in Poland,[22] approximately 25 times higher than those reported for Romanian samples included in this study.

Studies in Iceland have reported the lowest THMs concentrations in drinking water,[18] while the highest concentrations were reported in drinking water samples from Russia[23] and Romania (present study). The mean concentration for total THMs from Russia was 205±70 μg/L, this value exceeding by a factor of two, the maximum concentration allowed by the European norms.

In Romania, the OCPs concentrations in drinking water samples ranged from 0.004 to 0.354 μg/L, these results being in agreement with previous data reported for Romania,[4] but significantly higher when compared to other European countries.[21-30]

PAH levels in drinking water

The presence of PAHs in drinking water may be due to pyrogenic sources, which are likely derived from anthropogenic activities, such as the combustion-derived particles present in urban atmospheric dust or petrogenic, such as fuel oil or light refined petroleum products.

Table 2. Mean and range PAHs, THMs and OCPs concentrations in Romanian drinking water samples (present study) compared to previously reported levels for other European countries.

Location/ Year	Benzo(a)pyrene/ ng/L		ΣPAHs/ ng/L		ΣTHMs/ µg/L		ΣOCPs/ µg/L		*Ref.*
	Mean/ Range	No. Sampl.	Mean/ Range	No. Sampl.	Mean/ Range	No. Sampl.	Mean/ Range	No. Sampl.	
Greece/ 2000-2005	<2	40	<330	40	5-106	-	0.068	29	21, 24, 25
Poland/ 1999-2012	0-15	54	126-9815	54	2.1-36.9	10	0.072	102	5, 22, 26
Turkey/ 2010-2013	<0.53	8	<559	8	6.63±5.14 2.34-19.3	21	≤LOQ-0.042	21	20, 27
Spain/ 2009-2012	-	-	2.3–48.7	-	26.4 0.8–98.1	63	-	-	13, 19
Macedonia/ 2013	-	-	-	-	22.22 ± 12.06 0-45	45	0.018	12	28, 29
Iceland 2002-2012	1 - 26	312	4 - 80	325	0.35 – 1.4	317	0.045 – 0.055	12	18
Albania/ 2014	-	-	-	-	-	-	0.003 <LOQ-0.013	13	30
Russia/ 2003	-	-	-	-	205±70	-	-	-	23
Portugal/ 2015	-	-	-	-	1.7-97.7	33	-	-	31
France 2006-2007	-	-	-	-	5.7 – 67.8	284	-	-	32
U.K. 2000-2002 2005-2007	-	-	-	-	49.3 28.9	258	-	-	33
Hungary/ 2013	-	-	-	-	2.0 0.3 – 5.1	28	-	--	34
Romania/ 2013	-	-	-	-	17.8 1.87-94.2	40	0.045 0.007-0.354	40	**4**
Romania/ 2014-2016	2.291 ≤LOQ-21.7	47	53.5 6.18 – 96.2	47	48.7 3.2 – 197.3	47	0.039 0.004 – 0.240	47	**This study**

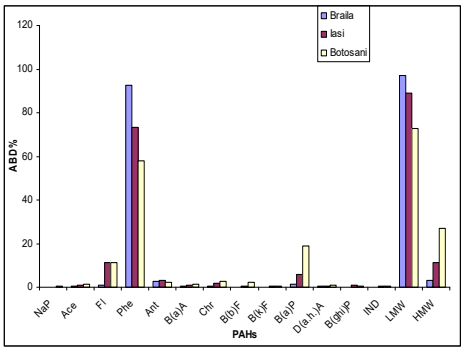

Figure 1. Abundance of individual PAHs, LMW and HMW in analyzed water samples from different areas of the Moldavian Region.

The most frequently detected PAHs in the drinking water samples were phenanthrene (Phe) (92.6%), benzo(a)pyrene [B(a)P] (18.9%), fluorine (Fl) (11.3%) and anthracene 3.08 (%) as can be seen in Figure 1. Different distribution of the presence of PAHs by counties was also evidenced. In the eastern area of the studied region (Braila), prevailed the lower molecular weight PAHs, LMW-PAHs (2-3 rings) (96%), in the center of the studied area (Iasi), the percentage of LMW-PAHs was lower (88%), while in the northern area (Botosani), an increased abundance of components with the high molecular weight PAHs, HMW-PAHs (4-6 rings) (27%) was recorded. Samples collected from Botosani evidenced higher than MAC benzo(a)pyrene levels.

Table 3. Source identification based on LMW over HMW ratio values for selected PAHs in drinking water samples.

Ratios	Pyrolytic	Petrogenic	Moldavian areas		
			Eastern	Center	Northern
LMW/HMW	Low	High	31.4	7.9	2.6
Ph/Ant	< 10	> 10	32.8	23.7	27.4
Chr/Pyr	< 1	> 1	2.4	1.8	1.73

In order to determine the possible PAH sources in water samples we have applied a diagnostic ratio method, which can evidence the source nature of pollution (petrogenic or pyrolitic)[35]. As can be seen from Table 3 data, the calculated LMW/HMW ratios for the three studied areas were between 2.6 and 31.4, and suggests that the sources of PAH contamination could be of petrogenic origin. This result is also confirmed by the ratios of Phe/Ant levels, which are higher than 10 and also by the ratios of Chr/Pyr levels, higher than 1.

A high percentage of LMW in the total PAHs (96%) and a high LMW/HMW ratio (31.4) suggest a petrogenic pollution of the drinking water sources, which, in the case of Braila County, might be attributed mainly due to the Danube River. In this case, river transport can be considered the main source of pollution with PAHs.

In the centre of Moldavia, Iasi County, the water sources are mixed, surface and underground, and the contribution of petrogenic pollution is lower than in the south of the studied region, which is suggested by the value of the ratio LMW/HMW, 7.9.

In the Northern Moldavia, Botosani County, groundwater represents the main drinking water source. A significantly lower ratio value for LMW/HMW (2.6) was noticed which suggests that the PAH sources might be both of pyrogenic and petrogenic origins. For this area, the abundance of the benzo(a)pyrene was much higher when compared to other studied areas, with the exceeding of the MAC being frequently encountered. These data suggest that PAHs might occur also from the combustion sources, such as coal, grass or wood combustion.

OCPs in drinking water

Even if the use of OCPs has been restricted or even banned throughout the EC, however, they are still detected in many environmental compartments, including drinking water. In Romania, starting from 1981,

the use of lindane and DDT has been banned, but due to their high persistence, OCPs can still be determined in the majority of analyzed samples.

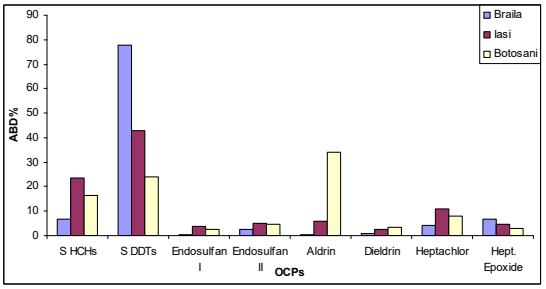

Figure 2. Abundance of OCPs in analyzed water samples from different areas of the Moldavian Region.

As can be seen in Figure 2, the highest detection rate of DDT and its metabolites was obtained in the southern Moldavia, respectively in Braila County, with a maximum concentration of ∑DDTs of 0.16 μg/L. The HCH isomers were detected with a higher frequency in the central area of Moldavia, with a maximum concentration of ∑HCHs of 0.019 μg/L. In the eastern Moldavia a higher abundance of aldrin was observed when compared to the other sampled areas, but their concentration did not exceed the MACs.

In order to identify the possible sources of water pollution with OCPs we evaluated several ratio of HCH isomers and DDT and its' metabolites.[36] The ratio of (DDD+DDE)/∑DDTs can be used to evaluate the recent use of the technical mixture of DDT and its persistence in the environment. A ratio of (DDD+DDE)/∑DDTs > 0.5 indicate a long-term use of DDT, but not necessarily a recent use. In our study, this ratio ranged between 0.5-0.9, indicating both excessive and long-term use of the DDT, but not necessarily a recent use.

Also, the low α-HCH over γ-HCH ratio obtained for the water samples included in this study, ranged between 0.1-0.7, suggesting that the HCHs are present in analysed water samples due to the historical use of lindane (usually 99% γ-HCH) and not due to atmospheric transport.

THMs in drinking water

THMs are mainly formed in drinking water as a result of chlorination of organic matter present in water supply stations. The most common THM is chloroform, which is the compound with the highest abundance in all analyzed water samples, as can be seen in Figure 3.

In the presence of bromides, brominated THMs are preferentially formed and the chloroform concentration decreases. This can be observed in our study especially for samples collected from the central area of Moldavia. In Iasi, the chloroform abundance was lower (44%) when compared to that determined in other studied areas, where abundance of about 65% of chloroform was observed. Simultaneously, significantly higher levels for bromoform and dichloromethane abundance were measured as evidenced in Figure 3.

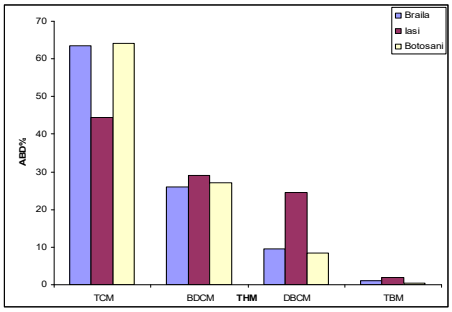

Figure 3. Abundance of THMs in analyzed water samples from different areas of the Moldavian Region.

In the central Moldavia, an exceeding of the MAC for THMs was observed in 29% of the analyzed samples and in the northern area, 10% of the analyzed samples. However, in the southern area, no exceeding of the

MAC was observed in collected samples. The high THM concentrations in the analyzed drinking water samples may be caused by organic pollution of water sources combined with excessive chlorination.

Conclusions

The present study reported for the first time the levels of PAHs in drinking water samples from Romania and further evaluated the sources and extent of pollution of drinking water from Eastern Romania, especially for rural areas. The calculated LMW/HMW ratios for the three studied areas suggest that the PAH contamination sources were mostly of petrogenic origin.

In order to identify the possible sources of OCPs water pollution, the (DDD+DDE)/∑DDTs ratio values indicated excessive and long-term use of DDT, but not necessarily a recent one.

The most commonly detected THM in drinking water was chloroform, with the highest abundance in all analyzed samples. Among the analysed samples, 12% have concentrations above the regulation limits for THMs.

References

1. EC DIRECTIVE 98/83/EC of 3 November 1998 on the quality of water intended for human consumption, Official Journal of the European Communities, L 330, 5.12.1998, p. 32-54;
2. Law no. 458/2002 regarding the drinking water quality, revised by Law 182/2011, published in Romanian Official Monitor, part I, no. 733 from 19 Octobers 2011;
3. Gurzau, A.E.; Popovici, E.; Pintea, A.; Dumitraşcu, I.; Pop, C.; Popa, O. Exposure assessment to trihalomethane from the epidemiological perspectives. *Carpathian J. Earth Environ. Sci.* **2011**, *6*, 5-12.
4. Dirtu, D.; Pancu, M.; Minea, M.L.; Sandu, I.; Dirtu, A.C. Occurrence and Assessment of Selected Chemical Contaminants in Drinking Water from Eastern Romania. *Rev. Chim. (Romania)* **2016**, *67*, 2059-2064.

5. Pawełczyk, A. Assessment of health risk associated with persistent organic pollutants in water. *Environ. Monit. Assess*. **2013**, *185*, 497–508.
6. Syafrudin, M.; Kristanti, R.A.; Yuniarto, A.; Hadibarata, T.; Rhee, J.; Al-onazi, W.A.; Algarni, T.S.; Almarri, A.H.; Al-Mohaimeed, A.M. Pesticides in Drinking Water - A Review. *Int. J. Environ. Res. Public Health* **2021,** *18*, 468-488.
7. Dirtu, A.C.; Cernat, R.; Dragan, D.; Mocanu, R.; Van Grieken, R.; Neels, H.; Covaci, A. Organohalogenated pollutants in human serum from Iassy, Romania and their relation with age and gender. *Environ. Int.* **2006**, *32*, 797-803.
8. Dirtu, A.C.; Covaci, A. Estimation of daily intake of organohalogenated contaminants from food consumption and indoor dust ingestion in Romania. *Environ. Sci. Tech.* **2010**, *44*, 6297-6304.
9. Dirtu, A.C.; Ali, N.; Van den Eede, N.; Neels, H. and Covaci, A. Country specific comparison for profile of chlorinated, brominated and phosphate organic contaminants in indoor dust. Case study for Eastern Romania. *Environ. Int.* **2012**, *49*, 1-8.
10. Kujlu, R.; Mahdavianpour, M. and Ghanbari, F. Multi-route human health risk assessment from trihalomethanes in drinking and non-drinking water in Abadan, Iran. *Environ. Sci. Pollut. Res*. **2020**, *27*, 42621-42630.
11. Ceretti, E.; Moretti, M.; Zerbini, I.; Villarini, M.; Zani, C.; Monarca, S.; Feretti, D. Occurrence and control of genotoxins in drinking water: a monitoring proposal. *J. Public Health Res*. **2016,** *5*, 769-781.
12. Legay, C.; Rodriguez, M.J.; Serodes, J.B., Levallois, P. Estimation of chlorination by-products presence in drinking water in epidemiological studies on adverse reproductive outcomes: a review. *Sci. Total Environ*. **2010**, *72*, 408-436.
13. Fernández-Navarro, P.; Villanueva, C.M.; García-Pérez, J.; Boldo, E.; Goñi-Irigoyen, F.; Ulibarrena, E.; Rantakokko, R.; García-Esquinas, E.; Pérez-Gómez, B.; Pollán, M.; Aragonés, N. Chemical quality of tap water in Madrid: multicase control cancer study in Spain (MCC-Spain). *Environ. Sci. Poll. Res.* **2017,** *24*, 4755-4764.
14. Feo, M.L.; Sprovieri, M.; Gherardi, S.; Sammartino, S.; Marsella, E. Polycyclic aromatic hydrocarbons and polychlorinated biphenyls in the harbours of Naples (Southern Italy): time and spatial distribution patterns. *Environ. Monit. Assess.* **2011**, *174*, 445-459.
15. Patel, A.B.; Shaikh, S.; Jain, K.R.; Desai, C.; Madamwar, D. Polycyclic Aromatic Hydrocarbons: Sources, Toxicity, and Remediation Approaches. *Front Microbiol.* **2020**, *11*, 562-581.
16. Xue, W.; Warshawsky, D. Metabolic activation of polycyclic and heterocyclic aromatic hydrocarbons and DNA damage: A review. *Toxic Applied Pharm.* **2005**, *206*, 73-93.
17. Solid Phase Extraction (SPE) – Application Guide, Macherey – Nagel, 2010, pp 16-25.
18. Gunnarsdottir, M.J.; Gardarsson, S.M.; St. Jonsson, G.; Bartram, J. Chemical quality and regulatory compliance of drinking water in Iceland. *Int. J. Hygiene Environ. Health*. **2016**, *219*, 724-733.

19. Kayali-Sayadi, M.N.; Rubio-Barroso, S.; Beceiro-Roldan, C.; Polo-Diez, L.M. Rapid Determination of PAHs in Drinking Water Samples Using Solid-Phase Extraction and HPLC with Programmed Fluorescence Detection. *J. Liquid Chrom. Related Tech.* **1996,** *19*, 3135-3146.
20. Yildirim, N.C.; Yildirim, N.; Kaplan, O.; Tayhan, N. Evaluation of Chemical and Microbiological Contamination Levels in Drinking Water Samples Collected from Towns in Tunceli, Turkey. *Int. J. Agric. Biol.* **2010**, *12*, 957-960.
21. Kanakia, M.; Nikolaou, A.; Makri, C.A.; Lekkas, D.F. The occurrence of priority PAHs, nonylphenol and octylphenol in inland and coastal waters of Central Greece and the Island of Lesvos. *Desalination*. **2007**, *210*, 16-23.
22. Kabzinski, A.K.M.; Cyran, J.; Juszczak, R. Determination of polycyclic aromatic hydrocarbons from water from Lodz. *Polish J. Environ. Studies*. **2002**, *11*, 695-706.
23. Egorov, A.I.; Tereschenko, A.I.; Altshul, L.M.; Vartiainen, T.; Samsonov, D.; LaBrecque, B.; Mäki-Paakkanen, J.; Drizhid, N.L.; Ford, T.E. Exposures to drinking water chlorination by-products in a Russian city. *Int. J. Hygiene Environ. Health*. **2003,** *206*, 539-551.
24. Golfinopoulos, S.K. The occurrence of trihalomethanes in the drinking water in Greece. *Chemosphere*. **2000**, *41*, 1761-1778.
25. Zambetoglou, K.; Papagianni, M.; Papaioannou, A.; Samara, C. Occurrence and removal of pesticides in the drinking water treatment plant of Thessaloniki, Northern Greece. *Fres. Env. Bull.* **2006**, *15*, 989-996.
26. Luks-Betlej, K.; Bodzek, D. Occurrence of Trihalomethanes, Particularly Those Containing Bromine, in Polish Drinking Waters. *Polish J. Environ. Stud*. **2002**, *11*, 255-260.
27. Demir, V.; Ergin, S. Occurrence and Assessment of Chemical Contaminants in Drinking Water in Tunceli, Turkey. *J. Chem.* **2013**, 238374.
28. Durmishi, H.B.; Daut, V.; Murtezan, I.; Agim, S.; Arianit, A.R. Variation of Trihalomethanes Concentration In Tetova's Drinking Water in the Autumn Season, Middle-East. *J. Scient. Res.* **2013**, *16*, 814-821.
29. Tomovska, T.; Nedelkova, M.; Stojkovska, K.; Presilski, S. Determination of Persistent Organochlorine Pesticides in Drinking Water Using LLE and GC/ECD. *J. Hygienic Eng. Design.* **2013**, *28*, 543-554.
30. Pine, O.; Nuro, A. Analysis of Some Organic Pollutants in Drinking Water using Capillary Gas Chromatography Technique. *Int. J. Curr. Microbiol. App. Sci.* **2016**, *5*, 702-709.
31. Melo, A.; Mansilha, C.; Teixeira, M.; Ferreira, I. Occurrence of Trihalomethanes in Chlorinated Waters from Different Sources Used for Urban Supply. *Food Sci. Tech.* **2016**, *4*, 57- 63.
32. Mouly, D.; Joulin, E.; Rosin, C.; Beaudeau, P.; Zeghnoun, A.; Olszewski-Ortar, A.; Munoz, J.F.; Welte, B.; Joyeux, M.; Seux, R.; Montiel, A.; Rodriguez, M.J. Variations in trihalomethane levels in three French water distribution systems and the development of a predictive model. *Water Res*. **2010,** *44*, 5168-5179.

33. Iszatt, N.; Nieuwenhuijsen, M.J.; Bennett, J.E.; Toledano, M.B. Trihalomethanes in public drinking water and stillbirth and low birth weight rates: an intervention study. *Environ. Int.* **2014**, *73*, 434-439.

34. *http://www.szegedivizmu.hu/en/environmental_protection/quality_and_composition_of_the_drinking_water_in_szeged/*

35. Nasher, E.; Heng L.Y.; Zakaria, Z.; Surif, S. Concentrations and Sources of Polycyclic Aromatic Hydrocarbons in the Seawater around Langkawi Island, Malaysia. *J. Chem.* **2013**, 975781.

36. Cai, S.R.; Sun, K.S.; Dong, S.Y.; Wang, Y.M.; Wang, S.; Jia, L. Assessment of Organochlorine Pesticide Residues in Water, sediment, and Fish of the Songhua River, China. *Environ. Forensics* **2014**, *15*, 352-357.