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PRAĆENJE I ODREĐIVANJE IZBRANIH HEMIJSKIH PARAMETARA U PODZEMNIM VODAMA

DETERMINATION OF SELECTED HEAVY METALS IN GROUNDWATER

IZVOD

Istraživanje i kontinuirano praćenje sadržaja nekih hemijskih parametara, kao što su joni teških metala Pb, Cd i Zn, u podzemnim vodama (izvorskim i vodama bunara), sprovedeno je primenom PSA metode za istovremeno određivanje. Sve dobijene vrednosti ispitivanih parametara na odabranim i ispravno koncipiranim mernim mestima bile su ispod ili u okviru granica MDK, i ako su varirale u zavisnosti od godišnjeg doba.

Ključne reči: teški metali, bunarske vode, prirodne izvorske vode, potenciometrijska analiza uklanjanja

ABSTRACT

The investigation and continuous monitoring of the content of some chemical parameters, such as heavy metal ions Pb, Cd and Zn, in groundwater (source and well water), was conducted using the PSA method for simultaneous determination. All obtained values of the tested parameters at the selected and correctly conceived measuring sites were below or within the limits of the MDK, and if varied depending on the season.

Key words: heavy metals, well waters, natural spring waters, potentiometric stripping analysis.

UVOD

U industrijskim vodama, zavisno od industrije, mogu se naći mnogi zagađivači. Ove vode mogu da sadrže tragove rude, gvožđa, koksa, karbonata, fenola i drugih, kao i jone olovnog metala, cinka, bakra, kadmijuma, koji kroz otpadne i iscrpljujuće vode idu do krajnjeg prirodnog ili veštačkog primaoca [1-3].

Na teritoriji Severnog Kosova i Metohije krajnji primalac je reka Ibar [4]. Rudarsko-metalurški hemijski kombinat, koji se sastoji od mnogih tehnoloških sistema i deponija, ima veliki uticaj na degradaciju vodene flore ove reke [5]. Rude deponije imaju heterogen hemijski sastav u smislu sadržaja teških metala i predstavljaju veliki ekološki balast. Njihov uticaj na rečne i podzemne vode ogleda se kroz ispiranje putem procednih i voda koje se slivaju sa površina. Industrijski otpad se obično nalazi u blizini reke. Zbog erozije, uticaja vodotoka i taloga, teški metali iz otpada se ulivaju u reku Ibar i infiltracijom u podzemne vode i aluvijalne ravni [6].

Podzemne vode aluvijalnog zemljišta su plitke, tako da su pod uticajem sastava rečne vode, industrijskih

INTRODUCTION

Depending on the industry, many pollutants can be found in industrial waters. These waters may contain traces of ore, iron, coke, carbonate, phenol and others, as well as ions of lead metal, zinc, copper, cadmium, which through waste and exhaust waters reach the ultimate natural or artificial recipient [1-3].

In the territory of Northern Kosovo and Metohija the final recipient is the Ibar River [4]. The mining-metallurgical chemical plant, consisting of many technological systems and landfills, has a great influence on the degradation of the aquatic life of this river [5]. Ore deposits have a heterogeneous chemical composition in terms of heavy metal content and are a major environmental ballast. Their impact on river and groundwater is reflected by flushing through process and surface waters. Industrial waste is usually located near the river. Due to the erosion, the impact of watercourses and sediment, heavy metals from the waste are poured into the Ibar River and infiltrated into groundwater and alluvial planes [6].

Groundwater of alluvial soil is shallow, so it is influenced by the composition of river water, industrial and municipal water, wastewater and

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i komunalnih voda, otpadnih voda i taloga (kiselih kiša) i često uzrokuju infiltraciju i mobilizaciju teških metala. Procesi u aluvijalnom zemljištu utiču na sorpciju/desorpciju teških metala. Akumulaciju teških metala u podzemnim vodama prate procesi rastvaranja, sedimentacije, fizičke, hemijske i biološke transformacije njihovih supstrata [7,8].

Teški metali uglavnom kroz zagađene vode dopiru do ekosistema [8,9]. Stepen kontaminacije primalaca može biti toliko ozbiljan da šteti zdravlju ljudi i životinja. Monitoring podzemnih voda je sastavni deo sistema koji štiti životnu sredinu od toksičnih efekata zagađivača, a posebno od uticaja teških metala [10].

Stanovništvo severnog dela Kosova i Metohije u gradovima i selima suočeno je sa ozbiljnim problemom vodosnabdevanja ili snabdevanja vodom iz gradske vodovodne mreže, a u takvoj situaciji vodosnabdevanje je obično iz obližnjih prirodnih izvora koji su retko podložni hemijskoj i biološkoj kontroli. Kontrola kvaliteta podzemnih voda takođe je direktno povezana sa zahtevima životne sredine i zdravljem ljudi.

Stoga je cilj ovog rada istraživanje i kontinuirano praćenje sadržaja nekih hemijskih parametara, kao što su joni teških metala olovo (Pb), kadmijum (Cd) i cink (Zn) u vodama bunara i prirodnih izvora na teritoriji severnog dela Kosova i Metohije. Pravilno dizajnirana mreža mernih mesta osigurala je njihovo sveobuhvatno praćenje i otkrivanje dugoročnih uzroka u ispitivanom periodu.

Voltammetrijska tehnika korišćena za utvrđivanje tragova teških metala u izvorskoj i bunarskoj vodi bila je Potentiometrijska striping analiza [11,12].

MATERIJALI I METODA

I) Određivanja u ovom radu sprovodena su sistemom za potenciometrijsku striping analizu, Stripping Analizer M1 (Tehnološki fakultet-Novi Sad, Simetry-Leskovac, Srbija). Primenjena je metoda istovremenog određivanja olova, kadmijuma i cinka.

II) Korišćeni su rastvori HCl (supprapur), HNO_3 (p.a.), KCl (supprapur), standardni rastvori Pb, Cd, Zn i Hg (1.000 g dm^{-3}, Supprapur), kompanije Mercke (Darmstad, Germany).

REZULTATI I DISKUSIJA

Rezultati određivanja hemijskih parametara u uzorku vode bunara i prirodene izvorske vode korišćenjem potenciometrijske striping analize (PSA) u periodu od aprila 2017. do januara 2018. godine na dvanaest mernih mesta u oblasti severnog dela Kosovske Mitrovice prikazani su u tabelama 1–9.

Istovremeno određivanje određenih hemijskih parametara, kao što su joni metala Pb, Cd i Zn pomoću PSA, izvršeno je u vodama bunara i prirodnim

sediment (acid rain) and often causes infiltration and mobilization of heavy metals. Processes in alluvial soil affect the sorption / desorption of heavy metals. The accumulation of heavy metals in groundwater is accompanied by the processes of dissolution, sedimentation, physical, chemical and biological transformation of their substrates [7,8].

Heavy metals mainly reach ecosystems through polluted waters [8,9]. The degree of contamination of recipients can be so severe that it harms human and animal health. Groundwater monitoring is an integral part of a system that protects the environment from the toxic effects of pollutants, and in particular from the effects of heavy metals [10].

The population of northern Kosovo and Metohija in cities and villages faces a serious problem of water supply or water supply from the city water supply network, and in such a situation water supply is usually from nearby natural sources that are rarely subject to chemical and biological control. Groundwater quality control is also directly linked to environmental requirements and human health.

Therefore, the aim of this paper is to investigate and continuously monitor the content of some chemical parameters, such as heavy metal ions lead (Pb), cadmium (Cd) and zinc (Zn) in the wells and natural resources in the northern part of Kosovo and Metohija. A properly designed network of measurement sites ensured their comprehensive monitoring and detection of long-term causes during the study period.

The voltammetric technique used to determine traces of heavy metals in spring and well water was Potentiometric striping analysis [11,12].

MATERIALS AND METHODS

I) The determinations in this paper were carried out by a system for potentiometric striping analysis, Stripping Analyzer M1 (Faculty of Technology-Novi Sad, Simetry-Leskovac, Serbia). The method of simultaneous determination of lead, cadmium and zinc was applied.

II) Solutions HCl (supprapur), HNO3 (p.a.), KCl (supprapur), standard solutions of Pb, Cd, Zn and Hg (1,000 g dm-3, Supprapur) from Mercke (Darmstad, Germany) were used.

REZULTATI I DISKUSIJA

The results of determining chemical parameters in a sample of well water and natural spring water using potentiometric striping analysis (PSA) from April 2017 to January 2018 at twelve measurement sites in the northern part of Kosovska Mitrovica are shown in Tables 1–9.

Simultaneous determination of certain chemical parameters, such as metal ions Pb, Cd, and Zn using PSA, was performed in well waters and natural spring waters. Measuring sites, when it came to wells,

izvorskim vodama. Merna mesta, kad su vode bunara u pitanju, obuhvatala su vode iz deset bunara od kamena i to: 1. Selo Žitkovac, 200 m od reke Ibar, 2 m od autoputa, staro 5 godina; 2. Selo Grabovac, 100 m od reke Ibar, u blizini autoputa, 30 godina; 3. Selo Žitkovac, 50 m od deponije Žitkovac, 200 m od reke Ibar; 4. Selo Rudare, 50 m od reke Ibar, 30 godina; 5. Selo Srbovac, 20 m od reke Ibar, 40 godina; 6. Selo Srbovac, 20 m od reke Ibar, 40 godina; 7. Selo Gornji Krnjin, 100 m od reke Ibar, 10 godina; 8. Selo Rudare, 80 m od reke Ibar, 25 godina; 9. Selo Grabovac, 30 m od reke Ibar, 25 godina; 10. Selo Grabovac, 30 m od reke Ibar, 25 godina.

Merna mesta za prirodne izvorske vode bile su: 1. Selo Grabovac, izvor iznad aluvijalnog zemljišta, 2. Devine vode, 10 km od Zvečana.

Praćenje navedenih parametara vršeno je od aprila 2017. do januara 2018. godine sa perjodima ponavljanja od četiri meseca (april, avgust, oktobar i februar). Rezultati eksperimentalnih određivanja predstavljeni su u Tabelama od 1 do 9. U okviru ovog ispitivanja vršeno je praćenje i vrednosti pH, merenje ove vrednosti vršeno je nakon uzimanja uzoraka. Izmerene vrednosti su takođe predstavljene u tabelama. Rezultati određivanja vrednosti pH, olova, kadmijuma i cinka u vodi iz bunara prikazani su u tabelama 1,3,5 i 7, a rezultati određivanja vrednosti pH, olova, kadmijuma i cinka u prirodnoj izvorskoj vodi prikazani su u tabelama 2,4,6 i 8.

included water from ten stone wells: 1. The village of Žitkovac, 200 m from the Ibar River, 2 m from the highway, 5 years old; 2. The village of Grabovac, 100 m from the Ibar River, near the highway, 30 years; 3. The village of Žitkovac, 50 m from the Žitkovac landfill, 200 m from the river Ibar; 4. The village of Rudara, 50 m from the river Ibar, 30 years; 5. The village of Srbovac, 20 m from the river Ibar, 40 years; 6. The village of Srbovac, 20 m from the river Ibar, 40 years; 7. Gornji Krnjin village, 100 m from the Ibar river, 10 years; 8. The village of Rudara, 80 m from the river Ibar, 25 years; 9. The village of Grabovac, 30 m from the river Ibar, 25 years; 10. The village of Grabovac, 30 m from the river Ibar, 25 years.

Measuring points for natural spring waters were: 1. The village of Grabovac, the source above the alluvial land, 2. Devine waters, 10 km from Zvecan.

These parameters were monitored from April 2017 to January 2018 with four-month repetition periods (April, August, October and February). The results of the experimental determinations are presented in Tables 1 to 9. Within this test, monitoring was carried out and pH values were measured after sampling. Measured values are also presented in the tables. The results of determination of pH, lead, cadmium and zinc in water from wells are shown in Tables 1,3,5 and 7, and the results of determination of pH, lead, cadmium and zinc in natural spring water are shown in Tables 2,4,6 and 8.

Tabela1. Rezultati određivanja hemijskih parametara u uzorcima vode bunara, april 2017, µg/dm3

Table 1. Results of determination of chemical parameters in the samples of water well, April 2017, µg/dm^3

Simple	1	2	3	4	5	6	7	8	9	10	MCL
Pb	3,17	2,02	6,43	1,97			1,13	3,24	1,07	6,81	10
Cd	0,69	0,84	1,89	2,27			1,47	1,48	1,38	2,66	3
Zn	28,03	39,12	149,21	59,33			178,56	177,92	98,16	247,77	3000

1 Selo Žitkovac, 200 m od reke Ibar, 2 m od autoputa, staro 5 godina; 2. Selo Grabovac, 100 m od reke Ibar, u blizini autoputa, 30 godina; 3. Selo Žitkovac, 50 m od deponije Žitkovac, 200 m od reke Ibar; 4. Selo Rudare, 50 m od reke Ibar, 30 godina; 5. Selo Srbovac, 20 m od reke Ibar, 40 godina; 6. Selo Srbovac, 20 m od reke Ibar, 40 godina; 7. Selo Gornji Krnjin, 100 m od reke Ibar, 10 godina; 8. Selo Rudare, 80 m od reke Ibar, 25 godina; 9. Selo Grabovac, 30 m od reke Ibar, 25 godina; 10. Selo Grabovac, 30 m od reke Ibar, 25 godina. Planirani uzorci 5 i 6 nisu uzeti zbog obilnih padavina

1 Village Zitkovac, 200 m from the river Ibar, 2 m from the highway, age 5 years; 2. Village Grabovac, 100 m from the river Ibar, near highway, 30 years; 3. Village Zitkovac, 50 m from the landfill Zitkovac, 200 m from the river Ibar; 4. Village Rudare, 50 m from the river Ibar, 30 years; 5. Village Srbovac, 20 m from the river Ibar, 40 years; 6. Village Srbovac, 20 m from the river Ibar, 40 years; 7. Village Gornji Krnjin, 100 m from the river Ibar, 10 years; 8. Village Rudare, 80 m from the river Ibar, 25 year; 9. Village Grabovac, 30 m from the river Ibar, 25 years; 10. Village Grabovac, 30 m from the river Ibar, 25 year: Planned samples 5 and 6 were not taken due to abundant precipitation

Tabela 2. Rezultati određivanja hemijskih parametara u uzorcima izvorske vode, april 2017, µg/dm^3

Table 2. Results of determination of chemical parameters in the samples of spring water, April 2017, µg/dm^3

Simple	Pb	Cd	Zn
1	1,73	1,34	79,01
2	2,09	1,52	38,97
MCL	10	3	3000

1. Selo Grabovac, izvor iznad aluvijalnog zemljišta, 2. Devine vode, 10 km od Zvečana

1. Village Grabovac, spring above the alluvial plane, 2. Devine vode, 10 km from Zvecan

Tabela 3. Rezultati određivanja hemijskih parametara u uzorcima vode bunara, avgust 2017, µg/dm3
Table 3. Results of determination of chemical parameters in the samples of water well, August 2017, µg/dm3

Simple	1	2	3	4	5	6	7	8	9	10	MCL
Pb	3,42	0,81	9,84	5,99	4,13	3,25	1,38	5,72	3,17	14,99	10
Cd	0,21	0,15	0,91	0,07	0,13	0,36	0,57	0,02	0,47	0,41	3
Zn	49,01	198,91	49,02	38,97	29,03	48,91	79,05	598,13	129,44	189,21	3000

1 Selo Žitkovac, 200 m od reke Ibar, 2 m od autoputa, staro 5 godina; 2. Selo Grabovac, 100 m od reke Ibar, u blizini autoputa, 30 godina; 3. Selo Žitkovac, 50 m od deponije Žitkovac, 200 m od reke Ibar; 4. Selo Rudare, 50 m od reke Ibar, 30 godina; 5. Selo Srbovac, 20 m od reke Ibar, 40 godina; 6. Selo Srbovac, 20 m od reke Ibar, 40 godina; 7. Selo Gornji Krnjin, 100 m od reke Ibar, 10 godina; 8. Selo Rudare, 80 m od reke Ibar, 25 godina; 9. Selo Grabovac, 30 m od reke Ibar, 25 godina; 10. Selo Grabovac, 30 m od reke Ibar, 25 godina.
1 Village Zitkovac, 200 m from the river Ibar, 2 m from the highway, age 5 years; 2. Village Grabovac, 100 m from the river Ibar, near highway, 30 years; 3. Village Zitkovac, 50 m from the landfill Zitkovac, 200 m from the river Ibar; 4. Village Rudare, 50 m from the river Ibar, 30 years; 5. Village Srbovac, 20 m from the river Ibar, 40 years; 6. Village Srbovac, 20 m from the river Ibar, 40 years; 7. Village Gornji Krnjin, 100 m from the river Ibar, 10 years; 8. Village Rudare, 80 m from the river Ibar, 25 year; 9. Village Grabovac, 30 m from the river Ibar, 25 years; 10. Village Grabovac, 30 m from the river Ibar, 25 year.

Tabela 4. Rezultati određivanja hemijskih parametara u uzorcima izvorske vode, avgust 2017, µg/dm^3
Table 4. Results of determination of chemical parameters in the samples of spring water, August 2017, µg/dm^3

Simple	Pb	Cd	Zn
1	3,14	0,91	39,12
2	2,03	2,37	48,71
MCL	10	3	3000

1. Selo Grabovac, izvor iznad aluvijalnog zemljišta, 2. Devine vode, 10 km od Zvečana
1. Village Grabovac, spring above the alluvial plane, 2. Devine vode, 10 km from Zvecan

Tabela 5. Rezultati određivanja hemijskih parametara u uzorcima vode bunara, oktobar 2017, µg/dm^3
Table 5. Results of determination of chemical parameters in the samples of water well, October 2017, µg/dm^3

Simple	1	2	3	4	5	6	7	8	9	10	MCL
Pb	1,89	0,79	7,11	3,65	4,81	6,32	0,99	3,71	4,02	24,09	10
Cd	0,06	0,24	0,21	0,06	1,01	0,87	0,06	1,73	0,59	0,79	3
Zn	29,01	38,99	19,94	39,01	33,8	48,9	38,89	399,01	258,9	568,99	3000

1 Selo Žitkovac, 200 m od reke Ibar, 2 m od autoputa, staro 5 godina; 2. Selo Grabovac, 100 m od reke Ibar, u blizini autoputa, 30 godina; 3. Selo Žitkovac, 50 m od deponije Žitkovac, 200 m od reke Ibar; 4. Selo Rudare, 50 m od reke Ibar, 30 godina; 5. Selo Srbovac, 20 m od reke Ibar, 40 godina; 6. Selo Srbovac, 20 m od reke Ibar, 40 godina; 7. Selo Gornji Krnjin, 100 m od reke Ibar, 10 godina; 8. Selo Rudare, 80 m od reke Ibar, 25 godina; 9. Selo Grabovac, 30 m od reke Ibar, 25 godina; 10. Selo Grabovac, 30 m od reke Ibar, 25 godina.
1 Village Zitkovac, 200 m from the river Ibar, 2 m from the highway, age 5 years; 2. Village Grabovac, 100 m from the river Ibar, near highway, 30 years; 3. Village Zitkovac, 50 m from the landfill Zitkovac, 200 m from the river Ibar; 4. Village Rudare, 50 m from the river Ibar, 30 years; 5. Village Srbovac, 20 m from the river Ibar, 40 years; 6. Village Srbovac, 20 m from the river Ibar, 40 years; 7. Village Gornji Krnjin, 100 m from the river Ibar, 10 years; 8. Village Rudare, 80 m from the river Ibar, 25 year; 9. Village Grabovac, 30 m from the river Ibar, 25 years; 10. Village Grabovac, 30 m from the river Ibar, 25 year.

Tabela 6. Rezultati određivanja hemijskih parametara u uzorcima izvorske vode, oktobar 2017, µg/dm3
Table 6. Results of determination of chemical parameters in the samples of spring water, October 2017, µg/dm3

Simple	pH	Pb	Cd	Zn
1	6,6	1,87	0,39	38,83
2	7,2	0,89	1,01	29,01
MCL	6,5-8,5	10	3	3000

1. Selo Grabovac, izvor iznad aluvijalnog zemljišta, 2. Devine vode, 10 km od Zvečana
1. Village Grabovac, spring above the alluvial plane, 2. Devine vode, 10 km from Zvecan

Tabela 7. Rezultati određivanja hemijskih parametara u uzorcima vode bunara, januar 2018, µg/dm3
Table 7. Results of determination of chemical parameters in the samples of water well, January 2018, µg/dm3

Simple	1	2	3	4	5	6	7	8	9	10	MCL
Pb	2,58	2,61	6,13	4,23	3,81	3,74	1,02	4,13	4,43	4,21	10
Cd	0,18	0,51	0,11	0,69	1,84	1,49	0,09	1,21	0,75	1,68	3
Zn	249,3	138,1	149,2	189,9	60,2	97,8	43,9	27,9	462,5	431,3	3000
pH	7,0	6,3	7,4	7,0	7,0	7,5	7,2	6,8	6,5	6,3	6,5-8,5

1 Selo Žitkovac, 200 m od reke Ibar, 2 m od autoputa, staro 5 godina; 2. Selo Grabovac, 100 m od reke Ibar, u blizini autoputa, 30 godina; 3. Selo Žitkovac, 50 m od deponije Žitkovac, 200 m od reke Ibar; 4. Selo Rudare, 50 m od reke Ibar, 30 godina; 5. Selo Srbovac, 20 m od reke Ibar, 40 godina; 6. Selo Srbovac, 20 m od reke Ibar, 40 godina; 7. Selo Gornji Krnjin, 100 m od reke Ibar, 10 godina; 8. Selo Rudare, 80 m od reke Ibar, 25 godina; 9. Selo Grabovac, 30 m od reke Ibar, 25 godina; 10. Selo Grabovac, 30 m od reke Ibar, 25 godina.
1 Village Zitkovac, 200 m from the river Ibar, 2 m from the highway, age 5 years; 2. Village Grabovac, 100 m from the river Ibar, near highway, 30 years; 3. Village Zitkovac, 50 m from the landfill Zitkovac, 200 m from the river Ibar; 4. Village Rudare, 50 m from the river Ibar, 30 years; 5. Village Srbovac, 20 m from the river Ibar, 40 years; 6. Village Srbovac, 20 m from the river Ibar, 40 years; 7. Village Gornji Krnjin, 100 m from the river Ibar, 10 years; 8. Village Rudare, 80 m from the river Ibar, 25 year; 9. Village Grabovac, 30 m from the river Ibar, 25 years; 10. Village Grabovac, 30 m from the river Ibar, 25 year.

Tabela 8. Rezultati određivanja hemijskih parametara u uzorcima izvorske vode, januar 2017, µg/dm3
Table 8. Results of determination of chemical parameters in the samples of spring water, January 2018, µg/dm3

Simple	pH	Pb	Cd	Zn
1	7,1	1,18	1,03	80,34
2	8,2	1,01	1,09	83,57
MCL	6,5-8,5	10	3	3000

1. Selo Grabovac, izvor iznad aluvijalnog zemljišta, 2. Devine vode, 10 km od Zvečana
1. Village Grabovac, spring above the alluvial plane, 2. Devine vode, 10 km from Zvecan

Tabela 9. Rezultati određivanja Pb, Cd i Zn u destilovanoj i česmenskoj vodi
Table 9. Results of determination of Pb, Cd and Zn in distilled and chesmen water, µg/dm3

Simple	Pb	Cd	Zn
Deionized water	0,00	0,00	0,00
Double distilled water	3,41	2,87	4,11
Distilled water	4,62	2,94	4,89
Tap water	9,13	3,54	11,95

Na osnovu prikazanih rezultata zaključeno je da je sadržaj odabranih određivanih metala u vodi svih posmatranih uzoraka ispod granice maksimalno dozvoljenog (MDK). Njihove vrednosti su varirale u zavisnosti od mesta uzorkovanja. Najveće vrednosti bile su na mernom mestu 10, u blizini reke Ibar (selo Grabovac, 30 m od reke Ibar, bunar star 25 godina).

Pošto industrijska postrojenja ne rade, to se može protumačiti činjenicom da se merno mesto nalazi u blizini deponije, koja se nalazi pored reke Ibar i na taj način je indirektno zagađena. Veće količine padavina dovele su do ispuštanja katjona sa deponije, njihove migracije u korito reke i dalje, infiltracije u podzemne vode i njihovog taloženja u bunar tokom dužeg perioda. Te vrednosti su bile u opsegu od 0,79 do 24,49 µg/dm^{-3} za Pb; od 0,02 do 2,72 µg/dm^{-3} za Cd i od 28,03 do 601,05 µg/dm^{-3} za Zn, mereno PSA metodom.

Based on the presented results, it was concluded that the content of selected determined metals in water of all observed samples is below the maximum permissible limit (MCL). Their values varied depending on the sampling site. The highest values were at measuring site 10, near the river Ibar (village Grabovac, 30 m from the river Ibar, well 25 years old).

As the industrial plants do not operate, this can be interpreted by the fact that the measuring site is located near the landfill, which is located next to the Ibar River and is thus indirectly contaminated. Higher rainfall led to the discharge of cations from the landfill, their migration into the river bed and beyond, infiltration into groundwater and their deposition into the well over a long period. These values ranged from 0.79 to 24.49 µg/dm^{-3} for Pb; from 0.02 to 2.72 µg/dm^{-3} for Cd and from 28.03 to 601.05 µg/dm^{-3} for Zn, as measured by the PSA method.

Analizirajući rezultate po perjodima uzorkovanja, sadržaj ispitivanih parametara u vodi svih bunara tokom prolećne (april 2017.), letnje (avgust, 2017.), jesenske (oktobar 2017.) i zimske (januar, 2018.) sezone bio je iznad polovine maksimalno dozvoljenog i varirao u zavisnosti od sezone. To se može objasniti vremenskim uslovima (kiša, topljenje snega) i pojavom infiltracije teških metala.

U istom periodu vrednost pH u vodi svih posmatranih bunara bila je u granicama MDK. Ova vrednost kretala se u rasponu od 6,5 do 7,9 od blago kisele, neutralne do slabo bazne sredine. Pošto je maksimalno dozvoljena pH u vodi od 6,50 do 8,50 to se može reći da izmerene vrednosti pH apsolutno pogoduju za migraciju jona ispitivanih metala kao i količini istih [4].

Rezultati ispitivanja izvorskih voda prikazani su u tabelama 3,4,6 i 8. Vrednosti takođe variraju u zavisnosti od mesta uzorkovanja. U selima i mestima izvan geografskog uticaja zagađivača (selo Grabovac, Devine vode), sadržaj je bio niži od maksimalno dozvoljene koncentracije MDK [14]. U nekim uzorcima može se javiti sadržaj jona i drugih metala u tragovima, ali bez uticaja na kvalitet ispitivane vode.

Radi poređenja, vršena su ispitivanja dejonizovane, bidestilovane, destilovane, kao i vode iz gradskog vodovoda na teritoriji opštine Zvečan (Tabela 9). Na osnovu poređenja prikazanih rezultata može se zaključiti da sadržaj Pb, Cd i Zn u vodama prirodnih izvora na severnom delu Kosova i Metohije ne prelazi MDK, pa se takva voda u pogledu ispitivanih metala, može koristiti kao voda za piće. Zbog toga ove izvorske vode ispunjavaju kriterijume za pitku vodu i mogu se koristiti bez prethodne pripreme i prerade [20, 21].

Dobijeni rezultati stoga daju originalni doprinos na polju analitički tačnih, odgovarajućih metoda za određivanje toksičnih metala u ekosistemu. Takođe, istraživanje je pokazalo da je primena PSA za istovremeno određivanje Pb, Cd i Zn od velikog značaja za definisanje uslova određivanja i značajno doprinosi teoriji i praksi, metodologiji uzorkovanja i pripreme u obliku jedinstvenog i odgovarajućeg uzorka za ostala analitička i hemijska određenja u polju vode.

ZAKLJUČAK

Istraživanje i kontinuirano praćenje sadržaja određenih hemijskih parametara kao što su joni teških metala Pb, Cd i Zn u bunarskim i prirodnim izvorskim vodama sprovedeni su na teritoriji severnog dela Kosova i Metohije. Pravilno odabrana mreža mernih mesta osigurala je njihovo sveobuhvatno praćenje i otkrivanje dugoročnih uzroka u periodu od aprila 2017. do januara 2018. Ispitivanja su rađena PSA metodom za istovremeno određivanje Pb, Cd i Zn. Za primenu ove metode, uslovi određivanja bili su definisani u okviru ranijih istraživanja.

Analyzing the results by sampling period, the content of tested parameters in the water of all wells during the spring (April 2017), summer (August, 2017), autumn (October 2017) and winter (January, 2018) seasons was above half of the maximum allowed and varied depending on the season. This can be explained by weather conditions (rain, melting snow) and the appearance of heavy metal infiltration.

In addition, during the same period, the pH in the water of all observed wells was within the limits of MCL. This value ranged from 6.5 to 7.9 from slightly acidic, neutral to slightly base medium. Since the maximum permissible pH in water is from 6.50 to 8.50, it can be said that the measured pH values are absolutely suitable for the migration of the ions of the tested metals as well as the quantities of them [4].

The results of spring water testing are shown in Tables 3,4,6 and 8. Values also vary depending on the sampling site. In villages and places outside the geographical influence of the pollutants (village Grabovac, Devine vode), the content was lower than the maximum permitted concentration of MCL [14]. In some samples, the content of ions and other trace metals may occur, but without affecting the quality of the water tested.

For comparison, tests were carried out on deionized, bidistilled, distilled, as well as water from urban water supply in the territory of Zvecan municipality (Table 9). Based on the comparison of the results presented, it can be concluded that the content of Pb, Cd and Zn in the waters of natural resources in the northern part of Kosovo and Metohija does not exceed the MCL, so such water can be used as drinking water for the metals tested. Therefore, these spring waters meet the criteria for drinking water and can be used without prior treatment and treatment [20, 21].

The obtained results therefore provide an original contribution to the field of analytically accurate, appropriate methods for the determination of toxic metals in the ecosystem. Also, research has shown that the application of PSA for the simultaneous determination of Pb, Cd and Zn is of great importance for defining the determination conditions and significantly contributes to theory and practice, sampling and preparation methodology in the form of a single and appropriate sample for other analytical and chemical determinations in the water field.

CONCLUSION

The research and continuous monitoring of the content of certain chemical parameters such as heavy metal ions Pb, Cd and Zn in well and natural spring waters were conducted in the territory of northern Kosovo and Metohija. A properly selected network of measurement sites ensured their comprehensive monitoring and detection of long-term causes between April 2017 and January 2018. Tests were performed using the PSA method for the simultaneous determination of Pb, Cd, and Zn. For the application of this method, the conditions

Sve dobijene vrednosti ispitivanih parametara na odabranim mestima su bile ispod ili u okviru granica MDK, iako su varirale u zavisnosti od sezone.

of determination were defined in the framework of earlier studies.

All obtained values of the tested parameters at the selected sites were below or within the limits of the MCL, although they varied depending on the season.

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