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Evaluation of heavy metal content in irrigation water of the Dukagjin Plain, Kosovo

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1. Abstract

This study was carried out for evaluation of irrigation water on heavy metal contents in Dukagjin Plain, Kosovo. Water samples were collected in clean bottles at 10cm depth from several irrigation sources (Rivers: White Drin, LumbardhiPejes, LumbardhiDecanit, Erenik, some reservoirs and canals). The samples collected were analyzed for heavy metal contents such as zinc, iron, copper, manganese, lead, nickel, cobalt, cadmium, chromium, and molybdenum, by Microwave Plasma Atomic Emission Spectrometry (MP-AES 4100). The findings indicated that there is no significant difference of heavy metal contents between irrigation water from canals, rivers and reservoirs. Copper, manganese, nickel, cobalt, lead and chromium were found in normal concentrations in all water sources, while zinc and iron were found in deficient concentrations. Cadmium and molybdenum is at recommended maximum concentrations.Therefore, these sources can be used for irrigation purposes without any hazardous effect on soil and plants.

Keywords: Irrigation water; heavy metals; toxic elements; Dukagjin Plain; Kosovo

2. Introduction

Heavy metals are defined as metallic elements that have a relatively high density compared to water [7]. They are also considered as trace elements because of their presence in trace concentrations in various environmental matrices [11]

In recent years, there has been an increasing ecological and global public health concern associated with environmental contamination by these metals [3]. Reported sources of heavy metals in the environment include geogenic, industrial, agricultural, pharmaceutical, domestic effluents, and atmospheric sources [10]. Also soil pollution from heavy metals is increased as a result of intensive use of irrigation water with high content in these metals. (Tamariz,1996; Mendez et al., 1997).It is known that irrigation is helpful for sustaining agricultural production in any place, but it is imperative that good quality water should be used to sustain the soil.

Not all trace elements are toxic, even in small quantities many are essential for plant growth (Fe, Mn, Mo, Zn). However, excessive quantities will cause undesirable accumulations in plant tissue and growth reductions. (FAO, 1985).

That's why monitoring trace elements in irrigation water is as important as monitoring salinity status because of their potential to build up in soil and be absorbed by plants thereby being introduced into food chain. When such happens, they constitute further risks to human and livestock in terms of health and wellbeing.

2.1 Study area

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The Dukagjin Plain is a semi-karst field that lies in the south-western part of Kosovo, covering 35% (3,891 km2) of country's total area. It is about 67 km long and 20-40 km wide and its average altitude is 450 m above sea level. It is surrounded by high mountain rangesof Bjeshket e Nemuna in the western part, Pashtrik in the southwest, theSharr Mountains in the south and southeast.

In the eastern part it borders the hilly region of Drenica which divides it from the Kosovo plain. White Drin is the main river that flows in this region,Dukagjin region is highly influenced by the hot air masses that come from the Adriatic Sea through the valley of White Drin river. The annual average temperatures vary from 11.3^{o}C (Peje) to 12^{o}C (Prizren). Average annual precipitation of this climatic area is 700 mm per year.

TheDukagjin plain is the most important agricultural region of Kosovo. Agriculture in this area relies heavily on irrigation. The main water sources for the aforementioned are the White Drin river, Peja'sLumbardh river, Decan'sLumbardh,Istog's Spring and Radoniq's lake.

Extensive research has not been conducted regarding the heavy metals content of the water for agricultural uses. Taking into consideration this fact, this research provides an evaluation for heavy metals of the water used for irrigation in the Dukagjin Plain.

3. Material and Methods

3.1 Collection of water samples

A total of 24 surface water samples were collected from sampling points in the cropping period of the peak dry season (July-August, 2015). Samples were collected from rivers (6 samples), reservoirs (4 samples)and canals (14 samples). The samples were collected in 1000 mL, clean plastic bottles. The bottles were kept air tight and labeled properly for identification. Aeration during sampling was avoided by stoppering the bottle quickly. Samples collected from study area were carefully transported to the laboratory and were preserved in a refrigerator for analysis.

3.2 Analytical procedure

Some parameters, such as EC, pH and temperature of the samples were measured on the spot using respectively portable EC-meter, pH-meter and thermometer.The analyses for heavy metals content (Zn, Fe, Cu, Mn, Ni, Co, Pb, Cr, Cd, Mo) in water samples were carried out by microwave plasma atomic emission spectrometry-MP-AES 4100 [18]. They were performed in the laboratory of Agricultural Institute of Kosovo between July and August 2015.

The heavy metals content of water samples were compared with'Recommended maximum concentration' of irrigation water [5]and limit values presented in **75/440/EEC and 2008/105EC Directives**[4, 6].

4. Results and discussion

Results from analyzed samples of water sources (rivers, reservoirs, canals) are shown on table 1 and table 2. On table 1 are displayed the mean values of pH and EC (Electric conductivity) with their limit values according to Guidelines for Interpretation of Water Quality for Irrigation [1]. On table 2 are shown analyses results of water samples by water sources, referring the mean values of heavy metals content and recommended maximum concentration of heavy metals in irrigation waters [4, 5, 6].

pH

The average pH valuesof water samples ranged from 6.83 ne 7.69, showing the alkaline nature of water. There is no significant differences between water sources (rivers, canals and reservoirs) and these values are within permissible limits for irrigation water [1].

Electrical Conductivity (EC)

The average electrical conductivity of irrigation canal water ranged from 0.211 to 0.380 dS/m. The average electrical conductivity of rivers of study area ranged from 0.215 to 0.360dS/m and in reservoirs ranged from 0.236 to 0.280 dS/m. All the water samples were found non-saline and will not contribute any harmful effect to agricultural land and crop [9].

EC values are included in "excellent" category of irrigation water classification, according to Wilcox [20]. Regarding to the 'degree of restriction on use', water has no restriction on use for irrigation, if values of EC < 0.7 dS/m [1, 2]. From this point of view, referring to EC values it

seems that water of the study area is suitable for irrigation, and it can be classified in "no restriction" category.

Trace elements

As it is shown by the results of analysesthere is heavy metals presence in all water samples from water sources which are used for irrigation in Dukagjini Plain.Their values vary by the type of metal and by the water samplesanalyzed. The maximum levels (ML) allowed for these metals in irrigation water are 2.0, 5.0, 0.20,0.20, 0.20, 0.05, 5.0, 0.10, 0.01 and 0.01mg/l for Zn, Fe, Cu, Mn, Ni, Co, Pb, Cr, Cd and Mo respectively [1, 5].

Table 2 shows that there are no significant differences in heavy metalscontentamong irrigation waters coming from rivers, reservoirs or canals. Study findings indicate that heavy metals content in irrigation water samples vary as follow: Mn ~ 0.1 mg/l, Mo 0.02-0.1, Zn 0.07-0.09 mg/l. All other elements are in concentrations lower than 0.02 mg/l (Table 2).

Comparison of results with recommended maximum concentration indicate that copper, manganese, nickel, cobalt, lead and chromium are in normal concentrations; while concentration of zinc (0.07 - 0.09 mg/l) and iron (0.01 - 0.02 mg/l) are considered in insufficient levels. Cadmium contents (< 0.02 mg/l) and molybdenum (< 0.02 – 0.1mg/l) are assessed in therecommended maximal concentrations.

The fact that the levels of some heavy metals in water is much lower than prescribed values does not translate into total safety of the water because the trace amounts detected for some elements is still worthy of consideration and further monitoring to ensure that levels do not exceed what has been detected. Monitoring should be on regular basis and different spatial and temporal settings because they are key factors with which concentrations vary.

Table 1.Average pH and EC of irrigation water in Dukagjin Plain

Water Samples	Location	Source of sample	pH	EC dS/m
1	Xerxe	Canal	7.50	0.242
2	BazeniGradisha	Reservoir	7.56	0.236
3	BazeniRezine	Reservoir	7.60	0.237
4	BabajBoges, lumiErenik	River	7.67	0.305
5	Bazeni No. 10, Bec	Reservoir	7.57	0.280
6	Rahushiq	Canal	7.35	0.258
7	Peje, LumiLumbardh	River	7.46	0.243
8	Loxhe	Canal	7.38	0.286
9	PejeLagjaHysni Rama	Canal	7.30	0.299
10	Peje, Fabrika e Birres	River	7.39	0.360
11	LumiLumbardh, ManastiriiDecanit	River	6.83	0.215
12	Isniq	Canal	6.98	0.265
13	Strellc	Canal	7.19	0.211
14	BurimiDrinitteBardhe	River	7.71	0.252
15	Vitomerice	Canal	7.46	0.241
16	Novoselle	Canal	7.38	0.270
17	Novoselle, LagjaThaci	Canal	7.47	0.277
18	Dubove	Canal	7.50	0.332
19	Gurakoc	Canal	7.41	0.320
20	KanaliGoges 1	Canal	7.69	0.355
21	KanaliGoges 2	Canal	7.67	0.380
22	Tomoc	Canal	7.46	0.319
23	Rudice, Kline	Canal	7.48	0.272
24	BurimiiIstogut	River	7.69	0.360
	Guidelines for Interpretation of Water Quality for Irrigation[1]		**Normal Range 6.5 - 8.5**	**None<0.7 Slight to Moderate 0.7-3 Severe >3**

[1]Adapted from Ayers and Westcott, 1985.

Table 2. Average heavy metals content of irrigation water in Dukagjin Plain

S#	Location	Source of sample	pH	Zn	Fe	Cu	Mn	Ni mg/l	Co	Pb	Cr	Cd	Mo
1	Xerxe	Canal	7.50	0.08	0.02	<0.02	<0.1	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
2	BazeniGradisha	Reservoir	7.56	0.07	0.02	<0.02	<0.1	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
3	BazeniRezine	Reservoir	7.60	0.07	0.02	<0.02	<0.1	<0.02	<0.02	<0.02	<0.02	<0.02	0.1
4	BabajBoges, lumiErenik	River	7.67	0.08	0.02	<0.02	<0.1	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
5	Bazeni No. 10, Bec	Reservoir	7.57	0.08	0.01	<0.02	<0.1	<0.02	<0.02	<0.02	<0.02	<0.02	0.04
6	Rahushiq	Canal	7.35	0.07	0.02	<0.02	<0.1	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
7	Peje, LumiLumbardh	River	7.46	0.08	0.01	<0.02	<0.1	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
8	Loxhe	Canal	7.38	0.08	0.02	<0.02	<0.1	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
9	PejeLagjaHysni Rama	Canal	7.30	0.09	0.01	<0.02	<0.1	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
10	Peje, Fabrika e Birres	River	7.39	0.08	0.02	<0.02	<0.1	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
11	Lumbardh, Man. Decanit	River	6.83	0.08	0.01	<0.02	<0.1	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
12	Isniq	Canal	6.98	0.08	0.02	<0.02	<0.1	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
13	Strellc	Canal	7.19	0.08	0.01	<0.02	<0.1	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
14	BurimiDrinitteBardhe	River	7.71	0.08	0.02	<0.02	<0.1	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
15	Vitomerice	Canal	7.46	0.08	0.01	<0.02	<0.1	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
16	Novoselle	Canal	7.38	0.08	0.02	<0.02	<0.1	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
17	Novoselle, LagjaThaci	Canal	7.47	0.07	0.01	<0.02	<0.1	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
18	Dubove	Canal	7.50	0.08	0.02	<0.02	<0.1	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
19	Gurakoc	Canal	7.41	0.08	0.01	<0.02	<0.1	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
20	Kanali Gog. 1	Canal	7.69	0.08	0.02	<0.02	<0.1	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
21	Kanali Gog. 2	Canal	7.67	0.09	0.02	<0.02	<0.1	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
22	Tomoc	Canal	7.46	0.08	0.01	<0.02	<0.1	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
23	Rudice, Kline	Canal	7.48	0.08	0.02	<0.02	<0.1	<0.02	<0.02	<0.02	0.03	<0.02	<0.02
24	BurimiiIstogut	River	7.69	0.08	0.02	<0.02	<0.1	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
	Recommended Maximum Concentration[1](mg/l)			**2.0**	**5.0**	**0.20**	**0.20**	**0.20**	**0.05**	**5.0**	**0.10**	**0.01**	**0.01**
	75/440/EEC and2008/105/EC* Directives (mg/l)			**3.0**	**0.30**	**0.05**	**0.05**	***0.02**		**0.05**	**0.05**	**0.001**	

[1]Adapted from National Academy of Sciences (1972) and Pratt (1972).

5.Conclusion

Heavy metals are present in all water samples from water sources that are used for irrigation in Dukagjini Plain. Their values vary according to the type of metal and to the analyzed sample.

The contents of heavy metals in surface waters used for irrigation in this region (rivers, reservoirs, channels) were found to be in normal concentrations.

Cadmium and molybdenum contents are on the recommended maximal concentrations.

Cadmium should be kept within recommended levels due to its potential for accumulation in plants and soil in concentrations which can be dangerous for human being.

Molybdenum is not toxic for plants in normal concentrations, but it could be toxic for livestock if forages are grown in lands with high concentration of molybdenum.

By this standard therefore, none of the water sources presents any potential risk hazard in terms of heavy metals content.

These water sources could be used for irrigation purposes without any hazardous effect in soil and plants.

Monitoring should be on regular basis and different spatial and temporal settings because they are key factors with which concentrations vary.

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