Research Article

Journal of Chemistry Letters

journal homepage: www.jchemlett.com

ISSN (online) 2717-1892

Evaluation of physico-chemical quality and metallic contamination level of epikarstic seepage waters in forest zone

Fatima Zahra Benhachem [a,b] *, Djamila Harrache [c]

[a] Department of hydraulic, Institute of sciences and technology, University Center of Maghnia, Algeria

[b] Laboratory for the Application of Organic Electrolytes and Polyelectrolytes (LAEPO), University Abou Beker Belkaid Tlemcen, BP119, 13000 Tlemcen, Algeria

[c] Department of chemistry, Faculty of exact sciences, University Djillali Liabes of Sidi Bel Abbes, Algeria

ARTICLE INFO

Article history:
Received 3 July 2020
Received in revised form 31 August 2020
Accepted 5 September 2020
Available online 5 September 2020

Keywords:
MTE
Rain
Mid-mountain
The infiltration
Road traffic

ABSTRACT

The present study is based on a quantification by Atomic Absorption Spectrometry (AAS), of metallic trace elements (MTE) in karstic water collected in a subhumid cavity following the wet deposition corresponding to the leaching of the atmosphere by rainwater. Our choice focused on a forest site located in mid-mountain, at the level of the forest of Hafir, located 15 Km in the south west of the city of Tlemcen (Algeria) and near a road traffic. In the light of the analytical results obtained, the presence in high concentrations of certain heavy metals such as cadmium Cd and nickel Ni in the rainwater, lead Pb and cadmium Cd in snow is reported in high concentrations. These waters loaded by these MTE, were able to infiltrate in the walls of the cavity and contaminate the water of the karst. All-in the rainwater and snow were collected on the exterior surface of the cavity. However, after rainfall and runoff, the infiltration water loads in Pb (0.15 mg/l), and Ni (0.044 mg/l).

For the other MTE: Mn, Co, Cu, Cd, Cr, Ag and Fe, they were detected in karstic water, but at levels below WHO recommended standards. These contents may reflect the release of these elements from the sediments of the cavity, remitted in suspension during the precipitation occurring in this period.

1.Introduction

During rainfall, rainwater loads in pollutants present in the atmosphere before leaching surfaces by runoff. The proportion of pollution contained in runoff derived from the polluted atmosphere is estimated between 15 and 25% [1]. Many authors Were interested in the quality of the runoff on the road, studies are numerous and diversified. Include among others [2, 3, 4, 5, 6]. Lead in road runoff is usually encountered in particulate form, or fixed to suspended solids, while zinc is predominantly present in dissolved form [7].

With reference to the quality of seepage water, the study carried out by [6] revealed a contamination of these waters by zinc and lead, particularly marked close to the edge of the roadway. According to the study of Legret et al (1994) of the Bègles rainwater infiltration site, has allowed to put in evidence the presence of metallic pollutants in significant quantities in the solids matter entrained by rainwater, in particular lead and zinc [8]. The term "rainwater" includes [9] meteoric waters, runoff of urban surfaces (roofs and roads), water discharged from overflows of sewerage sites and water discharged through the sewerage site. Other authors confirm the importance of runoff pollution on the road [10, 11, 12, 13].

2.Experimantal section

2.1 Presentation of the study area

The forest of Hafir is located in the South West of the city of Tlemcen. It belongs to the constituencies of the forests of Tlemcen, Maghnia and Tlemcen National Park. This forest extends over 1653 Ha owned to the communes of Ain Ghoraba and Sabra (see fig.1).

* Corresponding author. Tel.: +213552595444; e-mail: f.benhachem@yahoo.com

The type of soil encountered in the forest territory is the fersiallitic brown soil originating on limestone bedrock under the influence of an cold climate to less cold dry season climate. It is a heavy soil very poor in water reserves, rich in bases in particular in Ca^{+2}, Mg^{+2} and K^{+}, existing under climatic vegetation (of green oak, Aleppo pine) with a fairly dense undergrowth , moist and porous. It is a representative site of the context of contamination by atmospheric deposition (road traffic, fires). The region belongs to a sub-humid climate characterized by a cool winter and a dry summer: years of heavy rainfall are followed by periods of drought, which gives the region a very irregular water regime. The groundwater in the area is a source of drinking water.

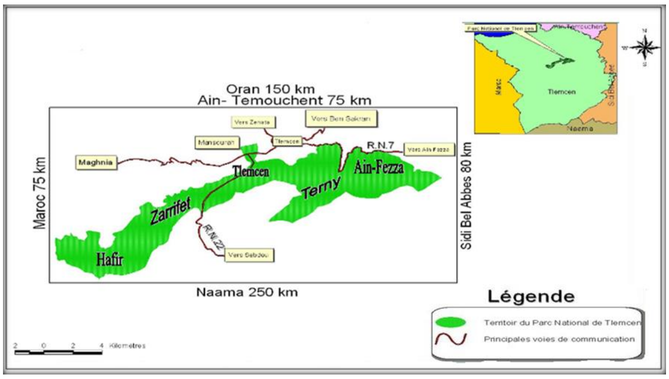

Fig 1. Location Map of the Hafir forest [14].

2.2. Sampling

The seepage karst waters crossing rocks with a thickness of 4 to 5m, were collected in a cavity of sub-surface, place called Ghar H'mam, located under a slope at the top of the oak forest, of an average elevation 1312 m at the following geographical location: Latitude: 34° 47'39.91 N Longitude: 1 ° 26'41.53' 'W. After sampling with a funnel, during 24h, karst waters of a volume of 3 liters were stored in glass bottles with teflon stoppers and then transported in a cooler at 4 ° C and protected from light for physico-chemical analysis, according to standardized protocols [15] and for a determination of heavy metals. Sampling of karstic waters was carried out at the end of the winter season. In fact, precipitation interfere when pollutants are transported to the ground and then to groundwater.

2.3. Physico-chemical characterization of water

The physico-chemical analysis of the seepage water consisted of the following measurements: T, pH (using a pH meter HACH Sens ion 3), conductivity (using a WTW conductivity meter, Multiline P4), salinity, turbidity (using a HACH 2100 N turbidimeter), alkalinity, total acidity, chlorides, total hardness, Bicarbonates, Magnesium, Chlorides, Sulphates, total iron, Manganese , Copper, and Pollution parameters: Ammonium, Nitrites, Phosphorus, the determination of the pollution parameters is carried out using a HACH DR / 2500 spectrophotometer.

2.4. Characterization of metals in water

Metering of metals in our samples was implement using an air / acetylene flame atomic absorption spectrophotometer (AURORA AI 1200).

3.Results section

The physicochemical characteristics of karstic water are summarized in Table 1. Karstic water has mainly a slightly alkaline bicarbonate character (pH = 7.89) within the range required by the WHO standard (6.5 - 8.5) and low turbidity (2.79 NTU). The conductivity value shows an average mineralization000 (under 1000 µS / Cm), rather soft.

It also appears that this water is calcium bicarbonated magnesian and therefore presents a typical profile of karstic waters. The chloride and sulphate contents are very low and well below the WHO standard.

On the other hand, the region undergoes the recurrence of overgrazing. We constated that the entrance of the sub-surface cavity served as a shelter for the shepherds whom, in addition, lit a wood fire to warm themselves during the winter. Under these conditions of intensive grazing, the rainwater which runs down and infiltrates into the walls of the cavity can be loaded with organic matter coming from the excreta and contaminate the seepage water. We debrief the impact of this pasture and the occupation of this part of the forest soil on the bacteriological quality of the water infiltrated in the karst of the cavity.

Sampling was carried out in wet weather respecting the conditions required for bacteriological analysis, namely : samplings sheltered from the wind in glass containers, transport of water samples at 4 ° C (Free from contamination, source of heat and light) and the analysis was carried out as soon as the samples arrived at the laboratory.

Finally, the results of the bacteriological analysis

Table 1. Results of the analysis of some physicochemical parameters of karstic waters

Parameters	**pH (at 14.1 °C)**	**χ (µS/Cm) (at 13.6 °C)**	**Turbidité NTU**	**TAC (mg/l $CaCO_3$)**	**TH mg/l of $CaCO_3$**	**Ca^{2+} mg/l of $CaCO_3$**	**HCO_3^- (mg/l)**	**Mg^{2+} (mg/l)**	**Cl^- (mg/l)**	**SO_4^{2-} (mg/l)**	**NH_4^+ (mg/l)**	**NO_2^- (mg/l)**	**P (mg/l)**
Values	7.89	524	2.79	245	185	160	245	6	42.54	17	0.02	0.013	0.32

Table 2. Results of the analysis of some bacteriological parameters of karstic water

Direct Overview		**Results obtained**		**Interpretation of sample result**
Color	/	Total Coliforms	NPP = 3	good bacteriological quality of water **(NPP < 5)**
Odor	/	E.Coli	Absence	
Other	/	Salmonelles	Absence	
Observations	/	Fecal Streptococci	Absence	

Table 3. Content of metallic elements in the water (infiltration, rain, snow, runoff)

Sample / Metallic element (mg/l)	Seepage water (Karstic)	RAIN	SNOW	Runoff water	WHO Standard (2006)
Co	0.15	0.048	/	0.012	/
Pb	0.15	/	0.32	0.08	0.01
Ni	0.044	0.54	0.003	0.094	0.02
Cu	0.04	/	/	/	2
Mn	0.038	0.035	0.002	0.04	0.4
Zn	/	/	/	2.53	3
Cd	0.001	0.01	0.002	0.003	0.003
Fe	0.01	0.013	/	4.65	0.3
Na	8.02	2.22	0.88	9.44	200
Mg	78.9	0.46	0.19	6.15	/
K	0.32	0.88	0.61	2.47	/
Ca	53	1.31	1.39	50	/
Cr	0.037	0.081	/	0.23	0.05
Ag	0.006	0.027	/	/	/

allowed us to notice that karstic water was free from pathogenic microorganisms (Table 2).

The results of the metering of metals in water (rain, snow and runoff) are reported in Table 3. After rain and runofll, the seepage waters loads with Pb (0.15 mg/l, 10 times the WHO standard) and Ni (0.044 mg/l, 2 times the WHO standard). For the other MTE: Mn, Co, Cu, Cd, Cr, Ag and Fe, they were detected in karstic water only after rainfall and snowmelt, but at levels below the standards recommended by WHO for drinking water quality. These contents may reflect the release of these elements from the sediments of the cavity, resuspended during precipitation occurred this period.

The presence in important concentrations of certain heavy metals, such as cadmium Cd and nickel Ni in rainwater, lead Pb and chrome Cr in snowmelt is reported in the literature [16, 17, 18]. These waters loaded by these MTE, were able to infiltrate into the walls of the cavity and contaminate the water of the karst , where the rain and snow have been collected on the outside surface of the cavity.

Runoff water recovered from the roadway is more loaded than rain and snow. It is characterized by a high content Pb, Ni, Fe, Cr content, well above the standard recommended by WHO (we have considered that runoff water can be drawn to seepage water, and the same standard had to be respected).

This contamination originates from the dry atmospheric deposition linked to road traffic [19, 6] and the wet deposition by leaching of the atmosphere by the rains and of the roadwat. We note that some MTE present in pavement runoff water come from erosion or corrosion by the rain of surfaces. By way of example, the supply of metals from surface wears [20, 21] . As for the contamination of the seepage water, it is incredible that it is made by the bias of runoff in pavement, seen the difference of the slopes and the morphology of the site.

4. Conclusion

The dispersion of MTE is an complex phenomenon where environmental impacts are difficult to identify and require multidisciplinary research approaches. However, forest soils in the karst regions, rich in organic matter, seem to constitute a barrier of protection of water resources. Forest fires, combined with intense anthropogenic activities and climate change, are apt to cause significant damage to the various interfaces of forest ecosystems in mid-mountain areas, particularly karstic waters that are highly vulnerable to pollutant infiltration, the contribution of rainwater and runoff, influence the evolution of the speciation of these pollutants and consequently their mobility and the associated potential risk.

References

[1] Y. Azzou , E. Alfakih , S. Barraud ,F-N. Alternative Techniques in rainwater sanitation . Choice, design, construction and maintenance . Ed. Tec and Doc, Lavoisier. Paris. 371 (1994).

[2] J.D. Baladès, M. Cathelain, P. Marchandise, J. Peybernard , J.C. Pilloy. Chronic pollution of runoff from intercity highways. Liaison Bulletin of the Laboratoires of the Bridges and Pavement, 140 (1985) 93-100.

[3] G. Stotz G. Investigations of the properties of the surface water run-off from highways in the FRG. *The Science of the Total Environment*, 59 (1987) 329-337.

[4] D. Grange , C. Rollin, N. Aires, J.P. Tabuchi. Comparative study of the impact on water quality and hydraulics of runofffrom conventional pavements and drainage asphalt. Proceeding 2nd International Novatech Conference, Lyon, 30 may-1er june, (1995) 369-376.

[5] M.E. Barrett, L.B. Irish , J.F. Malina , R.J. Charbeneau. Characterisation of highway runoff in Austin, Texas area. *Journal of Environmental Engineering*, 124 (1998) 131-137.

[6] C. Pagotto. Study on the emission and transfer in water and soil of metal trace elements and hydrocarbons in road domain. Doctoral thesis, University of Poitiers, 252 (1999).

[7] E.J. Elzinga , J.J.M Van Grinsven, F.A. Swartjes. General purpose Freundlich isotherms for cadmium copper and zinc in soils. *European Journal of Soil Science*, 50 (1999) 139-149.

[8] M. Legret, V. Colandini, D. Demare , J.D. Balades , H. Madiec. Pollution by heavy metals related to the infiltration of urban runoff in a porous pavement with a reservoir structure. *Environmental Technology*, 15 (1994) 1183-1191.

[9] J. Flores-Rodriguez . Toxic metals in urban rainwater: physico-chemical characteristics. Doctoral thesis, University of Paris XII - Val de Marne, 229 (1992).

[10] A. Nowakowska-Blaszczyk , J. Zakrzewski. The sources and phases of increase of pollution in runoff waters in route to receiving waters. Proceeding Seventh international conference on urban storm drainage, Hannover, Germany, I, (1996) 49-53.

[11] P.S. Mikkelsen, M. Häfliger, M. Ochs , P. Jacobsen, J.C. Tjell , M. Boller. Pollution of soil and groundwater from infiltration of highly contaminated stormwater -A case study (1996).

[12] S. Barraud, A. Gautier, A. Bardin, V. Riou. The impact of infiltration on soil and groundwater. A Case Study. Proceeding NOVATECH, Lyon, France, 4-6 Mai, 2 (1998) 449-456.

[13] Y. Mason, A.A. Ammann , A. Ulrich, L. Sigg. Behavior of heavy metals, nutrients, and major components during roof runoff infiltration. *Environmental Science Technology*, 33 (1999) 1588-1597.

[14] MPTNP. Management plan of Tlemcen National Park (2003).

[15] J. Rodier, Dunod, 7th edition, *Paris*. (1984)

[16] L. Lassabatère. Modification of the transfer of three heavy metals (Zn, Pb and Cd) in a soil resulting from a carbonated fluvio-glacial deposit by the introduction of geotextiles. Doctoral thesis. Lyon: INSA de Lyon, 252 (2002).

[17] F. Plassard, T.Winiarski. Petit-Ramel M. Retention and distribution of three heavy metals in a carbonated soil: comparison between batch and unsaturated column studies. *Journal of Contaminant Hydrology*, 42 (2000) 99-111.

[18] F. Valiron , J.P. Tabuchi . Control of urban pollution in rainy weather: State of Art. Paris: Tec & Doc Lavoisier, 564 (1992).

[19] V. Mottier, M. Boller,. Roof runoff - quality and dynamics of the polluting load - Bibliographic search. Report of the EAWAG. Dübendorf, Suisse, 45. Proceeding Seventh international conference on urban storm drainage, Hannover, Germany, 9-13 september, II, (1992) 707-712.

[20] S. Garnaud. Transfer and geochemical evolution of metallic pollution in an urban watershed. Doctoral thesis. Paris: National School of Bridges and Pavements, 396 (1999).

[21] B. Chocat. Recent prospects on urban sanitation and research needs related to sustainable water management in cities - Workshop 4: The city and its environment. In: Water and Territories Colloquium, Lyon, 9 and 10 January, 2 (2006).

How to Cite This Article

Fatima Zahra Benhachem; Djamila Harrache. "Evaluation of physico-chemical quality and metallic contamination level of epikarstic seepage waters in forest zone". Journal of Chemistry Letters, 1, 2, 2020, 59-62. doi: 10.22034/jchemlett.2020.113420