Vanadium and lithium contamination in freshwaters of the Conchos River in Chihuahua, Mexico

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Abstract

The hydraulic Conchos Watershed is essential for the inhabitants of the state of Chihuahua, Mexico. Nevertheless, evidence shows that the water that flows in the Conchos River is contaminated. The objective was to determine if Vanadium (V) and Lithium (Li) were present in the water of the Conchos River. During 2004 and 2005 six points were located in different tributaries for obtaining water samples. The points were Zaragoza (Z), Satevo (S), Florido (F), Parral (P), Chuviscar (CH) and Ojinaga (O). The samples were collected at 2-monthly intervals. Both elements were determined using an Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES). Variation in V pollution was observed between sampling location as well as in sampling dates. In 2004 highest values of V were observed in June (Z had 0.498 mg L⁻¹; S had 0.479 mg L⁻¹; F had 0.449 mg L⁻¹; P had 0.437 mg L⁻¹; CH had 0.412 mg L⁻¹; O had 0.473 mg L⁻¹) and in August samples (Z had 0.542 mg L⁻¹; S had 0.502 mg L⁻¹; F had 0.452 mg L⁻¹; P had 0.451 mg L⁻¹; CH had 0.447 mg L⁻¹; and O had 0.609 mg L⁻¹). In 2005 maximum V-values were noted in February samples reaching 0.545 mg L⁻¹ in Z; 0.502 mg L⁻¹ in S; 0.687 mg L⁻¹ in P; 0.411 mg L⁻¹ in CH; and 0.582 mg L⁻¹ in O. Lithium was detected at all points. The highest values were reported in October 2004 in O (0.707 mg L⁻¹ in October and 0.496 mg L⁻¹ in August) and P with 0.383 mg L⁻¹. In 2005, maximum concentrations of Li were observed in O reaching 0.344 mg L⁻¹ in February, 0.507 mg L⁻¹ in April and 0.396 mg L⁻¹ in June.

Keywords: *vanadium, lithium, Chihuahua, Mexico, metals.*

1 Introduction

The Vanadium (V) and Lithium (Li) are heavy metals that might be present in different concentrations in water of different ecosystems in the earth. The V constitutes about 0.01% of the earth's crust [1] while Li, the lightest metal is present in an average of 65 ppm on earth. In the particular case of V, the human is exposed to low levels of this element in different forms, but in the food a person may intake 10-20 micrograms daily, suggesting to be an essential element. For instance, fish contributed with an 11-34% of daily V ingestion in the inhabitants of the Adriatic coast [2]. In addition, some studies have shown that V is essential for goats and chicks [3]; nevertheless, the essentiality of V is still an open question, when it is showed that is toxic to some animals [4] like rainbow trout [5]. Likewise the V, the Li appears to be an essential trace element for some animals, hypothesizing a fundamental role in human by analogy. An interesting fact is that both elements have been considered for the treatment of human diseases, like diabetes, utilizing vanadium salts [6, 7] and the disease known as bipolar disorder using lithium [8-10]. The V is also believed to control high blood pressure [11].

Most surface waters contain some levels of V as well as Li. Highest concentration of V was reported in surface water of the Mount Fuji in Japan where 14.8 and 16.4 $\mu\text{g L}^{-1}$ were detected in two springs and a range of 17.7 to 48.8 $\mu\text{g L}^{-1}$ was observed in the water of five rivers [12]. Japan has so much volcano activity, so this fact may explain the V presence in the water as reported by Aiuppa *et al.*, [13] that found that much of the V presence might be a natural process, however, in other areas, anthropogenic activity must be responsible for V presence in the environment [14]. With respect to Li, generally this element is found in low concentrations in surface waters. In rivers of the United States of America was reported in concentrations of about 0.002 mg L^{-1} [15] while in study evaluating four segments of the Conchos River in Chihuahua, Mexico was found a range concentration of 14.3-119.9 $\mu\text{g L}^{-1}$ [16].

This paper gives an overview of the vanadium and lithium levels in waters flowing in six tributaries of the Rio Conchos of the State of Chihuahua, Mexico over a two years period. To our knowledge, this is the first time that these two elements are determined in the whole watershed. These results will help to different authorities, as well as the decision makers of different levels to analyze potential harmful effects of vanadium and lithium on human health, wildlife, environment or, in general, the suitability of the Conchos water for beneficial utilization.

2 Materials and methods

Water flow of the Rio Conchos originates in the mountain zone of the state of Chihuahua, Mexico, identified as the Sierra Tarahumara. The Conchos' stream flow descends from the 2,700 meters above sea level (masl) through the great plains with 1,000-1,500 masl, and finally, the flow joins the Rio Bravo/Rio Grande water in the city of Ojinaga at 720 masl. The Rio Bravo/Rio Grande

serves as the natural boundary between Mexico and the United States of America. The most important tributaries of the Rio Conchos are; the Rio Florido and the Rio Parral in the south of the state, the San Pedro and the Conchos in the central part, and the Río Chuviscar that flows in the middle of the city of Chihuahua. The flow of the tributaries located in the south is stored in the Boquilla Dam with a capacity of 2,903 million m³, the flow of the tributaries in the central part is stored in Las Virgenes Dam with a capacity of 348 millions of m³, and the El Granero Dam with a capacity of 356 millions of m³ stored the flows before joining the Rio Bravo/Rio Grande.

Six points along the Rio Conchos watershed were selected to obtain water samples during the years of 2004 and 2005. The water samples were obtained in a 2-month interval in each point; therefore, water samples were obtained in February, April, June, August, October and December every year. Point 1 was located in the Río Chuviscar (latitude 28° 49' 23.7"; longitude 105° 54' 57.0"; 1,279 masl) about 15 km east of the city of Chihuahua. Point 2 was located in the Rio San Pedro (latitude 27° 57' 13.2"; longitude 106° 06' 35.9"; 1,375 masl), approximately 5 km of the Satevo Town and before the water is capted in the Virgenes Dam. Point 3 was located about 2.5 km of Valle de Zaragoza town (latitude 27° 28' 15.5"; longitude 105° 42' 25.4"; 1,329 masl). The sampling point 4 was identified in the Rio Parral (latitude 27° 40' 03.4"; longitude 105° 12' 33.8"; 1,228 masl) about 30 km of the city of Parral. Point 5 was located in the Rio Florido (latitude 27° 40' 36.6"; longitude 105° 08' 37.4"; 1,225 masl) about 10 km south of the city named Camargo. Sampling point 6 was established near the city of Ojinaga (latitude 29° 34' 02.1"; longitude 104° 26' 46.1"; 786 masl) about 3 km above the junction with the flow of Rio Bravo/Rio Grande.

Water samples were collected in sterilized containers, preserved in a cool place and immediately transported to the laboratory of the Faculty of Zootechnic of the Autonomous University of Chihuahua where they were placed at about 4°C. The vanadium and lithium extraction of the water samples was done according to the Mexican Norm [17]. The concentration of both metals was using ICP optical emission spectrometry (Perkin Elmer 2100) in the laboratory of the National Institute for Research in Forestry, Agriculture and Livestock (INIFAP-Mexico).

An Analysis of Variance (ANOVA) was performed on values for both elements to determine year effect, bi-month effect, and location effect as well as the following interactions; bi-month*year, year*location and location*bi-month. In addition, descriptive statistics was used to visualize differences in concentration considering sampling points as well as bimonthly samples.

3 Results and discussion

In Figure 1 are showed the levels of V detected during the 2004 sampling. Its can be noted that the maximum level of V was observed in Ojinaga while minimum levels were noted in Parral and Florido rivers. In the particular case of Ojinaga, the highest level of V was observed in August (0.609 mg L⁻¹) and June (0.473 mg L⁻¹). The trend showed in 2004 is consistent in all sampling location

and all sampling dates, meaning that most of V presence in the water of the Conchos River is noted in summer time during the rainy season. In the six location points, the maximum level of V was detected in August; thus in Zaragoza the concentration was 0.542 mg L^{-1} ; in Satevo, 0.502 mg L^{-1} ; in Florido, 0.452 mg L^{-1} ; in Parral, 0.451 mg L^{-1} ; and in Chuviscar, 0.447 .

Figure 1: Levels of vanadium detected in six locations of the Rio Conchos in Chihuahua, Mexico during six months of the year 2004.

The water samples collected in 2005 resulted in different findings. In Figure 2, it is pointed out the levels of V during the 2005 sampling. It is obvious that maximum concentration of this element was observed in Parral during the sample of February with a concentration of 0.687 mg L^{-1} followed by the amount noted in Ojinaga where it was detected about 0.582 mg L^{-1} . During this year, the maximum V concentration was detected in the February samples; hence, in Zaragoza it reached 0.545 mg L^{-1} ; in Satevo, 0.502 mg L^{-1} ; and in Chuviscar 0.411 mg L^{-1} . Moreover, it can be observed that V was not detected in Florido samples and that the minimum amount of this element was detected in the locations Satevo. With respect to this element, statistical differences were found by year, bi-month, and the interaction of year*bi-month samples (Table 1). These principal effects are noted in Figure 1 and Figure 2.

There is a lack of historical information concerning the V levels in the Conchos River. The existence of this sort of data would help to analyze weather

the V amounts in the water have been constant or have increased in a certain period of time. If we assume no anthropogenic pollution in the whole watershed; then, the levels of V should be similar. Therefore, it could be said that we do not have information to said that there have been an anthropogenic effect in the Conchos River with respect to V levels. In general, the results presented here are higher than the findings of other environments. For instance, in the Tercero River in Argentina it was noted a level of V up to 0.109 mg L^{-1} [18]. In the Colorado River in the USA it was noted a V range of $0.2\text{--}49.2 \text{ } \mu\text{g L}^{-1}$ [19] while in Yangtze River in China it was detected 0.24 to $64.5 \text{ } \mu\text{g L}^{-1}$ [20].

Figure 2: Levels of vanadium detected in six locations of the Río Conchos in Chihuahua, Mexico during six months of the year 2005.

In Figure 3 it is presented the levels of Li detected in six locations of the Río Conchos during six monthly samples of 2004. The maximum levels were observed in Ojinaga with an amount of 0.707 mg L^{-1} during the October samples and in Zaragoza with 0.680 mg L^{-1} in the August sample. In general, the Ojinaga point reached the major levels of Li when it was observed values of 0.496 mg L^{-1} in August samples and of 0.437 mg L^{-1} in December samples. In Figure 4 it is presented the levels of Li detected in six locations of the Río Conchos during six monthly samples of 2005. It is obvious that maximum levels were observed in the sampling locations of Ojinaga and Chuviscar. These two sampling locations are closed to the cities of Ojinaga and Chihuahua. In the particular case of Ojinaga, it is a border city between the United States of America and Mexico where most drainage and runoff flows to the Conchos River. With respect to Chihuahua city, it has about a million inhabitants and some drainage flows in the Chuviscar tributary. According to the findings of this study it can be

Figure 3: Levels of lithium detected in six locations of the Rio Conchos in Chihuahua, Mexico during six months of the year 2004.

Figure 4: Levels of lithium detected in six locations of the Rio Conchos in Chihuahua, Mexico during six months of the year 2005.

Table 1: Analysis of Variance for vanadium and lithium concentration in water of San Pedro River of Chihuahua, México.

Vanadium					
Source	DF	Adj SS	Adj MS	F	P
Year	1	0.211250	0.211250	27.01	0.000
Location	5	0.065353	0.013071	1.67	0.178
Bi-month	5	0.663218	0.132644	16.96	0.000
Year*Bi-M	5	1.732206	0.346441	44.29	0.000
Year*location	5	0.020908	0.004182	0.53	0.748
Location*bi-M	25	0.134716	0.005389	0.69	0.821
Error	25	0.195554	0.007822		
Total	71	3.023204			
Lithium					
Source	DF	Adj SS	Adj MS	F	P
Year	1	0.08954	0.08954	3.88	0.060
Location	5	0.50326	0.10065	4.36	0.005
Bi-month	5	0.03046	0.00609	0.26	0.929
Year*Bi-m	5	0.17617	0.03523	1.53	0.217
Year*location	5	0.04409	0.00882	0.38	0.856
Location*bi-m	25	0.25435	0.01017	0.44	0.977
Error	25	0.57706	0.57706		
Total	71	1.67492			

hypothesized that Li amount is due to anthropogenic effects. With respect to Lithium concentration statistical differences were found only for location (Table 1) and none of the interactions tested were significant.

The results of the present study with respect to the level of Li are higher than previous studies reported by Bradford [21] who found Li levels of about 0.05 mg L⁻¹ in water of California, USA and for Feder [22] who reported Li levels of less than 10 µ L⁻¹ in Missouri, USA. Nevertheless, the most important aspect of these findings is the potential toxic effect in some organisms that live in water of the Conchos River when it is analyzed that Emery et al., (1981) supported a toxic effect of some insect larvae with levels of 0.4 mg L⁻¹. In addition, these researchers (Emery et al. [23]) hypothesized a toxic effect in rainbow trout with levels of Li of 0.6 mg L⁻¹.

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