EEET ECOLOGICAL ENGINEERING & ENVIRONMENTAL TECHNOLOGY

Ecological Engineering & Environmental Technology 2023, 24(9), 249–258
https://doi.org/10.12912/27197050/174036
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Received: 2023.09.13
Accepted: 2023.10.11
Published: 2023.11.15

Evaluation of the Concentration and Health Risks of Phosphates and Nitrates of a High Andean River

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ABSTRACT

In developing countries, river monitoring is very limited. Despite environmental and health problems, there is a paucity of information regarding the contaminants phosphates and nitrates. Thus, concentration and health risks, of phosphates and nitrates of the Ichu river waters, in Huancavelica, Peru, were evaluated. Sampling was carried out at six different points. Important water quality parameters were analyzed, such as pH, temperature, dissolved oxygen (DO) and electric conductivity (EC). The results revealed that the phosphate and nitrate varied between 0.475 to 0.575 mg/L and 11.10 to 14.00 mg/L, respectively. The concentration of phosphates and nitrates was 0.520±0.02 mg/L and 13.10±0.48, respectively. The Ichu River water had the quality that corresponded to its category, when compared to the permitted limits of the Environmental Quality Standards (EQS) for water. It did not present contamination according to the nutrient contamination index and the health risk was from chronic low intake. Besides, it presented a moderate relationship between nitrate and phosphate, due to the low concentration of phosphates during the dry season. What is new about this research is the approach to potential health risks of exposure to nitrates and phosphates, in a high Andean river in Huancavelica, Peru.

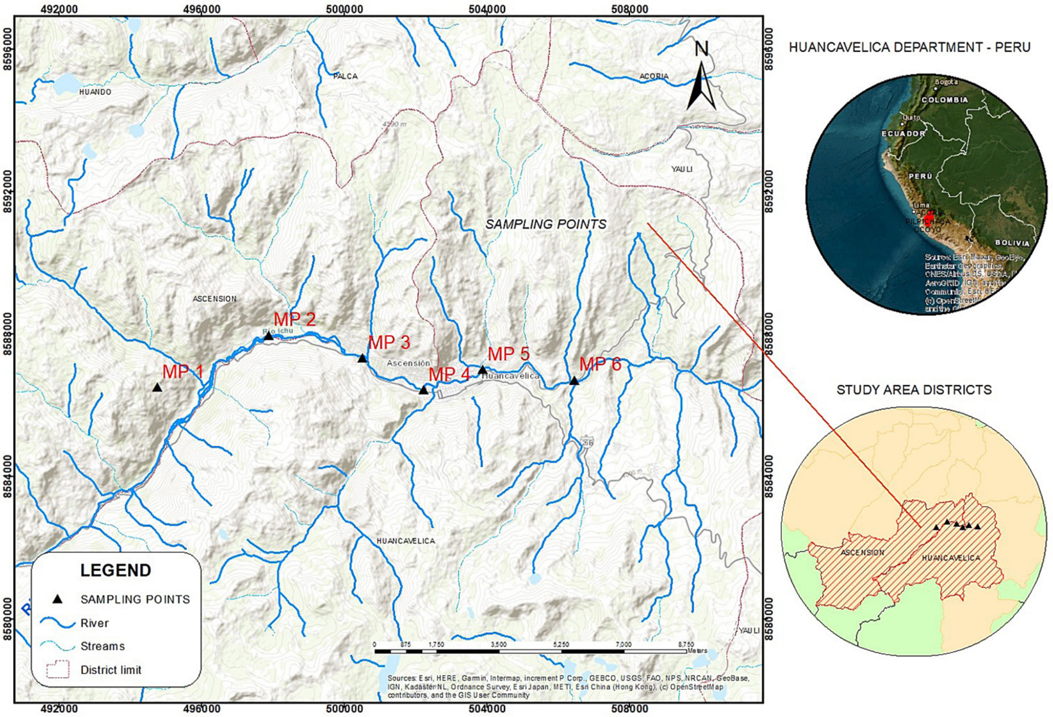
Keywords: Environmental Quality Standards, nutrient contamination, health risks, nitrate, phosphates, low water, river.

INTRODUCTION

Surface water is considered a fundamental natural resource for both human survival and development-related activities [Salem, 2021]. Rivers are the source of fresh water for any urban community, provide water, food resources and sustain human beings. Therefore, river water quality is a major environmental concern that must be preserved and monitored; the latter is a mandatory, but challenging task [Chakravarty & Gupta, 2021; Gupta et al., 2017; Parween et al., 2022]. Water quality is decisive for human well-being and health of ecosystems. The increasing deterioration of its quality is one of the most widespread and worrying environmental problems [Custodio et al., 2021]. In the last decades, a continuous deterioration in the quality of surface water has been noted, since it is more susceptible to contaminants from both natural and anthropogenic sources, such as the discharge of municipal and industrial wastewater, household waste disposed and irrigation drainage water, leading to clogging of urban rivers [Asha et al., 2020; Sekharan et al., 2022]. The transformation of the natural cycle of nitrogen and phosphorus, caused by anthropogenic activities, is one of the most fundamental environmental problems [Isiuku & Enyoh, 2020]. Some of the main pollutants of water bodies include nitrates and phosphates emanating from fertilizers, organic fertilizers and animal and human waste [De Girolamo et al., 2019]. When the concentrations of nitrate and phosphate ions in shallow water bodies are in excess, they lead to excessive algae growth, causing a high consumption of dissolved oxygen in the water. This leads to suffocation and death of aquatic plants as well as animals that decompose and deteriorate water quality. This process is called eutrophication [Leaf, 2018; Moshoeshoe & Obuseng, 2018; Vrzel et al., 2016]. Most rivers in developing countries face water pollution problems. Therefore, it has been difficult to achieve safe water quality by meeting standard allowable limits for industry, drinking water and agriculture [Kareem et al., 2021].

Water quality of a river can be assessed by monitoring various chemical, physical and microbiological variables [Tian et al., 2019]. Monitoring water quality involves frequent water sampling at various sites and determination of a large number of physicochemical parameters, which results in a large data matrix, which is often difficult to interpret [Kumar et al., 2020]. Many studies were carried out to evaluate water quality, including parameters such as pH, dissolved oxygen, turbidity, total dissolved solids, phosphates, nitrates and metals, grouped in indices [Othman et al., 2018]. Worldwide, water quality studies have increased; for example, in Turkey it has become a major problem in recent years [Sener et al., 2017]. In Peru, the National Water Authority is the entity in charge of monitoring water quality of rivers [ANA, 2017]. However, monitoring of water quality in different periods of time at the national level is still very limited, with a lack of information regarding the concentration of phosphates and nitrates.

The Ichu river is located in the region of Huancavelica, Peru. It is one of the important water resources for the city of Huancavelica, for drinking water supply, irrigation, fishing and fish farming. It crosses the central part of the city of Huancavelica; it is exposed to various sources of pollution, such as domestic and industrial effluent discharges, mining and agricultural operations that pollute water. As a result, different species, such as the trout, catfish, and frogs that used to live in the waters of Ichu River have now disappeared. In that sense, it is important to carry out constant monitoring of water quality at different times of the year, with greater emphasis on the dry season due to the low flow that it presents and being susceptible to contamination by eutrophication.



Sources: Esri, HERE, Garmin, Intermap, increment P Corp., GEBCO, USGS, FAO, NPS, NRCAN, GeoBase, IGN, Kadaster NL, Ordnance Survey, Esri Japan, METI, Esri China (Hong Kong), (c) OpenStreetMap contributors, and the GIS User Community

Figure 1. Geographical location of the sampling points in Ichu River, Huancavelica

However, there is a lack of studies focused on the evaluation of the concentration of phosphates and nitrates in surface waters of the Ichu River in Huancavelica. In addition, there is little monitoring of water quality in the urban environment of the city. In general, the studies focusing on potential health risks from nitrates and phosphates in high Andean rivers of Peru are lacking.

The objective of this investigation was to evaluate the concentration and health risks of phosphates and nitrates of surface waters of the Ichu River in dry season in the urban environment of the city of Huancavelica. Some physicochemical parameters were determined on site (Dissolved oxygen, Electric conductivity, Temperature and pH) and others ex situ (phosphates and nitrates) to compare them with the Environmental Quality Standards (EQS) for water, Category 3, vegetable watering and animal drinking [MINAM, 2017]. The results obtained contributed to assess the load of contamination by phosphates and nitrates as well as the risks to health. This study is the first research to address the potential health risks of exposure to phosphates and nitrates in Ichu River, in Huancavelica, Peru.

MATERIALS AND METHODS

Study area

The Ichu River is one of the main affluents of the Mantaro river; it is located in the central part of Peru; Huancavelica region, between the provinces of Huancavelica and Castrovirreyna. It is framed in the hydrographic field of the slope of the Atlantic Ocean, represented by the Mantaro river watershed. It lies between the coordinates UTM, System WGS84, Zone 18 to 12° 31′ 53″ south latitude and 74° 55′ 41″ west longitude (Figure 1). Its beginning is formed by the Astobamba and Cachimayo rivers between 2 850 to 4 955 m above sea level. On its way, it passes through the districts of Cercado of Huancavelica, Ascension, Yauli, Acoria, and the district of Mariscal Caceres, where it articulates with the Mantaro river.

Water sampling and analytical determination

The selected sampling points were located in the nascent, middle course and mouth of the micro watershed of the Ichu river, as well as before and after of the effluents. Six georeferenced monitoring points (MP) were established with the use of the Global Positioning System (GPS) (Table 1). In the urban environment, the sampling points PM-2, PM-3, PM-4 and PM-5, present the highest urban concentration along the Ichu River. For sampling, biosecurity measures were maintained, according to the water quality monitoring protocol (NWA, 2016). Six water samples were collected in total, during dry season in the year 2017. The physicochemical parameters determined on site were: dissolved oxygen (DO) (mg/ L), electric conductivity (EC) (µS/cm), temperature (°C) and pH, and were evaluated using portable equipment from Hanna Instruments (HI 991.301 pH/temperature Microprocessor, conductivity/ TDS HI 9835 Microprocessor and dissolved oxygen HI 9146 Microprocessor. The water samples for the analysis of phosphates and nitrates were collected in the bottles previously sterilized in an autoclave, at 110 atmospheres per 15 min (wet method). Each container was labeled with the information that ensured the identification of the samples, such as sampling point, date and time of sampling to then be placed in a cooler box with an ice pack at a temperature of 4°C for preservation during transport. Besides, preservation of each sample was achieved by adding 1.5 mL of concentrated nitric acid per liter of water (APHA, 2012). The samples under refrigerated conditions (4°C) were sent to the laboratory for analysis, accompanied by their chain of custody. The determination of phosphates and nitrates was performed by standard instrumentation methods of international analytical standards, ME-Stannous chloride test method for phosphates and ME-ion selective for nitrates (APHA, 2012).

Analysis of data

Data analyses were performed using Microsoft Office Excel and the SPSS Statistics v 20 software, using descriptive and inferential statistics. The mean and standard deviation were calculated for the different physicochemical parameters evaluated and presented in a table. The Shapiro-Wilk test was used to test the normal distribution at the 5% significance level using the SPSS Statistics v 20 software. In addition, to determine the water quality of the Ichu river, emphasis was placed on the parameters of phosphates and nitrates where their average values obtained for each sampling point were compared with the Environmental Quality Standards (EQS)

Table 1. Sampling points

Monitoring points	Coordinates UTM - ZONE 18S		Geographic reference
	EAST	NORTH	
MP-1	494 743.7	8 586 513.4	Reference point, drinking wáter collection EMAPA-HVCA
MP-2	497 880.2	8 587 972.0	Downstream (200 meters) of the municipal slaughterhouse (Chuñuranra)
MP-3	500 511.1	8 587 334.7	Height of the Pucarumi Sports Complex (Pucarumi - Ascensión)
MP-4	502 221.1	8 586 434.2	Before the bridge of the National School La Victoria of Ayacucho (Ascension)
MP-5	503 872.4	8 587 003.0	Under the Huancavelica army bridge (San Cristóbal)
MP-6	506 447.8	8 586 713.5	Ex - Santa Rosa bridge.

for water, Category 3, vegetable watering and animal drinking. Likewise, the health risks due to ingestion and dermal exposure of phosphates and nitrates. To test for significant differences between water bodies and season, a one-way analysis of variance was performed (ANOVA) with $p < 0.05$. The coefficient of variation (*CV*%) was calculated using the equation (1), as the ratio of the standard deviation (SDV) and the mean. The *CV* reports how the concentrations of nitrates and phosphates vary.

$$CV = \left(\frac{SDV}{Mean}\right) * 100 \tag{1}$$

Regarding the variation, it was classified as little variation (*CV*% < 20), moderate variation (*CV*% = 20-50) and high variation (*CV*% >50) [Verla et al., 2020]. Regarding the ratio of nitrate to phosphate (N:P) it was calculated to inform about the proliferation of algae and phytoplankton in water bodies. The nutrient pollution index (NPI), the risks to human health related to contamination and the risks to human health derived from the use of water for domestic activities were calculated. For the calculation of the NPI, Equation 2 was used.

$$NPI = \frac{Cp}{MACp} + \frac{Cn}{MACn} \tag{2}$$

where: $C_{n/p}$ – the average concentration of nitrate and phosphate at the sampling points, $MAC_{n/p}$ is the maximum allowable concentration taken from the WHO of 50 mg/L and 5 mg/L for nitrate and phosphate in surface waters, respectively. The NPI classification is categorized as NPI of <1 (without pollution), NPI of $1 \leq 3$ (moderate pollution), NPI of $> 3 \leq 6$ (considerable pollution) and NPI of > 6 (very high pollution) [Isiuku & Enyoh, 2020].

Humans can be exposed to nitrates and phosphates in surface waters by two means: by oral or ingestion and dermal route when they come into contact with water. Consequently, health risks were calculated from these two pathways. The risks by oral and dermal route are estimated from the chronic daily intake (CDI) per unit of weight expressed in Equations 3 and 4.

$$CDI_{oral} = \frac{C\frac{n}{p} * IR}{Bw_{A/N}} \tag{3}$$

$$CDI_{Dermal} = \frac{C\frac{n}{p} * SA * EV * CF}{Bw_{A/N}} \tag{4}$$

where: $C_{n/p}$ – the average concentration of nitrate and phosphate, *IR* – the rate of water intake that is 2 L/d for adults (*A*) and 0.67 L/d for children (*N*), Bw – the body weight for adults (Bw_A) and children (Bw_N), that is to say, 67.8 kg and 22.56 kg, respectively [ENAHO, 2022], K_i – the coefficient of dermal permeability in water (0.001 cm/h for adults and children), *SA* – the contactable skin Surface area (1 700 and 3 416 cm^2 for adults and children respectively), *EV* – Frequency of bathing (1 times/d), *CF* – the conversion factor (0.002 L/cm^3) [Yu et al., 2020].

RESULTS AND DISCUSSION

Determination of contaminants

In Table 2, the results of the physicochemical parameters of the river water in the dry season are shown. The reported results correspond to the mean and the standard deviation of three repetitions. The values are compared with the allowed limits of the water EQS, Category 3, vegetable watering and animal drinking. The pH is one of the important parameters, because it can affect the toxicity of some compounds in the

Table 2. Physicochemical parameters of the Ichu river water in the dry season

Monitoring Points	Physicochemical parameters (dry season)			
	pH	Temperature	DO	EC
	Units	°C	mg/L	μS/cm
MP - 1	7.5 ± 0.529^{a}	8.5 ± 0.265^{d}	7.21 ± 0.060^{b}	336 ± 7.00^{e}
MP - 2	6.1 ± 0.100^{ab}	12.1 ± 0.721^{c}	7.31 ± 0.044^{b}	624 ± 10.58^{c}
MP - 3	6.5 ± 0.200^{bc}	12.3 ± 0.500^{c}	9.76 ± 0.887^{a}	538 ± 22.61^{d}
MP - 4	7.1 ± 0.265^{ab}	14.6 ± 0.624^{ab}	9.60 ± 0.670^{a}	630 ± 20.52^{c}
MP - 5	6.5 ± 0.400^{bc}	12.8 ± 1.000^{bc}	10.95 ± 0.496^{a}	867 ± 9.640^{b}
MP - 6	6.8 ± 0.300^{abc}	14.7 ± 0.600^{a}	6.03 ± 0.295^{b}	1035 ± 22.61^{a}
Average	6.75	12.50	8.48	671.67
SDV	0.299	0.618	0.408	15.49
CV (%)	4.43	4.95	4.82	2.31
EQS	6.5–8.4	7.5–15	≥ 4	2500

Note: means with the same letters do not differ statistically for $p < 0.05$.

aquatic environment [Wu et al., 2018]. The average value per sampling point fluctuated from 6.1 to 7.5 units, with a mean and standard deviation of 6.75 ± 0.299 units, respectively. The pH values registered at the different monitoring points were significantly different ($p < 0.05$). With little variation according to the coefficient of variation (CV% =4.43). The pH values of the different sampling points were within the allowed limit of 6.5–8.4 unit [MINAM, 2017]. However, in MP-2 they were slightly below the water environmental quality standards range. The tendency to acidity shown in the lower part of the river could be the result of leachate and decomposition of plant remains, as well as soil biological activity. Therefore, pH variation in the present study could be due to leaching processes, soil conditions and natural water processes.

The temperature showed values between 8.5 to 14.7°C, with a mean and standard deviation of 12.50 and 0.62°C, respectively. It was found within the allowable limit of 7.5–15°C [MINAM, 2017]. The temperature registered at the different monitoring points was significantly different ($p < 0.05$). However, when evaluating the coefficient of variation, it was classified as little variation (CV% =4.95). Although water temperature is highly variable, it is an important parameter in water quality studies, since it affects the solubility of oxygen, as well as the rate of metabolic activities in organisms [Abd Ellah, 2020]. However, it is important to know the seasonal temperature changes which will allow determining the variability of the temperature both in dry and wet season. The values of dissolved oxygen (DO) ranged from 6.03 to 10.95 mg/L, with a mean and standard deviation of 8.48 and 0.408 mg/L, respectively. The DO values in the different monitoring points, were significantly different ($p < 0.05$). With little variation when evaluating the coefficient of variation (CV% =4.82). This parameter was found within the allowable limit of ≥ 4 mg/L [MINAM, 2017]. The DO is essential in water quality and the ecological health of aquatic ecosystems. Besides, during photosynthesis the oxygen produced in aquatic environments facilitates oxygen saturation [Ding et al., 2017]. However, a low value was found in MP-6 mainly, this refers to the anthropic activity that supports the river in its downstream course, accompanied by discharges of wastewater from various sources that increase microbial activity and accelerate organic matter degradation resulting in oxygen reduction in the river water. The values registered of electrical conductivity fluctuated between 336 to 1035 μS/cm, reaching an average and standard deviation of 671.67 and 15.49 μS/cm, respectively. The results reveal that the Ichu river waters did not exceed the allowable limit of 2500 μS/cm [MINAM, 2017]. These results are consistent with the work of Kükrer & Mutlu. [2019], who showed that EC >300 μS/cm values suggested high salinity with respect to surface water. Therefore, the variability of electrical conductivity values in river waters may be subject to the geological structure and precipitation in the watershed.

Figure 2, shows the phosphate content among the water samples from Ichu river. Phosphate concentration results did not meet the statistical assumptions of ANOVA (the normality and

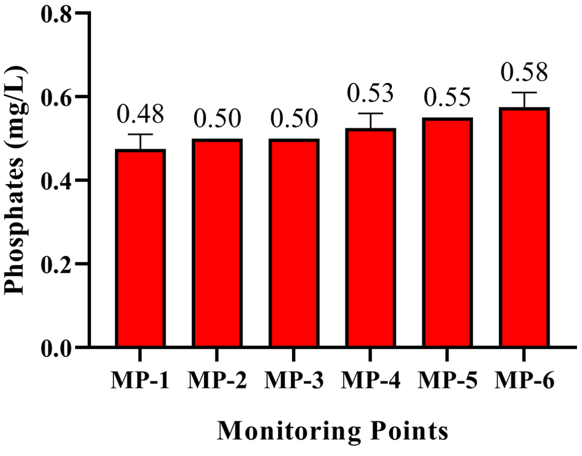


Figure 2. Results of the concentration of phosphates

homogeneity of variance), for this reason, the Kruskal-Wallis test was used to verify the hypothesis that the water samples collected in different places come from the same population. There was no significant difference ($p \geq 0.05$) between the samples at the six monitoring points studied.

The phosphate concentration ranged from 0.475 to 0.575 mg/L, reaching the average value and standard deviation of 0.52 and 0.02 mg/L, respectively. The results revealed that the water samples from the Ichu River did not exceed the permitted limits of 1 mg/L according to Peruvian regulations [MINAM, 2017]. Gupta et al. [2017], evaluated the waters of the river Narmda, Madhya Pradesh, India, and reported that the concentration of phosphates ranged between 0.01 to 0.52 mg/L, which was within the prescribed limit. When comparing these data, it can be seen that the maximum value of said study is consistent with the value of the mean phosphates found in the water samples from the Ichu river of the present study (0.52 mg/L). The natural presence of phosphates in water bodies is related to the decomposition of organic matter [D. Kumar et al., 2018]. However, higher concentration of phosphates could be attributed to the intense contribution of fertilizers and pesticides from agricultural lands, detergents found in waste and sewage effluents [Agbazue et al., 2015]. The critical concentrations for incipient eutrophication are between 0.306–0.612 mg/L PO_4^{3-} in Surface waters [Vásquez et al., 2016]. Besides, when the phosphate concentration exceeds 0.02 mg/L in lakes, the beginning of eutrophication and problems such as oxygen depletion, reduction of biodiversity, lower transmission of light and generation of algae blooms occur [Khalil et al., 2017]. The results of this study showed that phosphate concentrations could favor the increase of aquatic plants and algae, generating the eutrophication of water bodies [Alfonso et al., 2018]. Similarly, Pamei et al. [2022] mentioned that higher levels of phosphates generally contribute significantly to the eutrophication process in standing water, resulting in the loss of dissolved oxygen. Consequently, the water samples from Ichu river in dry season shown phosphate concentrations above the critical concentration for eutrophication according to reports in the scientific literature; however, they had the quality allowed in their category, according to Peruvian regulations.

In addition, Figure 3, shows the results of nitrate concentration in the water samples of the Ichu river. by not satisfying the statistical assumptions of the ANOVA (normality and homogeneity of variance), the Kruskal-Wallis test was used to verify the hypothesis that the water samples collected in different places come from the same population. There was no significant difference ($p \geq 0.5$) between the samples at the six monitoring points studied.

Nitrate concentrations fluctuated between 11.10 to 14.00 mg/L, with a mean and standard deviation of 13.10 and 0.48 mg/L respectively. The results were within the allowable limit for nitrates of 100 mg/L [MINAM, 2017]. Aganigbo et al. [2016] evaluated the surface waters in the area of Mbanabor, Anambra's watershed, southeast nigeria and reported a nitrate concentration ranging between 1.0 and 13.1 mg/L. When comparing the maximum value of the said study with the average value of the nitrate concentration, it agrees with the result found in the present research work, which was 13.10 mg/L. Nitrogen and its different forms in water are often used as important indicators to assess eutrophication pollution in ecosystems

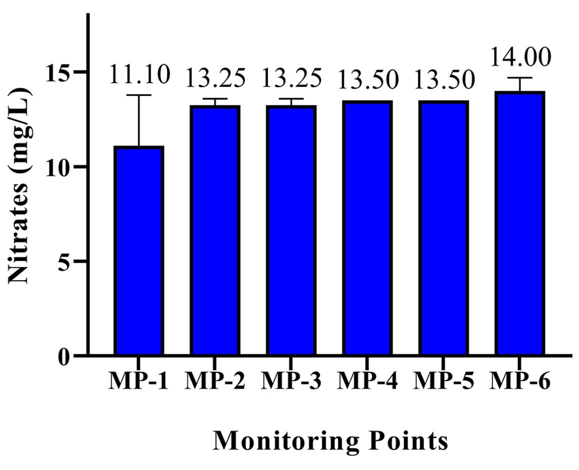


Figure 3. Nitrate concentration results

[Zhang et al., 2017]. The results support the different studies carried out in surface water bodies. Isiuku & Enyoh. [2020] registered nitrate levels ranging from 4.2 to 72.6 mg/L in dry season while in rainy season were between 3.2 and 55.6 mg/L, these data – when compared with the results obtained in the present study where the concentration of nitrates ranged between 11.10 and 14.00 mg/L – show a slight relationship. This may be due to the field of study and anthropogenic activities. In this sense, nitrate is the essential parameter for river water to show the state of contamination and human intervention [Singh et al., 2020].

Nutrient pollution index

The overall nutrient pollution index (NPI) for river water takes into account the possible effect of the addition of phosphate and nitrate in the environmental health. This helps to quickly estimate the overall quality of surface waters. The calculated NPI is displayed in Table 3. In dry season, at the sampling points studied in this research, according to the determined values of NPI, it is suggested that the Ichu river waters were found uncontaminated. Figure 4 shows the relationship between nitrate consumption and phosphate consumption (reduction ratio) during phytoplankton growth, explained from the Redfield relation that proposes fixed elements (N:P=16:1) for the sustained growth of aquatic organisms [Isiuku & Enyoh, 2020]. Therefore, phosphate was relatively insufficient and nitrate relatively excessive in the Ichu, Huancavelica river waters. The water was characterized by phosphate limitation.

Health risk assessment

Humans can be exposed to nitrates and phosphates in surface waters by two means: by oral ingestion or dermal route when they come into contact with water Therefore, health risks were calculated from these two pathways. Chronic daily intake (CDI) of nitrate and phosphate for adults and children in the water body via the oral ingestion and dermal routes of is presented in Table 4. CDI values greater than one always indicate chronic intake and therefore there are risks [Isiuku & Enyoh, 2020]. As a result, the CDI through oral ingestion showed low concentrations of phosphates and nitrates in dry season for both adults and children. Regarding the dermal route, a low chronic intake was shown.

Despite several contributions of information and analysis of contaminants, this study has some limitations. The parameters evaluated on site, as well as the phosphate and nitrate concentrations were determined in the dry season, not having information on these parameters in the wet season is a limitation for evalution ofthe temporary behavior. Therefore, future research should be carried out in times of drought (dry season) and flood (wet season). However, The novelty of the study is that it is the first investigation that addresses the potential health risks of exposure to nitrates and phosphates, for both adults and children, in Ichu river, in Huancavelica. This study lays the foundation for future research on the evaluation of contaminants such as phosphate and nitrates and the evaluation of risks to human health, in the Ichu river, from the Huancavelica region, Peru.

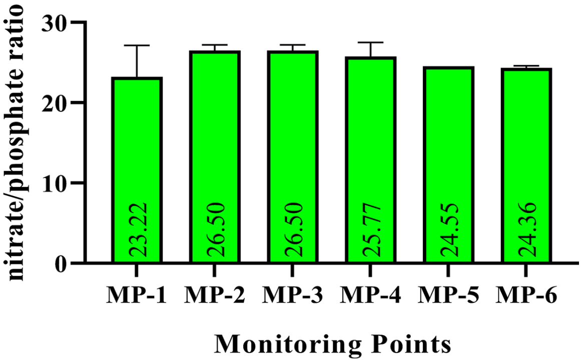


Figure 4. Nitrate to phosphate ratio of the Ichu river

Table 3. Contamination by nutrients index of the waters of the Ichu river in dry season

Monitoring points	Dry season	Observation
MP - 1	0.32	Without pollution
MP - 2	0.37	Without pollution
MP - 3	0.37	Without pollution
MP - 4	0.38	Without pollution
MP - 5	0.38	Without pollution
MP - 6	0.40	Without pollution

Table 4. Chronic daily intake of phosphates and nitrates in the dry season

Monitoring points	Age group	Phosphates	Nitrates
Oral route			
MP - 1	Adults	0.014	0.327
	Children	0.014	0.330
MP - 2	Adults	0.015	0.391
	Children	0.015	0.394
MP - 3	Adults	0.015	0.391
	Children	0.015	0.394
MP - 4	Adults	0.015	0.398
	Children	0.016	0.401
MP - 5	Adults	0.016	0.398
	Children	0.016	0.401
MP - 6	Adults	0.017	0.413
	Children	0.017	0.416
Dermal route			
MP - 1	Adults	2.382E-05	5.566E-04
	Children	1.438E-04	3.361E-03
MP - 2	Adults	2.507E-05	6.645E-04
	Children	1.514E-04	4.013E-03
MP - 3	Adults	2.507E-05	6.645E-04
	Children	1.514E-04	4.013E-03
MP - 4	Adults	2.633E-05	6.770E-04
	Children	1.590E-04	4.088E-03
MP - 5	Adults	2.758E-05	6.770E-04
	Children	1.666E-04	4.088E-03
MP - 6	Adults	2.883E-05	7.021E-04
	Children	1.741E-04	4.240E-03

CONCLUSIONS

The present study concluded that surface waters of the Ichu river in Huancavelica, Peru, showed phosphate contents above the critical concentration for eutrophication. However, it did not show contamination by phosphates and nitrates in the dry season, since the concentrations were below the maximum limit allowed by the Environmental Quality Standards for water, Category 3. In addition, the risk of chronic intake of phosphates and nitrates in children and adults was low. There was also no contamination according to the NPI evaluated. The concentration of phosphates and nitrates in the dry season in Ichu River is susceptible to increase due to anthropogenic contamination established in the Ichu river bed and therefore causes deterioration in its quality and the disappearance of species. In addition, more studies and water quality monitoring with a large sample size are needed to generate more data and more accurately report the status of phosphates and nitrates in the Ichu River water bodies.

Acknowledgments

To the National University of Huancavelica and to the Central Laboratory, for allowing the development of this project and access to laboratory material.

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