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Hydrochemical and microbiological evaluation of groundwater in an agricultural area of Ecuador

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Abstract: Hydrogeochemical and microbiological parameters of groundwater samples in the Paipayales agricultural community in western Ecuador were studied to evaluate groundwater origin, contamination, and suitability for domestic use and irrigation. The water wells studied are typically shared by multiple families which account for 37% of the total community population. A total of 31 parameters of water samples from the wells used by the community were analysed by four laboratories at the ESPOL University. The parameters analysed included microbiological and chemical compounds, along with physical characteristics typically influencing water quality. As regards the World Health Organization (WHO), U.S. Environmental Protection Agency (EPA), and Ecuadorian standards, all samples failed to meet the required concentrations for at least one compound. The chemical analysis showed eight elements (cadmium, aluminium, ammonia, iron, manganese, chloride, and bromide) exceeded the maximum limits for drinking water in at least one well. Seventy percent of sampled wells failed to meet the maximum permissible limits for at least one chemical parameter. Water in all wells showed the presence of microbiological contaminants. The high natural groundwater salinity limits the ability to use this groundwater for irrigation purposes. Water in open and closed wells shows different hydrochemical and microbiological patterns. The presence of domestic animals and the lack of protection for wells may influence the quality of water. It is highly recommended that the authorities increase water supply and storage capacity to improve the availability of drinkable water in rural communities in the area.

Keywords: agriculture, contamination, groundwater quality, microbiology, well

INTRODUCTION

Groundwater is a crucial resource for communities in arid and semiarid regions that do not receive regularly controlled water, and the access to it through wells is vital for maintaining regular consumption, daily activities, and agricultural production (Martínez-García, Jaramillo-Colorado and Fernández-Maestre, 2019). In agricultural areas, extensively utilised groundwater contains natural and anthropogenic agrochemical contaminants such as heavy metals and pesticides that affect water quality and its use for human consumption and irrigation of crops (Otero *et al.*, 2016; Martínez-García, Jaramillo-Colorado and Fernández-Maestre, 2019; Huang *et al.*, 2020). Additionally, the omnipresent remains related to the use of pesticides, such as agrochemical bottles and household waste, in the surroundings of wells also contribute to groundwater contamination.

The World Health Organization (WHO) included four heavy metal(oid)s, such as cadmium (Cd), arsenic (As), lead (Pb), and mercury (Hg), on its list of ten chemical elements hazardous to public health due to their high potential toxicity, even when present in trace amounts (WHO, 2014). For example, long-term intake of Cd-contaminated water causes Cd-accumulation in vital organs and tissues, including liver, kidney cortex, immune system, bones, and reproductive organs potentially causing cancer and cardiovascular diseases (Ikeda *et al.*, 2004). Mercury (Hg) produces teratogenic adverse effects interfering with the development of the foetus and causing developmental delays during childhood and attention deficits (WHO, 2017b). It has been reported that even low doses of Hg can produce harmful effects on the developing nervous system, cardiovascular, immune, and reproductive systems (WHO, 2017a; Osada, 2019). Aluminium (Al) is a common compound present naturally in geological settings and artificially in pesticides. It may harm human health causing pulmonary, gastrointestinal, cardiovascular, neurologic, and hematologic disorders after inhalation, ingestion, and water intake (Igbokwe, Igwenagu and Igbokwe, 2020).

Other metals such as copper (Cu), manganese (Mn), and zinc (Zn) are essential since they play important roles in biological systems. However, they can also produce toxic effects at high concentrations (Sobhanardakani *et al.*, 2017). For example, Mn is a common element in the Earth's crust and may occur naturally at high concentrations in groundwater but does not pose a health risk within natural limits (WHO, 2014). Yet Mn added to herbicides and fungicides in the agricultural environment can generate neurobiological alterations and problems in pregnancy (Takser *et al.*, 2004). Iron (Fe) and chrome (Cr) do not produce harmful effects on health. However, they are of concern due to their effects on the acceptability of water when present at high concentrations (WHO, 2014). Additionally, high concentrations of Fe and Mn in groundwater can affect the integrity of pump and well linings or coverage, causing possible breakdowns and consequently costly repairs, threatening the availability and quality of drinking water, and risks to public health (WHO, 2014).

Other elements such as excess chloride (Cl) and sodium (Na) can be harmful to crops (Machado and Serralheiro, 2017), and continued consumption of bromide (Br) at levels higher than the norm has been associated with kidney and thyroid carcinoma pathologies (WHO, 2014).

Sewage waste and microbiological contamination have direct negative impact on the quality of well water used for consumption and irrigation. Faecal indicators, such as faecal coliforms and *E. coli* (EC), reflect faecal groundwater contamination. In contrast, the total coliform count is not considered a reliable contamination parameter due to the number of bacteria irrelevant to human health, especially in tropical areas (WHO, 2014).

Numerous studies on groundwater pollution in arid and semi-arid areas have been carried out in the past decades. For example, Mthembu *et al.* (2022) reported a moderate pollution by heavy metals in almost 25% of samples in a semi-arid coastal aquifer in South Africa. Malek, Kahoul and Bouguerra (2018) reported an elevated groundwater physico-chemical and bacteriological pollution in a rural zone of north-eastern Algeria.

In comparison to some other regions worldwide, data on groundwater quantity and quality in Ecuador have been sparse and outdated. Many recent groundwater studies assessed the geogenic sources of solutes in the Andean aquifers (Guzmán *et al.*, 2016; Ruiz-Pico *et al.*, 2019), emphasising the impact of contamination (Bundschuh *et al.*, 2012). Moreover, vulnerable coastal aquifers have been affected by excessive exploitation by tourists, increasing salinity (Herrera-Franco *et al.*, 2020) and water resources affected by mining (Jiménez-Oyola *et al.*, 2021). Although consumption and irrigation are the priority uses of Ecuadorian water resources (Wingfield *et al.*, 2021), rural groundwater resources with a high degree of agricultural use have received little attention. Additional, aquifer contamination via latrines and human waste is common in Ecuadorian rural areas. One of the prominent examples is the alluvial aquifer of the Guayas Basin, located north of the largest city Guayaquil. Based on a set of geographical, land management, and groundwater nitrate contamination parameters, Ribeiro, Pindo and Dominguez-Granda (2016) stated that the fertiliser consumption substantially threatens the groundwater with nitrate contamination in the Lower Guayas area. In the typical Lower Guayas municipality of Santa Lucia, about 40 km north of Guayaquil, more than 50% of the population work in agriculture (PDOT, 2015). Santa Lucia is one of the cantons with the highest agricultural production in Ecuador, mainly rice cultivation (PDOT, 2015; Ribeiro, Pindo and Dominguez-Granda, 2016). Previous studies in Paipayales, a community covered by the study located in the Santa Lucia municipality, indicate that around 88.5% of the population makes a living essentially on rice cultivation (Calderón *et al.*, 2016). Therefore, domestic and agricultural water use is the main contentious issue (PDOT, 2015). The use of latrines for human waste is common in the rural area of Santa Lucia, and sewage generates high-level impact on the quality of well water used for consumption (PDOT, 2015).

This study aimed to evaluate the groundwater quality in the community of Paipayales, a representative rural and agricultural settlement in the lower basin of the Guayas River. Thus, the suitability of groundwater use for drinking and irrigation purposes, the impact of the well type, and, influence of distance from sanitary facilities on the groundwater quality is evaluated. Additionally, the article discusses water composition and correlations between the different compounds.

MATERIALS AND METHODS

STUDY AREA

The communities in this area are organised in enclosures, supported by the Autonomous Decentralised Municipal Government (Sp.: Gobierno Municipal Autónomo Descentralizado), and self-managed through different organisations, according to their objectives, and composed of local inhabitants. The main enclosure under the present study is Paipayales of 216 ha and 350 inhabitants. It is located 4 km from the rural parish of Santa Lucia (Fig. 1) in the Guayas Province, Ecuador. Eighty-nine percent of the land is used for rice-growing, followed by 0.2% mango, with only 6% forested area and 4% of land under forest regeneration (Fig. 1). Although many of the houses are traditionally built with a cane layer on a raised floor, most houses are made of brick. The Paipayales inhabitants are mostly small farmers; they operate 1–5 ha and produce rice during a year in two cultivation cycles of 2.5–3.5 months each. Access to water is from two sources. One is a tanker that provides drinking water for human consumption, delivered from the urban area of Santa Lucia municipality to the Paipayales enclosure every month. The alternative water source comprises wells, and it is used for irrigation and consumption purposes, such as cleaning, cooking, and drinking. The water runs out during the dry season in many of the wells. However, using the nearest well water is essential for families to maintain their basic activities. During adverse situations, families have relied on community support to meet their needs through this water source. Building a well involves investment that increases with the depth of the well, meaning a deeper well requires a greater investment. Examples of selected wells and their surroundings in the Paipayales community are depicted in Photo 1.

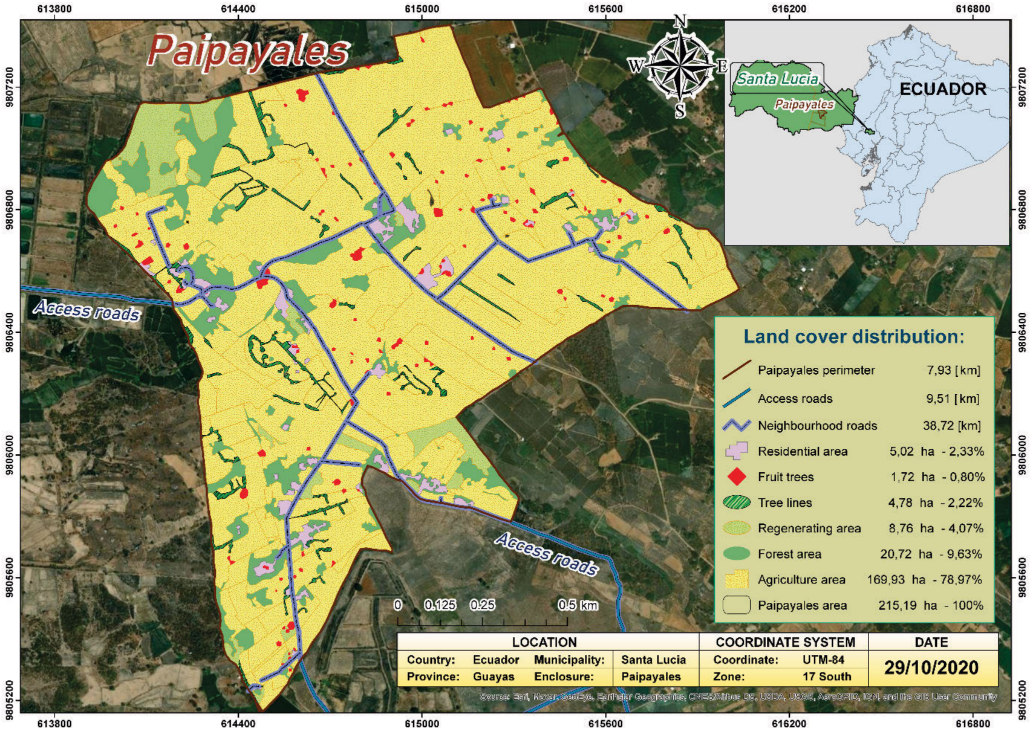

Fig. 1. Land cover distribution in the Paipayales community; source: Abner Valdivieso, Johnny Briones (Faculty of Earth Sciences, ESPOL)

Photo 1. View of the Paipayales area: A) open well, B) closed well, C) paddy field with empty bottles from pesticides, D) example of a dwelling in the Paipayales village (phot.: *R. Villalba Briones*)

DATA COLLECTION

The baseline information about water supply and use in the Paipayales community comes from bibliographic research, interviews with managers of the Autonomous Decentralised Municipality Government of Santa Lucia (Sp.: Gobierno Municipal Autónomo Descentralizado del Cantón Santa Lucía), and meetings with focus groups from the Paipayales community. Hence, we verified suspected problems, interviewed well users, and evaluated water resources available for the community. Interviews with local groups highlighted a concern about water resources. Well water was used for cooking, daily cleaning, and direct consumption when the monthly municipal tanker service was not available as scheduled due to the lack of piped water in the Paipayales community. Specific characteristics of the wells (depth, years of operation, type of well, etc.) and possible sources of contamination (animals, septic tanks, and crops) were recorded through a questionnaire survey among well owners.

Before the rainy season, thirteen privately owned wells were sampled from January to February 2020 (Fig. 2). They cover 37.4% of the Paipayales community population. Sampling wells were selected according to the density of households (Loaiciga *et al.*, 1992), the use of water (domestic and irrigation purposes), and types of wells (open and closed). The area and the sampling wells were privately owned and utilised for housing and agricultural purposes, primarily rice cultivation. While three open wells (P03, P04, and P06) had no cementation, allowing their water table to be in contact with the external environment, the remaining ten wells were protected by cementation, with the pump was connected to water through pipes.

All owners of the studied wells used a latrine based on a 3 m depth hole in the ground, with 6 wells located less than 20 m from the latrine. Eleven wells were surrounded by domestic animals such as pigs, chickens, dogs, as well as wild animals like bats or iguanas, or a pond destined for aquaculture. The distance of the wells from the latrines (*WD*) was measured to complement the hydrochemical and microbiological assessment. The distance varied from about 10 to 60 m, with an average distance of 35 m.

Samples were collected through the original tube of the well by activating the well pump. For wells not equipped with a pump a portable pump or extraction buckets provided by the well owner were used. The samples were stored in high-density polyethylene bottles for physical and chemical analysis, and in sterile bottles of 1 dm^3 for microbiological analysis. Moreover, a portable refrigerator with ice preserved the samples, which were delivered to the laboratories within a maximum of 6 h for processing.

LABORATORY ANALYSIS AND QUALITY ASSURANCE

A total of 31 parameters were evaluated, focusing on the most relevant factors for drinking and irrigation water quality. An overview of chemical parameters, corresponding analytical methods, as well as field and laboratory equipment is presented in Table 1.

Total coliforms, faecal coliforms, and *E. coli* were enumerated using the most probable number technique (APHA). Samples were inoculated in lactose broth (Difco Laboratories, Detroit, Michigan, USA). Positive tubes were confirmed in brilliant green bile lactose broth (Difco) for total coliforms and EC medium (Difco) for faecal coliforms. Enumeration of *E. coli* was performed in EMB agar (Difco) and confirmed by biochemical identification using indole, methyl red, Voges Proskauer, and citrate test. The analysis was performed in the Microbiology and Molecular Techniques Laboratory of the Faculty of Life Sciences (Sp.: Facultad de Ciencias de la Vida – FCV) at the ESPOL University.

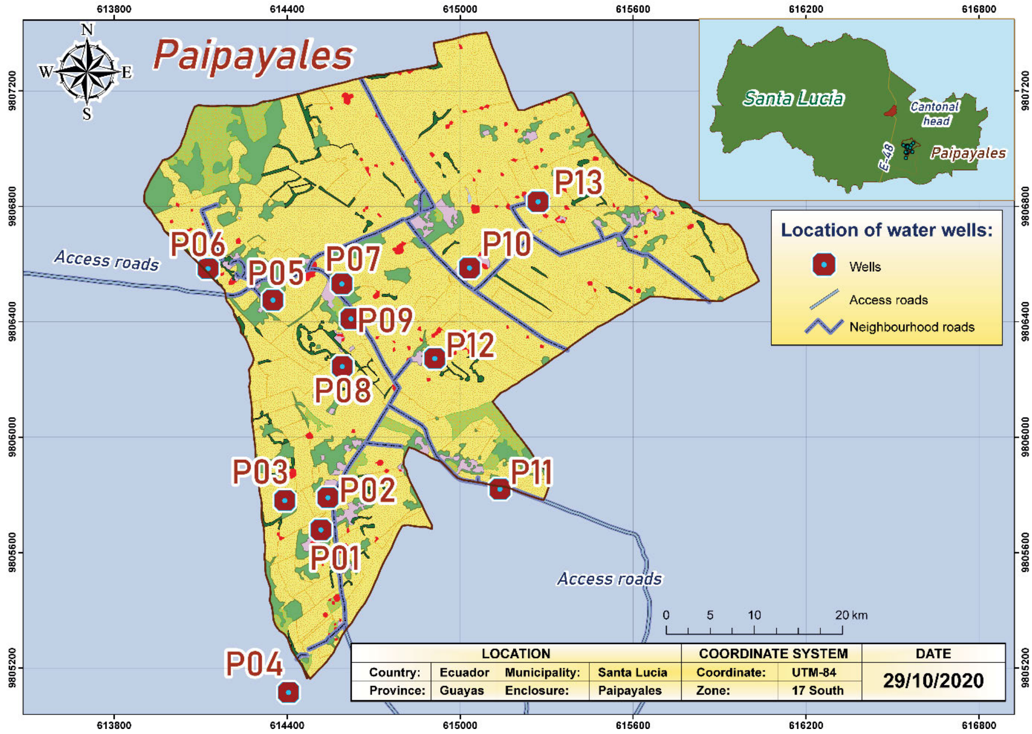

Fig. 2. Location of the sampled wells in the Paipayales community; source: Abner Valdivieso, Johnny Briones (Faculty of Earth Sciences, ESPOL)

Table 1. Overview of the analytical hydrochemical framework applied in this study

Parameter	Method	Instrument	Laboratory
Total dissolved solids (TDS)	direct measurement	HANNA HI 9829 multiparameter probe, Hanna Instruments, Woonsocket RI, USA	Centre for Water and Sustainable Development (CADS), ESPOL
Electrical conductivity (Cond)			
Salinity			
Biological oxygen demand (BOD)	ionic chromatography acc. to APHA 5210B	Metrohm 883 Basic Plus, Herisau, Switzerland	
Chemical oxygen demand (COD)	ionic chromatography acc. to APHA 5220D		
NH_4	ionic chromatography acc. to APHA 4110B		
Major ions (Ca, Mg, Na, K, Cl) and F, Br, Zn, Fe, Mn, Cu, Al, Cd, Cr	coupled plasma optical emission spectrometry ICP-OES	Perkin Elmer Optima 5300 DV, Waltham MA, USA	Ground Laboratory, Faculty of Life Sciences (FCV), ESPOL
NO_2^-, NO_3^- PO_4^{3-}, SO_4^{2-}, NH_3, HCO_3^-	spectroscopy	HACH DR2800, Ames IA, USA	Toxicological Research and Environmental Health Laboratory Faculty of Life Sciences (FCV), ESPOL
Total mercury (THg)	atomic absorption	Direct Mercury Analyzer, Milestone Inc., Milano, Italy	
Pb		Atomic Absorption Spectrophotometer AA400, Perkin Elmer, Waltham MA, USA	

Source: own elaboration.

Quality assurance procedures and precautions were implemented to ensure the reliability of the results. Thus, samples were carefully handled to avoid contamination. Glassware was acid cleaned, reagents were of analytical grades, and deionised water was used throughout the study. All metal analyses were performed in duplicate, and blanks (0.0001 ±0.00 mg·dm^{-3}) were also analysed.

DATA INTERPRETATION

The data were statistically analysed using the RStudio software version 1.3.1093 (RStudio Team, 2020). The maximum error of the ionic balance was 10%.

The microbiological parameters, total coliforms (TC) and faecal coliforms (FC), with values above the detection limit (>1600), were replaced with a value of 1999. One missing biological oxygen demand (BOD) value was predicted using linear regression with NH_4 as independent variable.

ASSESSMENT OF WATER QUALITY

The hydrochemical and microbiological parameters of the sampled groundwater were compared to the drinking water limits of the World Health Organization WHO (WHO, 2017a), U.S. Environmental Protection Agency (U.S. EPA, 2017), and the Ecuadorian standards (INEN, 2020). Various guidelines were considered to assess drinking water quality and provide comprehensive information about the influence of water intake on humans, as different countries and organisations establish different maximum permissible limits.

According to the Ecuadorian standards for drinking water (INEN, 2020), water for human consumption is defined as "Water used for drinking, preparing and cooking food, or other domestic uses, regardless of origin and supply, with physical, chemical and microbiological characteristics that guarantee its safety and acceptability for human consumption."

EVALUATION OF SALINITY AND SODICITY

The irrigation water quality was assessed using two diagrams and five indices related to salinity and sodicity. Saline irrigation groundwater causes the accumulation of dissolved salts in the soil and increases the soil osmotic potential and limiting the capacity of plants to absorb water. Additionally, this can lead to nutritional imbalances or toxicity due to specific ions. Elevated sodicity may destroy the soil structure through the swelling and dispersion of clay particles, forming low permeability layers. These layers restrict root growth, water infiltration, and enhance soil erosion, among other drawbacks (Paz *et al.*, 2020). A detailed description of the salinity and sodicity indices can be found in Rawat, Singh and Gautam (2018).

1. Sodium adsorption ratio (*SAR*)

The *SAR* is an irrigation water quality parameter determined from the concentrations of the main alkaline and earth alkaline cations (here expressed in meq·dm^{-3}) present in the water; it is defined as:

$$SAR = \frac{\mathrm{Na}^{+}}{\sqrt{\frac{1}{2}(\mathrm{Ca}^{2+} + \mathrm{Mg}^{2+})}} \tag{1}$$

Its concentrations are expressed in meq·dm^{-3}. The values were plotted in the log-Wilcox graph (Wilcox, 1958) that combines the ranges of conductivities and *SAR* in four levels of salinity hazard (C1–C4) and four levels of sodicity hazard (S1–S4). The plotting was performed using the Diagrammes software (Simler, 2009).

2. Percent sodium (%Na)

This alternative parameter to *SAR* is calculated as:

$$\%\mathrm{Na} = \frac{\mathrm{Na}^{+}}{\mathrm{Ca}^{2+} + \mathrm{Mg}^{2+} + \mathrm{Na}^{+} + \mathrm{K}^{+}}\ 100 \tag{2}$$

Its concentrations are expressed in meq·dm^{-3}. The classification of water is based on %Na as excellent (<20%), good (20–40%), permissible (40–60%), doubtful (60–80%) and unsuitable (>80%) (Rawat, Singh and Gautam, 2018).

3. Kelly index (*KI*)

Another alternative parameter to *SAR* is calculated as:

$$KI = \frac{\mathrm{Na}^{+}}{\mathrm{Ca}^{2+} + \mathrm{Mg}^{2+}} \tag{3}$$

Its concentrations are expressed in meq·dm^{-3}; $KI > 1$ indicates an excess level of Na^{+} in waters. Therefore, water with a $KI \leq 1$ has been recommended for irrigation, while water with $KI \geq 1$ is not recommended for irrigation due to alkali hazards (Rawat, Singh and Gautam, 2018).

4. Permeability index (*PI*)

Another alternative parameter to *SAR* is calculated as:

$$PI = \frac{\mathrm{Na}^{+} + \sqrt{\mathrm{HCO_3}^{-}}}{\mathrm{Ca}^{2+} + \mathrm{Mg}^{2+} + \mathrm{Na}^{+}}\ 100 \tag{4}$$

Permeability index can be grouped in three classes: class I (>75% – suitable), class II (25–75% – good) and class III (<25% – unsuitable). Water under class I and class II is recommended for irrigation (Rawat *et al.*, 2018).

5. Magnesium hazard (*MH*)

Excess concentration of magnesium in groundwater affects the soil quality by converting it into alkaline and therefore decreases the crop yield. It can be calculated as:

$$MH = \frac{\mathrm{Mg}^{2+}}{\mathrm{Ca}^{2+} + \mathrm{Mg}^{2+}}\ 100 \tag{5}$$

Values of $MH > 50\%$ is not recommended for irrigation purposes (Rawat, Singh and Gautam, 2018).

6. Potential salinity (*PS*)

This parameter focuses on salinity indicators Cl^{-} and SO$_4^{2-}$ and can be calculated as:

$$PS = \mathrm{Cl}^{-} + 0.5\ \mathrm{SO}_4^{2-} \tag{6}$$

Its concentrations are expressed in meq·dm^{-3}; $PS <$ 3 meq·dm^{-3} is an indication of the suitability of water for irrigation (Rawat, Singh and Gautam, 2018).

7. Gibbs diagram

The Gibbs diagram (Gibbs, 1970) summarises the evolution of groundwater chemistry with respect to principal dominant processes such as evaporation and/or saline water intrusion, water-rock interaction of younger waters and fresh rainwater recharge (Marandi and Shand, 2018). The variant of the Gibbs diagram constructed in this study includes the sum of total dissolved solids (TDS, in mg·dm^{-3}) and the ratio Na^{+}/(Ca^{2+} + Na^{+}).

CLUSTER ANALYSIS

The hierarchical agglomerative cluster analysis was applied to identify natural grouping of elements with similar characteristics. The data sets were standardised (centred and normalised). Euclidean distance was used as a dissimilarity measure, the Ward method was employed for agglomerative clustering to maximise homogeneity within clusters. The resulting groupings are shown in a dendrogram, which illustrates the distances (heights) between clusters.

MATRIX CORRELATION

Correlation analyses among parameters were conducted to identify patterns in the composition of well water and influences of different origins, including geological, agrochemical use, microbiological inputs, physical characteristics, and environment of the wells. This analysis utilised Spearman's rank correlation coefficient (−1; 1). Correlation coefficient values above 0.5 and below −0.5 were considered statistically significant at 0.05 and 0.10 significance levels, respectively. Other correlation values were considered non-significant (Cohen, 2013).

RESULTS AND DISCUSSION

CHEMICAL AND MICROBIOLOGICAL GROUNDWATER COMPOSITION

The chemical and microbiological composition of the groundwater in the wells of Paipayales is summarised in Figure 3 and Table S1.

Chemical analyses. Eight of thirteen wells sampled had concentrations that exceeded the WHO maximum permissible limits (MPL) for water consumption. These limits were exceed for Fe (four wells), Mn (three wells), Cd (five wells), THg (six wells), and Al (seven wells). Moreover, seven of the wells had at least one parameter above the EPA permissible levels for drinking water. EPA permissible levels for drinking water were exceeded in three wells for BOD (5 mg·dm^{-3}) and in seven wells for COD (10 mg·dm^{-3}). Six wells had Mn, THg and Cd concentrations above permissible levels for drinking water with respect to the Ecuadorian standards. Concentrations of THg were above WHO maximum permissible levels (1 μg·dm^{-3}) in seven wells (P03–P08 and P13) and exceeded the U.S. EPA MPLs (2 μg·dm^{-3}) in two wells (P04 and P13).

In the three open wells (P03, P04 and P06), five chemical parameters exceeded the WHO MPL in each well, and three chemical parameters exceeded the U.S. EPA MPL in each well. Additionally, BOD and COD exceeded the EPA benchmark in the closed wells. The three open wells also exceeded Ecuadorian standards for THg and Al (INEN, 2020). Of the ten closed wells, six had water quality that did not meet U.S. EPA standards, five did not meet WHO standards, and two did not meet Ecuadorian standards.

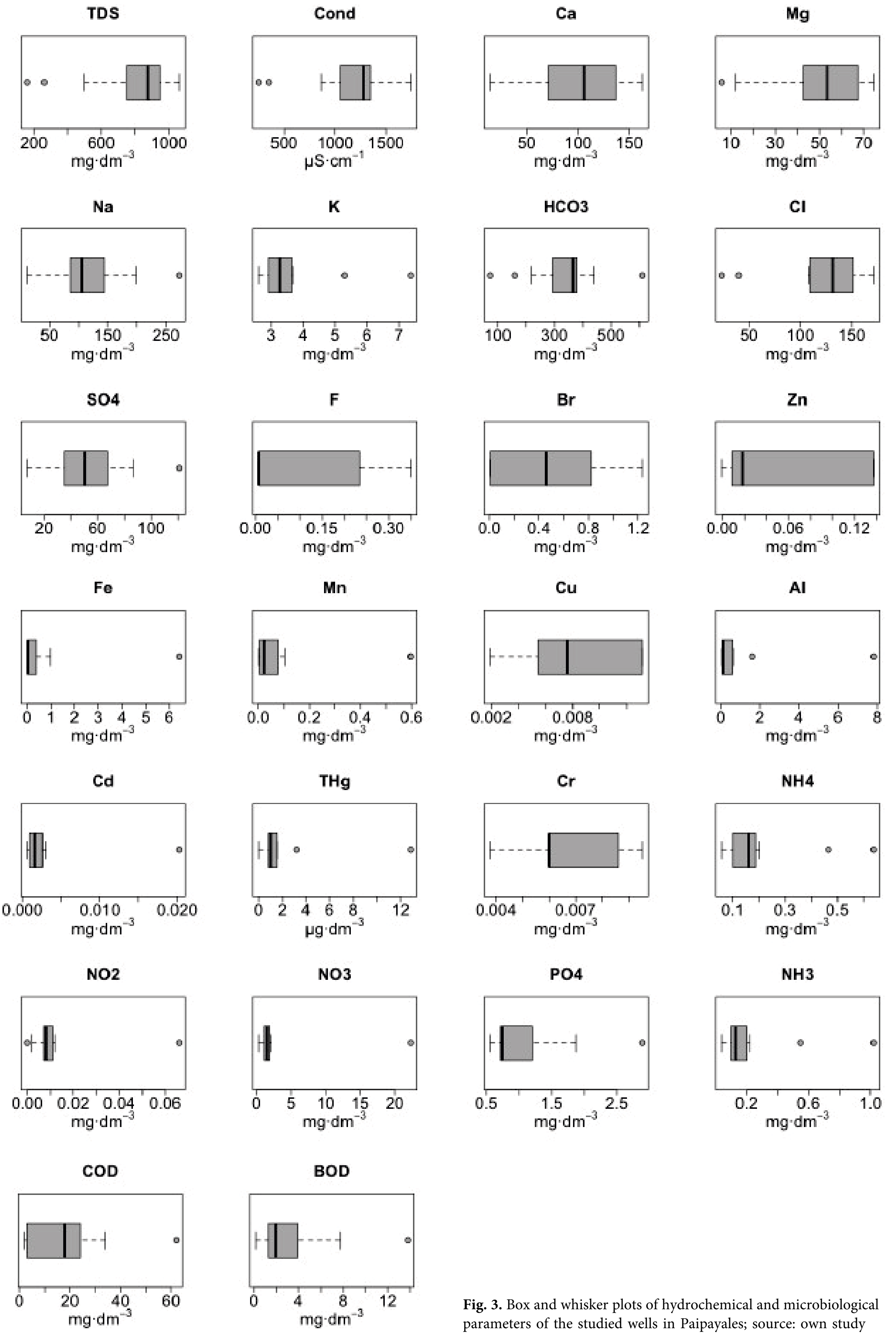

Fig. 3. Box and whisker plots of hydrochemical and microbiological parameters of the studied wells in Paipayales; source: own study

Microbiological analyses. Total coliforms, faecal coliforms, and *E. coli* were detected in all the samples ($N = 13$) with values between 5.50 and >1600 MPN·(100 cm^3)$^{-1}$ – Table S1.

The microbiological load exceeded regulatory limits in 100% of the cases, which largely consistent with the proximity of septic tanks within 20 m or less. Water from all wells was used for human consumption and, additionally, for irrigation in 69.2% of instances. The presence of *E. coli* indicates recent faecal contamination. According to the WHO and the Ecuadorian regulation, *E. coli* should not be present in water intended for human consumption (WHO, 2017a). According to Ecuadorian regulations and the values found for TC and FC, the water can be used for human consumption after conventional treatment. Wells can also be used for agricultural or irrigation purposes. Although water quality can vary rapidly and all systems show occasional failures, the presence of this pathogen in all wells indicates a widespread problem. However, in rural water supply systems, *E. coli* due to faecal contamination is a recognised recurring issue and should not be detected in water designated for human consumption in samples of 100 cm^3 (WHO, 2017a). The proximity of the wells to the crops, septic tanks, and the presence of free domestic animal husbandry around the water wells used for consumption may have caused undesirable contamination. A 20-meter buffer zone was established as a safe distance from family septic wells to prevent infiltration of microbiological loads. This distance significantly reduces the presence of microbiological agents of human faecal origin, such as EC, FC, and BOD (Knappett *et al.*, 2011). The influence of the well depth, being irregular, could not be verified. Generally, deeper wells exhibited a lower microbiological load. Moreover, the wells were not chlorinated, as chlorination is not a common practice prior to their use in the area. However, microbiological degradation of organochlorine pesticides decomposes the molecules, liberating chlorides (Fuentes *et al.*, 2010).

ANALYSIS OF SODICITY AND SALINITY HAZARD

The analysis of the quality of the irrigation groundwater reveals that almost all samples belong to category S1 of low sodium water (SAR = 0–10), which can be used for irrigation on almost all soils with low risk of developing harmful levels of exchangeable sodium (Fig. 4). Only one well (P02) reveals a higher SAR. The overall low SAR is related to elevated Mg concentrations (average Ca/Mg = 0.83), presumably originating from infiltrated river waters transporting Mg dissolved from volcanic rocks along the upper Daule River course. Despite the overall low sodicity hazard level, most groundwater samples belong to the high-salinity water category C3 (750 < Cond < 2250 μS·cm^{-1}), indicating waters that cannot be used on soils with restricted drainage without further application of salinity regulation measures. Only two open wells (P03 and P04) contain low or low-medium salinity (Cond < 750 μS·cm^{-1}) groundwater, which can be used for irrigation of most crops. The low conductivity of water in the open wells is affected by precipitation water inflow prior to and during the sampling campaign.

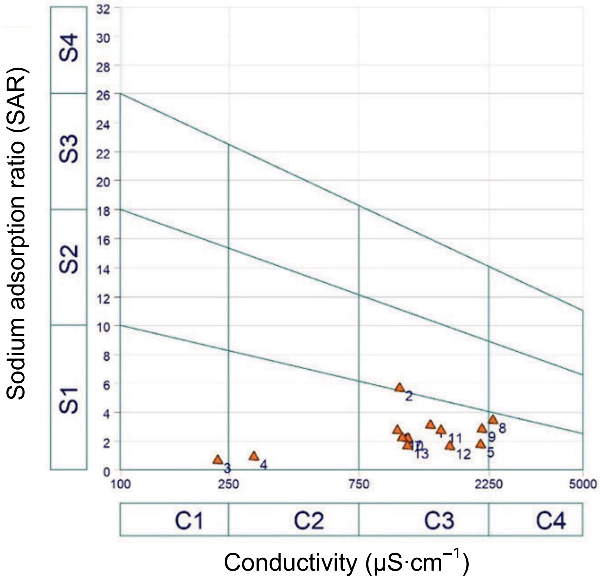

Fig. 4. Log-Wilcox diagram of the salinity and sodicity hazard in groundwater samples from Paipayales; conductivity ranges and sodium absorption ratio (SAR) in four levels of salinity hazard (C1–C4) and four levels of sodicity hazard (S1–S4); 1–13 = the numbers of wells P01–P13; source: own study

Ratios which include concentrations of Ca^{2+}, Mg^{2+}, SO_4^{2-} and Cl^- indicate that those ions constitute the major salinity sources in groundwater in the target area. The SAR and %Na of all wells indicate permissible quality for irrigation, the indices of salinity that include Mg^{2+}, Ca^{2+}, and Cl^- show that these components are the dominant salinity sources, lowering the quality of groundwater designated for crop irrigation. Among the five salinity indices applied, the groundwater in the open wells (P03, P04, P06) shows three or four values above the permissible level. Most of the wells exhibit unsuitable conditions with respect to the potential salinity index (PS), presumably of geogenic origin and a high influence of evaporation (see also the Gibbs diagram, Fig. 5). Another possible source of sulphates and chlorides can be attributed to artificial pesticides.

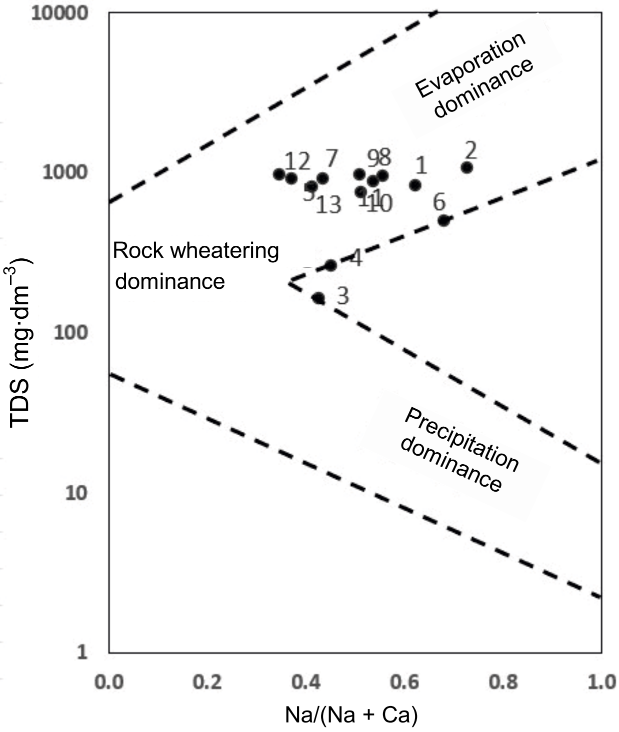

Fig. 5. Gibbs diagram of groundwater quality in the studied wells in Paipayales; 1–13 = the numbers of the wells P01–P13; source: own study

CLUSTER ANALYSIS

The analysis of 30 hydrochemical and microbiological parameters (Tab. S1) identified two main clusters of open and closed wells (Fig. 6).

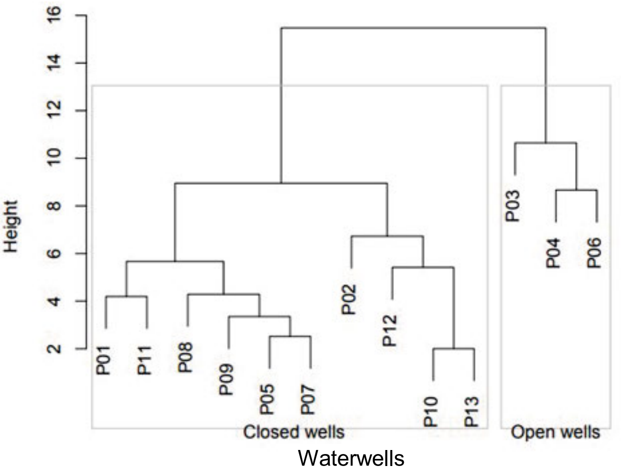

Fig. 6. Cluster diagram showing similarity between two main groups of wells in Paipayales; P01–P13 = wells; source: own study

Water in all open wells showed unacceptable concentrations for human consumption in at least three heavy metals present in agrochemicals, such as Cd, Al, Mn, and Fe. Five of ten closed wells had concentration over the maximum permissible level (MPL) for the same compounds.

CORRELATION AMONG PARAMETERS

The correlation analysis was carried out in two steps: first, jointly for both clusters of open and closed wells, and second, separately for closed wells.

Open and closed wells. The chemical composition of both categories of wells revealed various levels of correlations (Fig. 7). The TDS was significantly positively correlated to geogenic water-rock exchange indicators such as conductivity, Ca^{2+}, Mg^{2+}, Na^{+}, HCO_3^{-}, Cl^{-}, and SO_4^{2-}. These parameters, which are directly related to interactions with solid materials underground, showed (except Ca^{2+}, Mg^{2+}, and HCO_3^{-}) a significant negative correlation with metals (except Zn, Cd and Cr and Cu with Na). Additionally, Al showed a strong positive correlation with Cd, Mn, and Fe and less strong with Cu, while the correlation with Cr was very low (insignificant). Moreover, Zn showed a significant negative correlation with *F* (−0.612). A high positive correlation among almost all metals (except Cr and Zn) could be explained by the recurrent presence of Cd, Al, Mn, and Fe in agrochemicals, especially pesticides. These compounds could be directly introduced into the water through the air, without interacting with other subsurface solids. The COD showed a high correlation with almost all metals (except Cr and Zn), but no correlation with microbiological elements. The prevalence of microorganisms might indicate heterogenic and stochastic sources. Moreover, Cr was more related to the TDS and other inorganic major ions. The TDS and Cond analyses had a similar outcome due to their compositional similarity. Additionally, they showed a highly significant negative correlation with almost all metals (except Zn, Cr), NH_3, and COD.

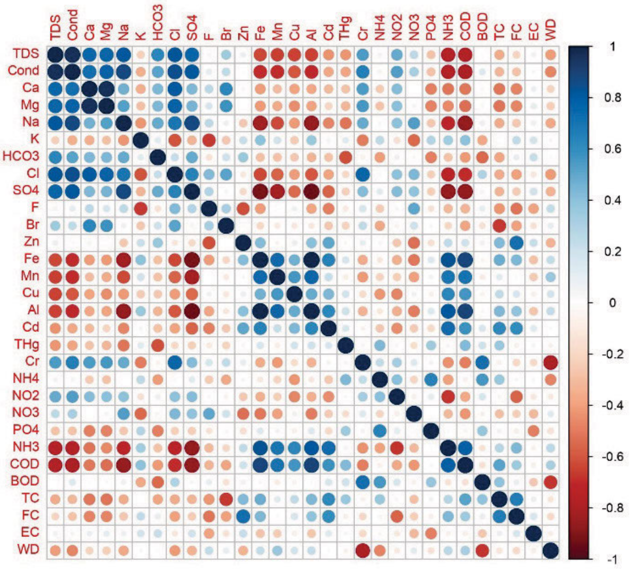

Fig. 7. Correlation gradient matrix between chemical and microbiological concentration from 13 closed and open wells in Paipayales; red indicates a negative correlation and blue indicates a positive correlation; point size represents the correlation value (with maximum size indicating a correlation of 1 and minimum 0); source: own study

Three parameters, namely Na, TDS, and Cond, exhibited a high negative correlation with almost all metals (except THg, Cr, Zn and Cd), NH_3, and COD. The following metals: Al, Mn, Fe, Cu, and Cd are typically present in pesticides and could be directly introduced into the water without substantial water-rock interaction. Negative significant and non-significant correlations were also found between the metals and geogenic compounds (except Zn and Cr). Potassium (K) had no correlation with other ions, possibly due to its presence in fertilisers. However, K had a high negative correlation to *F*, which is also utilised in certain types of fertilisers.

Like other microbiological indicators, *E. coli* (EC) showed no clear correlation with any chemical or other microbiological parameters. Other identified correlations include: a) a low negative correlation between PO_4 and EC, b) a high negative correlation between Br and TC, and c) a casual high positive correlation of Zn with FC. The heterogeneity and predominant presence of microorganisms in many wells could be due to a high number of spills and various anthropogenic or animal farm influences.

Closed wells. The analysis of correlations in the closed wells (Fig. 8) showed stronger correlations between various parameters in comparison to the joint correlation analysis of both open and closed wells (Fig. 7). Fe and Mn are the two metals that showed a strong positive correlation, while Cd had a significant positive correlation with Fe and NH_3 and a non-significant correlation with Al and Zn. Cadmium occurs naturally in all agricultural soils and is a typical compound found in fertilisers (Roberts, 2014). Potassium showed no correlation with other ions, indicating the fertiliser origin. The predominantly geogenic parameters such as TDS, Cond, Ca, Mg, Na, SO_4, and Cl showed a high positive correlation between them (except Ca and Mg with Na and SO_4). Microbiologic compounds showed correlation among themselves, but no correlation with the increasing distance from the latrine (*WD*). However, *WD* showed negative correlation with TDS, Cond, NH_4, NO_2, Cl, and BOD, which are parameters related to human waste and latrines (Fig. 8).

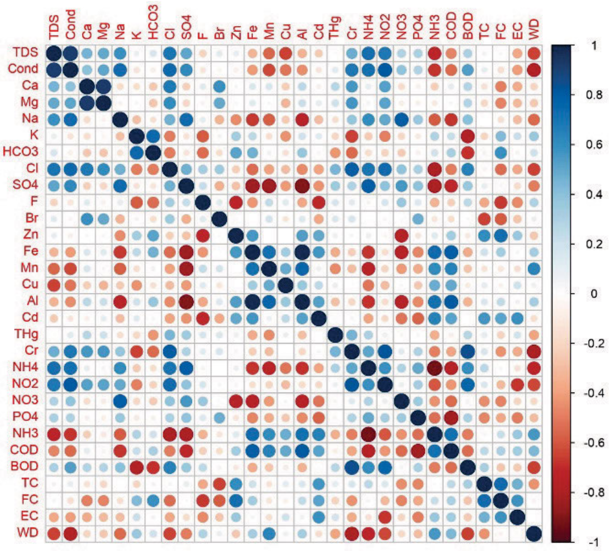

Fig. 8. Correlation gradient matrix between chemical and microbiological concentrations from 10 closed wells in Paipayales; explanations as in Fig. 7; source: own study

No significant linear correlation was found between the distance of the well from the latrine and the microbiological values. All samples showed high microbiological values because most wells are close to septic tanks or latrines. Several studies on other rural areas of the world have noted the impact of latrines on microbiological contamination. For example, Knappett *et al.* (2011) recommended maintaining 20 m as a key distance between the well and the latrine to minimise groundwater contamination.

CONCLUSIONS

The water from the thirteen sampled wells is unsuitable for human consumption due to its hardness and high concentrations of various contaminants, including manganese (Mn), cadmium (Cd), total mercury (THg), chlorine (Cl), bromine (Br), aluminium (Al), iron (Fe), and ammonium (NH_4), all exceeding permissible values.

The data support the hypothesis that the groundwater from Paipayales is affected by high natural geogenic salinity and that several trace metals (i.e. Cd and THg), microbiological and other water quality parameters (NH_4) exceeded environmental benchmarks.

At the same time, the high degree of natural groundwater salinity limits the ability of using this groundwater for irrigation purposes. While the sodicity hazard remained relatively low, the salinity hazard values indicated an elevated risk posed by irrigation waters from the closed wells. Irrigation channels from the Daule River is one possible engineering solution to avoid increase in salinity in soils designated for rice cultivation.

The groundwater in Paipayales showed various hydrochemical and microbiological patterns in open and closed wells. The findings supported the need to protect wells and prevent anthropogenic groundwater contamination to meet water quality standards for human consumption and irrigation.

This study highlighted the importance of geological origin when comparing open and closed wells. In addition, heavy metals showed different correlations depending on the origin of geogenic ions in both scenarios. Some compounds traditionally present in agrochemicals (Fe, Cd, Al, K, F), pesticides, and fertilisers affected the hydrochemical patterns in all wells and closed wells matrix. The external input of these contaminants affects water quality, and thus its responsible use should be promoted among farmers.

The distance between the well and the latrine (*WD*) shows more correlation with the compounds related to faeces in closed wells. This result can be explained by the additional contamination surface runoff to the open wells, typically from domestic and wild animal wastes.

The following solutions can be recommended to improve and maintain the quality of drinking and irrigation water in the community of Paipayales: a) to improve the supply of water to the community from the Santa Lucia Municipality, and b) to increase the water storage capacity by building water tanks. Additionally, other strategies, such as rainwater harvesting and dry toilets, should be fostered to avoid faecal contamination of drinking water. Further development of irrigation channels from the nearby the Daule River might serve as a logical alternative for irrigation purposes.

SUPPLEMENTARY MATERIAL

Supplementary material to this article can be found online at: https://www.jwld.pl/files/Supplementary_material_Villalba.pdf

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CONFLICT OF INTERESTS

All authors declare that they have no conflict of interests.

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