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An integrated assessment of water quality in a land reform settlement in northern Rio de Janeiro state, Brazil

Thayana Paranhos Portal^a, Marcos Antonio Pedlowski^b, Cibele M. S. de Almeida^a,
Maria C. Canela^{a,*}

^a *Laboratório de Ciências Químicas, Universidade Estadual do Norte Fluminense Darcy Ribeiro (UENF), Campos dos Goytacazes, Rio de Janeiro, Brazil*

^b *Laboratório de Estudos do Espaço Antrópico, Universidade Estadual do Norte Fluminense Darcy Ribeiro (UENF), Campos dos Goytacazes, Rio de Janeiro, Brazil*

* Corresponding author.

E-mail address: mccanela@uenf.br (M.C. Canela).

Abstract

The Zumbi dos Palmares land reform settlement lacks modern facilities for water and sewage treatment. Local farmers often use shallow wells as alternative source of water supply, because the water table is reasonably high in the region. This work presents a multivariate analysis assessment of physicochemical and bacteriological parameters and pesticide residues in water samples collected from these shallow wells. The physicochemical parameters analyzed were: conductivity, pH, DOC (dissolved organic carbon), nitrate, turbidity, and bacteriological analysis measuring total and fecal coliforms. The results show non-compliance with Brazilian legal standards in most samples where low pH values were found, characterizing the presence of acidic waters. Another example of non-compliance is the presence of total and fecal coliforms in for drinking water in most of the samples and, in some cases, very high values (2,400 CFU). Some wells showed high conductivity values, probably associated with a history of oceanic intrusion. Analyses determining the contamination by pesticides show the presence of ametrine, atrazine, methyl parathion, carbaryl and hexazinone.

The concentration for these compounds ranged from 0.14 to 1.17 $\mu\text{g/L}$. Ordinance No 2914/2011 from the Brazilian Ministry of Health establishes the acceptable limits for atrazine and methyl parathion as 9 $\mu\text{g L}^{-1}$ and 2 $\mu\text{g L}^{-1}$. None of these exceeded the allowable Brazilian and European limits. However, for the other two pesticides, the European Legislation (Council Directive) recommends the maximum allowable concentration of 0.1 $\mu\text{g L}^{-1}$ and, 0.5 $\mu\text{g L}^{-1}$ for total pesticides. Our samples that were above the quantifiable limit of 50 ng L^{-1} , were also above the European limit values. Our results therefore suggest that water gathered from shallow wells at the Zumbi dos Palmares settlement is not proper for consumption without proper disinfection treatments.

Keywords: Analytical chemistry, Environmental science

1. Introduction

Groundwater has become an important alternative source of drinking water, in regions where the supply infrastructure is precarious [1]. The quality of groundwater is linked to several aspects. Among these, is the residence time in the rocks surrounding the water source and the land use. The latter include concentration of nutrients, micro-organisms and other chemical components controlling the composition of the recharge waters. Moreover, factors like rainfall amount and anthropic activities, such as the direct discharge of pollutants, also interfere with groundwater quality [1, 2]. Agricultural activities are important sources of groundwater contamination, mainly through use of pesticides and nitrogen compounds [3, 4].

According to the National Survey of Brazilian Households [5], while 78.6% of the urban households are connected to existing water distribution networks, only 44% are also connected to sewage treatment networks. The National Water Agency (ANA) estimates that until 2016, 16% of the Brazilian population lived in rural areas and consumed 33.4 m^3/s of water collected from wells, cisterns and other isolated sources for their basic needs [6]. Although rural household consumed 15 times less water than urban counterparts, the highest consumption volume (868.3 m^3/s or 78.3%) came from rural areas of agriculture and livestock, suggesting a possible ground water contamination due to runoff. Water quality is a concern for most rural households consuming water without treatment and without quality control.

Brazilian water quality diagnostic relies on the limits established by the Ordinance 2914/2011 of the Ministry of Health [7]. The basic parameters listed in that ordinance are pH, turbidity, electrical conductivity, dissolved organic carbon and microbiological contamination [2, 8]. Microbiological contamination is a common problem for Brazilian rural areas. Wells used for water sampling are usually old and improperly sealed. In addition, they are often located near sources of

contamination (e.g., animal breeding areas and cesspools) [9]. Water contamination via microorganisms is one of the main mechanisms for the dissemination of diarrheal diseases [9, 10].

In addition to the basic parameters, nitrogen has gained prominence in rural regions because of its strong impact on groundwater quality [6, 11]. Nitrogen is present in agricultural activity as well as sewage. The high concentration of nitrogen in drinking water can cause damage to human health. Newborns and adults lacking some intestinal tract enzymes, are affected the most by Methaemoglobinaemia, a disease that can lead to death in acute cases [12]. Recently, pesticides from agricultural; activities have been of greater concern because of their presence in groundwater through point and non-points sources. However, very little is still known about these contamination sources [1, 2, 3, 4].

The main objective of the present study was to measure water quality in shallow wells built by family farmers at the Zumbi dos Palmares land reform settlement. The water quality potability parameters were based on analysis of pesticide contamination associated to agriculture inputs (fertilizers and pesticides) and, the lack of basic sanitation infrastructure.

2. Materials and methods

2.1. Reagents and chemicals

High purity standards of pesticides ($\geq 99\%$): Hexazinone, parathion methyl, atrazine, ametryn, captan, carbaryl, as well as, the internal standard triphenyl phosphate were purchased from Sigma Aldrich. The pesticide grade solvents, acetonitrile and methanol, were supplied by Tedia. Every material used in this study was previously washed with ultrapure water (MILLI-Q) and alkaline Extran (Merck 3%).

The samples were filtrated using glass fiber filters (Sartorius Stedim Biotech, Germany) to remove the particulate material. For the microbiological analyzes, the samples were collected directly in the field, without filtration, using sterile flasks and taken directly to the laboratory to undergo analytical procedures. Cartridges used in the extraction were SPE ODS-C18 (Agilent Technologies) containing 1,000 mg of sorbent. Gas argon (5.0–99.999 Vol.%, Air Liquide) was used to evaporate the samples. Stock standard solutions were prepared with mix of pesticides in acetonitrile at concentration of 200 mg/L. The working solutions were prepared in high and low concentrations 100, 50, 20, 10 and 5 mg/L (High concentration) and 2, 1, 0.5 and 0.2 mg L⁻¹ (Low concentration).

2.2. Study area and sampling

The Zumbi dos Palmares settlement is in the municipalities of Campos dos Goytacazes and São Francisco do Itabapoana on the Northern Fluminense region (Fig. 1) in Brazil.

The Zumbi dos Palmares settlement is the result from the occupation of a large farm belonging to a single landholder and, organized by the Landless Rural Workers Movement (MST), in April of 1997. A federal decree transferred the property from its private owner to the federal government in October of 1997 and later transformed into a land reform settlement. The National Institute of Colonization and Land Reform (INCRA) partitioned the original landholding in 1998. The Zumbi dos Palmares settlement received a total 506 families that were distributed in five nuclei. The distribution of individual land plots occurred in mid-1998. Farmers immediately began to implement diversified agricultural systems, but with the predominance of monocultures of pineapple, cassava and sugarcane [13]. In recent years, sugarcane and pineapple have become the main source of these farmers' income. The increased use of chemical fertilizers and pesticides are related to the economic dependence on monocultures. Technical extension services to minimize the risks of human and environmental contamination are lacking [14].

At the Zumbi dos Palmares settlement, drinking water is available from shallow wells built near each household and from five artesian wells built by INCRA to meet collective demands, such as crop irrigation. Silva and Sacomani identified, as early as 2001, which most wells in the settlement, were not properly sealed and consequently, were vulnerable to contamination [8].

Water sampling was carried out in shallow wells that were built along paved and unpaved roads. Despite the fact that the Zumbi dos Palmares settlement was divided

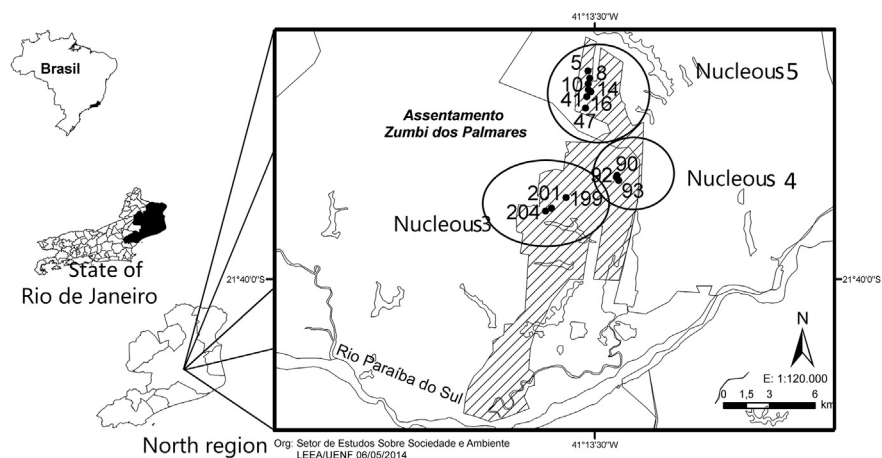


Fig. 1. Map of the Zumbi dos Palmares settlement, highlighting the nuclei and surveyed lots.

into five subdivisions a.k.a “núcleos”, samples were taken mainly from *nuclei* 3, 4 and 5 due to their higher agricultural activity (Fig. 1). Water samples were collected in four sampling series to include wet and dry periods in 2012 and 2013 (Table 1).

2.3. Solid-phase extraction (SPE) for pesticide analyses

To establish the best extraction conditions, we tested 3 types of elution solvents (methanol, acetonitrile and methanol/acetonitrile (1:1)). At first, cartridges were conditioned with 3 aliquots (2.5 mL) of each solvent, 10 mL of ultrapure water followed by 1 L of the sample or fortified ultrapure water were passed through the solid phase at 8 mL min⁻¹. The SPE was cleaned with 10 mL of ultrapure water and the pesticides were eluted with 3 aliquots (2.5 mL) of the same solvents used in conditioning step. The extract was carefully evaporated to dryness with argon, and 50 µL of internal standard were added and re-suspended to a final volume of 500 µL of the tested solvents. All analyses were done in triplicates. Samples were extracted 24 hours after being collected in the field.

2.4. GC-MS analysis of pesticides

Pesticides were analyzed in a Shimadzu GC-2010 system coupled to a Shimadzu GCMS-Q Plus mass spectrometer with an electron impact ion (EI) mode at 230 °C. The chromatographic separation was carried out in a capillary column (BPX5, SGE, USA, 30 m × 0.25 mm ID, 0.25 µm DF) and helium was used as the carrier gas. The temperature of the capillary column was set at 100 °C, which was increased to 280 °C at 15 °C/min and then to 300 °C at 6.5 °C/min. A sample volume of 1 µL was injected with a split ratio of 10. The analysis was also carried out in SIM (Selective Ion Monitoring) mode. For each pesticide, we used three significant ions for quantification: ametryn – 227, 212 and 68 m/z; atrazine – 200, 215 and 173 m/z; hexazinone – 171, 128 and 83 m/z; parathion methyl – 109, 125 and 263 m/z; captan – 77, 79 and 149 m/z; and Carbaryl – 115, 116 and 144 m/z. The mass spectrometer operated with electron energy of 70 eV. Two analytical curves were used to quantify the pesticides, one in aqueous phase and other in organic phase. After that, the samples were injected using the same parameters presenting better results studied in this work to evaluate the best recuperation of the compounds.

Table 1. Data of Campaigns along the years 2012 and 2013 and average rainfall.

Campaigns	Date	Average rainfall (mm)
I	(may/12); (sep/12)	0
II	(nov/12); (dec/12)	3.9 e 0
III	(july/13)	11.6
IV	(oct/13)	0

2.5. Physicochemical parameters analysis

The analyses of the parameters: conductivity, fecal and total coliforms, pH and turbidity were made on the same day samples were collected. Conductivity analyses used a conductivity meter (Bio Cristal, model: CA150) with constant of cell of $k = 1$. Turbidity used nephelometric methods though of a portable turbidimeter Chemetrix 1000 P. The pH analyses used a potentiometric method (Micronal mod. B374). Finally, the microbiological analysis used the multiple tube dilution technique according to section 9221 from Standard Methods [15].

Nitrate and nitrite concentrations were measured using an Ion Chromatography (Metrohm, 844 UV/VIS Compact IC) and the DOC (Dissolved Organic Carbon) was determined using (TOC 5000 Shimadzu). Samples were conserved with concentrated phosphoric acid and at low temperature. Analyses were carried out according standard analysis methods [15].

2.6. Statistical analyses

Principal Component Analysis (PCA), Factor Analysis and dendrogram was used to assess the correlation between the different parameters studied. The software program used was Statistica 7.0 from StarSoft Inc, USA. Means and standard deviations were calculated to provide additional data analysis.

3. Results

3.1. Physicochemical parameters and microbiology analyses

The results for each parameter used to assess water quality are presented in Fig. 2. Table 2 shows the parameters and their standard values recommended by current legislation and the average rainfall of the 5 days before each sampling (UENF/

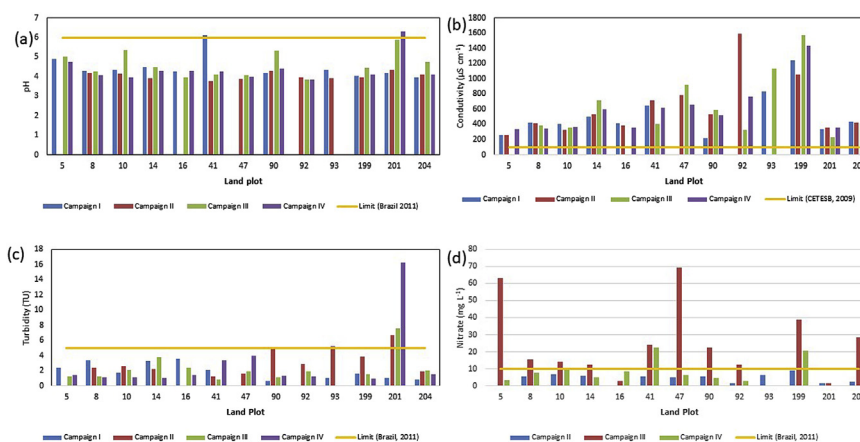


Fig. 2. Results for physical chemical parameters (a) pH; (b) conductivity; (c) Turbidity; (d) Nitrate.

Table 2. Maximum values allowed by Brazilian laws.

Parameter	Legislation	Maximum value allowed	Range (average)
Conductivity	CETESB/2009	100 $\mu\text{S cm}^{-1}$	222–1575 (584)
Turbidity	2914/2011 – MS	5 UT	0.67–16.20 (2.61)
pH	2914/2011 – MS	0 UFC	3.77–6.31 (4.38)
Fecal and total coliforms	2914/2011 – MS	0 UFC	0–2400 (62.2/249.3) ^a
Nitrate	2914/2011 – MS	10 mg L^{-1}	0.45–69.1 (13.0)
Nitrite	2914/2011 – MS	1 mg L^{-1}	0.001–0.01 (0.005)
DOC	CONAMA 357/2005 – IBAMA	3 mg L^{-1}	1.75–43.2 (8.46)

^a Average related to fecal and total coliforms, respectively.

Pesagro Meteorological Station). These results show for most samples, the values falling outside the limits established by the Ministry of Health Ordinance Number 2914 of 2011 [11].

In the case of pH, the values are predominantly low, indicating the predominance of water with acidic characteristics. Acidic water has a strong influence on ecosystems and groundwater, since it increases the solubility of toxic metals and nutrients. The acidic water's corrosive behavior limits its overall use [16].

Conductivity is the measurement of the water's capacity to conduct electric current. It is a good indicator of the amount of salts in the water column [17]. According to São Paulo State Basic Sanitation Technology and Pollution Control Agency (CETESB), conductivity values greater than $100 \mu\text{S cm}^{-1}$ indicate an impacted environment or waters with corrosive properties [17]. Another factor influencing the conductivity is the mineral composition of soils, recharge rates, or even, saline intrusion. Most of our conductivity results are above CETESB's limit value. Consequently, sampled wells can be classified as being of medium to high salinity [18, 19] (Fig. 2). Similar results were found in shallow wells in Africa [20, 21]. High water conductivity may be also related to soil characteristics. The settlement contains area of past marine transgression [22]. Nuclei 3 and 4 presented the highest conductivity values for land plot 199. In the third sampling, plot 92 presented a considerable increase in conductivity, coinciding with a rainy period (Table 1). In addition, high salt concentrations were also observed in land plots 93 and 199. This was not an expected result. Usually the salinity of wells increases, as recharge decreases [19]. But since these were very shallow wells, ion leaching from the surface might have had an immediate effect on conductivity values.

With respect to turbidity (Fig. 2c), the values were found below the limit recommended by Ordinance no. 2914/2011 - 5 TU (turbidity unit). Plot 201 was the exception,

exhibiting high values. Interestingly, this was the only sample collected from a deep well drilled by INCRA to supply several farms with water. The presence of suspended material may be associated with the inorganic matter from a well drilling. Usually, water turbidity indicates the presence of particulate matter in suspension or the presence of microorganisms. In this case, we observed the presence of inorganic particles (sand, silt, clay). Microbiological results showed that there were also no microorganisms.

Nitrate concentration samples presented high values mostly in the third sampling, in a pattern distinct from the others: maximum of 69.1 mg L^{-1} as nitrate, two of which exceeded the limit of Ordinance 2914/2011 (Fig. 2d). The World Health Organization (WHO) establishes a limit of 50 mg L^{-1} of NO_3^- for drinking water [23].

The most common sources of nitrate in groundwater are septic tanks and agricultural fertilizers. Contamination is probably related to the leaching of soil fertilizers once the highest concentration was found in periods of rainfall. As it will be show below, samples also showed the presence of coliforms. High concentrations of nitrate in well water occur in association with health problems, in particular for children [24, 25]. Walton [26] describes reports of 278 cases of methaemoglobinaemia in children in the United States. Bourchard et al. [27] reported high concentrations of nitrate associated with increased incidence of congenital malformations, in Canadian and Australian studies. Rheinheimer et al [28] showed results obtained from groundwater in the Brazilian state of Rio Grande do Sul, had higher concentrations of nitrate, but none exceeding 22 mg L^{-1} of NO_3^- (5 mg L^{-1} of N-NO_3^-). Higher values of nitrate found in shallow wells of Paraná state had maximum of 40.22 mg L^{-1} of NO_3^- [29].

Dissolved Organic Carbon (DOC) presented values higher in the samples mainly from the third sampling period, marked by the occurrence of rains (Table 2). In this period there was an increase in the concentration of organic and particulate matter carried to the groundwater [2].

The increase in the consumption of synthetic fertilizers and pesticides was expected to lead to the increase in the concentration of nitrate in soils and, consequently, also to greater transport to superficial and subterranean aquatic bodies [30, 31].

While coliform bacteria are indicators of fecal contamination and the presence of other pathogenic organisms, their presence can pose risk of infectious diseases dissemination [32]. In both Brazilian and other international regulations, the result of any test detecting the presence of these microorganisms must be negative, especially when water is used for drinking water [33, 34]. According to Stukel [25], the poor conservation of wells can cause microbiological contamination. Most farms at the Zumbi dos Palmares settlement have wells close to livestock and poultry. Most surveyed wells showed positive results for the presence of fecal and total coliforms,

which may have been contaminated by septic tanks and domestic animals raised in the vicinity of the wells (Fig. 3).

3.2. Statistical assessment of results

The results show a statistical relationship between electrical conductivity and nitrate concentration using the Pearson correlation coefficient (Fig. 4a). Similar correlation results were observed by Rulkens et al [35] and Vervoort et al [36]. These authors observed an increase in nitrate concentrations and electrical conductivity when water sources are close to areas of intense application of agrochemicals.

We also observed an inverse correlation between turbidity and DOC (Fig. 4a). Turbidity is associated with the degree of attenuation in the intensity in which a light beam is absorbed or scattered in a water column. Thus, turbidity is usually associated with the presence of suspended solids, organic matter and, in some cases, microbiological contamination of aquatic ecosystems [17]. However, the inverse correlation between these two variables shows that the turbidity is related to the presence of suspended particles of inorganic origin (i.e., sand, silt, clay), which could have resulted from the type of well construction and lack of impermeabilization of its side walls [17, 21].

Fig. 4b shows the direct relation of fecal and total coliform, pH and turbidity. It is possible to observe that pH is strongly correlated to turbidity, and an increase in

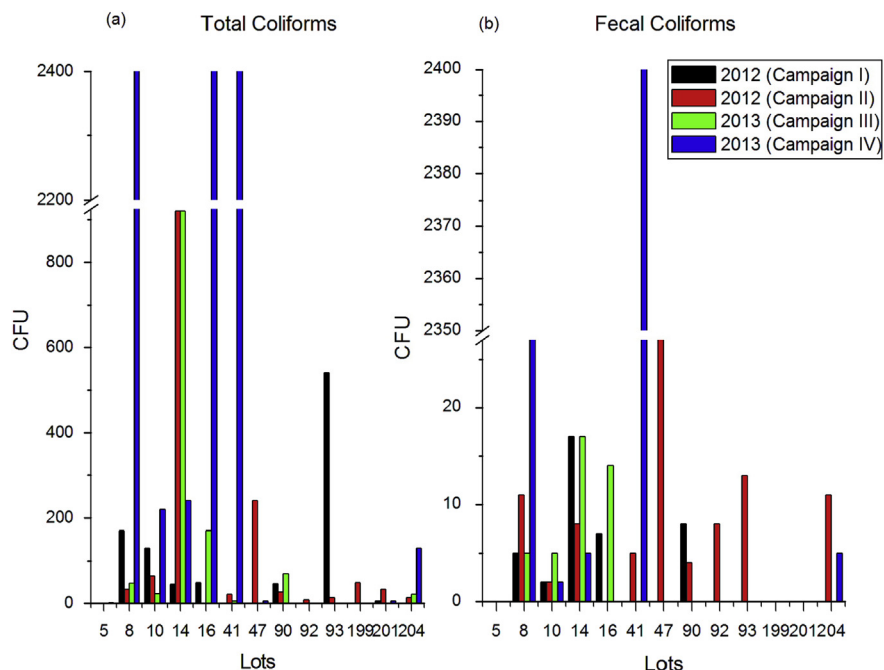


Fig. 3. Results for fecal coliforms – (a) Total Coliforms; (b) Fecal coliforms.

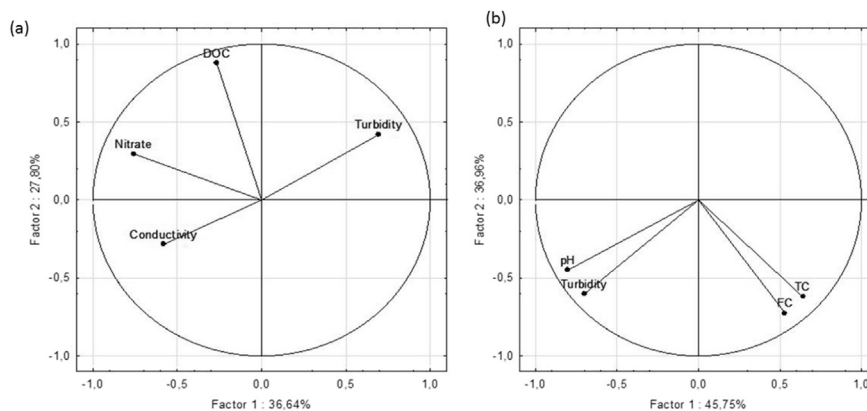


Fig. 4. Pearson Correlation — (a) Correlation between physicochemical analysis; (b) Correlation between pH, turbidity and fecal (FC) and total coliforms (TC).

turbidity (inorganic particles) causes an increase in pH values. The inverse is evident in land plot 201, where a deep well collects water from below the rock layer which protects the water table from infiltration and contamination [37]. As a result, the well in plot 201 has low conductivity and is less susceptible to anthropogenic sources of contamination. This also explains the negative correlation between turbidity and the presence of coliforms.

Fig. 5 shows a dendrogram where the Euclidean distances among the variables are represented, more specifically, the relationship between nitrate and conductivity. The proximity between these two variables is probably caused by contamination from anthropic sources. The increase of nitrate concentration causes the increase of the conductivity. The distancing of the variable turbidity is related to the groundwater depth which is more protected from human interferences.

3.3. Pesticide analyses

3.3.1. Validation procedure

Table 3 shows the limits of detection, quantification and regression data of the analytical curves in the organic and aqueous phases. Correlation coefficients above 0.999 indicate a good analytical curve quality [38, 39]. The values obtained for each pesticide parameter showed that the method presented a good adjustment of the data for the regression line. The LD and LQ range obtained was 25–500 ng L⁻¹ and 50–1,000 ng L⁻¹.

The solvent that presented the best result for extraction of pesticides from SPE was acetonitrile (Fig. 6) which was used in the recovery test and in the samples. The concentration used in the recovery test was 100 µg L⁻¹ for all pesticides.

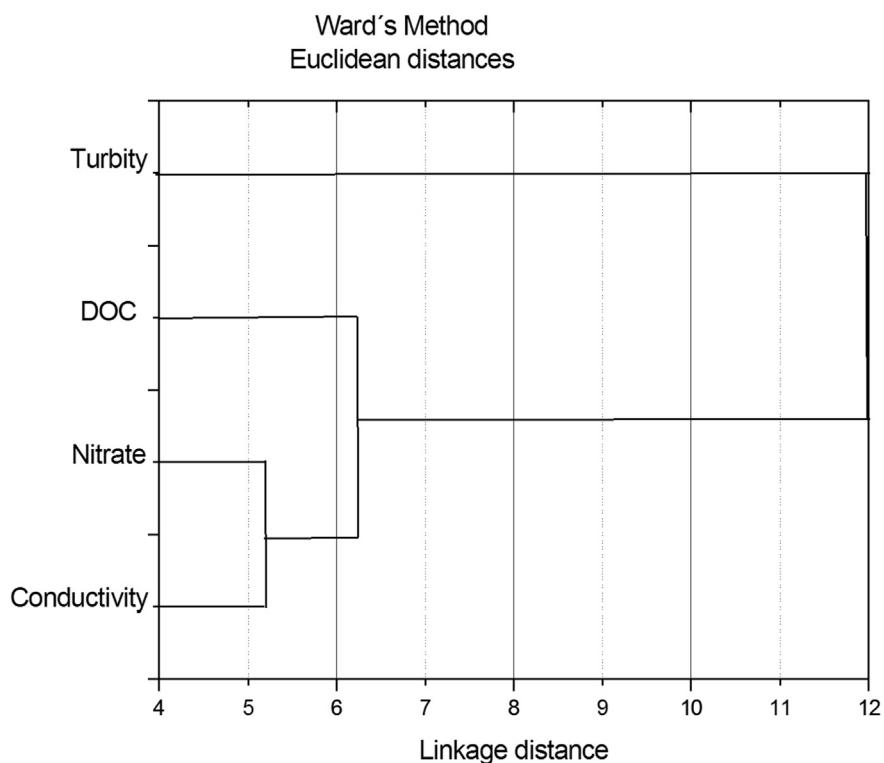


Fig. 5. Dendrogram for the studied variables.

Recovery tests for captan (70%) are not presented in Fig. 5 because this pesticide was added later to the study. The acceptable recovery rates for pesticides residues range from 70 to 120% [40]. The recovery rates for the pesticides in this study ranged from 70 to 101%.

3.3.2. Pesticides analysis in shallow well water

Atrazine, carbaryl, hexazinone, methyl parathion and ametryn were found in our samples. Pesticides quantification was carried out using the analytical curves of

Table 3. Regression equations and limits of detection and quantification.

Pesticides	LD*/LQ** ng L ⁻¹	Regression equation (AP)	R (AP)	Regression equation (OP)	R (OP)
Atrazine	25/50	$Y = 3.3912x - 4.9028$	0.9956	$Y = 3.2339x + 26.982$	0.9949
Ametryn	100/250	$Y = 2.886x - 47.04$	0.9885	$Y = 4.4515x + 6.3628$	0.9958
Captana	500/1,000	$Y = 3.428x - 27.284$	0.9962	$Y = 4.8409x - 11,127$	0.9968
Carbaryl	25/50	$Y = 4.5999x - 56.007$	0.9907	$Y = 3.0252x - 39.063$	0.9160
Hexazinone	25/50	$Y = 4.5571x - 4.9028$	0.9973	$Y = 8.9735x - 7.6665$	0.9971
Methyl parathion	250/500	$Y = 4.5818x - 33.551$	0.9958	$Y = 4.6633x - 24.26$	0.9989

*LD – Limit of detection; **LQ – Limit of Quantification; AP – Aqueous Phase; OP – Organic Phase.

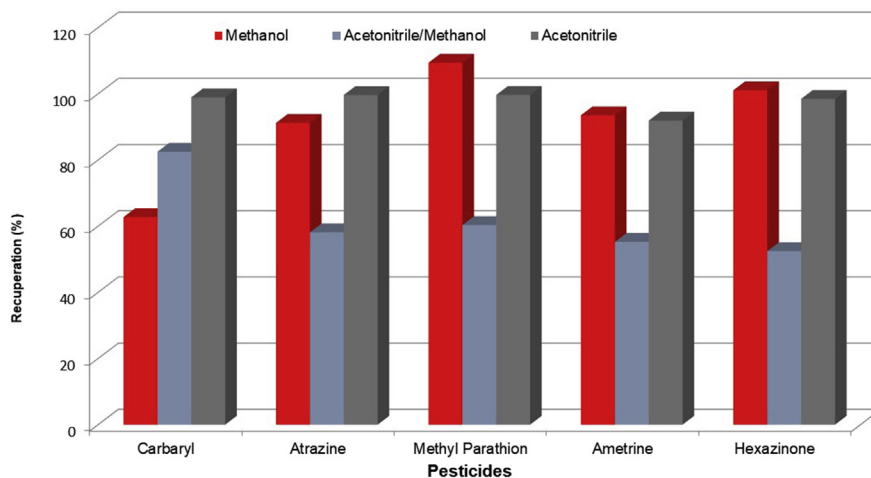


Fig. 6. Recovery test of pesticides for solvent selection.

the organic and aqueous phase standards. The concentrations of pesticides are presented in Table 4. Pesticides were absent in all samples collected in the second sampling. This result is probably associated to an extensive dry season that occurred before water was collected. To increase the detection of small quantities, the samples from sampling 3 and 4 were concentrated to 100 μL , while in the previous sampling samples were concentrated to 500 μL to allow the identification of pesticides not previously detected.

Table 4. Results for the presence and quantification of atrazine, carbaryl, hexazinone and methyl parathion.

Lots	Atrazine ($\mu\text{g L}^{-1}$)	Carbaryl ($\mu\text{g L}^{-1}$)	Hexazinone ($\mu\text{g L}^{-1}$)	Methyl parathion ($\mu\text{g L}^{-1}$)
5	<50*	Nd	<50**	(0.4)* and (1.176)**
8	<50*	<50**	<50*	nd
10	<50* and <50**	Nd	<50*	nd
14	(0.112)*	<50**	<50*	<50*
16	<50* and (0.07)**	Nd	<50*	nd
41	<50* and <50**	Nd	<50*	nd
10	nd	nd	nd	2.00
92	0.400	0.390	0.186	0.442
199	0.435	0.473	0.177	0.590
201	0.389	0.361	0.140	0.547
204	0.470	0.390	nd	0.733
Superficial water	<50**	Nd	0.302	nd

*1^a Campaign; ** 3^a Campaign; nd – Not detected; < 50 – below the detection limit (50 ng L^{-1}).

Regarding the pesticides found in our samples, the Brazilian Ordinance 2914-MS only establishes a limit for atrazine ($2 \mu\text{g L}^{-1}$). The concentrations found for atrazine are within the established limits [7]. However, compared to the limits found in legislation from other parts of the world, such as from the European Union [34], these samples have concentrations that exceed the acceptable limits. The European regulation accepts a maximum of $0.1 \mu\text{g L}^{-1}$ for a specific pesticide and $0.5 \mu\text{g L}^{-1}$ for the total concentration of pesticides. Methyl parathion alone was found to have $1.18 \mu\text{g L}^{-1}$ in a single sample from the third sampling.

Atrazine was found in plots 14, 16, 92, 199 and 201. Its presence is believed to have negative effects on human health due to the fact this compound can act as an endocrine disruptor and, for that reason it should not be present in the drinking water [41]. Another pesticide found in land plots 92, 199 and 201 was carbaryl, which rapidly degrades to α -naphthol when released into the environment. The problem is the resulting metabolite is more dangerously toxic than carbaryl's original active ingredient [42, 43].

4. Conclusions

The results from our analyses of shallow wells at the Zumbi dos Palmares settlement showed that several samples had values beyond the limits stipulated by the Brazilian legislation regulating the quality of water used for drinking water. In addition, we also observed significant relationships among different variables pointing to a process of water contamination caused by manmade sources. In the specific case of fecal coliforms, many water samples reached the maximum limit of quantification (2,400 CFU). This finding is important since fecal coliforms are often associated to the presence of other pathogens harmful to human health.

Nitrate also presented high values during rainy periods, a result probably associated with the leaching of fertilizers from soils surrounding wells. The results from pesticide analyses also indicate that drinking water at the Zumbi dos Palmares is being impacted by a predominance of agricultural activities. In spite of that, the two of the pesticides found in our samples had concentrations that were within the limits established by Brazilian laws. A comparison to the European legislation levels, these pesticides exceeded the accepted maximum values. This result is important because it shows the need for improvement in Brazilian law regulating the acceptable limits of exposure to pesticides present in drinking water.

In summary, we suggested that water quality assessment in rural areas of developing countries must move beyond the traditional concern with biological contamination. It must also include other variables such as fertilizers and pesticides.

Declarations

Author contribution statement

Thayana Paranhos Portal: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Wrote the paper.

Marcos Antonio Pedlowski, Maria C. Canela: Conceived and designed the experiments; Contributed reagents, materials, analysis tools or data and interpreted the data; Wrote the paper.

Cibele M. S. de Almeida: Analyzed and interpreted the data; Wrote the paper.

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Competing interest statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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