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PAPER

The impact of point source pollution on shallow groundwater used for human consumption in a threshold country†

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Many developing and threshold countries rely on shallow groundwater wells for their water supply whilst pit latrines are used for sanitation. We employed a unified strategy involving satellite images and environmental monitoring of 16 physico-chemical and microbiological water quality parameters to identify significant land uses that can lead to unacceptable deterioration of source water, in a region with a subtropical climate and seasonally restricted torrential rainfall in Northern Argentina. Agricultural and non-agricultural sources of nitrate were illustrated in satellite images and used to assess the organic load discharged. The estimated human organic load per year was 28.5 BOD_5 tons and the N load was 7.5 tons, while for poultry farms it was 9940-BOD_5 tons and 1037-N tons, respectively. Concentrations of nitrates and organics were significantly different between seasons in well water (*p* values of 0.026 and 0.039, respectively). The onset of the wet season had an extraordinarily negative impact on well water due in part to the high permeability of soils made up of fine gravels and coarse sand. Discriminant analysis showed that land uses had a pronounced seasonal influence on nitrates and introduced additional microbial contamination, causing nitrification and denitrification in shallow groundwater. P-well was highly impacted by a poultry farm while S-well was affected by anthropogenic pollution and background load, as revealed by Principal Component Analysis. The application of microbial source tracking techniques is recommended to corroborate local sources of human *versus* animal origin.

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Environmental impact

Sources of contamination including poultry farms and animal rearing without waste treatment, inadequate/scattered solid waste disposal, wastewater effluents, and settlements without sewer systems were identified in a peri-rural area in Salta, Argentina. A unified strategy involving satellite images and environmental monitoring was used to evaluate the pollution in the environment. The land use activities represent a high contamination risk for shallow groundwater and for the whole environment since the water tables are not deep and the soils are highly permeable. The location of farming activities close to waterways represents a high risk for drinking water supplies in Northern Argentina and other countries with similar geologic and climatic zones. Interventions are needed to improve water quality and thereby decrease the morbidity rate of diseases attributable to environmental causes.

Introduction

Worldwide, increasing anthropogenic activities put pressure on natural resources, thus exacerbating the likelihood of disease and other public health risks. In addition to the increased water demand by a growing population, agriculture, animal, and manufacturing activities also contribute to the pollution of surface water and groundwater.[1] The United Nations (UN) has recognized access to clean water and sanitation as a fundamental human right, based on the concern that 884 million people live without access to safe drinking water and more than 2.6 billion lack access to basic sanitation.[2] This deficiency explains why each year 1.5 million children under the age of five die as a result of water- and sanitation-related diseases.[1,3] For example, in Latin America the increasing urban population and rapid urbanization associated with unplanned urban centers and peri-urban settlements have exceeded the government's ability to expand the infrastructure related to sanitization and supply of potable water,[4–6] limiting available options to provide adequate access to good-quality water. Moreover the urban–rural gap related to drinking water supply is larger in developing countries, where in rural areas eight out of ten people are still without access to an improved drinking water source.[1]

In many developing and threshold countries, the water from shallow wells is used directly without treatment or after insufficient treatment in both peri-urban and rural communities.[7–9] Furthermore, in these settlements on-site sanitation, usually pit latrines and/or septic tanks, is the typical treatment for human excreta, representing an obvious source of fecal contamination in water supplies.[10] Microbiological contamination of shallow well water used for human consumption could also be due to inadequate management of waste generated by agricultural practices, livestock, poultry farms, and manufacturing. The main route of exposure for infectious diarrhea is oral–fecal. Parasites, bacteria and viruses have long been recognized to be the principal agents responsible for causing persistent diarrhea.[11]

These intensive land uses can also lead to chemical contamination by the introduction of different chemical substances to the environment such as pharmaceuticals (including hormones, aspirin, ibuprofen, and antibiotics), fertilizers, and pesticides. It is well known that intensive agriculture, unsewered sanitation and nitrogenous fertilizers in cropping systems contribute nitrates to groundwater. The exposure to high nitrate levels in drinking water may cause several health hazards in humans and animals.[12] Soil characteristics such as porosity play a crucial role in the fate of contaminants and influence whether they reach an aquifer of surface receiving water. Therefore, the water quality of shallow groundwater wells is a result of combined factors, all of which can influence the mechanism by which pathogenic microorganisms and chemical pollutants enter the water.[7]

Like many other cities in Latin America, the city of Salta, located in the northwest of Argentina, has undergone rapid growth in the last few decades. The population expanded to occupy semi-rural areas where water and sanitation are not available. The water supply in these areas relies on the use of shallow wells as a source of domestic water and pit latrines are employed for sanitation. The water is used for many purposes: domestic in the poorest areas (drinking, hygiene, cooking, watering plants, and vegetables that are grown for self-consumption, animals, *etc.*), recreational with children as the main users, and livestock maintenance.

The objectives of this study were (i) to determine the effect of agricultural and/or human fecal pollution on the quality of source water in a semi-rural area; (ii) to link specific land uses and location of wells to the quality of shallow groundwater; and (iii) to evaluate the importance of key parameters such as seasonal rainfall and soil characteristics on water quality. Monitoring campaigns were conducted over a full one-year period on water sources of different origins within a semi-rural area of Salta. Multivariate data analysis was applied to identify the most important parameters affected by anthropogenic or natural pollution.[13]

Materials and methods

Description of the study region

The Lerma Valley is located in the northwest of Argentina. It is an intramontane graben (basin), situated within the eastern mountain chains of the Andes in the province of Salta. Geographically it is between the latitudes 24° 22′ and 25° 43′ S and the longitudes 65° 15′ and 65° 48′ W. The area of study is 2038.5 ha, approximately 10 km away from the capital city of Salta (Fig. 1). The study area was selected as part of the recharge zone of the catchment with increasing anthropogenic activities that are putting public health at risk.[14]

According to Köppen classification, the climate subtype is Cwb (humid with warm summers and dry winters). The climate is characterized by hot summers with temperatures of up to 40 °C; winters are dry and temperatures are rarely below zero. This subtropical climate has a marked seasonal variation. It is characterized by a mean annual precipitation of between 600 and 1200 mm, mostly restricted to the rainy season.[15] Around 80% of torrential rains are concentrated from December to March (Fig. S1†). This fact presents a limitation for the availability of water from surface sources. The soils are incipient, A–C profile, coarse texture, overly drained, and filled with inhomogeneous quaternary sediments. The depth of the groundwater table decreases in an easterly direction. The Arenales River runs through the study area, where the main uses of the river are as a water source for a drinking water plant, agricultural irrigation, and livestock maintenance. After that, the river crosses Salta city and continues to discharge in Cabra Corral dam, which provides water for hydroelectric energy and other uses (irrigation, recreation) to downstream locations. The poor water quality of the river and an associated channel were reported previously, together with high incidence rates of diarrhea in the area.[14] As the tap water provided by the treatment plant is intermittent during the day (for just a few hours), people usually also use groundwater from shallow wells of less than 10 m depth. There is no sewerage in the area; septic tanks and pit latrines are the only method of sanitation, often located up-gradient from the shallow wells. One third of the total population of 4500 inhabitants is rural and is heterogeneously distributed around the whole region.

Identification of sources of contamination and estimation of load

Point sources of contamination were identified using a Global Positioning System (GPS). Non-agricultural sources such as the waste disposal network, animal wastes (including livestock and

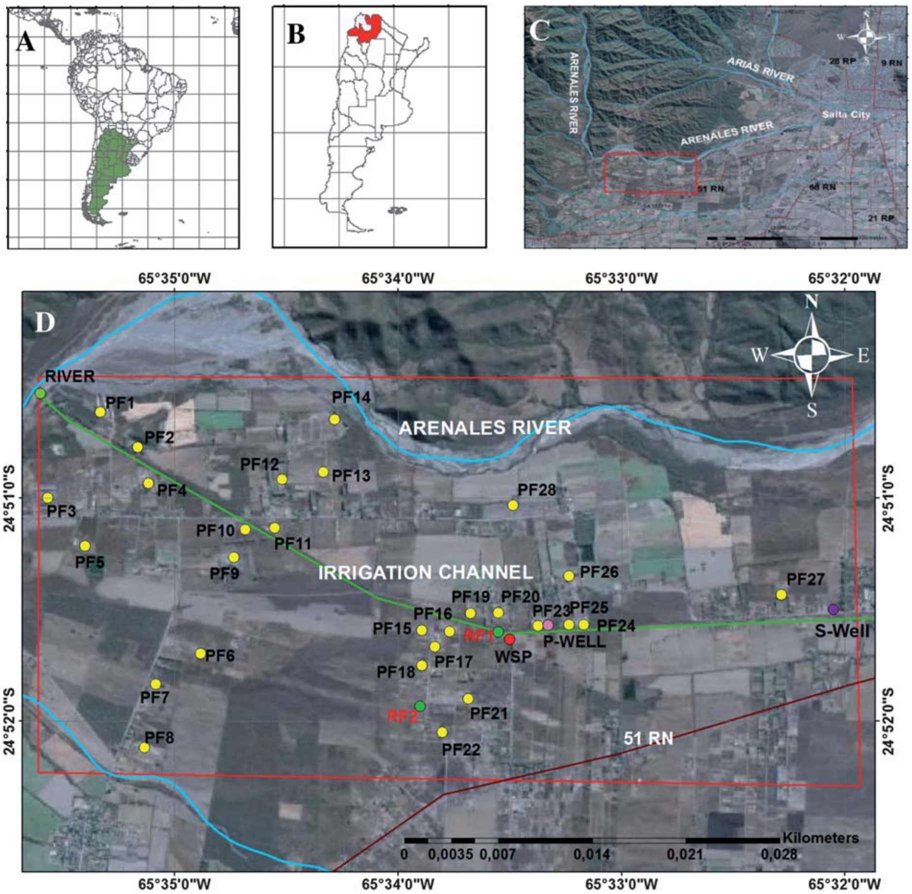

Fig. 1 Geographical location of the study area: (A) Argentina in South America, (B) Salta Province in Argentina, (C) Study area in Salta and (D) location of the poultry farms (PF) and shallow wells studied (RN: National Road; WSP: Wastewater Stabilization Pond; RF: Rearing Farming [swine]).

human excreta), and river–aquifer interactions are considered important factors that indirectly enrich nitrates in groundwater.[16]

Within the study area, sites that were considered as pollution sources were poultry farms and animal rearing without waste treatment, inadequate/scattered solid waste disposal, wastewater effluents, and settlements without sewer systems (human excreta). This information was illustrated in satellite images and used to evaluate the organic and nutrient loads discharged into the environment. The organic load discharge for poultry farms was estimated following standard tables suggested by the World Health Organization[17] and U.S. Department of Agriculture[18] as 4.6 kg BOD_5 per hen per year, and for domestic effluent of people not connected to a sewer system as 6.9 kg BOD_5 per person per year. We estimated 0.41 kg N per hen per year and 3.3 kg N per person per year as the nutrient loads for poultry farms and human waste, respectively, according to standard tables.[18] Data from the National Population Census served to estimate the number of inhabitants in the study area. The number of birds was estimated based on satellite images and field observations to calculate the area covered by farms and considering a density of ten birds per m^2 (personal communication from producers).

Study sites and sampling scheme

Two wells were selected for this study, one from a private home (called P-well) located immediately downstream of a poultry farm (and hence impacted by farm waste disposal practices), and the other from the school of the area (called S-well), where children spend the day and have breakfast and lunch. The distance between the two wells is 2120 m and both are used for drinking water. The septic tank of the school is 10 m upstream from the shallow well used as a supply of potable water. For comparison, additional samples were analyzed from the Arenales River as it enters the area of study (just before water is diverted to the irrigation channel and before it receives the impact of all the agricultural activities). Hence it was possible to use the river as the water quality reference, since it provides the main recharge water of the shallow aquifer and residence time is short. Thus, a total of three sites (the two wells and one site at the river) were sampled monthly for an entire year, from March 2008 to February 2009 (36 samples in total). As the wells are less than 10 m in depth, they reach their lowest levels at the end of the dry season (October–November).

Physical and chemical analysis

Physico-chemical parameters such as temperature, pH, conductivity, salinity, turbidity, and dissolved oxygen were measured *in situ* using a U-10 Horiba multiparametric probe. Pre-cleaned (with distilled water) plastic 5 L bottles, rinsed three times with the water to be studied, were used to collect the water samples for physical and chemical analysis. Well-water samples were taken directly from the well without pumping, using a bottle fitted with a weight at the base, carefully avoiding the contamination of samples by any surface scum.[19] The samples were kept in ice-cold containers and transported to the laboratory within 2 h for further processing. Suspended, dissolved, and total solids, nitrates, ammonium, carbonates, bicarbonates, hardness (as calcium carbonate), magnesium, calcium, and absorbance at 254 nm were determined in the laboratory to complete the physicochemical characterization. The Abs_{254} was used as an indicator of the aggregate concentration of UV-absorbing natural organic matter (NOM), using humic acid (Fluka) as a surrogate to obtain a standard curve. All the measurements were performed following Standard Methods described by APHA.[19]

Microbiological analysis

The microbiological quality of water was assessed by the determination of Total and Thermotolerant Coliforms (TC and TTC, respectively) as indicator bacteria, according to the National Water Legislation that follows the WHO *Guidelines for Drinking Water Quality*.[20]

Water samples of 100 mL were grabbed aseptically, using sterile plastic containers. Collected samples were kept refrigerated in the dark and analyzed within 4 h. TC and TTC were estimated using the Most Probable Number (MPN) method described in Standard Methods[19] by cultivation in MacConkey broth at 37 °C for 48 h and 44 °C for 24 h, respectively. Enumerations were expressed as MPN per 100 mL.

Statistical analysis

Data manipulation, merging of datasets and statistical analyses were performed using SPSS version 17.0.0 software (SPSS Inc., USA, 2008). A box–whisker diagram was used to present seasonal variation of ionic constituents, physico-chemical and microbiological parameters from river and well water samples. Data analysis was carried out using non-parametric tests, since the data were not normally distributed ($p < 0.001$). Goodness-of-fit to normal distribution was tested for all water quality data using the Shapiro–Wilks W-test applying the statistical package InfoStat version 2010.[21] The Kruskal–Wallis test was used to determine the seasonal variations in certain parameters from all monitoring sites. The Spearman rank correlation coefficient (r) was calculated to compare parameters and determine their degree of association. This approach is commonly applied in environmental monitoring studies and shows no loss of power compared to parametric tests.[22]

In addition, multivariate statistical analysis was applied to assess the water quality variations to investigate and identify the impact of potential pollution sources in the three sampling sites. The chemometric evaluation was performed by two techniques: Principal Component Analysis (PCA) and Discriminant Analysis (DA) with InfoStat software.[21]

Results and discussion

Land use description and estimation of contamination

There are several known point sources and diffuse sources of pollution in the area; most of them contribute to both organic and NO_3^- contamination of surface water and groundwater. Poultry farming is an important economic activity within the rural community, and the total poultry farm density in this region is higher than in the rest of the province.[25] Twenty-eight poultry farms were recorded scattered throughout the study area (Fig. 1) and none of them had waste treatment. Typically, animal excreta are either deposited directly onto the soil (open dumping) or dumped into the river. This practice adds a potential source of nitrates to groundwater in the area. Our calculations suggest that the total poultry population would produce a considerable amount of organic material (9940 BOD_5 tons per year) and nitrogen (1037 N tons per year). Also, 46% (13 in total) of the poultry farms are located beside the irrigation channel, representing a high potential source of contamination of surface water.

The estimated human organic load was 28.5 BOD_5 tons per year and the N load was 7.5 tons per year. The onsite sanitation systems constitute a potential hazard to the environment, particularly to the soil and the groundwater, depending on their design and maintenance. Fecal matter tends to accumulate in a specific location and precipitation facilitates the dispersion of the contaminants (microorganisms and nitrogen). The solid waste is subjected to anaerobic decomposition while the liquids tend to infiltrate into the soil thereby reaching the water.[26,27]

Taken together, land use activities represent a high contamination risk for shallow groundwater and surface water because the water table ranged from less than 2 to 7 m in the wet and dry seasons, respectively. In addition, this area belongs to the recharge zone of one of the most important aquifers that supplies water to the capital city. Sediments are formed by fine gravel and coarse sands, resulting in a high permeability zone. According to Foster and Hirata[28] the vulnerability of this area is extremely high.

Surface and shallow groundwater quality

Sixteen physico-chemical and microbiological parameters were measured for a total of 36 water samples and compiled as surface water (12 samples) and groundwater (24 samples, including the S-well and P-well) (Table S1†). Each dataset was also divided into wet season (November to March) and dry season (April to October) to determine any seasonal variations in water quality parameters (Fig. S1†). As expected, the temperature of the river was strongly affected by ambient temperature with mean temperatures of 17.4 °C (±2.8) in the wet and 12.5 °C (±2.9) in the dry season. Groundwater temperatures were stable at 19.5 °C (±1.9) and 18.6 °C (±0.6) in the wet and dry seasons, respectively. The Kruskal–Wallis test revealed statistically significant differences ($p < 0.05$) for most of the parameters determined – with the exception of ammonium and total coliforms – between river and well water.

Both types of water – groundwater from shallow wells and surface water from the river, which provides water to recharge the aquifer – were classified according to a Piper diagram as calcium–magnesium–bicarbonate (results not shown). For all of these minerals, groundwater contained higher concentrations than did surface water (Table S1†). This was probably due to the dissolution of those minerals from the soil during the infiltration even though the residence time in the water table is short. The high concentrations of these ionic species together with higher concentrations of nitrates in the wells also resulted in higher conductivities (Fig. 4a and b). In fact, the Spearman coefficients showed that there was a strong correlation between them and with conductivity, concentration of dissolved oxygen and total and dissolved solids, and in some cases with turbidity and temperature (Table 1). The maximum permissible conductivity for drinking water established by WHO[20] is 1400 μS cm^{-1}, a limit that was not reached by any of the samples analyzed in this study (100–1000 μS cm^{-1}).

Seasonal influences on water quality

Natural levels of EC found in surface water were lower than 230 μS cm^{-1} and elevated values generally represent anthropogenic influences. Average EC increased during the dry season in surface water due to the river's low flow during this time, which led to an increase in concentration of dissolved salts. Conversely, in shallow groundwaters the EC increased in the wet season. In this case the non-mineralized recharge waters could not dilute ionic species, due to the fact that rainfall produced runoff with transport of animal excreta and removal of human excreta from pit-latrines. This was confirmed since concentrations of calcium, magnesium and acid carbonate did not differ significantly between seasons in well water. In contrast, nitrates and organic material (Abs_{254}) did show significant differences (P values of 0.026 and 0.039, respectively) according to the Kruskal–Wallis test.

The Kruskal–Wallis test revealed statistically significant seasonal variations of pH, conductivity (EC), dissolved oxygen (DO), temperature, total solids (TS), total dissolved solids (TDS), nitrates, and NOM for shallow well water and also for EC, turbidity, temperature, TS, suspended solids (SS), calcium, acid bicarbonate, and thermotolerant coliforms (TTC) for the river samples (Table S1†).

Interestingly, only EC, temperature and TS varied significantly between seasons for both groundwater and surface water. Nonetheless median concentrations during the wet season tended to increase for all measured parameters. Lack of statistically significant differences, *e.g.*, for TC and TTC, between seasons can be attributed to the great variability of measurements in wells (Fig. 3). The levels of TC found in groundwater were all in excess of the Argentinean guideline of <3 MPN per 100 mL.[29] TC constitute a serious risk to consumers of shallow groundwater or untreated surface water. Water quality in rural areas is frequently poorly maintained in both developing/threshold and industrialized nations that depend on private water supplies for their drinking water.

In rural areas, high nitrate levels are usually correlated with livestock production and agricultural activities such as fertilizing.[30] The NO_3^- concentration in the shallow groundwater was higher during the rainy season. Kim *et al.* (2009) reported that nitrate-contaminated alluvial groundwater underneath the agricultural area was enriched with calcium ion,[31] which was also verified in this study (Table S1†). The increase in total hardness, mainly due to Ca^{2+}, in shallow well water can be explained by the weathering of the rocks by water, the dissolution of chemical fertilizers used in crops,[32] and nitrification of reduced nitrogen from manure.[31] Nitrification was suspected due to the correlation observed between calcium and nitrate values and a decreasing pH (Table S1†). During this process protons (H^+) are released along with NO_3^-, which enhances the dissolution of minerals resulting in higher calcium ion concentrations.[31]

Argentinean legislation establishes a range of pH from 6.5 to 8.5 as a permitted level for drinking water.[29] Although no health-based guideline pH value was proposed by WHO since it usually has no direct impact on consumers, it is one of the most important operational water quality parameters. The pH of groundwater (Table S1†) was considerably different from that of the river, which did not have a seasonal impact. Conversely, the pH in shallow groundwater was significantly impacted by season ($p = 0.018$). During the wet season it decreased and only 33% of the samples were below the national guideline.

The local guideline for turbidity is 3 NTU,[29] while 5 NTU is permitted by WHO.[20] This parameter showed great variability in the river and concentrations were much higher during the wet

Table 1 Correlation matrix among the physico-chemical (pH, EC, Turb, DO, Temp, TS, TDS, SS, NH_4^+, NO_3^-, Ca^{2+}, Mg^{2+}, HCO_3^-, and Abs_{254}) and microbial (TC and TTC) parameters of shallow groundwater ($n = 24$). Spearman's rank correlation coefficient (below the main diagonal) and probability (up the main diagonal)

	pH	EC	Turb	DO	Temp	TS	TDS	SS	NH_4^+	NO_3^-	Ca^{2+}	Mg^{2+}	HCO_3^-	TC	TTC	Abs_{254}
pH	—	0.398	0.048	0.010	0.916	0.995	0.767	0.166	0.410	0.677	0.455	0.642	0.538	0.033	0.020	0.863
EC	−0.181	—	0.154	0.000	0.001	0.000	0.000	0.778	0.113	0.000	0.000	0.002	0.000	0.145	0.242	0.128
Turb	**0.408**^{a}	0.300	—	0.951	0.498	0.082	0.035	0.838	0.044	0.017	0.103	0.006	0.143	0.505	0.825	0.136
DO	**0.516**^{b}	**−0.792**^{b}	0.013	—	0.130	0.002	0.006	0.369	0.078	0.032	0.000	0.003	0.000	0.028	0.108	0.370
Temp	−0.023	**0.653**^{b}	0.145	−0.318	—	0.000	0.000	0.345	0.917	0.002	0.002	0.281	0.088	0.553	0.970	0.596
TS	−0.001	**0.932**^{b}	0.362	**−0.608**^{b}	**0.669**^{b}	—	0.000	0.661	0.154	0.000	0.000	0.004	0.002	0.161	0.269	0.033
TDS	0.064	**0.903**^{b}	**0.433**^{a}	**−0.548**^{b}	**0.708**^{b}	**0.951**^{b}	—	0.664	0.272	0.000	0.000	0.010	0.003	0.307	0.436	0.015
SS	−0.292	0.061	−0.044	−0.192	−0.202	0.094	−0.093	—	0.062	0.958	0.858	0.376	0.756	0.729	0.834	0.878
NH_4^+	0.176	0.332	**0.414**^{a}	−0.367	0.022	0.300	0.234	0.386	—	0.294	0.162	0.000	0.095	0.910	0.394	0.713
NO_3^-	0.090	**0.811**^{b}	**0.481**^{a}	**−0.438**^{a}	**0.606**^{b}	**0.905**^{b}	**0.938**^{b}	−0.011	0.223	—	0.000	0.024	0.048	0.649	0.715	0.005
Ca^{2+}	−0.160	**0.938**^{b}	0.341	**−0.739**^{b}	**0.602**^{b}	**0.826**^{b}	**0.794**^{b}	−0.038	0.295	**0.667**^{b}	—	0.004	0.000	0.152	0.172	0.218
Mg^{2+}	0.100	**0.604**^{b}	**0.542**^{b}	**−0.576**^{b}	0.229	**0.570**^{b}	**0.515**^{b}	0.189	**0.709**^{b}	**0.459**^{a}	**0.563**^{b}	—	0.004	0.627	0.778	0.313
HCO_3^-	−0.132	**0.759**^{b}	0.308	**−0.757**^{b}	0.356	**0.609**^{b}	**0.578**^{b}	0.067	0.348	**0.408**^{a}	**0.834**^{b}	**0.566**^{b}	—	0.056	0.293	0.135
TC	**−0.436**^{a}	0.306	−0.143	**−0.449**^{a}	0.127	0.295	0.218	0.075	0.024	0.098	0.302	0.104	0.395	—	0.000	0.773
TTC	**−0.471**^{a}	0.248	−0.048	−0.336	0.008	0.235	0.167	0.045	−0.182	0.079	0.288	0.061	0.224	**0.764**^{b}	—	0.612
Abs_{254}	−0.051	0.427	0.419	−0.260	0.155	**0.570**^{a}	**0.631**^{a}	0.045	−0.108	**0.706**^{b}	0.351	0.291	0.420	0.085	0.149	—

^{a} Indicates significant level at $p < 0.05$ (2-tailed). ^{b} Indicates significant level at $p < 0.01$ (2-tailed).

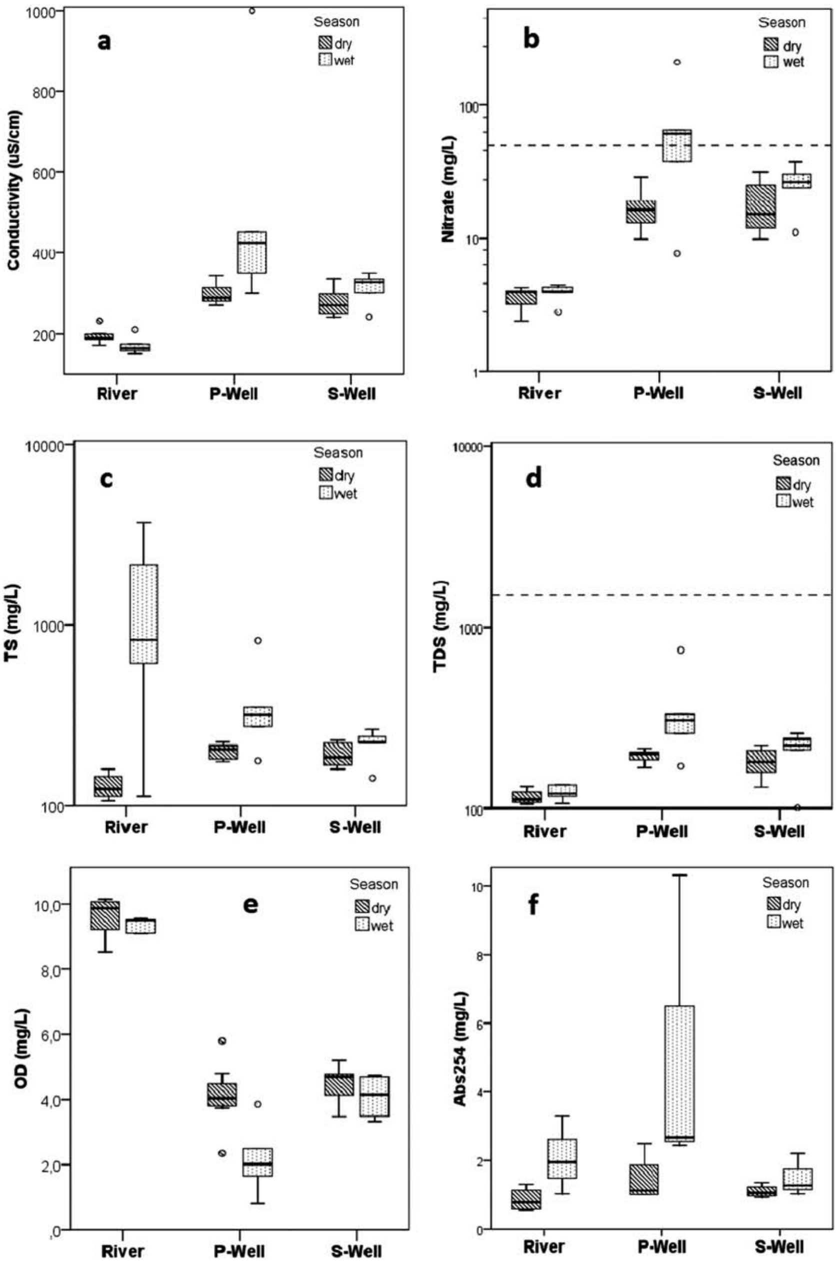

Fig. 2 Physico-chemical parameters of the three sites sampled (river, P-well, and S-well): (a) conductivity, (b) nitrate concentration, (c) total solids (TS), (d) total dissolved solids (TDS), (e) dissolved oxygen (DO), and (f) natural organic matter measured as absorbance at 254 nm (Abs_{254}). The broken line represents the drinking water guideline in Argentina 45 mg NO_3^- L^{-1} (b) and 1500 mg L^{-1} (TDS, d).

season. The intense precipitation during this period caused the suspension of solids (see TS and SS in Table S1† and Fig. 2c), which were carried into the river. This increased the flow and turbulence avoiding sedimentation and facilitating the resuspension of the river bed. During the summer the river looked like chocolate milk due to the high amount of natural mineral clays (illite, kaolin and vermiculite) suspended in it (Fig. 2c), of which magnesium is one of the main components. Despite the high turbidity in the river, it was below 7 NTU in the wells, even during the wet season, thanks to the filtration ability of the soil, which retained a great portion of the suspended solids.

All the water samples were below 1500 mg L^{-1} for TDS (Fig. 2d), which is the drinking water guideline in Argentina.[29] There is no health-based guideline proposed by WHO since reliable data on possible health effects associated with the ingestion of TDS in drinking water are not available. However, the presence of TDS in drinking water above 1000 mg L^{-1} may be objectionable to consumers.[20] Unlike another report,[33] in this study rainfall enhanced the dissolution of chemicals into the water body, thereby increasing TDS values in groundwater.

It is known that microorganisms tend to adsorb to solids, which provide protection for them, hence ensuring longer survival in the environment. Therefore, the diminution of solids by filtration of rainfall or surface water through the soil to become groundwater was expected to enhance the elimination of microorganisms. However, the experimental results showed the opposite situation,

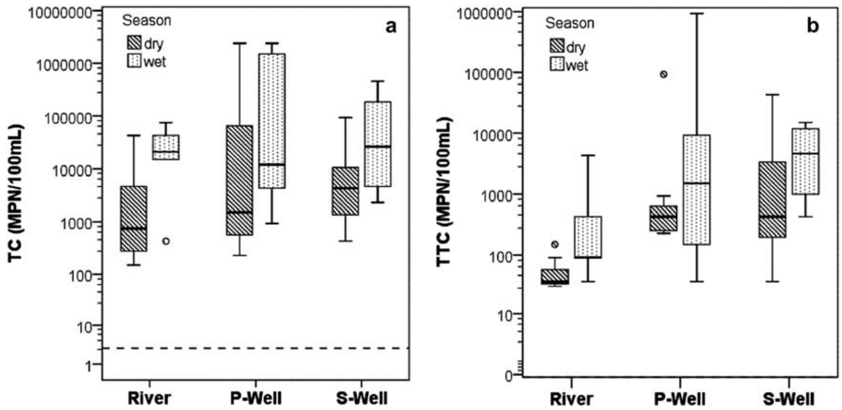

Fig. 3 Microbiological parameters of the three sites sampled (river, P-well, and S-well): (a) total coliform concentration (TC) and (b) thermotolerant coliform concentration (TTC). The broken line represents the drinking water guideline in Argentina for TC <3 MPN per 100 mL.

indicating that the path followed by water through the soil introduced additional microbial contamination (see TC and TTC in Table S1†). This effect was stronger for the P-well (closer to a farm) than for the S-well (Fig. 3). A similar effect was observed in the decreased DO in the wells, especially for the P-well during the wet season (Fig. 2e), which was in agreement with the marked increment of the NOM measured as Abs_{254} (Fig. 2f).

Ammonia in the environment originates from metabolic, agricultural and industrial processes. Degradation of BOD is also a source of nutrients (NH_4–N) that can be oxidized with additional oxygen consumption. In the literature the term ammonia includes both the non-ionized (NH_3) and the ionized (NH_4^+) species. Ammonia is very soluble in water and in the pH range of most natural waters will exist principally as ammonium ion (NH_4^+). Thus, as ammonium ion was more likely to be in the waters we studied, we only investigated the presence of this ionized species. Natural levels in groundwater and surface water are usually below 0.2 mg L^{-1} according to WHO.[34] All the samples, except for two from the dry season in P-well, were below the acceptable level, and there were no significant differences between concentrations of ammonium ions in different water bodies.

Impact of land use on shallow well water quality

The river water did not have an important nitrate contribution to the analyzed system and the average nitrate concentration did not change significantly between seasons. It was at least one order of magnitude smaller than the corresponding values in the groundwater for the wet season, while the difference was not as great for the dry season. The nitrate concentrations found in groundwater were strongly affected by the land use. The increment of NO_3^- during the wet season was remarkable, especially with the first heavy rainfall (in December for this particular monitoring year) eluting salts, organic matter, and microorganisms from the soil (Fig. 4). This effect was more pronounced in the P-well (Fig. 4a), which was directly influenced by several poultry farms located upstream. Due to weathering and open dumping, a considerable amount of soluble forms of nitrogen were leached into deep soil layers especially during wet months of the year. After the peak of the first flush, the decreased concentration might be due to the dilution effect observed with the increment of the water table or by a natural denitrification process. Nitrate concentration can be attenuated under reducing conditions and NOM presence in the aquifer.[31]

The S-well was probably impacted by the septic tank located around 10 m upstream from the well (Fig. 4b). Nitrate and thermotolerant coliform concentrations were high for both seasons, perhaps due to the high contributions from students attending the school (from March to the middle of July and from August to the middle of December), and also to the wet season precipitation flushing the septic tank. The lowest values, found in August, were probably the consequence of the closed school during the winter vacations (two weeks in July).

The increase in coliform counts (TC and TTC in Table S1†) during the wet season was as expected.[8,9,33] An important factor could be the poor quality of well and sanitary seal construction, allowing the rain to wash contamination accumulated at the surface down into the well.[35] The higher coliform concentration during the wet season could also be due to the movement of contaminants into water bodies by rainwater through recharge and runoff from pollution sources such as waste dumps and pit latrines located upstream and close to water points.[33] Dzwairo *et al.*[36] found that the impact of unlined pit latrines on groundwater quality can reach a lateral distance of as far as 25 m.

The poor microbial water quality of the river and of the irrigation channel is affecting public health in the community. The incidence rates of diarrhea cases and parasitosis in 2005 at the Herrera Hospital in Campo Quijano (where the regional health center is located) were 500.3, 738.9, 279.4, and 78.6‰ for children of <1, 1, 2–4, and 5–9 years old, respectively.[14] Land use, waste management, sanitation, water management, water use, and hygiene are factors that cannot be separated from water quality. Together with the global health situation associated with poverty (malnutrition, accessibility to the health system, population settlements in areas without sanitary services and susceptibility to flooding, among others), they contribute to the observed high incidence of diarrhea cases.

Spatial and seasonal assessment of water quality by discriminant analysis

Canonical Discriminant Analysis was carried out to assess the spatial (surface water and groundwater) and seasonal (dry and wet) variabilities in groundwater. The three more correlated

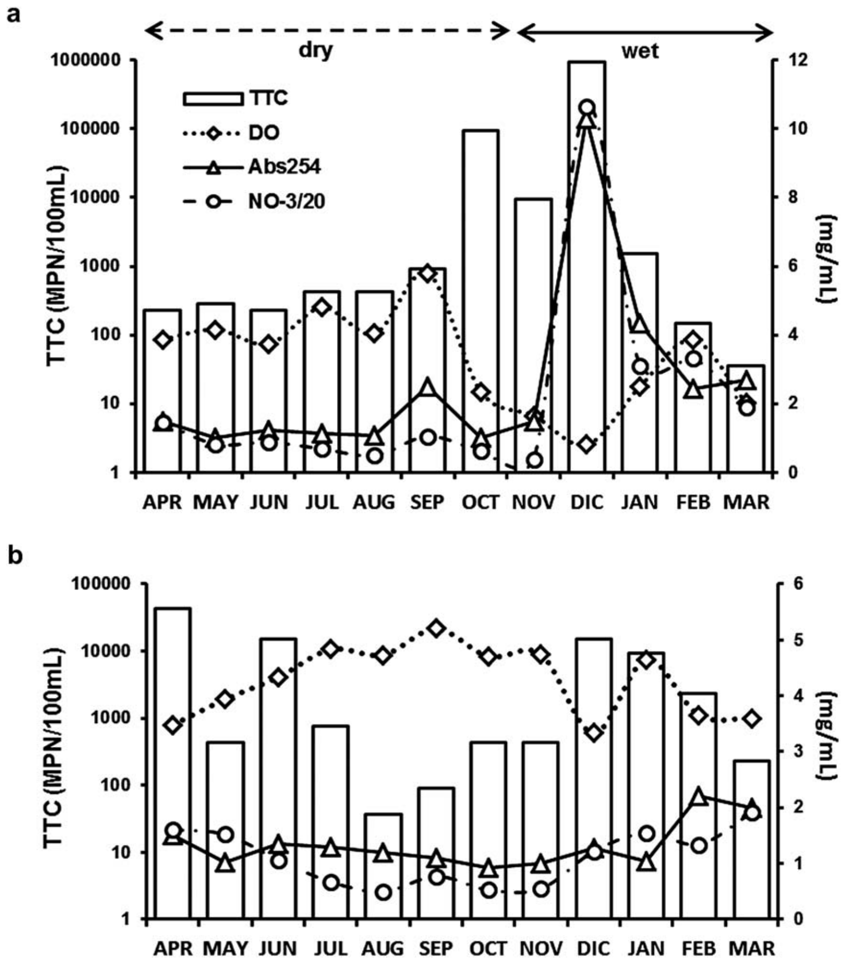

Fig. 4 Variation of thermotolerant coliforms (TTC), dissolved oxygen concentration (DO), natural organic matter (Abs_{254}), and nitrate concentration (NO_3^-) along the monitoring year in shallow groundwater: (a) P-well and (b) S-well. The dry and wet seasons are indicated. Nitrate values were divided by 20 in order to fit them in the axis scale.

parameters (EC, TS and TDS) were eliminated from the analysis and the coliform density estimation was transformed (LnMPN). As there were three classification groups (study sites), two canonical discriminant functions (DF_1 and DF_2) were obtained. The value of every discriminant variable coefficient was standardized to determine the relationship between the discriminant variables and functions (Table 2). Coefficients exceeding 0.8 were considered significant. Eigenvalues for both DFs exceeded 1.0. These two DFs together accounted for 100% of total variance between groups. DF_1 (recognition capacity of 93.12% of the difference) was defined by three discriminant variables with high score coefficients; Ca^{2+}, DO, and HCO_3^-. DF_2 explained just 6.88% of the variance and its main contributor variables were bicarbonate and Abs_{254}. This factor distinguished between groundwater samples. DF_1 discriminated principally between surface water and groundwater with opposite sign centroids (Table 2) and best characterized the river water with low concentrations of the main ions (calcium and bicarbonate), and a high concentration of oxygen according to the condition of the mountain river, located in the head basin (Fig. 5). These variables are combined in a factor accounting for a natural process.

The discriminant analysis approach allowed for the graphical representation of the canonical scores of sample observations and the relationships among the groups (Fig. 6), which may be used to assign a new observation to an existing group.[23] The canonical scores of a new individual would be determined for the first two DFs and its position could then be plotted.[37] The plot showed that the samples from the three sites were well differentiated, with only one case belonging to P-well wrongly assigned to S-well, representing 4.35% of total error in the cross-classification.

For a better understanding of the variability of groundwater quality – our main interest – DA was carried out to assess the spatial and seasonal variations by treating the two wells (P-well and S-well) and seasons (dry and wet), separately. Thus, DF spatial (DF_e) and DF seasonal (DF_s) were obtained (Table 3). The main variables used to discriminate between the two wells in DF_e were thermotolerant coliforms, pH, HCO_3^-, and ammonia. However, other parameters with medium high scores were Mg^{2+} and DO. Taking into account all these variables, it is possible to associate this factor with processes of nitrification and denitrification that could be occurring in S-well and P-well, respectively. In P-well with a minor concentration of dissolved oxygen, the increase of HCO_3^-, which tends to have a slightly higher pH, could likely be caused by the denitrification mediated by microbial oxidation of organic carbon.[31] This phenomenon may

Table 2 Total standardized canonical coefficients between two canonical discriminant functions (DF_1 and DF_2) and discriminant variables. Centroids in the discriminant space obtained for each site. Boldface coefficients are the most significant (>0.80)

Variable	DF_1	DF_2
pH	0.38	0.26
Turbidity	−0.16	0.43
DO	**0.87**	−0.10
Temperature	−0.51	−0.58
SS	0.71	0.36
NH_4^+	0.09	−0.02
NO_3^-	−0.51	−0.48
Ca^{2+}	**0.89**	−0.17
Mg^{2+}	0.30	−0.18
HCO_3^-	**−0.81**	**1.52**
Abs_{254}	0.50	**0.84**
LnTC	0.65	−0.22
LnTTC	−0.19	−0.56
Eigenvalue	18.04	1.33
Variance (%)	93.12	6.88
Cumulative variance (%)	93.12	100
Centroid in the discriminant space		
P-well	−3.26	1.37
River	5.61	0.10
S-well	−2.62	−1.35

explain the decrease of nitrates after the peak of the first rainfall. Meanwhile, in S-well a process of nitrification could have been happening. Nitrification of reduced nitrogen from manure (NH_4^+) released protons along with NO_3^-, which decreased pH and allowed for the dissolution of minerals and the release of magnesium under acidic conditions.[31] In addition, low pH could be caused due to the contamination from the area upstream of the S-well. The cross-validation of the discriminant function gave 4.35% of total error, which represented a good classification.

In the seasonal assessment, DF_s had great contributions from nitrates, calcium, bicarbonates and turbidity (Table 3). In this situation the discriminant function classified all the cases correctly (100%). Seasonal discrimination was strongly influenced by the wet season in which most parameters showed high concentrations despite turbidity. As previously stated, this was related to the process of mineral dissolution (typically occurring in groundwater) and also with the input of pollution sources from anthropogenic activities taking place in the area.

It is worth noting that in contrast to using the Kruskal–Wallis test, the usefulness of DA lies in the reduction in the number of variables that could explain most of the variabilities in water quality.

Assessment of land use contributions to water quality by principal component analysis

Principal Component Analysis was carried out to identify factors influencing the quality of surface water and groundwater. The 16 variables were taken into account for PCA, which was applied separately for the three sampling sites and was carried out on the normalized dataset to eliminate the effect of the data measurement scale.[24] According to Kaiser's Criterion,[38] only PCs having eigenvalues greater than unity were considered of significant influence (Table 4). PC loadings on the table are interpreted as correlation coefficients between the variables and the factors, and represent how important a variable is for the obtained component. This interpretation is more reliable due to the fact that correlation eliminates errors caused by the different measurement scales for each kind of variable. Following the criteria of Liu and coworkers[39] only loadings with strong correlation were considered; in this case factor loadings higher than 0.70 were regarded as significant.

PCA results for surface water samples showed that 61% of the total variance was explained by two factors (Table 4). The first one, accounting for 46% of the data variance, had a high positive

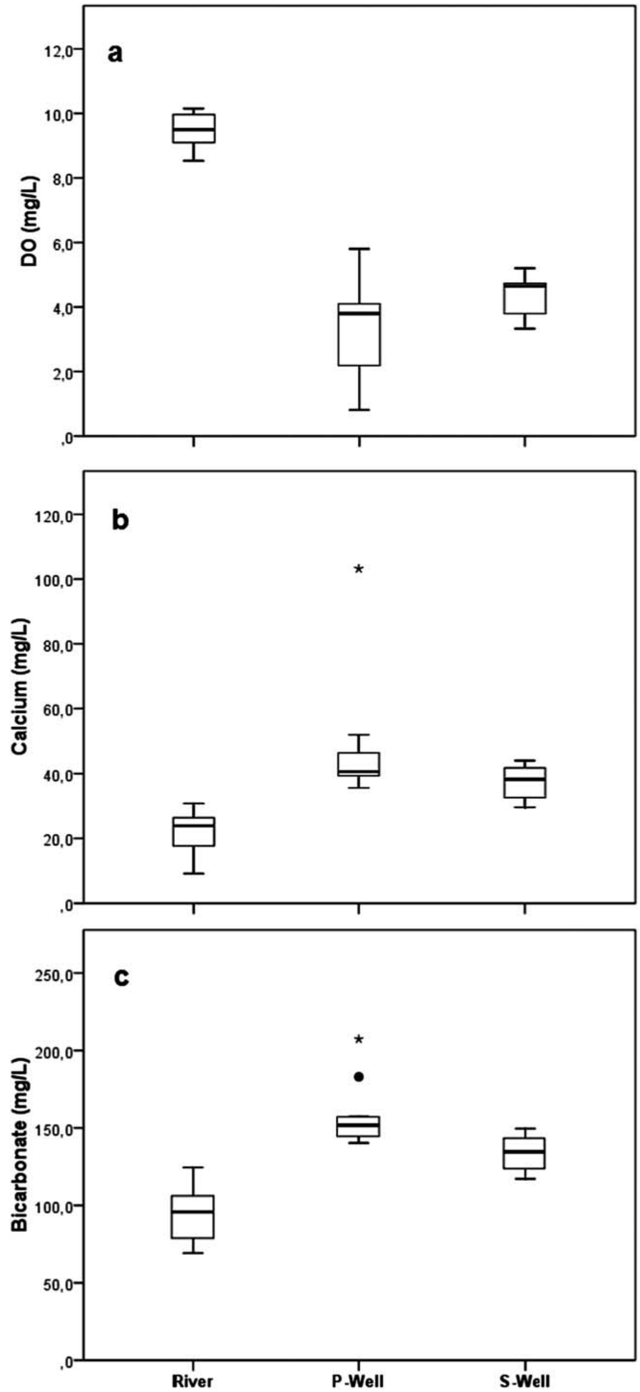

Fig. 5 Box plots of selected discriminating parameters (DF_1) identified by DA in the three sampling sites. (a) Dissolved oxygen; (b) calcium and (c) bicarbonate.

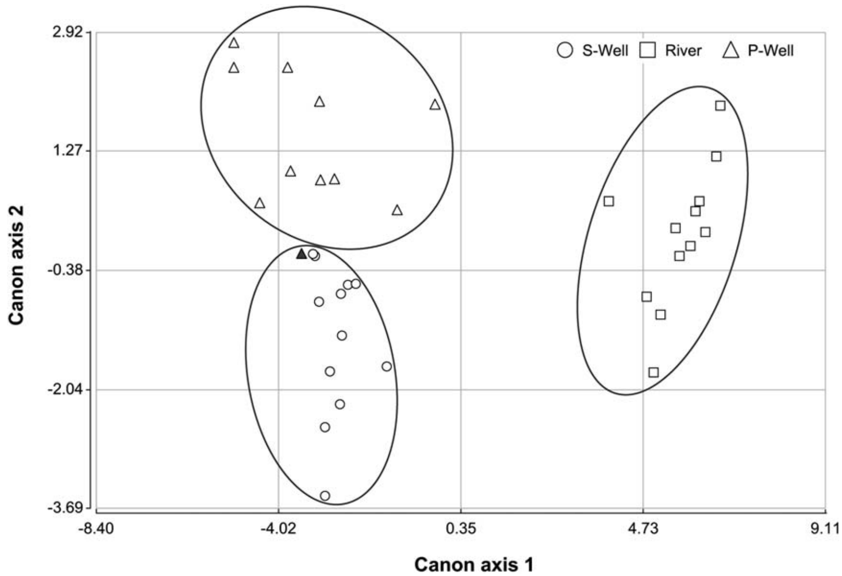

Fig. 6 Canonical discriminant analysis plot of three sites studied (river, P-well and S-well) in two discriminant functions (▲ represents the only wrong assigned case in the discriminant space).

Table 3 Total standardized canonical coefficients between two canonical discriminant functions and discriminant variables for spatial (DF_e) and seasonal (DF_s) variability in shallow groundwater. Boldface coefficients are the most significant (>0.80)

Variable	DF_e	DF_s
pH	**−1.03**	0.31
Turbidity	−0.53	**1.65**
DO	0.77	−0.49
Temperature	0.41	−0.35
SS	−0.45	0.77
NH_4^+	**0.94**	0.14
NO_3^-	−0.06	**−2.13**
Ca^{2+}	−0.28	**1.80**
Mg^{2+}	0.68	−0.37
HCO_3^-	**−1.21**	**−1.73**
Abs_{254}	0.32	0.29
LnTC	−0.66	0.33
LnTTC	**1.44**	−0.39

loading for turbidity, TS, SS, and LnTCC. According to Hong *et al.*[40] these variables were related with external processes that increase solid concentrations in surface water such as the runoff from drainage basins and re-suspension of sediments due to rainfall. In addition, these data provided evidence that suspended solids facilitate the survival of thermotolerant coliforms by adsorption, protecting them from UV radiation and others threats and providing inorganic and organic nutrients attached to the particles.[40] Other variables contributing to PC1 with negative loadings were Ca^{2+}, HCO_3^-, and EC. Since our water was calcium–magnesium–bicarbonate according to Piper classification, these ions (Ca^{2+} and HCO_3^-) were the main contributors to conductivity of surface water. Based on others reports[24,40,41] it is possible to establish that PC1 may represent the association between rainfall and the process of erosion and drag of particles during the wet season resulting in an external contribution for solids, coliforms, and dilution of minerals in the river. The second factor, PC2, was responsible for 15% of the total variance and had only temperature with a significant loading. However, it is worth noting that ammonia and total coliforms were variables with high positive loadings. This was unexpected due to the positive correlation between temperature and coliforms caused by the well-known increase in the die-off rate for indicator bacteria with the temperature.[42] However, the presence of ammonia may suggest a fresh contamination from wild animal activity that increases the source of bacteria with high temperatures.

The results of PCA for P-well water samples showed that the first component (PC1) accounted for over 39% of the total variance in the dataset and had high positive factor scores for EC, TS, TDS, NO_3^-, temperature, Ca^{2+} and Abs_{254}. This relationship can be explained by poultry contamination due to the impact of the farm upstream from the well. Especially during the summer (high temperature) wet season as was mentioned before, heavy rainfalls recharge groundwater with inputs of nitrates, calcium and organic material from the top soil fully covered with bird excrement, leading to the increase in the concentration of TS, TDS and EC. Also, this impact was confirmed by the fact that, despite the ascent of the water table level due to recharging, conductivity and concentrations of ions increased, although the concentrations could be expected to decrease due to dilution. The second factor, accounting for about 26% of the total variance, consisted of positive loading for bicarbonates, thermotolerant and total coliforms and negative loading for pH (Table 4). This factor may represent the microbiological contamination of the well and the negative relation with pH supports the common notion that the presence of bicarbonates favors an ideal pH for the survival of the bacteria.[40] The third factor accounted for 11% of the total variance and had only magnesium as an important variable, which could be related to water–rock interactions,[24] as Mg^{2+} in groundwater primarily comes from dissolution of the mineral that forms the bedrock and clays in this area. The three factors analyzed explained 76% of the total variance.

Table 4 Factor loadings from Principal Component Analysis of standardized water quality dataset for the three sampling sites. Boldface loadings are the most significant (>0.70)

Sites	River					P-well				S-well			
Variables	PC 1	PC 2	PC 3	PC 4	PC 5	PC 1	PC 2	PC 3	PC 4	PC 1	PC 2	PC 3	PC 4
pH	0.10	0.39	−0.53	0.42	0.49	−0.39	**−0.77**	0.08	−0.05	0.24	**0.86**	−0.01	0.37
EC	**−0.85**	0.38	−0.32	−0.02	−0.11	**0.99**	−0.02	−0.04	−0.04	**0.96**	−0.09	−0.11	−0.03
Turb	**0.94**	0.14	0.12	0.11	−0.18	−0.09	−0.70	0.41	−0.40	0.52	0.48	0.25	0.17
DO	−0.48	−0.39	0.09	0.53	−0.44	−0.51	−0.68	−0.05	−0.27	**−0.79**	0.37	−0.35	0.24
Temp	0.52	**0.72**	−0.05	−0.21	−0.26	**0.82**	−0.11	0.03	0.36	0.38	0.36	−0.55	−0.25
TS	**0.84**	−0.09	−0.41	0.02	−0.27	**0.93**	−0.27	0.11	0.03	**0.96**	0.06	−0.02	0.03
TDS	0.62	0.03	−0.54	0.42	0.19	**0.89**	−0.40	0.01	0.07	**0.95**	0.08	−0.16	0.13
SS	**0.84**	−0.09	−0.41	0.02	−0.27	0.41	0.37	0.46	−0.46	−0.65	−0.17	0.45	−0.37
NH_4^+	0.22	0.68	0.33	−0.24	0.30	−0.22	0.06	0.65	0.60	0.32	0.54	0.65	−0.18
NO_3^-	0.62	−0.35	0.25	0.35	0.37	**0.89**	−0.42	−0.05	0.02	**0.95**	0.08	0.02	−0.05
Ca^{2+}	**−0.89**	0.09	−0.29	−0.22	−0.03	**0.81**	0.37	−0.05	−0.21	**0.99**	0.02	−0.07	0.06
Mg^{2+}	−0.03	0.45	0.47	0.69	−0.16	0.33	−0.30	**0.74**	−0.01	**0.80**	0.27	0.23	−0.19
HCO_3^-	**−0.88**	0.35	−0.20	0.09	−0.10	0.38	**0.77**	0.34	−0.28	**0.94**	−0.13	0.12	−0.11
Abs_{254}	0.60	0.06	0.66	−0.14	−0.01	**0.75**	−0.21	−0.51	0.06	0.66	−0.22	−0.34	−0.47
LnTC	0.60	0.62	−0.08	0.09	−0.19	−0.06	**0.73**	0.10	0.46	0.46	**−0.78**	0.08	0.21
LnTTC	**0.84**	−0.24	−0.28	−0.38	−0.005	−0.05	**0.84**	−0.10	−0.37	0.54	−0.56	0.20	0.50
Eigenvalue	7.32	2.35	2.07	1.58	1.03	6.21	4.21	1.76	1.42	8.68	2.64	1.39	1.04
% Variance	46	15	13	10	6	39	26	11	9	54	17	9	6
Cumulative % variance	46	61	74	84	90	39	65	76	85	54	71	80	86

In the case of PCA for S-well, the two first factors together accounted for 71% of the total variance and the other two factors with an eigenvalue greater than 1 did not show any loading higher than 0.70. The PC1 accounting for the 54% of the data variance had a high positive loading for calcium, conductivity, total solids, total dissolved solids, nitrates, bicarbonates, and magnesium; meanwhile dissolved oxygen was negative. The second factor accounting for the 17% of the total variance represented the microbial contamination of the well. The data from PC1 suggests that processes such as mineral dissolution, weathering and pollution from anthropogenic activities are occurring in this well. Similar results were obtained in other reports.[24,31,40,41] The presence of calcium, magnesium and bicarbonates indicates dissolution of minerals bearing these ions during recharge of the aquifer by rainfall. These ions in the component are related to weathering.[13,24,41] The presence of nitrates may represent contamination from human activities, since any natural source of it was identified in the region. In addition, the negative relationship with oxygen concentration suggested that a contamination process – for instance, organic matter degradation – is taking place in the water-well.

Conclusions

• The location of farming activities close to waterways represents a high risk for drinking water supplies in Northern Argentina and other countries with similar geologic and climatic zones.

• The most important exceedances of regulatory levels were related to thermotolerant and total coliforms (36 out 36 samples), nitrates and pH.

• There are two factors that make this peri-rural area near Salta an area of extreme vulnerability. First, soils are formed by fine gravels and coarse sands, resulting in a high permeability zone. Second, the land use activities identified represent a high contamination risk for shallow groundwater and for the whole environment since the water tables were measured at a few meters, from less than 2 to 7 m in the wet and dry seasons, respectively.

• PCA and CDA analysis of complex datasets identified pollution sources/factors and helped us to understand temporal/spatial variations in water quality, allowing for an effective management of this vital resource.

• Simple steps can improve public health risks in these regions. They are to regulate and control farming activities and solid waste disposal, to improve the sanitation system, and to monitor nitrates, coliforms and pH. With such data in hand it is possible to intervene to improve water quality and thereby decrease the morbidity rate of diseases attributable to environmental causes.

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