



Assessing the vulnerability of groundwater resources in semiarid lands of central Argentina

Jorgelina Ceferina Montoya¹ · Carolina Porfiri¹ · Zinda Edith Roberto¹ · Ernesto Francisco Viglizzo²

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Abstract

Groundwater resources in semiarid lands of central Argentina are currently threatened by contamination from agricultural pesticides. The objectives of the present work were: (a) to estimate groundwater recharge on a monthly basis to identify periods of high susceptibility of the aquifers to be polluted, (b) to assess groundwater vulnerability to pollution using the Generic and Pesticides DRASTIC GIS-based model for each recharge month previously identified, (c) to quantify the presence of atrazine, imazapyr, glyphosate, and its metabolite AMPA in groundwater, and (d) to check the application of the DRASTIC model in the semiarid lands of central Argentina. According to the estimation of groundwater recharge, the vulnerability of aquifers increases during March, April, and November. The six resultant vulnerability maps revealed that groundwater is under “high-to-moderate” risk of pollution in the study area. About 47 and 88% of the total area is highly vulnerable, according to the Generic and Pesticides DRASTIC maps, respectively. Atrazine and imazapyr were quantified in groundwater at concentrations greater than $0.1 \mu\text{g l}^{-1}$ in four of the analyzed compounds. Potential pollution of groundwater was conditioned by the spatial variability of geomorphological features, and influenced by others variables such as the intensity of herbicides use and the physicochemical properties of the compounds. In the present study, groundwater pollution is in line with the DRASTIC maps.

Keywords Vulnerability · Groundwater · Semiarid · Recharge · Herbicide residues

Introduction

Groundwater pollution is a major global concern for the environment and human health, particularly in arid and semiarid regions where groundwater represents the main water source. Groundwater quality is generally under considerable risk of pollution as it is susceptible to those activities taking place on the soil or near the ground, especially in intense use of pesticides–agriculture (Székács et al. 2015; Shakerkhatibi et al. 2014; Vonberg et al. 2014; Battaglin et al. 2014).

Semiarid lands of central Argentina have poor surface water resources, and therefore, groundwater is the primary drinking water source for both urban and rural populations. During the last 25 years, an intensification of agriculture has taken place due to the adoption of a no-till technological package, that is, the introduction of genetically modified soybeans (tolerant to glyphosate), no-tillage systems (Alvarez and Steinbach 2009; Díaz-Zorita et al. 2002), and the intense use of synthetic pesticides (Viglizzo et al. 2011). This modern agriculture has been successful in increasing yields but has also caused extensive environmental damage like groundwater pollution by the intensive use of pesticides (Özkara et al. 2016; Aktar et al. 2009). Since semiarid lands of Argentina are characterized by an intensive farming with high inputs of pesticides, the natural quality of groundwater is under substantial threat. Thus, due to the significance of the groundwater for human communities, protection against anthropogenic pollution is of crucial importance (Asare-Donkor 2016; Lamastra 2016).

In understanding the nature of groundwater pollution by pesticides, it is necessary to consider not only land-use, soil,

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✉ Carolina Porfiri
porfiri.carolina@inta.gob.ar

¹ Instituto Nacional de Tecnología Agropecuaria, Anguil, La Pampa, Argentina

² CONICET/INCITAP Instituto de investigaciones en ciencias de la tierra y el ambiente productivo, Santa Rosa, La Pampa, Argentina

climate, and aquifer properties, but also intrinsic properties of pesticides. The idea that the geological environment protects groundwater and, therefore, it is not vulnerable to human activities prevailed for a very long time (Vrba 2002). This had serious long-term consequences on groundwater quality over many countries, and nowadays, groundwater pollution by pesticides is a worldwide problem. Although groundwater constitutes the main water source in the study area, its conservation and protection is not considered a priority. Therefore, groundwater vulnerability studies are considered as a new scope for research in central Argentina. The combination of land-use and hydrogeological factors is known as the vulnerability of groundwater to contamination. In general, groundwater vulnerability assessments are aimed at determining the tendency or likelihood for contaminants to reach a specified position in the groundwater system after introduction at some location above the uppermost aquifer (Liggett and Sonia Talwar 2009). Groundwater vulnerability is a concept, not a measurable property. It is the tendency or likelihood of contamination occurring in the future, and, thus, must be inferred from surrogate information that is measurable.

The semiarid Pampas Plain is an extended geographical region characterized by very small slopes lower than 0.01% (Jobbágy et al. 2008) and including a wide cover Quaternary sediments (Zárate 2003). The phreatic aquifers conform by quaternary deposits (Pampean loess) exposed to an intensive agricultural land-use. Thus, aquifers are susceptible to contaminants due to a shallow water table and because of the high permeable lithology. The surface materials consist mainly of permeable sands, which have a little capacity to hinder chemical migration, and water table is shallow, which favors short transit times of herbicides from the land surface to the groundwater system. Although aquifers are very important in the study area, the vulnerability of the aquifers to pollution by organic pollutants was never studied.

Although several vulnerability assessment techniques have been developed, DRASTIC system is the best known (Aller et al. 1987). This index is one of the simplest methods related to groundwater vulnerability, based on seven geological and hydrological parameters that comprise, among others, the vadose zone, the soil horizon, the relief terrain, and recharge capacity of soils.

DRASTIC index has been modified by many researchers and scientists based on geological and hydrogeological settings, climate conditions, and other special situations. It can be used in a wide variety of regions like agricultural, arid, semiarid, and basaltic zones (Shirazi et al. 2012). The index has been applied for mapping groundwater vulnerability in aquifers of semiarid areas across the world, such as Northern Tunisia (Boukari et al. 2017), Northwestern China (Wen et al. 2009), Egypt (2009), Ethiopia (Tilahun and Merkel 2010), Turkey (Ersoy and Gultekin 2013), and

Jordan (Mohammad 2017). However, the method has a serious limitation, because it does not consider the distribution, intensity, and duration of the recharge events.

DRASTIC index considers the net recharge estimation on annual basis (Aller et al. 1987). However, mean annual precipitation is lower than potential evapotranspiration in semiarid regions (Simmers et al. 1997). Water balance method, on annual basis, results in no groundwater recharge at all. To obtain those moments in which aquifers are more vulnerable, the original proposal/approach of the present study was to identify the time of the year where water excess might occur. Thus, instead of annual net recharge, monthly recharge was calculated.

Rainfalls in semiarid regions are seasonal and unpredictable, and long periods of water deficit may be disrupted by sudden pulses of water excess related to short episodes of intense rainfall (Salas 2000). Inevitably, those pulses cannot be properly represented by average annual figures (Alderwish and Dottridge 1998) and pollutant flows to groundwater may be underestimated in some periods (Simmers 1997). The calculation of water balance during those short periods of water excess appears to be the way to deal with this issue (Hendrickx and Walker 1997).

The general purpose of the present work is to assess the vulnerability of the Quaternary aquifer system related to agricultural pesticides contamination using the Generic and Pesticide DRASTIC models. Determining different vulnerability zones in the aquifers would help planners and decision makers to address areas that need to be protected and to set priority levels of management. Moreover, determining vulnerability zones is a primary step for decision-making support for planners and land managers. At the same time in this study, multiple groundwater samples were collected from different vulnerable zones, and three herbicides were analyzed to check DRASTIC outcomes.

Consequently, the specific objectives of this study were: (a) to estimate groundwater recharge on a monthly basis, to identify the periods of high susceptibility of the aquifers to be polluted, (b) to assess groundwater vulnerability to pollution using the Generic and Pesticides DRASTIC GIS-based model for each recharge month previously identified, (c) to quantify the presence of atrazine, imazapyr, glyphosate, and its metabolite AMPA in groundwater, and (d) to check the application of the DRASTIC model in the semiarid lands of central Argentina.

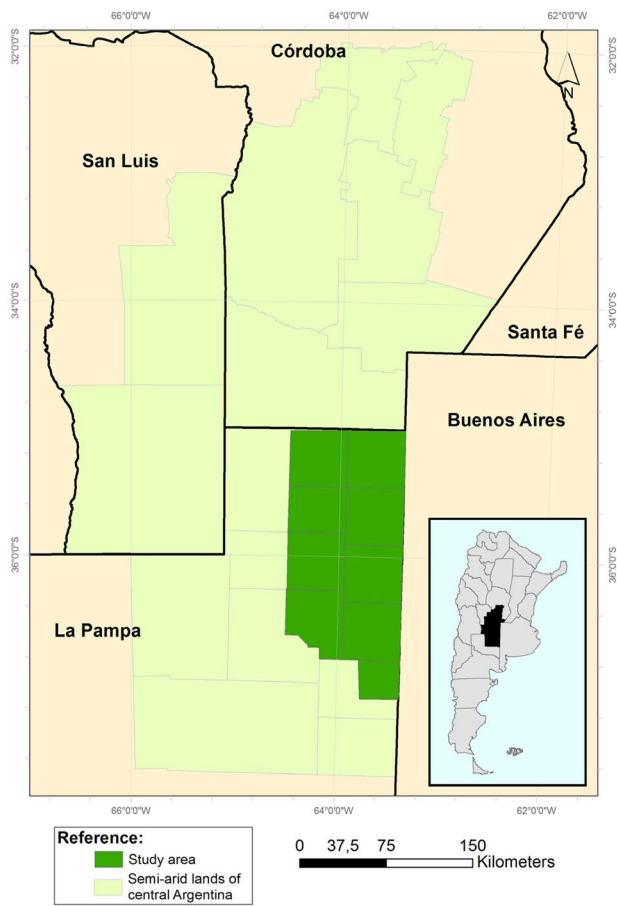


Fig. 1 Location of the study area

Materials and methods

The study area

The study area of 27,612 km² is displayed between 63° and 64° 15'W and 35°–37° 15'S coordinates, and involved several districts of La Pampa province in the semi-arid lands of central Argentina (Fig. 1). The region is typical of the eolian sedimentary landscapes of the Inland semi-arid Pampa (Soriano et al. 1991).

The climate of the study region is semi-arid temperate, with a mean annual temperature of 16.2 °C. Mean temperatures for the coldest (July) and warmest (January) months are 16 and 33 °C, respectively. Winds are more intense and frequent during the warm season, inducing the occurrence of high daily evapotranspiration rates (Díaz-Zorita et al. 2002). Most rainfall occurs between the spring and fall seasons (October–March), and average precipitation decreases from 800 to 600 mm per year along an NE-to-SW axis. Rainfall amounts are highly variable between years, typical of semi-arid regions (Simmers 1997). Rainfall amounts are highly variable between years, typical of semi-arid regions. Mean

annual rainfall is lower than the annual potential evapotranspiration, around 1000 mm per year, FAO Penman–Monteith equation (Allen et al. 1994). Thus, the hydrologic Climatic Balance is negative and results in no groundwater recharge at all. In semi-arid areas, a long periods of water deficit may be disrupted by short but intense rainfall episodes triggering abrupt pulses of water excess (Salas 2000) that, eventually, could carry agriculture pollutants to groundwater. The predominant soils of the study area, Entic Haplustolls, do not present any significant restriction to crop growth, as they are sandy well drained and deep (> 150 cm). Sand content usually exceeds 70% and the soil organic matter in the top horizon is < 1.5% (INTA-SAGyP, 1990).

The study area is conformed by a complex sand dunes system (Sand Sea) (Holocene age) (Iriondo 1990). Winds have favored the accumulation of this sandy mantle with variable thickness that delineates a gentle rolling plain (Smedley et al. 2000). The geomorphology shows a relatively uniform and softy waved plain with micro-reliefs composed by small hills and depressions.

Two geomorphological units have been described by Cano et al. (1980): (1) the Sandy eolian Plain (SP) situated in the North East of the region, and (2) the Calcrete Plain (CP) in the North Central. The parental materials of soils are mainly eolic sediments with a low clay and high silt content. Fernandez et al. (2008) described ten soils of the same area, which differed considerably in their profile depth (ranging from 0.60 to 2.00 m) and had also very different textures (sand contents between 450 and 830 g kg⁻¹). The soil's water storage capacity (WSC) showed similar variability according to texture and soil depth, ranging from a minimum of 70 mm to a maximum of 189 mm. However, in contrast to what might have been expected, sandy soils had higher WSC than loamy soils, due to their deeper profiles. Sandy soils are mostly found in the SP region where rainfall is higher and soil depth is not limited by a calcrete layer. CP soils have finer loamy textures but are shallow due to calcite presence. The calcrete layer with lowest depth of 0.6 m limited the WSC of the soil at 70 mm, whereas site with deeper soil profile of 2.00 m had a WSC of 189 mm.

The aquifer system is conformed by eolian deposits of the Holocene and consists of two layers which are hydraulically connected (Mariño and Schulz 2008). The upper layer is a permeable sand underlying to a lesser permeable silts and silty-to-sandy sediments with variable amounts of calcium carbonate that reach a thickness up to 100 m. Loess sediments forms the main phreatic aquifers that supply fresh water to urban and rural communities (Martínez and Osterrieth 2013). The thickness of the upper sand layer in the landscape ranges between 15 m in dunes and 2–3 m in depressions (Malan 1983). In the western sector, there is a calcrete/rocky layer close to surface underlying the loess deposits. Calcrete formation is characterized by a low permeability,

scarce of well-developed drainage, and a false water table can eventually be stored upper the calcrete formation. How-

Finally, DRASTIC index (DI) is made up of the sum of the products of ratings (R) and weights (W) of the seven parameters according to the following equation:

$$\text{DRASTIC Index} = D_R D_W + R_R R_W + A_R A_W + S_R S_W + T_R T_W + I_R I_W + C_R C_W. \quad (1)$$

ever, Calcrete fissures and fractures allow water percolation until reaching the real water table (Giai et al. 2002).

In general, the water table depth range from 0 to 10 m in the Eastern and to 20–25 m in the central part of the area (Hernández Bocquet 2009). The geomorphology of the landscape exerts strong influences on soil and the shape of the water table which follows the configuration of land topography. High sectors of the sandy relief behave as recharge areas, whereas depressions behave as discharging areas of the aquifers (Miglianelli 1984). While the water table deepens and land depressions remain dry during dry periods, the water table rises reaching the ground in low areas during the wet ones (Tanco and Kruse 2001). In the NE area, the flat topography constrains surface drainage and together with a semiarid climate determines the presence of a shallow water table along most of the landscape.

Soybean [*Glycine max* (L.), sunflower (*Helianthus annuus* L.), maize (*Zea mays* L.), and wheat (*Triticum aestivum* L.)] are the dominant crops of the region. During the last decade, the adoption of minimum tillage and no-tillage soil management schemes spread over the study area, accompanied by a more intense use of potentially contaminant pesticide and fertilizer inputs (Viglizzo et al. 2011).

DRASTIC model

One of the most widely used groundwater vulnerability assessment methods is the DRASTIC index, developed by the US Environmental Protection Agency (EPA) (Aller et al. 1987). The acronym DRASTIC corresponds to the initials of the seven hydrogeological parameters involved: Depth to water, net Recharge, Aquifer media, Soil media, Topography, Impact of vadose zone media, and hydraulic Conductivity of the aquifer.

DRASTIC index (DI) includes two versions: the Generic DRASTIC index (DGI), and the Pesticides DRASTIC index (DPI). DGI evaluates potential pollution based on the weighted combination of these parameters. The typical ratings (R) range from 1 (less potential contamination) to 10 (the highest potential contamination). Each of these parameters has a particular effect on the potential vulnerability visible in a subjective rating. This rating is then scaled by a weighting factor (W) varying from 1 (least significant) to 5 (most significant). The weight multipliers are used to indicate the relative importance of each layer. DPI was designed to be used when the activity of concern is the application of pesticides in an area. The difference between the two indexes is expressed in the relative weights of the seven DRASTIC factors.

The resulting DRASTIC index (DI) represents a relative measure of groundwater vulnerability: the higher the DI, the greater the potential groundwater pollution.

To better represent the local hydrological characteristic of semiarid lands of central Argentina, the rating system was modified based on bibliography data listed below, and the weight for the seven parameters were consistent with the original DRASTIC method. The data finally used in the DRASTIC model of this study are listed in Table 1.

For the conditioning of the different layers involved in the calculation of the DRASTIC index, we used data from public agencies and several regional studies. These regional works included geological (Rocca et al. 2006; Zárate 2003; Iriondo 1990; Cano et al. 1980; Linares 1980), hydrogeological (Mariño and Schulz 2008; Martínez and Osterrieth 2013; Provincial Water Agency (APA); Smedley et al. 2000), soil (Fernandez et al. 2008; SAGyP-INTA et al. 1990; Cano et al. 1980), and topographic studies (Roberto et al. 2008); as well as climatologic data (Area of Climatology from INTA-Ing. Covas meteorological station).

Generic and pesticide DRASTIC maps of the study area

To elaborate the generic and pesticide DRASTIC maps, the ArcGIS 9.2 software was used. Data were transferred into spatial raster data by applying an inverse distance-weighting interpolation technique. The seven resulting raster maps were reclassified using the assigned rates. Then, the reclassified layers were used as input parameters for the raster calculator function. The DRASTIC index for the given area was calculated by multiplying each parameters rating by the assigned weights that reflects the relative contribution of each factor to the contamination process (general and pesticides).

DRASTIC index allows modifying the original hydrogeological parameters to the setting which described a specific area. The standard DRASTIC index values range between 23 (26 for pesticides DRASTIC) and 226 (256 for pesticide DRASTIC), corresponding to a minimum and maximum vulnerability (Lobo-Ferreira and Oliveira 1998). The variables rating allow the user to adjust the value based on more specific knowledge (Aller et al. 1987). Thus, the key factors and criteria underlying the elaboration of the existing vulnerability maps were different for different countries (Lobo-Ferreira 2000). In this work, three vulnerability categories

Table 1 Hydrogeological settings, rates, and weights of the DRASTIC model parameters used in semiarid lands of central Argentina

Parameter	Generic weight	Pesticide weight	Modified range	Rating
<i>D</i> (m)	5	5	< 10	9
			10–20	7
			20–50	5
			50–100	2
			> 100	1
<i>R</i> (mm month ⁻¹)	4	4	0–12	1
			13–24	3
			25–36	5
<i>A</i>	3	3	Sandy deposits	6
			Silty sand deposits	5
<i>S</i>	2	5	Sandy	9
			Loamy sand, sandy	8
			Loamy sand	7
			Loamy sand and loam	6
			Sandy loam, loam, and loamy sand	5
<i>T</i> (%)	1	3	0–2	10
<i>I</i>	5	4	Sand	8
			Sand and calcrete	7
			Calcrete	6
<i>C</i> (m day ⁻¹)	3	2	Sandy sediments 10–20	4
			Silty sand deposits < 10	2

were used: high (180–226), moderate (100–159), and low (23–99). The key factors considered for groundwater pollution were: shallow unconfined aquifer and, permeability and attenuation capacity of the unsaturated zone. According to these factors, high vulnerability is characterized as follows: shallow groundwater levels (< 10 m) and high permeability related to sandy soils and sandy vadose zone. On the contrary, low vulnerability is related to deep groundwater levels (> 50 m), loam and sandy loam soil texture, and the presence of a calcrete layer in the vadose zone. Intermediate rating values between these two contrasting scenarios delineate the moderate category.

Depth to water table

Depth to water is the distance from the ground surface to the water table. It determines the depth of materials that pollutants must go through before reaching the water table (Rahman 2008). Therefore, the longer the distance to water table, the lesser the chance of pollutants to arrive to the water table and higher the probability to be attenuated. Water table digital map (scale 1:100,000) was provided by Roberto et al. (2008). This map was then reclassified according to the range and weight of the parameters as shown in Table 1 (Fig. 2). In the study area, depth to water is lower than 10 m in the eastern part, between 10 and 20 m in the central areas and, higher than 100 m in Western lands.

Net recharge

To calculate the net recharge, the soil water balance method (Thorntwaite 1948) was applied using the Agroagua Software, Version 5 (Forte Lay et al. 1996). Data were provided by the Agrometeorology Area of INTA (G. Covas Experimental Station) in Anguil, La Pampa province. The storage capacity was calculated referred to 1 m depth or up to the calcrete layer (if it was the case) when soil profile was less than 1 m depth. We performed 26 water balances (one for each soil profile or site) across the study area. Related to the temporal scale of the study, we used a 48-year data series (1961–2008) for 12 profiles (locations), and a 17-year data series (1961–1977) and a 28-year data series (1980–2008) for the remaining two profiles.

In agreement literature cited from other semiarid regions of the world, water balance tends to be negative when expressed on annual basis. Nevertheless, in certain months of the year, precipitation can exceed potential evapotranspiration and soil water storage may increase and net recharge may occur. Therefore, for each particular month, a mean data series of water excess was calculated as it is shown in Table 2.

Walkowiak and Solana (1989) used a simple method to characterize those geographical regions with high inter-annual variability rainfall. They calculated probability of rainfall occurrence on a monthly basis. We employed the

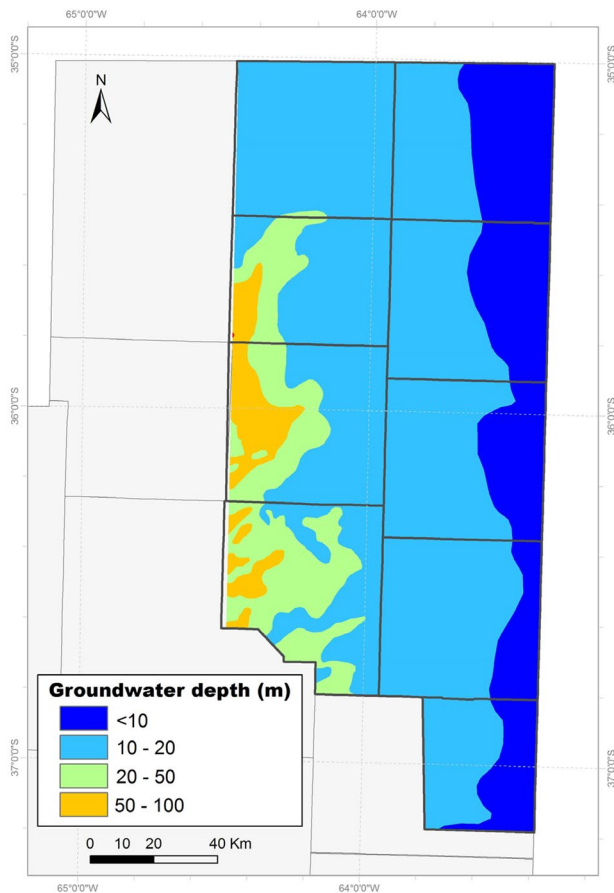


Fig. 2 Distribution of water table depth in the study area

same method but using the water excess, instead of rainfall, estimated by the water balance. This approach allows obtaining a degree of prediction of excess water occurrence. Thus, a key issue was used to detect the frequency of water excess events for each month, and this resulted from the ratio between the number of water excess events in 1 month and the total number of months in the time series (Eq. 2; Table 3). Finally, a monthly based recharge map was elaborated using the product of the average of water excess and the frequency of the events. This standardizing procedure was used to build a data layer that expresses the probability of net recharge events occurrence for each month and each location. Those results, displayed both on time and space scales, represented the so-called vulnerability maps. Three net recharge classes were determined for March (0–12, 12–24, and 24–36 mm), and two classes for April and November (0–12, 12–24 mm). The corresponding rating values were 1, 3, and 5 (Table 1):

$$f_i = \frac{M_i}{M_i^T}, \quad (2)$$

where f_i is the frequency of events of excesses in month i , M_i is the number of excess events in month i , and M_i^T is the total number of month i in the register.

Net recharge is one of the layers with higher weight, because water is the principal vehicle for leaching and transporting contaminants, so those months with a more frequent occurrence of water excess were selected.

Aquifer media

Aquifer media control the contaminant fate. High permeability generally leads to lower pollutant attenuation capacity. To obtain the aquifer media map (1:500,000), we used both the geological map of La Pampa Province (Cano et al. 1980) and a study of Zarate (2003). As shown in Fig. 3, the quaternary aquifer media are mainly composed of sandy sediments and silt sandy deposits. The hydraulic conductivity of aquifers ranges from 20-m day⁻¹ in those lands rich in sandy sediments (Castro and Schulz 2009) to 10-m day⁻¹ in lands where sandy-silt sediments predominate (Auge 2005) (Fig. 5). Therefore, based on the geological description, the aquifer media were classified according to the criteria of Table 1.

Soil

Soil has a significant impact on the amount of recharge, the amount of potential dispersion and the purifying process of contaminants (Lee 2003). Soil data were obtained from the “Atlas de Suelos de la República Argentina” (SAGyP-INTA et al. 1990). Five surface texture classifications were identified in the study area, (displayed in Fig. 4). The assigned DRASTIC ratings and weight are listed in Table 1.

Topography

Topography is expressed in the form of slope in the DRASTIC model. Low-sloped lands tend to retain water for a longer period than the high-sloped ones, and then, infiltration and contaminant migration increase as slope decreases. At regional scale, the study area is extremely flat, with slopes of < 0.01% (Jobbágy et al. 2008).

The slope map was developed from the Digital Elevation Model (DEM) from SRTM (Shuttle Radar Topography Mission). Slope parameter (from W to E) at the regional scale is < 2%, and thus, it is represented by only one terrain relief class (rating 10), as showed in Table 1.

Impact of vadose zone

The vadose zone is the portion of the geological profile above groundwater surface (phreatic) (Poehls and Smith 2009). According to Boulding and Ginn (2004), the vadose

Table 2 Mean water excess for data series

Soil profile	Months											
	J (mm)	F (mm)	M (mm)	A (mm)	M (mm)	J (mm)	J (mm)	A (mm)	S (mm)	O (mm)	N (mm)	D (mm)
Alvear	44.53	60.25	73.51	49.80	49.48	33.55	16.96	10.81	32.04	29.02	39.19	72.84
Anguil1	39.03	26.28	36.36	35.68	14.10	46.25	48.58	23.55	10.83	30.19	23.37	48.06
Anguil2	28.06	25.49	37.33	34.10	21.63	24.63	37.36	26.87	25.15	30.76	18.28	44.73
Anguil3	28.91	32.48	37.20	45.36	23.83	31.14	35.05	29.41	25.82	24.87	23.78	37.32
Anguil4	18.33	31.00	42.07	34.09	11.51	24.71	62.87	24.10	40.75	29.91	28.50	79.61
Anguil5	32.70	26.40	34.89	30.67	17.83	41.76	44.48	24.43	21.19	28.57	25.09	77.66
Catriló	61.52	30.48	55.28	47.74	28.58	17.55	32.11	35.24	34.22	48.13	34.35	67.08
Cereales	61.57	44.62	41.78	15.56	15.02	13.85	0.00	17.95	26.32	47.63	30.25	35.55
Larroudé	26.98	46.16	46.67	38.09	28.05	25.83	18.27	13.08	35.14	32.08	33.96	34.65
Macachín1	27.57	40.63	59.75	28.17	21.76	9.86	16.56	38.86	42.94	25.82	20.41	38.61
Macachín2	32.36	44.49	50.56	30.60	23.40	12.58	19.87	23.14	60.88	28.59	29.60	25.03
Macachín3	50.73	45.55	43.73	31.57	18.04	11.76	10.07	31.44	54.45	21.98	27.75	43.97
Martini1	144.60	21.68	39.97	69.75	7.97	18.53	43.95	2.87	36.15	44.10	54.33	150.50
Martini2	85.75	11.80	59.45	78.85	25.48	14.00	4.10	2.80	31.70	41.90	58.15	146.00
Martini3	61.33	26.12	60.84	35.62	42.12	18.38	5.15	18.14	32.34	32.04	24.64	30.23
Martini4	79.00	29.60	61.46	75.30	20.35	14.68	50.45	5.03	29.47	44.73	37.00	81.85
Pico1	17.09	40.40	46.77	45.06	23.66	14.28	19.66	9.53	18.27	26.93	35.80	47.80
Pico2	26.74	51.38	73.53	46.44	23.96	13.75	20.03	10.54	33.67	25.07	38.54	50.73
Quemú	39.93	37.66	57.04	50.52	38.25	18.23	9.55	27.18	24.25	46.21	37.53	35.83
Realicó	28.86	22.81	33.25	40.80	31.36	19.96	15.10	12.34	36.80	21.27	57.86	68.35
Riglos	36.98	58.91	54.59	27.63	22.92	13.03	20.61	18.91	61.27	25.43	34.11	58.41
StaRosa	35.00	19.18	52.94	30.73	23.99	34.78	30.35	10.79	39.08	40.51	33.66	51.84
Trenel1	25.13	44.90	62.89	43.97	30.07	6.67	28.71	14.74	39.62	24.13	41.64	42.60
Trenel2	26.93	38.85	60.99	36.07	18.94	8.07	12.39	17.24	44.22	27.56	43.75	58.21
Trenel3	18.68	38.49	52.07	35.80	29.78	6.45	35.43	17.02	53.02	27.23	41.42	57.84
Winifreda	55.90	19.30	60.91	44.79	28.00	29.00	40.68	41.10	21.55	43.63	42.09	74.00

zone is the significant reservoir for the capture, storage, and release of contaminants. Many processes that influence the potential pollution take place in the vadose zone. The characteristic of this zone controls the passage of the contaminants to the aquifer and their potential attenuation. The vadose zone stratigraphy was obtained from the Natural Resources Inventory of La Pampa Province (Cano et al. 1980; Zarate 2003). In the study area, the vadose zone media are conformed by calcrete, sand, and calcrete and sandy deposits. Ratings were then multiplied by the weight of the vadose zone parameter (Table 1) to generate the vadose zone index map (Fig. 5).

Hydraulic conductivity of the aquifer

This parameter represents the groundwater mobility capacity inside the saturated media (Civita and De Maio 2000); in other words, it expresses the ability of the aquifer materials to transfer water and control the contaminants movement throughout the aquifer. Aquifers of high hydraulic

conductivity are more vulnerable to contamination than those of low conductivity. The hydraulic conductivity of aquifers ranges from 20-m day⁻¹ in those lands rich in sandy sediments (Castro and Schulz 2009) to 10-m day⁻¹ in lands where sandy-silt sediments predominate (Auge 2005). The hydraulic conductivity map shows assigned ratings that range between 2 and 4 (not shown) (Table 1).

Groundwater sampling

To check the DRASTIC index, three herbicides and one metabolite were selected as the primary control parameters (contaminants). In natural conditions, herbicides are not found in groundwater and they usually infiltrate from the surface layer. Thus, for testing the vulnerability assessment, 95 groundwater wells were sampled from 16 farms located in different vulnerability zones of the study area (Fig. 6). Samples were analyzed for Atrazine (ATZ), Imazapyr (IMZ), Glyphosate (GLY), and aminomethylphosphonic acid (AMPA). Farms were selected according to the intensity of herbicides use. Farms with low input of herbicides (LIH)

Table 3 Frequency of occurrence of water excess events

Soil profile	Months											
	J	F	M	A	M	J	J	A	S	O	N	D
Alvear	0.25	0.15	0.40	0.48	0.21	0.15	0.10	0.08	0.17	0.29	0.23	0.10
Anguil1	0.04	0.06	0.21	0.25	0.13	0.12	0.07	0.09	0.10	0.13	0.13	0.10
Anguil2	0.35	0.31	0.54	0.46	0.31	0.23	0.15	0.23	0.23	0.35	0.42	0.33
Anguil3	0.43	0.41	0.63	0.46	0.35	0.26	0.19	0.18	0.31	0.44	0.46	0.35
Anguil4	0.13	0.13	0.38	0.32	0.23	0.15	0.06	0.17	0.13	0.17	0.19	0.15
Anguil5	0.06	0.07	0.22	0.29	0.15	0.13	0.07	0.12	0.10	0.15	0.13	0.10
Catriló	0.13	0.09	0.43	0.47	0.28	0.21	0.19	0.15	0.21	0.26	0.32	0.17
Cereales	0.18	0.29	0.59	0.47	0.35	0.24	0.00	0.12	0.29	0.41	0.47	0.24
Larroudé	0.18	0.19	0.38	0.38	0.22	0.13	0.15	0.06	0.10	0.26	0.18	0.15
Macachín1	0.13	0.31	0.44	0.35	0.42	0.21	0.19	0.15	0.21	0.25	0.40	0.19
Macachín2	0.23	0.33	0.52	0.44	0.44	0.21	0.23	0.17	0.23	0.31	0.44	0.23
Macachín3	0.15	0.33	0.44	0.40	0.44	0.21	0.19	0.17	0.23	0.31	0.44	0.19
Martini1	0.03	0.14	0.34	0.21	0.24	0.10	0.07	0.10	0.07	0.17	0.10	0.07
Martini2	0.09	0.04	0.35	0.17	0.17	0.09	0.04	0.09	0.09	0.22	0.09	0.09
Martini3	0.17	0.39	0.65	0.48	0.26	0.17	0.17	0.22	0.22	0.43	0.35	0.30
Martini4	0.07	0.21	0.38	0.21	0.28	0.14	0.07	0.14	0.10	0.21	0.17	0.14
Pico1	0.19	0.21	0.40	0.35	0.25	0.17	0.17	0.13	0.15	0.23	0.17	0.17
Pico2	0.17	0.19	0.40	0.35	0.23	0.17	0.17	0.10	0.13	0.23	0.15	0.17
Quemú	0.13	0.21	0.43	0.31	0.22	0.16	0.15	0.16	0.22	0.32	0.34	0.22
Realicó	0.18	0.16	0.28	0.37	0.15	0.16	0.16	0.07	0.09	0.19	0.12	0.12
Riglos	0.33	0.38	0.60	0.54	0.48	0.23	0.29	0.25	0.25	0.40	0.48	0.23
StaRosa	0.06	0.02	0.06	0.17	0.04	0.02	0.04	0.02	0.04	0.08	0.17	0.13
Trenel1	0.08	0.08	0.31	0.27	0.13	0.06	0.15	0.10	0.13	0.17	0.23	0.15
Trenel2	0.17	0.17	0.40	0.46	0.19	0.13	0.15	0.21	0.13	0.29	0.27	0.19
Trenel3	0.17	0.17	0.40	0.46	0.19	0.13	0.15	0.21	0.13	0.29	0.27	0.19
Winifreda	0.06	0.08	0.19	0.19	0.06	0.06	0.08	0.08	0.04	0.15	0.15	0.10

are those with a low but no absence use of herbicides. On the contrary, farms with high inputs of herbicides (HIH) are completely dependent of the herbicides application for weed control. Farms with HIH and LIH were selected and sampled in SP and CP. Sixty-nine samples were collected from the SP area: 41 with HIH and 28 with LIH. Twenty-six samples were collected in the CP (13 with HIH and with 13 LIH) (Fig. 6). The number of samples in the study area was not balanced, since there were different number of farms with different number of wells each. Therefore, the percentage is referred to the total samples of each sampling area.

Samples were obtained from windmill water pumps. Windmills extract water not beyond 12 m of depth. Wells were pumped for a minimum time of 15 min before the water sample was collected. Samples were collected in plastic bottles and transported to the laboratory in refrigerated containers. Then, they were filtered through microfilters (0.22-mm-pore-size) and placed in 1.5-ml glass vial. Finally, they were frozen under dark conditions until their analysis.

Chemical analysis

Two analytical methodologies were used to quantify the target compounds: GLY, AMPA, ATZ, and IMZ. For GLY and AMPA, a precolumn derivatization with 9-fluorenylmethylchloroformate was used and the quantification was done by UPLC–MS/MS (ACQUITY UPLC[®] Waters) (Quatro Premier XE) (Zelaya et al. 2011). To analyze IMZ and ATZ, the technique by direct injection was employed, performed by high-performance liquid chromatography in a Waters[®] ALLIANCE 2695 separation module equipped with a XBridge C18 3.5 μ m particle size, 2.1 \times 100 mm column (Waters). A mobile phase A:water/acetonitrile 98:2 + 0.5% of formic acid—phase B: acetonitrile + 0.5% of formic acid (flow of 0.300 ml/min) were used and molecules were analyzed in a coupled Quattro mass spectrometer Waters[®] XE Premier-Micromass (Mode ESI+ MRM for 2 transitions per analyte). The system was controlled by Masslynx Micromass spectrometry software. Quantification limits for GLY and AMPA were 0.10, and 0.30 and 0.25 ppb for ATZ and IMZ, respectively.

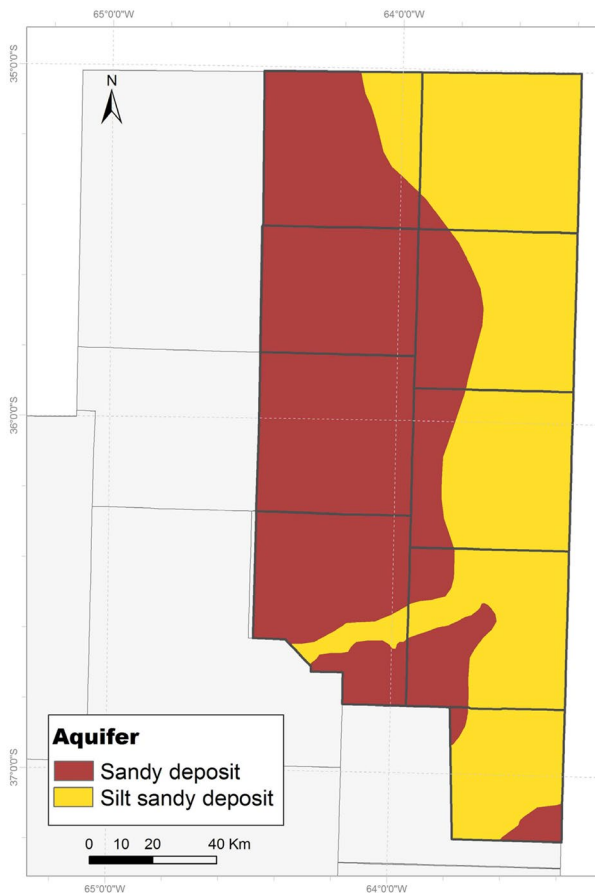


Fig. 3 Map of sediments of the aquifer media

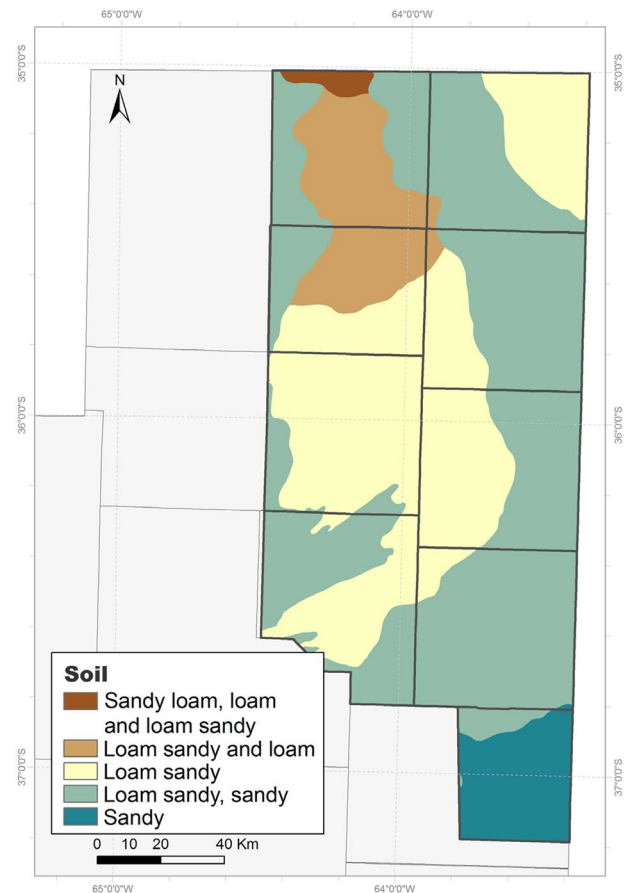


Fig. 4 Soil texture types of the study area

Results and discussion

According to the estimation of water excess in the study area, the groundwater is naturally recharged by rains during late spring (November) and summer (March), and also during the fall season (April). Since the annual rainfall distribution shows an important concentration in spring–summer (60–75%) and in autumn–winter (25–40%), groundwater recharge follows the natural pattern of seasonal rain fluctuation. Water excess followed the following order: March > April > November. The recharge layers of March, April and November are shown in Fig. 7 a, b and c.

Recharge is crucial to understand the potential groundwater pollution process. It is the principal vehicle for leaching and transporting contaminants to the water table. Thus, during March, April, and November, the risk of groundwater pollution would increase in the study area. Groundwater resource management cannot be undertaken without a quantification of the recharge process and its seasonality (Robins 1998).

Groundwater recharge is higher in NE lands than in W ones, which is closely related to rainfall distribution. Likewise, water excess in the study area is higher in N Sector

in contrast to W lands. This is because coarser-textured soils like in SP have small store capacity and water excess moves rapidly to groundwater (Kennett-Smith et al. 1994). Whilst finer texture soils like in CP can store more amounts of water, discharging water excesses slowly. Because of the small field capacity and high infiltration, the water excesses in sandy soils are replenished much more quickly than those soils with loam texture. Thus, groundwater recharge is greater on sandy soils, increasing percolation losses and, therefore, pesticides mobility through oil profile.

Vulnerability maps for March, April, and November months obtained by the application of the DGI (Fig. 8a–c) and the DPI (Fig. 9a–c), evidenced that aquifers of the study area are susceptible to be polluted. The DGI scores vary from 119 to 200; whereas DPI values ranged from 139 to 200. According to the results of the groundwater vulnerability assessment, the study area can be divided in two zones: moderate vulnerability (interval 100–159) and high vulnerability (interval 180–266). The percentage of low vulnerability zones was less than 2%.

The DGI maps showed that 47.2, 46.4, and 46.7% of the area are highly susceptible to pollution for March, April, and

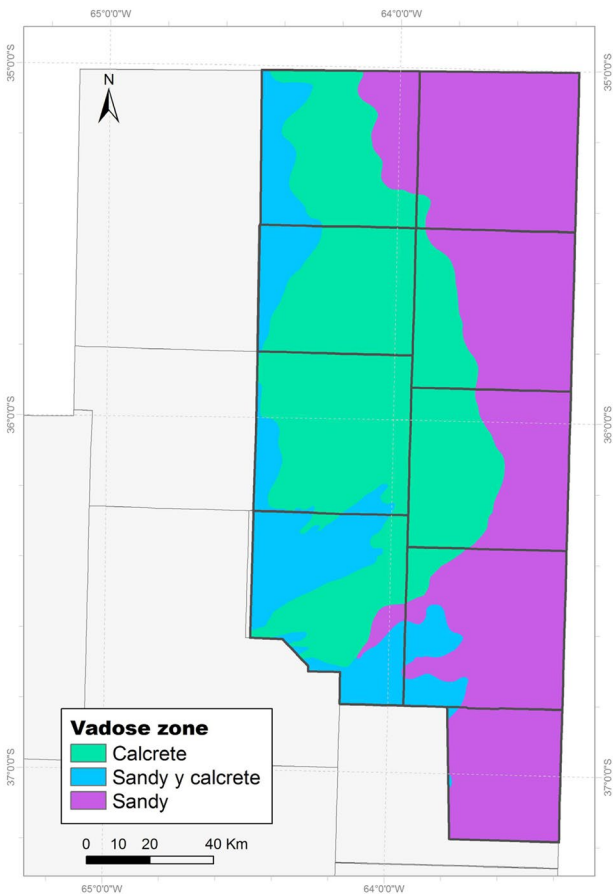


Fig. 5 Characteristics of the vadose zone of the study area

November, respectively. The remaining area was then classified as moderate vulnerability, as less than 2% presented low-to-moderate vulnerability. The DPI maps revealed that 93.7 and 91% of the area has high risk of pollution for March and April, respectively, and 79% of the area show high vulnerability in November. In the present study, the amount of recharge did not show differences regarding the impact in aquifers vulnerability. The difference between the water excess for the 3 months was not greatly enough to produce a remarkable impact in the estimation of vulnerability.

Based on the hydrogeological conditions, the six vulnerability maps of the present study showed that Eastern lands are highly vulnerable, while central and Western lands rather involve moderate vulnerability classes. High vulnerability of E lands can be explained by a combination of shallow water tables, highly permeable soils, a predomination of sandy components in the vadose zone, and positive water balances in March, April, and November. The same characteristics define the high vulnerability of the Dire Dawa groundwater basin zones, a semiarid region of Ethiopia (Tilahun and Merkel 2010).

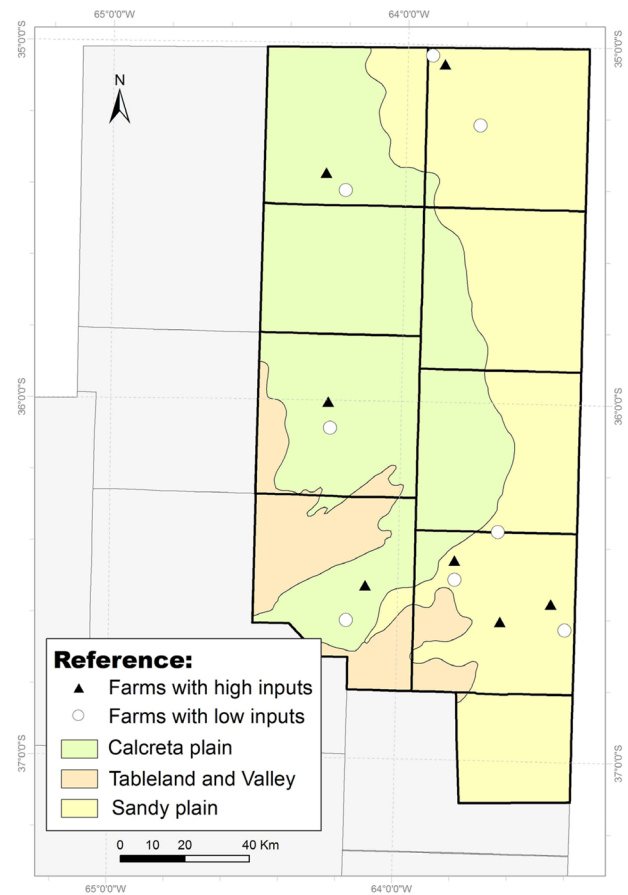


Fig. 6 Location of sampled farms with high and low inputs of herbicides in the study area

The moderate vulnerability of Central and Western lands can be explained by a combination of a deep water table (> 10 m), a low recharge rate, and a little permeable calcrete layer. For instance, Giai and Visconti (2002) studied the formation of the calcrete Plain Subregion of La Pampa Province and its hydrological behavior, demonstrating that the calcrete layer is porous with limited permeability. Calcrete formation can retain water for some time, being permeable in some degree and water can percolate through fractures reaching groundwater (Giai and Visconti 2002). This situation leads to the formation of a false water table from which water is able to drain down through fissures and then recharges the phreatic aquifer.

The different productive aptitude of the agroecological regions of the study area defines different technological characterization of the productive systems. The SP region represents the major potential productive zone, with simple soils that have a good organic matter availability (Lorda et al. 2008), being annual cropping the predominant productive activity. On the contrary, the CP zone



Fig. 7 Maps of recharge (mm month^{-1}) for: **a** March, **b** April, and **c** November

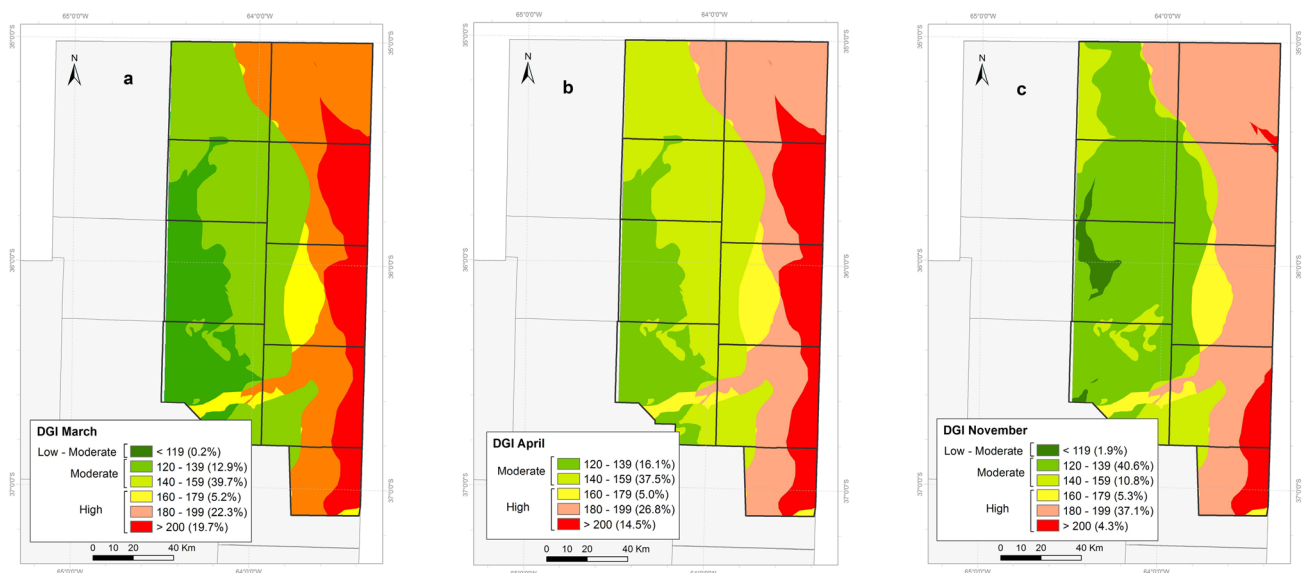


Fig. 8 Maps of the intrinsic aquifer vulnerability (DGI) for: **a** March, **b** April, and **c** November

is characterized by a lower aptitude for crop production. Therefore, since the higher aptitude of SP zone, systems productions are subject to high input of technologies such as pesticides and fertilizers. Nowadays, a tendency to a permanent agriculture of annual crops is observed. The intensification of human activities increases the risk of groundwater contamination (Saidi et al. 2010).

DRASTIC index may be used for a preventive purpose through the prioritization of areas where groundwater protection is a critical issue for the analysis of land-use activities at regional scale. While the original version of DRASTIC

described the spatial vulnerability of lands, we incorporated a temporal scale in our study to identify periods of higher vulnerability and to implement precise management strategies regarding the dominant crops such as soybean, maize, and sunflower. Although November is a highly vulnerable month that corresponds to the sowing date of summer crops, it appears to be less vulnerable than March and April. At this moment, the conjunction of environmental and productivity factors indicates a yellow light related to the risk of groundwater contamination in this region.

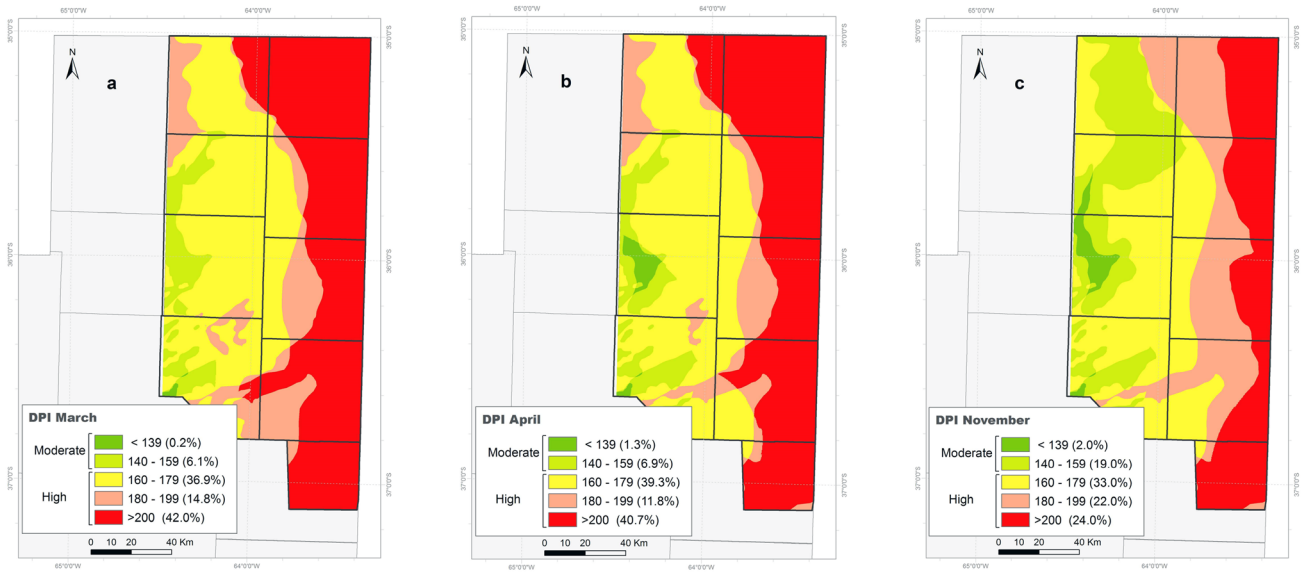


Fig. 9 Maps of the pesticides aquifer vulnerability (DGI) for: **a** March, **b** April, and **c** November

DRASTIC index check

Of 95 water samples analyzed, 18% had quantifiable levels of herbicides. ATZ (13.60%) was the most frequently detected compound in groundwater samples followed by IMZ (3.10%). GLY was quantified in 1.0% of the samples and AMPA was not detected. ATZ concentrations ranged from 0.30 to 16.0 $\mu\text{g l}^{-1}$, and IMZ residues varied among 0.25–6.42 $\mu\text{g l}^{-1}$. GLY was found in one well at 0.67 $\mu\text{g l}^{-1}$. All polluted samples exceeded the EU limit for individual pesticides in drinking water: 0.1 $\mu\text{g l}^{-1}$ (European Directive 98/83/EC). Since the quantification limits of the analytical method for ATZ and IMZ are above 0.1 $\mu\text{g l}^{-1}$, the water

quality criteria for drinking water established to protect human health were exceeded by both herbicides.

Herbicides detection in groundwater was related to some extent with the lithology and the intensity of herbicide use. Overall, there was a coincidence between the higher percentages of herbicides detected in water samples obtained in the SP zone which is in line with the vulnerability DRASTIC pesticide maps. Regarding herbicide use, higher proportion of polluted samples was related to high inputs farms. In the SP zone, 26.0 and 17% of the samples were polluted with ATZ, for HIH and LIH, respectively. In the CP zone, HIH farms (moderate vulnerability), 7.7% of water samples had ATZ. On the contrary, in water samples of LIH farms, herbicides were not detected (Table 4).

Table 4 Number and percentage of samples polluted; maximum and minimum concentrations levels of herbicides in groundwater samples

Herbicides	Sandy plain			Calcrete plain			
	Intensity of herbicide usage						
	High	Conc ($\mu\text{g l}^{-1}$) Max–min	Low	Conc ($\mu\text{g l}^{-1}$) Max–min	High	Conc ($\mu\text{g l}^{-1}$) Max–min	Low
Atrazine	7	0.3–6.5	5	0.30–16.1	1	0.33	0
%	17.1		17.8		7.7		0.0
Imazapyr	3	0.2–6.4	0	–	0	–	0
%	7.3		0.0		0.0		0.0
Glyphosate	1	0.7	0	–	0	–	0
%	2.4		0.0		0.0		0.0
AMPA	0	–	0	–	0	–	0
%	0.0		0.0		0.0		0.0
No. of samples	41		28		13		13
Total residues hal%	26.8		17.8		7.7		0

Since about 1970, ATZ has been heavily used in agriculture production in Argentina. Atrazine is the single most widely herbicide used in corn, applied to fields before crop emergence, after crop emergence, or at both times. Besides, atrazine is applied for weed control during the non-crop periods in chemical fallow. Even though atrazine is not labelled for weed management in soybean production, and the farmer takes a risk applying atrazine in chemical fallow for weed control within plots where soybean is going to growth. Considering the large quantities and the high intensity of inputs used in the study area, higher concentrations of herbicides would have been expected in groundwater.

ATZ is a weak base compound with a moderate-to-strong adsorption to soil (Satpute et al. 2015), and a moderate solubility of water and mobility through soil profile (Delwiche et al. 2014; Schwab 2006; Kruger et al. 1993). Herwing et al. (2001) reported that once adsorbed in soil, ATZ persists there over long periods and it desorbs only gradually. During transport through soil profile, especially when it is still in the root region in the first 10 cm of the vadose zone, some dissipation occurs, until reaching the water table of the unconfined aquifer. Atrazine has been found in surface water and groundwater. A great number of studies have monitored the concentrations of atrazine in groundwater over the last 3 decades (Van Maanen et al. 2001; Guzzella et al. 2005; Tappe et al. 2002; Shomar et al. 2005; Székács et al. 2015). ATZ residues detected in the present study coincide with concentrations found in different regions of the world. Due to its impact on groundwater, atrazine has been banned in many countries, and consequently, producers and environmental scientists have focused their attention on possible substitutes. However, in Argentina, it is still widely used (SAGPyA 2001).

IMZ have become widely used more recently in Argentina (registered in 2003) due to the adoption of imidazolinone-tolerant crops (Clearfield® crops) (Tan et al. 2005). Because it is a relatively new class of herbicide and due to their low application rate (80 g ha^{-1}), we would have expected to find lower concentrations in groundwater. The environmental concerns about imidazolinone herbicides have been raised regarding to their anionic character. As a consequence of their amphoteric structure, imidazolinone herbicides are predominantly in the anionic form at pH levels typical of many agricultural soils (Mangels 1991). Because of that, imidazolinone are very mobile in soil (Porfiri et al. 2015; Reginato et al. 2005; O'Dell et al. 1992) and may leach to the groundwater. To date, a few reports of imidazolinone herbicides have been published related to their detection in groundwater. For example, Battaglin et al. (1998), studied the occurrence of imidazolinone in groundwater in the Midwestern United States, and imazethapyr was detected at concentrations less than $0.10 \mu\text{g l}^{-1}$, while IMZ was not detected. It is important to notice that the highest residues

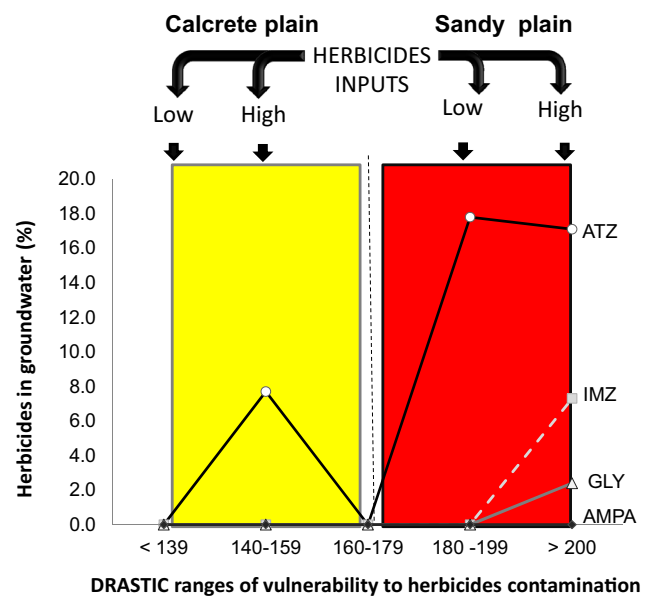


Fig. 10 Percentage of atrazine, imazapyr, glyphosate, and its metabolite AMPA in groundwater of sandy and calcrete plains, under low (LIH) and high (HIH) input conditions, and their correspondence with DRATIC pesticide vulnerability estimations

of ATZ in groundwater ($16.1 \mu\text{g l}^{-1}$) and IMZ in some wells ($6.52 \mu\text{g l}^{-1}$) could be caused by point sources, such as an accidental leak or an inappropriate disposal.

Despite the heavy use of glyphosate in no-tillage systems and glyphosate-resistant crops in the past 20 years in agricultural lands of central Argentine, only one sample of 95 tested wells had GLY. These results were expected, since GLY and AMPA are not likely to move to groundwater due to their strong adsorptive characteristics. Glyphosate has also been detected in groundwater on rare occasions. Battaglin et al. (2014) recently reported that of a total amount of 1171 groundwater analyzed samples from 807 different sites; glyphosate was detected only in 5.8% and AMPA in 14.3%.

By visual inspection of Fig. 10, we can elucidate that the groundwater potential pollution is conditioned by the spatial variability of geomorphological features (SP and CP), influenced by others variables such as the intensity of herbicide use (HIH and LIH), and the physicochemical properties of the compounds. The groundwater pollution is in line with the DRATIC maps.

Conclusions

The present work addresses the vulnerability assessment of the Quaternary aquifer system. Generic and Pesticide DRATIC GIS-based models were applied to assess the groundwater vulnerability of agriculture and other activities on the land surface. DRATIC maps were checked against

herbicides detection in the underlying aquifers to the study area.

According to recharge monthly estimation, the aquifers vulnerability of the semiarid lands of central Argentina would increase during March, April, and November. Consequently, the Generic and Pesticide DRASTIC models were applied for those months. The vulnerability maps revealed that groundwater is under a high-to-moderate vulnerability to pollution. On average, Generic and Pesticides DRASTIC maps display that 47 and 88% of the entire area is highly vulnerable to pollution, respectively. The northern part of the study area is dominated by high-pollution vulnerability class, and this is very strongly related to shallow groundwater systems, high permeable sediments, and net recharge.

DRASTIC pesticide model was tested using herbicides concentration data of groundwater as a proxy of pollution risk. In relation to this, several water samples were collected from farms widely distributed in the area, previously classified according to the intensity of herbicide use. In general, groundwater quality is currently affected by residues of herbicides, as evidenced by positive detections of these compounds. Atrazine and imazapyr were detected at concentrations that exceeded the $0.10 \mu\text{g l}^{-1}$ limit. Herbicides occurrence is related to the intensity of agricultural activity, physicochemical properties of the compounds, highly permeable soils, shallow water table, and net recharge. The results reveal that there is clear relationship between herbicide pollution and the intense use of these compounds. Atrazine and imazapyr were found at higher proportions in high inputs herbicides farms. Moreover, the higher frequencies of detection of these compounds in groundwater were positively correlated with areas of high vulnerability to pollution, coinciding with the sandy plain region.

Pesticides DRASTIC maps are representative of the real susceptibility of the shallow aquifers of the semiarid lands of central Argentina. The results of the present study indicate that more attention is needed concerning management of agricultural lands and water resources, and for that, monitoring of groundwater quality is urgently needed. The present study may provide useful information and criteria for decision-making and management of water resources to protect groundwater quality.

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