ORIGINAL ARTICLE

# Groundwater chemical pollution risk: assessment through a soil attenuation index

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**Abstract** Aquifer vulnerability is frequently estimated through methodologies that don't consider most physical and chemical soil parameters. A soil attenuation index is proposed to estimate groundwater chemical pollution risk, that takes into account organic carbon content, pH, cation exchange capacity, clay content, phreatic depth and landscape position. The attenuation index is constructed by a methodology similar to that developed for water quality index. P, Mn and Zn concentrations in groundwater from selected places were used to validate the proposed index.

**Keywords** Soil properties · Groundwater protection · Soil attenuation index · Aquifer vulnerability

## Introduction

Chemicals are transported through the unsaturated zone dissolved in water that infiltrates from the land surface and percolates to the water table. The concentration of the contaminant crossing the water table will be different from the concentration of leachate emanating from the source because of the physical, chemical and biological mechanisms mainly occurring in the unsaturated zone (UZ) i.e.,

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filtration, adsorption, desorption, solution, dilution, oxidation, precipitation, biological transformation, etc.

In any given area, groundwater is vulnerable to contamination from anthropic activities.

Groundwater vulnerability is a function of the geologic setting of an area, as this largely controls the amount of time that has passed since the water fell as rain, infiltrated through the soil, reached the water table, and began flowing to its present location. This amount of time is called the residence time of the groundwater. Most sources of contamination are located on or near the land surface, and are of quite recent origin from a geological perspective.

Different land uses (industrial, agricultural and urban use) in a semiurban region in the surroundings of Buenos Aires city (Escobar, province of Buenos Aires), impact in a different way on soil and water. In a previous paper, we have studied soils located in different landscape positions in this area to evaluate their properties and their ability of P adsorption (Heredia and Fernández Cirelli 2006).

Some methods to evaluate vulnerability assessment, like GOD method (Foster and Hirata 1988), the Irish approach (Daly and Drew 1999) or AVI method (Van Stempvoort et al. 1993), consider only some characteristics of the soil and unsaturated zone such as clay content. The approach based on delineation of protection zones for groundwater supply systems considers to some extent groundwater flow and contaminant transport processes within the saturated zone (Derouane and Dassargues 1998). Other methods to assess aquifer vulnerability like DRASTIC (Aller et al. 1985), SINTACS (Civita and De Regibus 1995), EPIK (Doerfliger and Zwahlen 1997) consider only thickness, texture and mineralogy.

Various natural, physical processes, and chemical reactions that operate in the soil, unsaturated, and saturated zones, may cause the pollutant to change its physical state

and chemical form. These changes may attenuate the degree of pollution. Especially in soil and the unsaturated zone, some mechanisms may affect the contaminant concentration much more than in the saturated zone (Gogu and Dessargues 2000).

Actually, the evaluation systems in use neglect important parameters like other significant soil properties (i.e., organic matter content, pH value) or sorption processes. Transport and degradation processes have not been taken into account for potential pollution assessment. Chemical properties of soils and unsaturated zone may improve the diagnosis of the potential pollution risk.

The comparison of each one of the evaluated parameters (phreatic depth, landscape position, clay content, cation exchange capacity, organic carbon, pH) to determine the relative capacity of attenuation of the contamination in the soils is a complex task. It is important to develop a methodology for soils based on the one used for the determination of water quality index (Conesa Fdez Vitora 1993). In this index, the different parameters are normalized and then combined in a unique number that facilitates the water quality comparison.

The objective of this work was to determine the physical and chemical properties that are related with the soil buffer capacity and classify the soils in function of their capacity of reduction of the contamination through the development of a soil attenuation index.

## Materials and methods

Escobar county (Fig. 1) has 178,155 inhabitants and 30,300 ha. Population increased 180 % between 1970 and 1991 (INDEC 2001). Urban areas account for 7,486 ha.



**Fig. 1** Map of Buenos Aires province (Argentina) with indication of studied area

While rural areas account to 15,114 ha. Industrial activity is important and 233 establishments have been reported (CDI 2006).

The soil profiles, and groundwater under study are located between 34° 18′S and 58° 51′ W to 34° 24′S and 58° 44′W, in the geomorphologic unit called Rolling Pampa (Pampa ondulada) which has a wet climate (mean annual precipitation is 900 mm) and a mean temperature of 16°C.

From the geological point of view, the Rolling Pampa is a sedimentary basin where Cretaceous, tertiary, Plio-Pleistocene and Pleistocene sediments are superimposed over the Precambrian crystalline basement.

The pampean sediments or pampean loess, Medium and Upper Pleistocene (SAGyP-INTA 1989), are of special importance in the chemical composition of the groundwater. Pampean loess is of volcanic pyroclastic origin and has been transported by winds to the actual place of deposition. The most important components are plagioclases, quartz, orthoclase, volcanic ash, volcanic glass shards, calcium carbonate as calcite, altered feldspars, fragments of volcanic rocks, and organogenic opal; the clay fraction is composed of illite (Iñiguez and Scoppa 1971).

Soil samples were collected in the soil trench during January 2004 (summer) from undisturbed sites, located in different places in Escobar county (Garín, Maschwitz, Belen de Escobar, Loma Verde and Matheu).

They were air dried, sieved to pass 2 mm and analyzed for extractable phosphorus (Pe, Bray-Kurtz 1 method), pH (1:2.5 soil: water relationship), organic carbon (OC) (Walkley-Black method), cation exchange capacity (CEC) and exchangeable iron (Fe), manganese (Mn), zinc (Zn), copper (Cu) (Amonium Acetate 1N pH 7.0) and clay content (Bouyoucous method) were determined by standardized methods (Sparks 1996; USDA 1996).

Water samples of Pampeano aquifer were collected in May 2004 ($n$: 34, between 9 and 30 m depth) and Cu, Fe, Mn and Zn, were determined with an ICP-OES Perkin Elmer Optima 2000 DV. Soluble phosphorous (P) in groundwater samples was determined (Murphy and Riley 1962).

Soil attenuation index (SAI)

The different soil parameters require a normalization step, where each parameter is transformed into a 0–100% scale. The next step is to apply relative weight factors that reflect the importance of each parameter as an indicator of the soil attenuation capacity.

The SAI combines in a unique number (index) the different parameters to facilitate the comparison (Conesa Fdez Vitora 1993).

Parameters used for the construction of SAI were: landscape position, phreatic water depth, clay content,

CEC, OC and pH. They were combined in the following equation:

$$SAI = \frac{\sum C_i \times P_i}{\sum P_i}$$

where $C_i$ is the value assigned to each parameter after normalization, where 100 is the maximum punctuation and 10 the minor. $P_i$: is the relative weight assigned to each parameter. The scale varies from 1 to 4, where 4 is most important (i.e., phreatic depth), while a value of 1 means that the parameter has a smaller impact (i.e., landscape position).

## Results and discussion

Soils were classified according to soil taxonomy (Soil Survey Staff 2003), as previously described (Heredia and Fernández Cirelli 2006).

The soils are in two landscape positions, upper (U) and lower (L) part of the field. The U-soils are: 1, 2, 4, 5, 6, 7 and 10. The L-soils are: 3, 8 and 9 (Table 1 and Fig. 2).

Hewitt and Shepherd (1997) have developed a structural vulnerability index for Australian soils. They identified four soil attributes: total organic content, phosphate retention, clay content and dry factors (wetness). Other
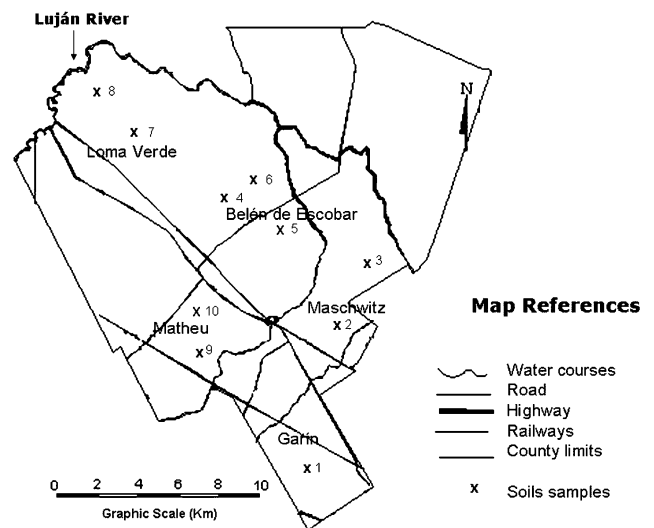


Fig. 2 Map of Escobar county and soil sampling places

authors developed soil indexes to improve soil quality and soil land uses (Año Vidal et al. 2002).

In our work, the objective was to study the effect of soil on groundwater quality and how the construction of an attenuation index may improve the vulnerability models used up to now.

The first step in the construction of SAI was the normalization of the selected parameters (Table 2).

For phreatic layer, a 2 m depth was considered the most vulnerable depth since water may rise by capillarity in clay and loamy soils. On the other hand, phreatic groundwater deeper than 20 m was considered of very low vulnerability. This parameter was given the highest relative weight since it is of utmost importance for the arrival of pollutants to the water table.

The position in the landscape gives an idea of the unsaturated zone thickness and consequently the thickness that pollutants should transit until the water table. It complements the phreatic water depth and was given a relative weight of 1. The U-soils (20–30 masl) were given the maximum value of normalization factor (100), the minor corresponds to those L-soils located near the rivers and streams of the area (5 masl) and the intermediate values are presented in the Table 2.

Formation and stabilization of peds needs a clay content of 15 %. As the clay content increases the capacity of pollutant retention of the soil also increases. This parameter deserved a relative weight of 3 due to its important function in the retention of contaminants.

For CEC that represents the soil capacity to retain ions, a normalization factor of 10 was given to soils with a CEC value less than 5 $cmol_c$ $kg^{-1}$, which are considered of low retention of nutrients and contaminants. The highest

**Table 1** Soil identification and classification

| Location | Identification | Coordinates | Taxonomic classification |
|---|---|---|---|
| Garin | 1 (U) | 34°24′53.9″S 58°44′36.7″W | Typic Argiudoll |
| Maschwitz | 2 (U) | 34°22′42.3″S 58°44′40.6″W | Entic Hapludoll |
| Maschwitz | 3(L) | 34°21′46.9″S 58° 44′05″W | Aquic Hapludoll |
| Belén de Escobar | 4 (U) | 34°20′11.9″S 58°48′06.7″W | Typic Argiudoll |
| Belén de Escobar | 5 (U) | 34°20′34.4″S 58°46′53.9″W | Typic Argiudoll |
| Belén de Escobar | 6 (U) | 34°20′05.2″S 58°47′15.6″W | Udarent |
| Loma Verde | 7 (U) | 34°18′53.1″S 58°51′07.9″W | Typic Argiudoll |
| Loma Verde | 8 (L) | 34°18′38″S 58°51′18.8″W | Typic Natraquoll |
| Matheu | 9 (L) | 34°23′36.8″S 58°49′06.1″W | Mollic Fluvaquent |
| Matheu | 10 (U) | 34°22′48.3″S 58°48′48.3″W | Typic Argiudoll |

**Table 2** Parameters considered for the construction of the SAI, relative weight and proposed normalization factor

| Parameter | Relative weight (Pi) | Normalization factor (Ci) | | | | |
|---|---|---|---|---|---|---|
| | | 100 | 75 | 50 | 25 | 10 |
| Phreatic depth (m) | 4 | >20 | 10–20 | 5–10 | 2–5 | <2 |
| Landscape position (m) | 1 | >20 | – | 10–20 | 5–10 | <5 |
| Clay (%) | 3 | >50 | 30–50 | 20–30 | 15–20 | <15 |
| CEC (cmolc kg$^{-1}$) | 3 | >25 | 17–25 | 10–17 | 5–10 | 0–5 |
| OC (g kg$^{-1}$) | 3 | >30 | 20–30 | 15–20 | 7.5–15 | 0–7.4 |
| pH | 2 | 6.6–7.5 | 5–6.5/7.6–8.5 | | | >8.5/<5.0 |

Selective criteria have been used to normalize the different parameters

normalization factor (100) was given to soils with CEC above 25 cmol$_c$ kg$^{-1}$. The given relative weight was 3, since CEC is directly related to the capacity of retention of ions of the exchange complex.

Normalization factor for OC ranged from 10 for those soils with values lower than 7,4 g kg$^{-1}$, to 100 for soils with OC values higher than 30 g kg$^{-1}$. The given relative weight was 3 since OC gives a very clear idea of the complexation capacity, has a clear incidence on aggregate stability and affects pore stability in the edaphic system.

Several authors (Huddleston 1996; Gan 2002) found that combined effect of leaching potential and sorption potential determined a soil sensibility with respect to groundwater vulnerability and these factors depend on texture and organic matter content.

For soil pH, the maximum value (100) was assigned to pH between 6.6 and 7.5, while 75 was given to slightly to moderately acid soils and slightly to moderate alkaline soils. For strongly and very strongly acid and alkaline pH values, the normalization factor was 10 because extreme pH values promote colloidal instability and affect the porous systems. Also, low pH increases the mobility of most trace elements. The relative weight for pH was 2 since together with CEC gives an idea of the saturation of

the colloidal complex and the possibility of movement of toxic elements in the soil.

Phreatic depth (Table 3) is considered from the land surface since this value is more representative of the transit of the pollutant through the unsaturated zone. Piezometric levels of the area are shown in Fig. 3. The landscape position was evaluated in situ considering the topographical chart of the area. Other parameters were determined in our laboratory according to the previously described methods. The values corresponding to each of the parameters needed for the construction of the index are shown in Table 3.

Each of the parameters in Table 3 was normalized according to the criteria above described (see Table 2 for normalization factors). Values obtained are shown in Table 4.

SAI was calculated for each soil taken into account, the normalization value of the analyzed parameters and the corresponding relative weight previously assigned to each of them (Table 5).

The hierarchical levels established for SAI were as follows: SAI between 0 and 25 corresponds to a soil of very low retention capacity; between 26 and 50, low retention capacity; 51 to 75, moderate retention capacity,

**Table 3** Value of variables analyzed for each necessary soil for the construction of the soil attenuation index

| Soil | Phreatic water depth (m) | Landscape position (m) | Clay content[a](%) | CEC[b](cmol$_c$ kg$^{-1}$) | OC[c](g kg$^{-1}$) | pH[c] |
|---|---|---|---|---|---|---|
| 1 | 10 | 15 | 56 | 16.7–17.0 | 13.5 | 6.4 |
| 2 | 10 | 8 | 42.5 | 7.7–8.2 | 8.1 | 6.4 |
| 3 | 0.5 | 4 | 45 | 15.6–13.6 | 17.5 | 6.5 |
| 4 | 30 | 28 | 50 | 17.0–23.2 | 12.4 | 6.7 |
| 5 | 30 | 26 | 51 | 17.1–19.2 | 13.2 | 6.2 |
| 6 | 6 | 20 | 30 | 18.0–11.0 | 7.8 | 7.9 |
| 7 | 4 | 9 | 40 | 13.1–14.6 | 23.6 | 6.9 |
| 8 | 3 | 4 | 32.5 | 15.9 –12.1 | 26.9 | 7.4 |
| 9 | 0.6 | 3 | 41 | 20.0–15.1 | 30.0 | 8.8 |
| 10 | 6 | 20 | 50 | 17.0–12.0 | 18.3 | 6.3 |

[a] It corresponds to B horizon or to the depth inside the 100 cm profile depth (argilic horizon or clay layer)

[b] It corresponds to A and B horizon

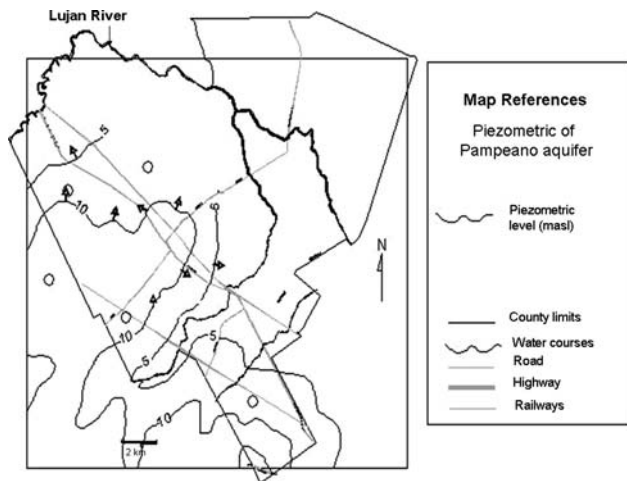[c] It corresponds to A horizon or first 20 cm soil depth

**Fig. 3** Piezometric map of Pampeano aquifer (adapted from Silva Busso et al. 2004)

**Table 4** Normalization value of the analyzed parameters

| Soil | Phreatic water depth | Landscape position | Clay content | CEC | OC | pH |
|------|----------------------|--------------------|--------------|-----|-----|-----|
| 1 | 50 | 50 | 100 | 50 | 25 | 75 |
| 2 | 50 | 25 | 75 | 25 | 25 | 75 |
| 3 | 10 | 10 | 75 | 50 | 50 | 75 |
| 4 | 100 | 100 | 100 | 75 | 25 | 100 |
| 5 | 100 | 100 | 100 | 75 | 25 | 75 |
| 6 | 50 | 50 | 75 | 50 | 25 | 75 |
| 7 | 25 | 25 | 75 | 50 | 75 | 100 |
| 8 | 25 | 10 | 75 | 50 | 75 | 100 |
| 9 | 10 | 10 | 75 | 50 | 75 | 10 |
| 10 | 50 | 75 | 100 | 50 | 50 | 75 |

and values between 76 and 100 would indicate that the soil has high retention capacity.

According to the SAI values, the studied soils can be classified as is shown in Table 6. U-soils have a moderate

**Table 6** Classification of the soils under study according to SAI

| SAI | Soil number |
|-----|-------------|
| Low | 8 > 6 > 2 > 9 > 3 |
| Moderate | 4 > 5 > 10 > 1 > 7 |

SAI, with the exception of soil 2 (sandy soil) and soil 6 (Udarent soil), while the L-soils have lower SAI.

None of the evaluated soils enters inside the category of very low or high soil attenuation index.

In order to validate the constructed SAI, the soil behavior in relation to the contamination with P and heavy metals and their impact on the groundwater, was analyzed.

Soil 10 was selected as an example of soil with moderate SAI. It was evaluated for P, Mn and Zn contamination. Extractable Mn in soil was 6.55 mg kg$^{-1}$, while in Pampeano aquifer its concentration was under the detection limit (<4 µg L$^{-1}$). Extractable Zn was up 1 mg kg$^{-1}$ while in groundwater its concentration was 35.8 µg L$^{-1}$, indicating a reduction of Zn content of 28 times. Extractable soil P value was in this soil of 38.6 mg kg$^{-1}$, in soil solution it ranged between 0.12 and 1.18 mg L$^{-1}$ (mean value 0.32 mg L$^{-1}$) and in the groundwater it was of 0.07 mg L$^{-1}$ (Heredia and Fernández Cirelli 2006).

Soil 2 was selected as an example of a soil with low SAI. Extractable P soil content was 73.8 mg kg$^{-1}$, while P concentration in groundwater was 0.258 mg L$^{-1}$, indicating a smaller soil attenuation capacity in comparison with soil 10.

On the other hand, we analyzed the relationship between land use, soil type, and its corresponding SAI, P and trace metals in the Pampeano aquifer (Table 7) in different places in Escobar county.

The lowest SAI value corresponds to Maschwitz soils, with the highest manganese and phosphorous concentration in groundwater. In this area, the land use is mainly urban;

**Table 5** Calculation of the SAI for the soils in study

| Soil | Phreatic water depth | Landscape position | Clay content | CEC | OC | pH | $\sum$ | SAI |
|------|----------------------|--------------------|--------------|-----|-----|-----|--------|-----|
| 1 | 200 | 50 | 300 | 150 | 75 | 150 | 925 | 57.8 |
| 2 | 200 | 25 | 225 | 75 | 75 | 75 | 675 | 42.2 |
| 3 | 40 | 10 | 225 | 150 | 150 | 75 | 650 | 40.6 |
| 4 | 400 | 100 | 300 | 225 | 75 | 100 | 1200 | 75.0 |
| 5 | 400 | 100 | 300 | 225 | 75 | 75 | 1175 | 73.4 |
| 6 | 200 | 50 | 225 | 150 | 75 | 75 | 775 | 48.4 |
| 7 | 100 | 25 | 225 | 150 | 225 | 100 | 825 | 51.6 |
| 8 | 100 | 10 | 225 | 150 | 225 | 100 | 810 | 50.6 |
| 9 | 40 | 10 | 225 | 150 | 225 | 10 | 660 | 41.3 |
| 10 | 200 | 75 | 300 | 150 | 150 | 75 | 950 | 59.4 |

**Table 7** Mean values of trace metals and phosphorous in groundwater

| Locality | Copper μg L$^{-1}$ | Manganese μg L$^{-1}$ | Iron μg L$^{-1}$ | Zinc μg L$^{-1}$ | Phosphorus mg L$^{-1}$ |
|---|---|---|---|---|---|
| Loma Verde | 30.7 | 1.0 | 24.5 | 474.2 | 0.231 |
| Belén de Escobar | 12.5 | 5.5 | 95.5 | 202.0 | 0.031 |
| Matheu | 18.5 | 2.3 | 78.8 | 245.9 | 0.036 |
| Garín | 9.3 | 8.1 | 123.4 | 283.8 | 0.133 |
| Maschwitz | 13.3 | 380.4 | 12.8 | 102.4 | 0.236 |

there are also greenhouses and nurseries with horticultural crops.

In Loma Verde, soils have low SAI but higher pollutant inputs because of meat factories and vegetables greenhouses. In this case, groundwater presents the highest copper, zinc and P concentrations values.

In spite of Garín's soil moderate SAI value, the highest iron concentration in groundwater is found in this place. This fact may be explained by the high pollutant inputs because of metal industries as well as nurseries.

On the other hand, in Matheu and Belén de Escobar with higher SAI soils than the other studied places, both metal and P concentration in groundwater are lower although pollutant input is also high due to industries, nurseries and urban population.

From the above results, it is evident that soils with low SAI are those that have higher concentration of P and trace metals in groundwater (Maschwitz and Loma Verde), while those with relatively higher SAI (Matheu and Belén de Escobar) show lower concentration. Iron concentration in Garín is explained through the high inputs of this metal due to industrial activities, which overcomes the soil attenuation capacity.

The constructed SAI gives a number easy to understand for everyone, and based on scientific criteria for soil quality. This index would be an useful and simple tool to evaluate the attenuation capacity of soils in places where anthropic activities may have a strong impact on the groundwater, improving the evaluation of groundwater vulnerability through the existing methods.

## Conclusions

Conclusions that arise from this first approach to determine a soil attenuation index (SAI) are:

– The soil attenuation index was developed following the methodology used for water quality index.
– Physical and chemical soil parameters relevant to pollutant sorption were taken into account.
– The developed SAI was validated considering phosphorous and trace metal groundwater contents.

– Further studies are required to evaluate the use of the constructed SAI to evaluate groundwater vulnerability to organic xenobiotics, such as plaguicides.
– Nitrate groundwater vulnerability cannot be assessed by this methodology because this mobile ion is not retained by organic matter or clays.

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