GROUNDWATER SALINIZATION IN THE HARBOUR AREA GRABEN IN MAR DEL PLATA, ARGENTINA. HYDROGEOCHEMICAL PERSPECTIVE

D. E. MARTÍNEZ[1, 2] ✉, H.E. MASSONE[1] and E. M. BOCANEGRA[1,3]

[1]Coastal and Quaternary Geology Certre, Mar de Plata National University, Argentina. E-mail: demarti@mdp.edu.ar
[2] National Council for Scientific and Technical Research (CONICET), Argentina
[3] Scientific Research Commission of the Buenos Aires Procince (CIC), Argentina

Abstract

Mar del Plata lies on the Atlantic Coast of Argentina and has a permanent population of 700,000 inhabitants. Water supply for all uses is derived from groundwater, exploited from a phreatic multilayered aquifer. Seawater intrusion takes place mainly in the downtown area, up to 2,500 m from the coastline. In the harbour area a salinization process affecting a short number of wells has also been observed. This area is a structural graben, isolated from the seaside by a quartzitic horst. The chemistry of the salinization process is different from that observed in the downtown area, where TDS reach values up to 7,000 mg/L, while the maximum value in the harbour area is 2,700 mg/L. These observations and the fact that the quartzitic horst does not allow marine intrusion into the graben, makes it necessary to consider other hypotheses, such as the rising salinization from Miocene sediments and salinization as a result of the exploitation in a closed underground basin. The second hypothesis could be supported by the increase in the nitrate content, but the geochemical model requires the dissolution of about 3 mmol/L of halite, which is considered improbable. The rise of waters derived from Miocene formations is evidenced by the presence of green clays and sands in the well logs. The concomitance of both processes appears as a reasonable hypothesis.

Keywords: Mar del Plata, overexploitation, upward salinization, fish industry

Introduction

Mar del Plata is the main seaside resort in Argentina. Its permanent population is around 700,000 inhabitants, reaching up to 1,000,000 inhabitants during the summer season. It is on the seaside of the Atlantic Ocean, at 38º00´lat S and 57º35´long W, placed in an area that corresponds to the last spurs of

✉ Corresponding author

the Tandilia range (Figure 1). The Tandilia range is a chain of low altitude mountains (maximum height 600 m), following a NW-SE direction in the Province of Buenos Aires. The range is formed by metamorphic Precambrian basement rocks, overlaid by a sedimentary sequence of Lower Paleozoic age, which crops out in the Mar del Plata area forming the hydrogeologic bedrock. A sedimentary sequence of Upper Tertiary and Quaternary age, mainly formed by aeolian and fluvial silt and fine sand, completes the stratigraphy and forms the aquifer unit.

The city gets its fresh water supply for all uses from underground resources present in the detritic aquifer system. That has led to intensive exploitation of groundwater resources that has brought a salinization problem, mainly due to seawater intrusion. Seawater intrusion was analyzed in previous works (Bocanegra *et al.*, 1993; Mérida, 2002), considering the evolution of the piezometric levels.

Two depression cones were identified, one corresponding to the downtown area and the other in the surroundings of the Mar del Plata's harbour. Both depression cones were related to salinization processes, but they were found to be different in some aspects (Bocanegra *et al.*, 1993). The harbour area is isolated from the seaside by an outcrop of orthoquarzites, which prevents marine intrusion. Field data show that these rocks could be considered as impermeable, since typical yields are about 1 m^3/h. This geological situation and the different chemical evolution of the salinization processes have led to assess other hypotheses to explain the salinization process in the harbour area. This work is mainly focused in the analysis of possible origins of groundwater salinization in the harbour area.

Historical perspective of the salinization problem

The criteria for groundwater exploitation used since the beginning of the XX century were based on the need for drinking water in cities with demographic growth rates of 100,000 inhabitants per decade. Since 1945, as a consequence of unrestricted exploitation, accelerated saline intrusion has been registered in the city centre, reaching a displacement of 150 m/year and, in some wells, an increase of 2,000 mg/L/year in the chloride content. Extraction continued on a larger scale, reaching 137 wells under exploitation in 1970.

Consequently, a new lay-out for exploitation was planned, starting gradually in 1969 and in 1970, with a set of wells to the north of the city, among La Tapera and Santa Elena Creeks (Figure 1). In this period, a significant drawdown of water levels in the wells near the exploitation axis took place, and pumping systems had to be placed deeper.

The water quality in the suburban and rural area underwent a significant degradation, caused by an increase in the concentration of nitrate exceeding 90 mg/L, as well as by bacteriological contamination in private wells located in suburban neighbourhoods without sewage system. Furthermore, there was a 10 m recovery of the piezometric levels in the urban area caused by the cessation of exploitation in those wells with high chloride content. This situation led to water logging in the basement of some buildings of the city, creating the need for continuous drainage.

As a consequence, in 1992 a new area of groundwater exploitation was proposed to the south of the city, and, in early 1993, a new management strategy was designed, which aimed at achieving an integral but

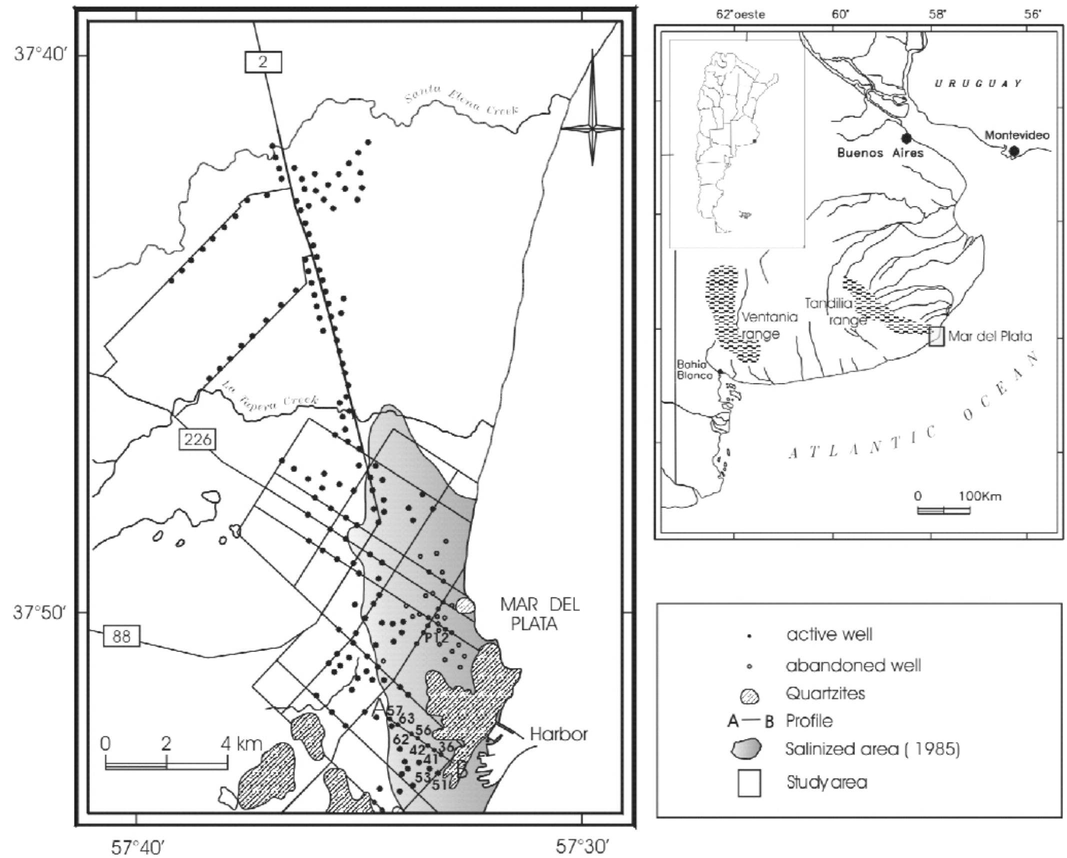


Figure 1. Location map.

rational development of the hydrological resources. This new production strategy was based on two fundamental concepts: flow balance for each hydrologic basin and pumping suitability for the critical discharge. This exploitation policy, while maintaining the "supply-extraction" balance, avoided the accelerated drawdown of the piezometric levels and thus prevented the quick "deepening-expansion" process of the depression cone. The distance between wells, which historically was 400 m, reached 600 m – 700 m, and therefore, reduced the interference that produced less drawdown and greater efficiency in pumping systems.

Hydrogeological background

The geology of the Southern spurs of the Tandilia range is dominated by two main types of rocks: a Lower Paleozoic sequence of orthoquartzites and a Cenozoic sequence of silt and silty-sand sediments. Orthoquartzites show an alternation of tectonic grabens and horsts. Three fault systems are recognized in this bedrock, with NW-SE; NE-SW and W-E trends to which three joints systems are associated (Teruggi y Kilmurray, 1980).

The detritic aquifer behave both as unconfined and multilayer. It consists of Pleistocene-Holocene loess sediments of silt-sand and very fine-grained sandy textures with a permeability of 10-15 m/d and a transmissivity of about 700 m^2/d. Its thickness varies from 70 to 100 m, resting on Miocene marine sediments in some areas; while in other areas they rest on the hydrogeological bedrock, made up of lower Paleozoic orthoquartzites (Sala *et al.*, 1980). In the harbour area, several wells were built in the graben (known as El Barco basin). Between the coast and El Barco graben there is a horst of orthoquartzites; it is a hydrological barrier which prevents direct connection with the sea. Figure 2 shows a W-E topographic profile and a schematic stratigraphic sequence in seven wells. An alternation of aquitard (silty-clayed) and aquifer (sandy-silty) levels can be identified in each one. Miocene sediments were reached only in well 41.

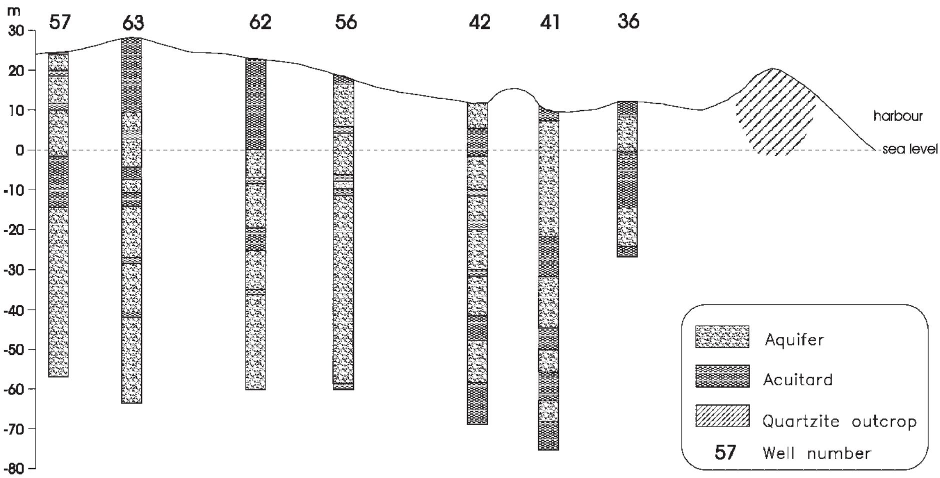


Figure 2. Schematic geological profile of the harbour graben.

Hydrogeochemistry of seawater intrusion process

The geochemistry of seawater intrusion process was analyzed in previous works by Bocanegra (1993) and Martínez and Bocanegra (2002). Mixing ratios obtained on the basis of the chloride (conservative ion) contents showed different seawater proportions according to the distance to the coast line, with a maximum of about 5%. The comparison between the observed concentrations in salinized waters and in a theoretical conservative mixture, indicated that some geochemical processes should be considered to explain the observed groundwater composition.

In the papers mentioned above, the seawater intrusion process was modelled using NETPATH (Plummer *et al.*, 1991) and PHREEQM (Nienhuis and Appelo, 1991), taking into account the mineralogy of the aquifer. The most important processes affecting groundwater composition are calcite precipitation and cation exchange. Iron sulphide precipitation and organic matter oxidation appears as secondary processes, needed to explain the sulphate decrease in the mixed water. The proportion of iron sulphide precipitation obtained in the models was 0.5 to 0.6 mmol/L.

Calcite precipitation is consistent with the lower carbon contents found and the calculated saturation indexes (SI). Calcite SI remains about 0-0.3 in all the samples, showing equilibrium or a slight over-saturation. Moreover, calcite phase is widely present in the aquifer mineralogy, mainly as caliche concretions. Calcite precipitation involves the transference to the solid phase of about 2.0 mmol/L.

Cation exchange appears as the most important process regulating groundwater composition, especially favoured by a high cation exchange capacity of the sediments, of about 23-40 meq/100g. It involves mainly, as a result of the saltwater intrusion, between 4 and 5 mmol/L of sodium uptake and calcium release. Magnesium is also adsorbed, replacing sodium at the exchange surfaces at high seawater proportions (about 0.7 mmol/L).

Methods

In order to study the salinization problem in the harbour area and to analyse the proposed hypothesis for the origin of salinization, different methods and tools have been used. A wide database is available, including chemical water analyses of all the deep exploitation wells since the starting of operation in the 1980s. A classical analysis was carried out, including Piper diagrams, time series and different maps showing the temporal and spatial hydrochemical evolution. Also, the well logs are available, and a geological cross-section was drawn. Finally, some codes for hydrogeochemical modelling were used to test the processes involved in each hypothesis on the origin of salinization. The codes used were NETPATH (Plummer *et al.*, 1991) and PHREEQC2.0 (Parkhurst and Appelo, 1999).

Results

In Figure 3 a well considered to be representative of the salinization process in the downtown area (P12) is compared with well 51, located in the harbour area, using Stiff and trilinear diagrams. A different evolution can be observed. The salinization process started at the same time in both wells, but the evolution of well P12 is towards the seawater composition, while the evolution of P51 shows a proportionally higher increase in the sulphate concentration. The composition of groundwater in the wells at the beginning of the exploitation and when the salinization occurred is shown in Table 1.

The chemical composition of the salinized wells around the harbour area (36, 41, 42, 51, 53 and 56) was plotted in a Piper diagram (Figure 4). The chemical evolution observed in these wells shows a slightly different trend for well 51, for which the sulphate increase is important, and the rest of the wells show a more defined trend towards chloride waters. The cation triangle does not show important changes, all

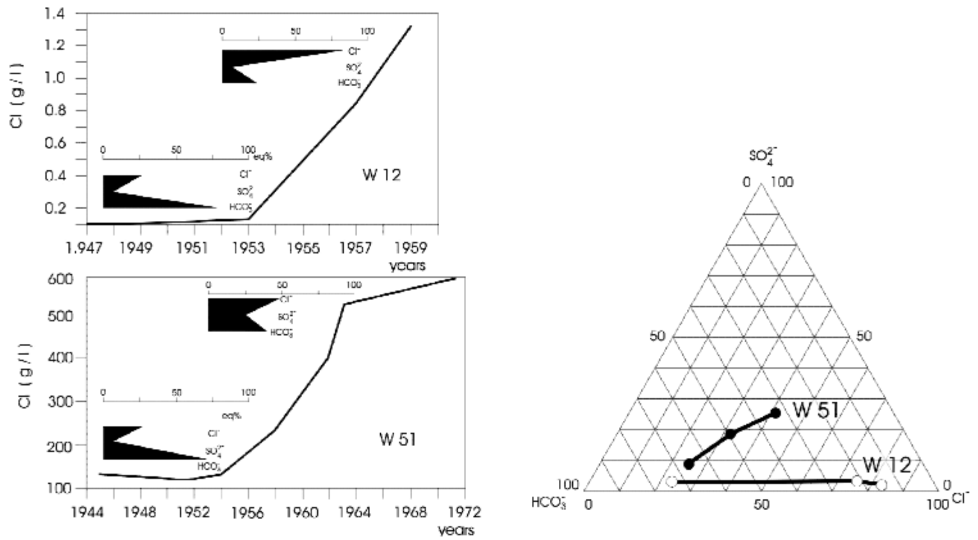
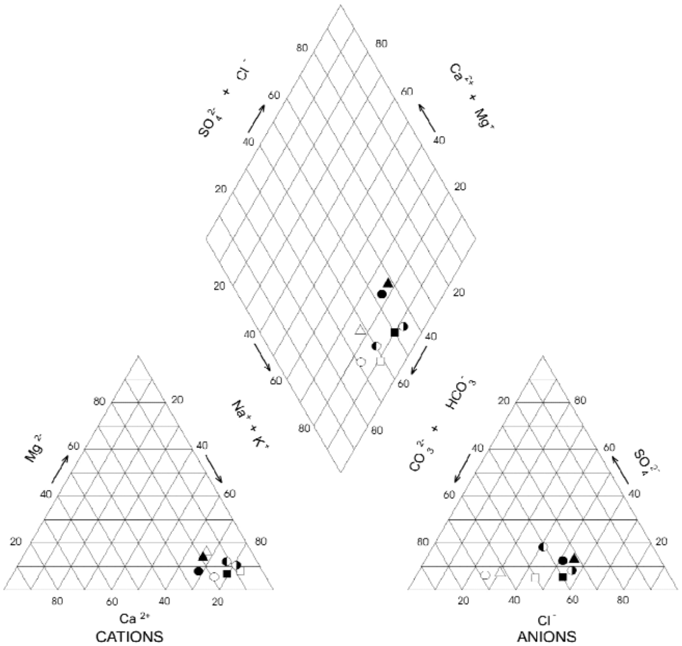


Figure 3. Anionic evolution of waters of a representative well of the downtown area (P12) and well 51 in the harbour area. The points included in the anionic triangle correspond, from left to right, to years 1948, 1953 and 1959 (well P12) or 1964 (well W51).



well year			
△ 36 1948	○ 41 1948	□ 42 1948	◐ 51 1948
▲ 36 1955	● 41 1978	■ 42 1978	◑ 51 1974

Figure 4. Piper diagram showing the water composition of wells located in the harbour area.

waters remain within the sodium type. Published Piper diagrams for the salinized waters in the downtown area (Martínez and Bocanegra, 2002), showed a trend from initial sodium waters to mixed cation waters, as a result of the exchange process described above.

Another interesting analysis performed was the hydrograph of the concentration of chloride, sulphate and nitrate ions from the starting of operation in 1948, until 1978. These hydrographs identify the beginning of the salinization process in the harbour wells and the relative importance of these ions during the salinization (see figures 5, 6 and 7).

The geochemical code NETPATH (Plummer *et al*., 1991) was used to identify hydrochemical models capable of explaining the observed hydrochemical evolution in the harbour area. Inverse models have been performed simulating different probable conceptual models to explain the observed salinization. The lack of data about the composition of the water contained in Miocene formations was an important limitation in this issue.

The initial attempt was to simulate the salinization of the wells in this area using the same model applied to explain the salinization of downtown wells, considering freshwater-seawater

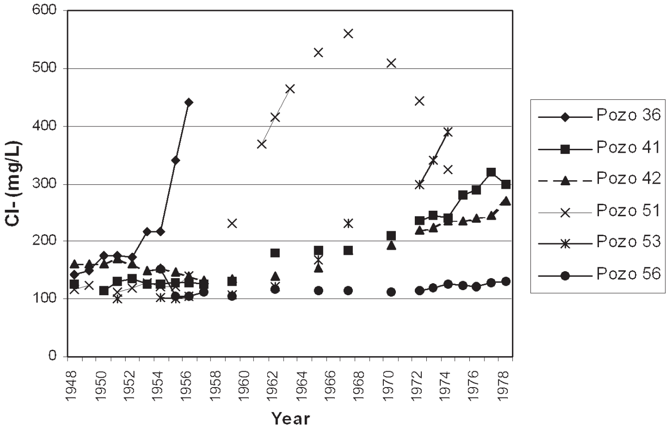


Figure 5. Chloride contents evolution in wells of the harbour area.

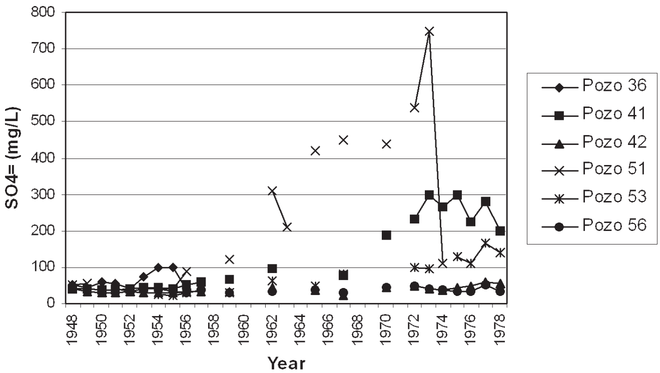


Figure 6. Sulphate contents evolution in wells of the harbour area.

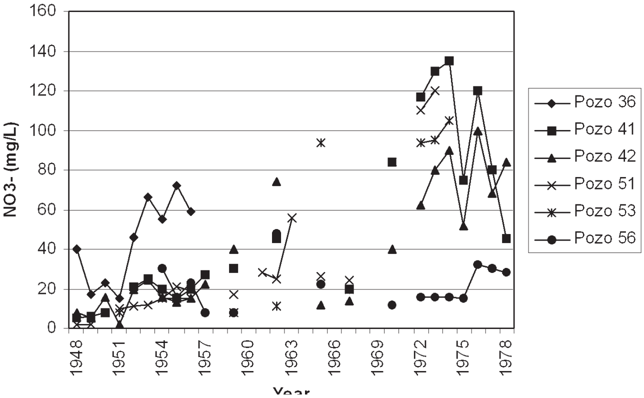


Figure 7. Nitrate contents evolution in wells of the harbour area.

Table 1: Groundwater composition (in mg/L) of some selected wells at the operation start and when the water was salinized. Total Dissolved Solids (TDS) expressed as residue on evaporation at 105ºC. Concentrations in in mg/L. nd: non-determined.

WELL	YEAR	pH	TDS	Na	Mg	Ca	Cl	SO_4	NO_3	NO_2	HCO_3	SIO_2
W 36	1948	7.7	870	276	16	40	142	53	40	<0.05	518	63
W 36	1953	7.7	1190	368	26	56	216	74	66	nd	545	60
W 36	1955	7.7	1496	432	24	61	340	101	72	nd	504	76
W 41	1948	7.8	882	298	8	36	125	40	5	<0.05	575	60
W 41	1967	7.8	1340	345	16	37	185	76	20	<0.01	576	73
W 41	1978	7.7	1460	391	33	40	284	182	45	0.03	604	0
W 42	1948	7.8	900	322	7	28	160	39	8	< .05	541	53
W 42	1972	7.8	1160	371	11	24	220	47	62	<0.01	504	25
W 42	1978	7.5	1156	331	14	20	248	57	84	0.08	510	nd
W 51	1948	7.6	866	254	8	17	116	52	2	< .05	472	nd
W 51	1966	7.8	2287	647	55	84	560	450	24	<0.01	566	67
W 51	1970	7.3	2250	649	53	86	510	440	84	<0.01	436	47
W 51	1974	7.4	1625	515	22	19	324	110	120	< .01	590	40
W 53	1954	7.8	805	264	7	13	102	27	15	nd	462	55
W 53	1965	7.8	995	315	12	30	168	48	94	< 0.01	505	72
W 53	1974	7.3	2360	667	48	91	390	96	105	<0.01	579	52
W 56	1954	7.6	975	314	16	34	131	39	30	<0.01	553	56
W 56	1965	7.8	985	333	7	18	115	37	22	<0.01	583	67
W 56	1978	7.5	901	358	8	24	130	29	26	<0.01	560	nd

mixing, but this could not be achieved because of the code did not find any satisfactory model. If freshwater-seawater mixing is simulated taking as initial solutions those of the wells before their salinization and as final solutions those of the salinized wells, and the same processes used in downtown area are considered, the obtained results are: the seawater proportion in the mixing should be about 1–2%, calcite dissolution in the range of about 0.9 to 1.7 mmol/L, cation exchange involves calcium uptake and sodium release in the order of 0.7 to 3.3 mmol/L. As it can be observed, the chemical evolution of the waters in harbour area shows a sulphur increase, then the sulphide precipitation process used in downtown wells in not possible.

A different conceptual model is necessary, which includes gypsum dissolution instead of iron sulphide precipitation, calcite dissolution instead of calcite precipitation, and different trends in the exchange processes, with calcium uptake and sodium release instead of calcium release and sodium uptake observed in the marine intrusion process. To simulate the chemical evolution from initial freshwaters to saline waters, just considering reactivity against mineral phases, large amounts of halite dissolution are needed. The saturation indexes relative to mineral phases obtained with PHREEQC2.0 (Parkhurst and Appelo, 1999) show that the waters in the harbour area are slightly undersaturated with respect to calcite and amorphous silica, and undersaturated with respect to gypsum.

Discussion

Trilinear diagrams (figures 3 and 4) show a change of water type in groundwater samples. This change is the result of an increase in dissolved salt, as it can be see in figures 3, 5, 6 and 7. Noticeably, Figure 3 shows that the salinization of the wells started at the same time in the harbour area and downtown, this being related in both areas to the development of the aquifer exploitation. Groundwater salinization in downtown area has been attributed to seawater intrusion, and this phenomenon was widely supported by many evidences, mainly hydrochemical ones. Nevertheless, as it has been pointed out, the geological structure of the harbour graben led to consider the occurrence of marine intrusion as highly improbable in the area.

The presence of saline water in marine Miocene age sediments was initially mentioned by Stappenbeck (1926). In some areas of the Pampa plain, the rise of waters, leading to the salinization of the overlying formations has been stated (Mauro and Sanchez, 2003). Then, the raising of waters from Miocene formations was proposed as a probable source for the presence of saline waters. Green sediments that could be assigned to the Miocene deposits were observed in the log of well 41, but not in the other wells, probably due to the fact that they were not deep enough. Sulphate concentrations, higher than those expected from marine intrusion, especially in well 51, were taken as an indication of water rise from Miocene formations. However, the Piper diagram (Figure 4) and the sulphate evolution graph (Figure 6) show that the exceptional sulphate increase does not take place in other wells of the area. The low iron concentrations, mostly below the detection level of 0.05 mg/L, are non-consistent with a sulphate increase due to iron sulphide oxidation. Moreover, as a consequence of iron sulphide precipitation a pH change should take place, but this phenomenon has not been observed.

Figures 5 to 7 show the evolution in the concentration of chloride, sulphate and nitrate respectively, show that the first salinized well is well 36, followed by well 51. These wells are the closest to the quartzitic barrier and the seaside, which might suggest that marine intrusion took place, and the very low permeability of quartzites might not be such. But it is noticeable to see that there is a rise in the nitrate concentration that can not be assigned to seawater intrusion because seawater has very low nitrate contents. On the other hand, the attempts made in order to apply to the harbour's waters the same hydrogeochemical models tested in downtown area has failed. However, some mass balance models considering seawater mixing were obtained, but including sulphate dissolution. The presence of gypsum in the sediments has not been mentioned in the well logs; thus the dissolution of gypsum as dissolved sulfphur source should be discarded, thus leading to discard the marine intrusion hypothesis as well.

As mentioned before, no data of the Miocene waters are available and then a mixing model could not be performed. Nevertheless, this hypothesis is still strongly considered due to the different type of salt increase observed, mainly the sulphate increase, and to the presence of those Miocene sediments described in the drilling profiles of the wells. The salinization resulting from Miocene waters upward in other areas of the Pampean plain has produced saline waters with high sulphate contents (Mauro and Sanchez, 2003; Tuchneider *et al.*, 2004).

Nitrate increase could not be explained by the rise of water from the Miocene sediments, and then other alternative hypotheses were needed. Two possibilities appear in this case, the first is the contribution from organic matter included in some sediments corresponding to an old pond and alluvial plains, and the other one is from wastewater produced by the fish industry in the zone. This wastewater composition was summarized by González *et al*. (1983), with a mean value for total nitrogen content of about 300 mg/L. The concordance of the nitrate increase with the water salinization could be just the result of a temporal coincidence between the development of intensive groundwater exploitation and the industrial activity of local fisheries.

Conclusions

According to the observed results, it is possible to discard marine intrusion as a source for the salinization of groundwater in the harbour area. The main objection to this hypothesis comes from the increase in sulphate contents over the theoretical mixture, which can not be explained by gypsum dissolution (no gypsum recognized in the well logs) or sulphide oxidation (no pH changes in agreement with this process). A combination of different processes appears as responsible of the salinization phenomenon, all of them as a consequence of the aquifer overexploitation. These processes are: 1) raising of saline and high sulphate bearing waters from Miocene formations. As mentioned, the lack of data about the composition of the water contained in Miocene formations impede to test an integrated mass-balance model for this hypothesis, 2) oxidation and leaching of organic matter which gives a part of the observed nitrate increase, 3) pollution by fish filletering wastewater.

The presence of Miocene sediments in the graben according to the log of well 51 and the similarity among the observed salinization features and some Miocene waters, upward salinization phenomena in other areas of the Pampa, initially supports the Miocene origin hypothesis. New well drilling and sampling techniques will be necessary to confirm this hypothesis.

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Topic 6.

Management of coastal aquifers