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Evaluation of groundwater contamination beneath an urban environment: The Besòs river basin (Barcelona, Spain)

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Abstract

The urban groundwater of the central Besòs river basin (the La Llagosta aquifer) has become contaminated due to the infiltration of wastewater from septic tanks and sewage networks, and by industrial activities located in urban areas.

The groundwater hydrogeochemistry of the La Llagosta aquifer was characterized using isoconcentration maps, hydrogeochemical diagrams (Piper, Schoeller–Berkaloff) and by analyzing hydrogeochemical changes along a flow-path that crosses an urban and peripheral industrial area in the main alluvial aquifer (the La Llagosta unit). The evolution of cations, anions and heavy metals along the flow path and the use of the PHREEQC numerical code indicate a complex set of geochemical processes, which result from the interaction between the sources of pollution, the groundwater flow and the mineral composition of the aquifer materials.

The contaminated groundwater below the urban areas shows high contents of NO_3^- (90–100 mg/L) and an increase in the concentrations of Ca^{2+} and Mg^{2+} which coincides with a decrease in pH.

The Eh shows greater variation than the pH along the flow line studied, with values ranging between 56 mV in the industrial area and 370 mV in the urban area. The area with the lowest Eh value coincides with the highest concentrations of dissolved Fe (4.7 mg/L) and Mn (0.22 mg/L).

Keywords: Groundwater; Hydrogeochemistry; Urban environment; Nitrates; Heavy metals

1. Introduction

Groundwater contamination has major implications for health and the environment in urban areas. This contamination may be due to urban stormwater infiltration, the uncontrolled leakage of wastewater and septic tanks, and industrial activities (Robertson et al., 1991; Jeong, 2001; Rivett et al., 2002; Dechesne et al., 2004). The groundwater beneath polluted urban areas may be contaminated by heavy metals and trace elements and may contain a wide variety of organic compounds, all of which have a major effect on the water supply and the environment (Custodio, 1997; Vidal et al., 2000).

In addition, the uncontrolled release of wastewater from septic systems and urban sewers is a major source of recharge in terms of volume in some urban aquifers (Edmunds et al., 2002; Foster and Chilton, 2004). Wastewater and septic system effluents contain high concentrations of dissolved organic carbon (DOC), ammonia, pathogens and organic micropollutants, as well as heavy metals and trace elements, particularly in the case of the release of industrial wastewater into sewer systems.

When wastewater and septic system effluents migrate through an unsaturated zone and reach a saturated zone, the nitrification of NH_3, the release of N and P from organic compounds and the oxidation of DOC yield high concentrations of NO_3^-, PO_4^{3-}, CO_2 and other groundwater contaminants (Ptacek, 1998), although it is also very common to find high levels of Cl^-, Na^+, Ca^{2+}, K^+, alkalinity, dissolved organic carbon and low levels of pH and dissolved oxygen.

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In wastewater infiltration zones, the Eh can be low, ranging from 30 to 200 mV. This can give rise to high concentrations of dissolved Fe and Mn, which is the result of the reductive dissolution of Fe (III) oxyhydroxide and Mn (IV) oxides from aquifer sediments (Ptacek, 1998; Amirbahman et al., 2003), and the mobilization of some contaminants together with As, which is adsorbed to solid oxyhydroxides (Navarro and Carbonell, 2004). In addition to ammonium oxidation, the degradation of dissolved organic carbon (DOC) will consume dissolved oxygen in the unsaturated and saturated zones, resulting in an increase in the partial pressure of CO_2 that may affect carbonate hydrogeochemistry and carbonate mineral solubility (Robertson and Cherry, 1992; McQuarrie and Sudicky, 2001; McQuarrie et al., 2001). In carbonate-poor sediments, the pH decrease cannot be buffered by calcite dissolution, and this may lead to heavy metal mobility (Robertson and Blowes, 1995).

In this paper, the main objective is to identify the contamination processes related to groundwater in the urban areas in the central Besòs river basin (the La Llagosta aquifer) and to describe the hydrogeochemical changes that are taking place in the groundwater flow. In order to do so, we studied the main cation evolution (K^+, Ca^{2+}, Mg^{2+}), NH_4, electrical conductivity and Eh, which were compared to the concentrations of metal polluting agents (Fe, Mn and Ni) that were found. The saturation indices of calcite, dolomite, ferrihydrite and siderite in the groundwater flow were studied using the PHREEQC code.

1.1. Site location, climatology and geology

The Besòs basin lies to the north of Barcelona (Fig. 1) and has a surface area of approximately 1000 km^2. The area to the immediate north of the city of Barcelona is densely populated and highly industrialized.

The climate of the area studied is typically Mediterranean, with a considerable variation in mean monthly temperatures: the coldest month is January, with a mean temperature of 7.5 °C, and the hottest is July, with a mean temperature of 23 °C. The mean annual precipitation in the area is 609 mm and the potential evapotranspiration values stand at approximately 800 mm/year. The mean monthly hydrometeorological water balances that were conducted (Navarro, 2003) provide useful rainfall values in the region of 21–26% of the precipitation, and the runoff coefficient was estimated to be around 10% of the mean annual precipitation. The main stream flows of the Besòs river basin are characterized by their great irregularity; thus, the maximum flow occurs in the form of floods in the autumn and spring. The mean annual flow of the River Besòs was 128.8×10^6 m^3 for the 1969–1970 to 2000–2001 period.

The Besòs basin (Fig. 1) runs along a north–south axis and crosses three main geo-structural units: the Catalan coastal range, the pre-coastal depression and the pre-coastal range.

The coastal range runs in a NE–SW direction parallel to the coast, and consists mainly of Hercynian granites and granodiorites. Due to the alpine fracture tectonics, these materials form a horst above the pre-coastal depression as a result of the distension phase to which the Catalan coastal range was subjected during and after the Oligocene. The pre-coastal depression consists of a block downthrown by the NE–SW fault, along which flows the River Mogent (the main tributary of the River Besòs on its left bank), and the parallel fault that marks its boundary with the pre-coastal range. The depression is infilled by Miocene sediments and piedmont deposits and by the Quaternary river terraces that have formed on top of the Tertiary deposits. These materials reach a thickness of 1000 m in the central area of the Besòs river basin.

The Quaternary alluvial materials are unevenly arranged on top of the Miocene sediments and are associated with a series of river terraces resting on and flanked by this base. There are three terraces (Navarro, 1989) associated with silt deposits of colluvial origin. The age of the Quaternary materials ranges from the Riss/Würm interglacial for the upper terrace to the Holocene for the lower terrace. The river terraces develop on palaeochannels cut into the impermeable Tertiary base that reaches a maximum depth of 15 m below the surface of the terrain. In the La Llagosta aquifer, the terraces are made up of arenaceous deposits with a thickness of 10–15 m.

1.2. Hydrogeology

The groundwater flow in the La Llagosta alluvial aquifer mainly occurs in the base gravels, which are usually saturated, and aquifer recharge is basically attributable to groundwater inflows from other aquifers and recharge from rivers and irrigation canals. Moreover, discharge is mainly caused by groundwater outflows to deltaic aquifers and extraction from wells.

The alluvial aquifers show transmissivity values that range from 100 to 1400 m^2/day (PHPO, 1985; REPO, 1971), an average thickness on the order of 3–8 m, and an effective porosity of 10–14%, resulting in a mean storage capacity of about 57×10^6 m^3. Groundwater extraction reached about 37.3×10^6 m^3 per annum in the 1984–1985 period, but had dropped substantially at the time of writing (2005) to 22×10^6 m^3 per year, due to the gradual abandonment of public supply catchments and the decrease in some areas of extraction for industrial purposes.

The groundwater flow in the La Llagosta aquifer was determined by water level measurements taken in about 120 piezometers and active industrial and water supply wells. The water table is shallow (1.5–4 m below ground level) and the average linear groundwater velocity was calculated using the Darcy equation.

On the basis of a hydraulic conductivity of 150 m/day and a hydraulic gradient of 0.01, the mean Darcy velocity

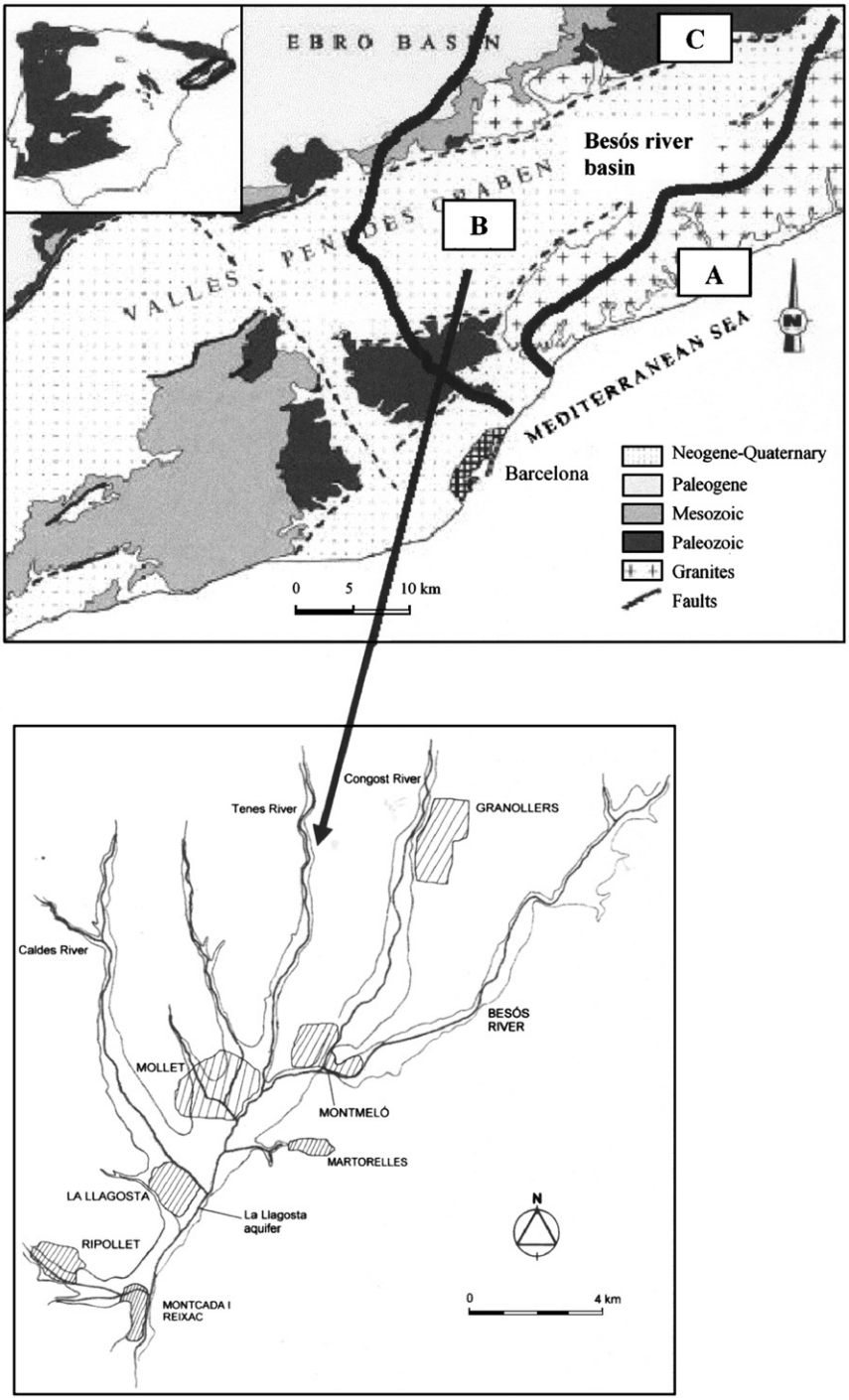

Fig. 1. Map of the Besòs river basin and location of the main urban areas in the La Llagosta aquifer. (A) coastal range, (B) pre-coastal depression, (C) pre-coastal range. The hatched areas indicate the current (2006) extension of the main urban developments located in the La Llagosta aquifer and its surrounding areas. Modified from Cardellach et al. (2002).

of these aquifers is 1.5 m/day, with a pore velocity of 10.7 m/day for a porosity of 0.14. The hydraulic balance in the alluvial aquifers indicates a recharge of $46.6 \times 10^6\,m^3/yr$ and the possibility of increasing exploitation by $18.9 \times 10^6\,m^3/yr$ beyond the present extraction.

The alluvial aquifers in this region have been known to have pollution problems for some years, although the hydrogeochemical processes affecting the groundwater have not been studied sufficiently (Navarro et al., 1991a).

2. Methods

At the end of 2002 and the beginning of 2003, a sampling campaign was conducted in the various alluvial systems

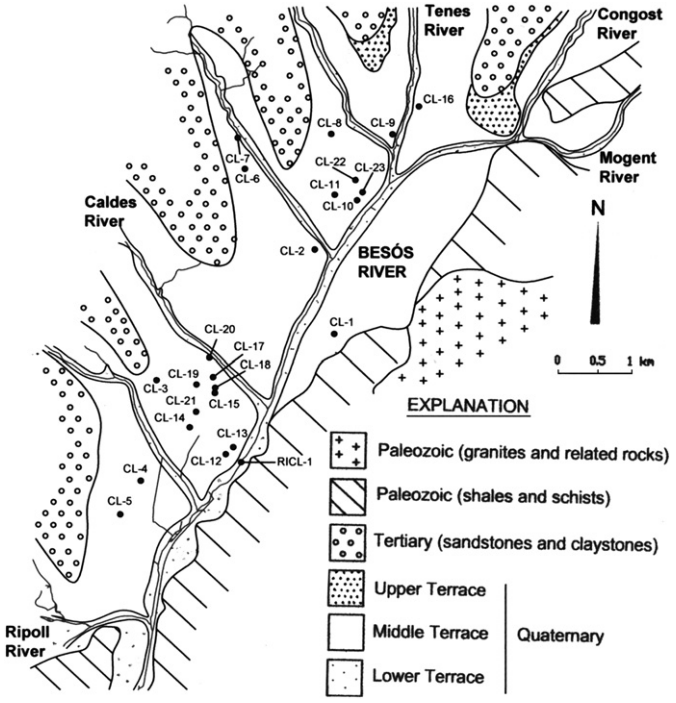

Fig. 2. The La Llagosta alluvial aquifer and groundwater sampling points used in this study. CL-1 to CL-23: well samples RICL-1: River Besòs sample.

(Fig. 2). The main hydrogeochemical results for the La Llagosta aquifer are shown in Table 1.

The tests carried out and the testing methods followed are shown in Table 2. Electric conductivity, temperature, pH and Eh values were obtained as field data for the points sampled.

All the samples were filtered using cellulose nitrate films of 0.45 μm in diameter, and stored at 4 °C. Their pH, temperature, oxidation–reduction potential and electric conductivity had been determined previously. The pH was measured potentiometrically and the pH-meter was calibrated before each reading.

Conductivity was determined using a conductimeter calibrated with NaCl for each effluent sample. The oxidation–reduction potential was measured using an ORP-meter with a combined platinum electrode. The acidified samples (ultra trace HCl, pH = 1.9) were analyzed using the ICP-MS method at the University of Barcelona, to determine their cation, heavy metal and trace element content.

The concentrations of NO_3^-, NO_2 and NH_3 were determined using colorimetric analysis techniques, and the concentrations of Cl^- and $SO_4^=$ were determined using ion chromatography.

All reported values had an ionic balance below 5%, and the accuracy of the ICP-MS analyses was controlled using

Table 1
Hydrogeochemistry of the La Llagosta aquifer wells

Sample	pH	Eh	Cl^-	NH_4	NO_2	NO_3^-	SO_4^{-2}	HCO_3^-	Ca^{2+}	Mg^{2+}	Na^+	K^+
CL-1	7.2	521	137	0.5	0.01	55.7	138	384	90.1	10.7	43.0	2.9
CL-2	7.1	285	309	3.0	0.02	23.6	148	403	114.5	20.3	211.6	11.3
Cl-3	7.2	265	184	0.3	<0.01	151	254	384	200.9	56.7	128.4	5.6
CL-4	7.1	219	186	0.5	<0.01	81	166	421	189.1	44.3	110.6	2.6
CL-5	7.2	72	176	0.5	0.06	72.1	192	445	213.3	41.8	109.7	1.5
CL-6	7.0	370	46.4	1.0	<0.01	86.1	164	409	186.2	32.7	37.9	0.9
CL-7	7.1	257	72.6	0.5	<0.01	99.3	140	418	185.3	40.2	47.9	2.2
CL-8	7.1	275	117	0.6	<0.01	67.6	145	378	190.2	33.6	73.7	0.9
CL-9	7.2	200	160	0.6	<0.01	14	103	369	148.3	25.2	59.2	5.0
CL-10	7.0	219	188	0.6	<0.01	17.9	158	482	154.8	28.3	143.7	5.1
CL-11	7.1	215	122	0.4	<0.01	23	125	485	153.8	34.5	85.1	4.2
CL-12	7.4	42	223	0.5	0.02	30.5	1300	403	477.5	108.3	123.9	17.2
CL-13	7.3	89	259	3.0	<0.01	18.3	168	470	139.5	24.9	183.9	10.2
CL-14	7.8	105	272	0.6	<0.01	21.8	130	415	123.9	35.3	149.4	6.6
CL-15	8.1	112	57.3	0.17	<0.01	8.4	105	171	63.2	8.3	47.9	23.2
CL-16	7.5	110	105	0.7	<0.01	23.3	108	323	105.8	22.9	63.5	4.9
CL-17	7.4	76	243	0.3	<0.01	18.9	128	390	112.5	27.4	151.1	8.8
CL-18	7.7	56	252	0.3	0.02	17.6	137	397	123.4	30.2	155.4	10.0
CL-19	7.8	56	199	0.4	<0.01	24.2	117	384	99.0	24.7	138.2	8.9
CL-20	7.9	100	254	0.5	<0.01	35.4	136	378	120.6	29.2	152.8	12.3
CL-21	7.8	81	258	0.4	<0.01	25.6	123	390	114.6	30.1	153.5	7.4
CL-22	7.4	91	131	0.3	<0.01	9.1	115	470	128.8	27.9	92.8	5.2
CL-23	7.7	114	158	0.4	<0.01	19.7	147	397	125.2	26.7	111.5	5.4
RICL	8.2	106	403	15.7	1.38	21.2	162	433	131.3	25.1	245.1	21.0

Sample	Fe	Mn	Ni	Pb	Zn
CL-1	480	29.0	<20	22.0	87.5
CL-2	190	9.0	20	12.0	47.5
CL-3	70	1.0	<10	4.0	13.5

Table 1 (*continued*)

Sample	Fe	Mn	Ni	Pb	Zn
CL-4	60	2.0	10	2.0	33.5
CL-5	240	34.0	30	2.0	951.5
CL-6	110	4.0	<10	1.5	59.5
CL-7	80	2.0	<10	2.5	49.0
CL-8	40	<1	<10	<1.0	16.5
CL-9	50	1.5	<10	1.0	24.0
CL-10	50	2.5	10	23.0	58.5
CL-11	40	4.0	<10	4.0	41.5
CL-12	110	224.5	24.0	21.5	54.5
CL-13	170	909.2	14.7	9.4	53.7
CL-14	20	5.1	<10	3.3	15.5
CL-15	2540	628.8	18.5	54.0	1044.1
CL-16	30	2.8	14.0	4.6	124.8
CL-17	4740	11.4	66.3	5.9	83.3
CL-18	40	224.3	<10	3.2	48.8
CL-19	20	1.6	<10	2.4	120.3
CL-20	110	10.7	<10	2.4	146.4
CL-21	20	1.4	<10	2.2	44.1
CL-22	50	670.2	15.2	1.6	35.3
CL-23	30	5.4	10.5	2.8	214.3
RICL	130	217.9	33.9	2.3	92.4

Eh: mV; Cl^-, NH_4^+, NO_2, NO_3^-, SO_4^{-2}, HCO_3^-, Ca^{2+}, Mg^{2+}, Na^+, K^+: mg/L; heavy metals: μg/L.

Table 2
Parameter and analysis methods used in the analysis of groundwater samples

Elements/parameter	Method
Ca, K, Na, Mg, Sr, Fe	ICP-OES[a]
Mn, Ni, Pb, Zn	ICP-MS[a]
Chloride	St. M. 4110 C[b]
N as NH_4^+	UNE 77028[b]
Nitrate	St. M. 4500-NO3 B[b]
Sulphate	St. M. 4110C[b]
Bicarbonate	St. M. 2320 B[b]
VOCs (non-chlorinated)	HRGC/FID[b]
VOCs (chlorinated)	HRGC/ECD[b]

[a]Laboratory of the University of Barcelona (ICP-MS).
[b]Laboratory of the Consortium for the Defense of the Besòs Basin.

appropriate laboratory standards, and each batch was checked by means of reference standards.

3. Results and discussion

3.1. General hydrogeochemistry

The groundwater was hydrochemically characterized using the Piper hydrochemical diagrams (Fig. 3) and Schoeller–Berkaloff, Stiff diagrams and several isocontent maps. The Piper diagram of the groundwater in the La Llagosta aquifer shows the existence of the following three main groups of waters:

(1) Calcium bicarbonate waters, located mainly in the northern sector of the aquifer, which correspond to the water coming from the aquifer systems of the River Tenes, the Riera Seca de Mollet and the Riera de Gallecs.
(2) Sodium–calcium chloride–bicarbonate waters, the most extreme case of which is the water from well CL-2 at the confluence of the Riera de Gallecs and the River Besòs, which has a very similar chemistry to that of the surface water, as far as the predominant elements are concerned.
(3) Calcium–sodium bicarbonate–chloride waters, which are midway between the previous two types in the diagram.

Note that the Cl^- and Na^+ content increases downstream of the groundwater flow, with the exception of well CL-9, which appears to receive extra Cl^-, as we move from the palaeochannels of the River Tenes and the Riera Seca de Mollet to the center of the basin.

The spatial distribution of electric conductivity shows an upward trend downstream of the groundwater flow over time. Fig. 4 shows the evolution over time of the electric conductivity value in the period 1997–2003 for three wells on the La Llagosta industrial estate. Conductivity increased considerably in that period, at least in the area of the wells.

The isonitrate concentration map (Fig. 5) shows the highest concentrations below La Llagosta and Mollet urban areas, reaching values of 90–100 mg/L of NO_3^-. In these areas significative amounts of faecal coliforms, *Escherichia coli* and *Bacteroides fragilis* bacteriophages and *Clostridium perfringens* were detected in groundwater (Navarro et al., 1991b), suggesting the possibility of wastewater and/or septic-system effluent infiltration. An increase in the hardness of the groundwater was detected in

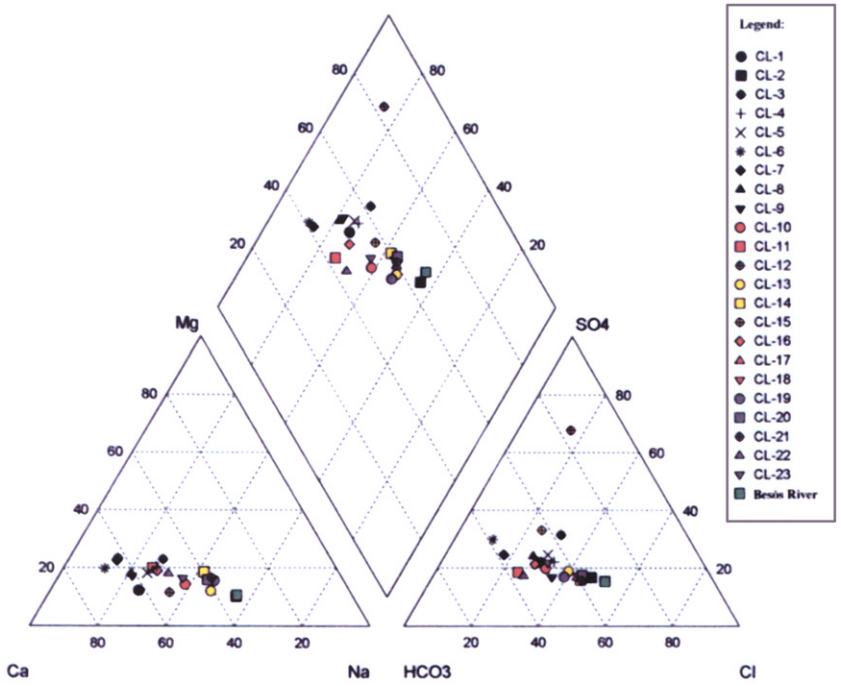

Fig. 3. Piper hydrogeochemical diagram of groundwater samples of the La Llagosta alluvial aquifer unit. CL-1 to CL-23: well samples RICL-1: river Besòs sample.

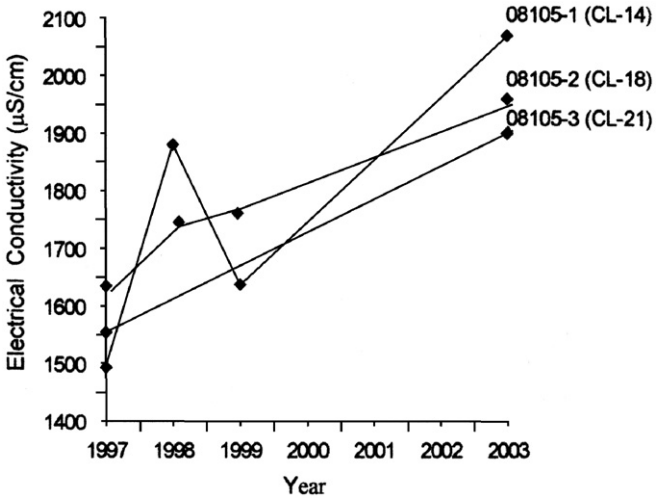

Fig. 4. Evolution of electric conductivity in selected sampling points of the La Llagosta aquifer.

built-up areas (Sant Pere de Reixac, La Llagosta, Mollet del Vallès and Montmeló), which roughly coincides with the NO_3^- distribution. This suggests that the groundwater is contaminated by leakage from the sewer network.

The areas with high nitrate content and total hardness may be explained in terms of the two basic reactions that occur if there is an infiltration of wastewater when the medium is oxidizing: the oxidization of organic matter (CH_2O) and the nitrification of ammonium. Thus, the total oxidation of wastewater that has a mean ammonia concentration of 37 mg/L may produce a concentration of 127 mg/L of NO_3^- in contaminated groundwater. Since the nitrate concentrations in the contaminated areas were 90–100 mg/L, the observed differences may be attributed to dilution caused by mixing with upstream non-contaminated groundwater and the hydrodynamic dispersion effects. These processes tend to lead to an increase in CO_2 and the possible partial dissolution of the solid material of the aquifer and a significant increase in NO_3^- in the groundwater, since the uncontaminated groundwater shows a low concentration of NO_3^- (about 20 mg/L).

As for contamination by organic compounds, the study detected contamination by halogenated volatile solvents (trichloroethene, tetrachloroethene and 1,1,1-trichloroethane) and trihalomethanes (chloroform and bromodichloromethane). The spatial distribution of the total content of the solvents (trichloroethene + tetrachloroethene) is shown in Fig. 6. Note that the values in excess of 10 µg/L were located on the industrial estates of La Llagosta, Mollet del Vallès and Montmeló. The highest values were found on the industrial estate of Mollet del Vallès; the content of well CL-11 was particularly significant, with 61.9 µg/L of tetrachloroethene, 2.2 µg/L of trichloroethene and 1.1 µg/L of 1,1,1-trichloroethane.

3.2. Evolution of groundwater in urban and industrial areas

In order to evaluate the impact of urban and industrial areas on groundwater quality, the evolution of groundwater geochemistry was analyzed along a flow line that crosses an urban and peripheral industrial area in the La Llagosta alluvial aquifer unit (Fig. 5). The evolution of the main cations (K^+, Ca^{2+}, Mg^{2+}) and the ion nitrate (Fig. 7) shows the expected phenomena associated with the

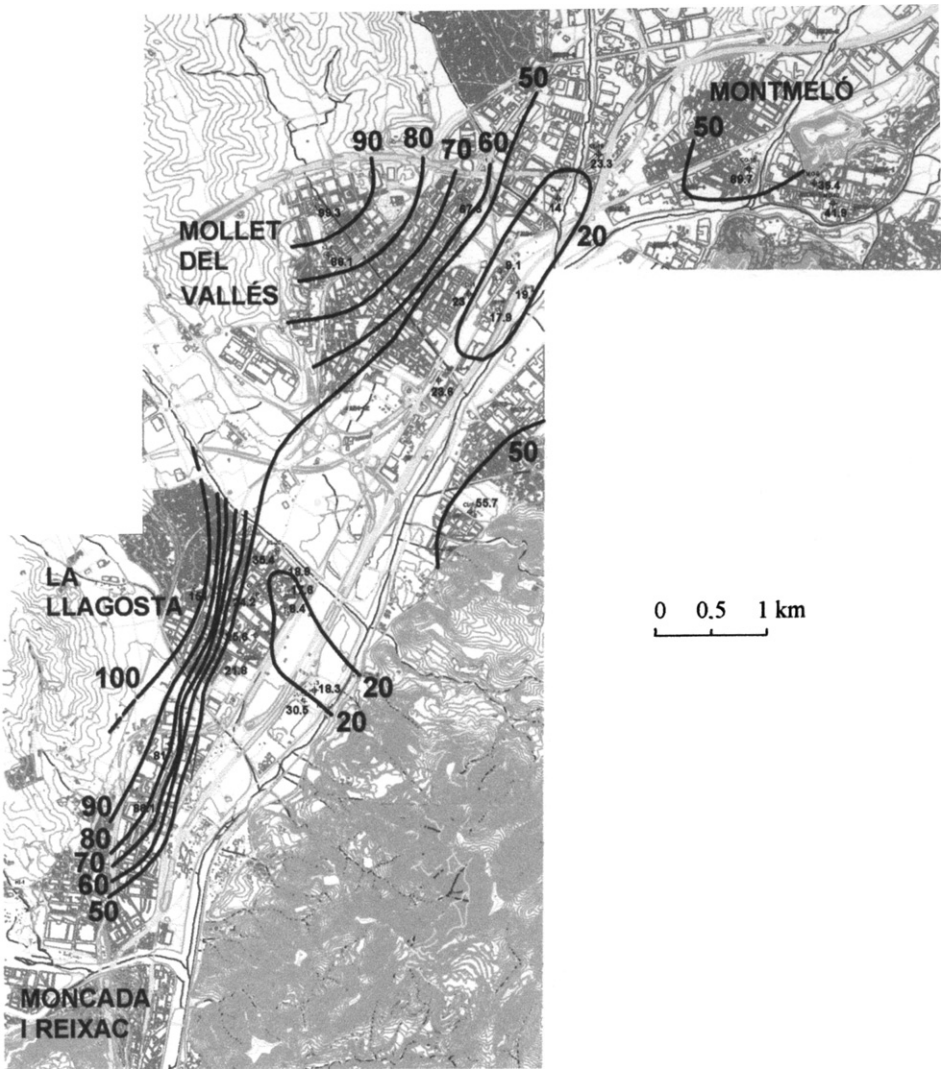

Fig. 5. Isonitrate concentration map of the La Llagosta alluvial aquifer unit (values in mg/L).

infiltration of wastewater through the unsaturated and saturated zone, which, due to the nitrification of the ammonium and the oxidization of the dissolved organic matter, leads to an increase in the concentrations of NO_3^-, CO_2 and H^+ and other dissolved matter. Thus, high concentrations of nitrates, which reached values of 90 mg/L, were detected in the urban part of the flow line (points CL-7 to CL-2 in Fig. 7). These concentrations drop and level off at around 20 mg/L when the groundwater moves away from the built-up areas and enters the industrial area (points CL-17 to CL-14).

If we compare the evolution of the urban and industrial areas, there is a clear increase in the concentrations of Ca^{2+} and Mg^{2+} in the urban area, coinciding with a decrease in pH (Fig. 7) caused by the degradation of organic matter and the nitrification of ammonium. The drop in pH in a medium rich in carbonate sediments such as that studied here is likely to be accompanied by the dissolution of the carbonate minerals, and therefore by an increase in dissolved Ca^{2+} and Mg^{2+}. This phenomenon is suggested by the high concentrations of dissolved Ca and Mg in comparison with the concentrations of these cations outside the urban area and under the industrial facilities.

The Eh shows greater variation than the pH along the flow line, with values ranging from 56 mV in the industrial area to 370 mV in the urban area (Fig. 8). The area with the lowest Eh value coincided with the area in which there was the highest concentration of dissolved Fe and Mn (Fig. 8). Beneath the main industrial area the Eh is low, ranging between 56 and 105 mV, and this zone coincides with elevated concentrations of dissolved Fe in well CL-17 (4.7 mg/L) and dissolved Mn in well CL-18 (0.22 mg/L). Therefore, the Eh–pH conditions under the industrial area can permit a considerable iron concentration in groundwater. Besides, the wastewater infiltration from industrial sewage networks suggests the possibility of the

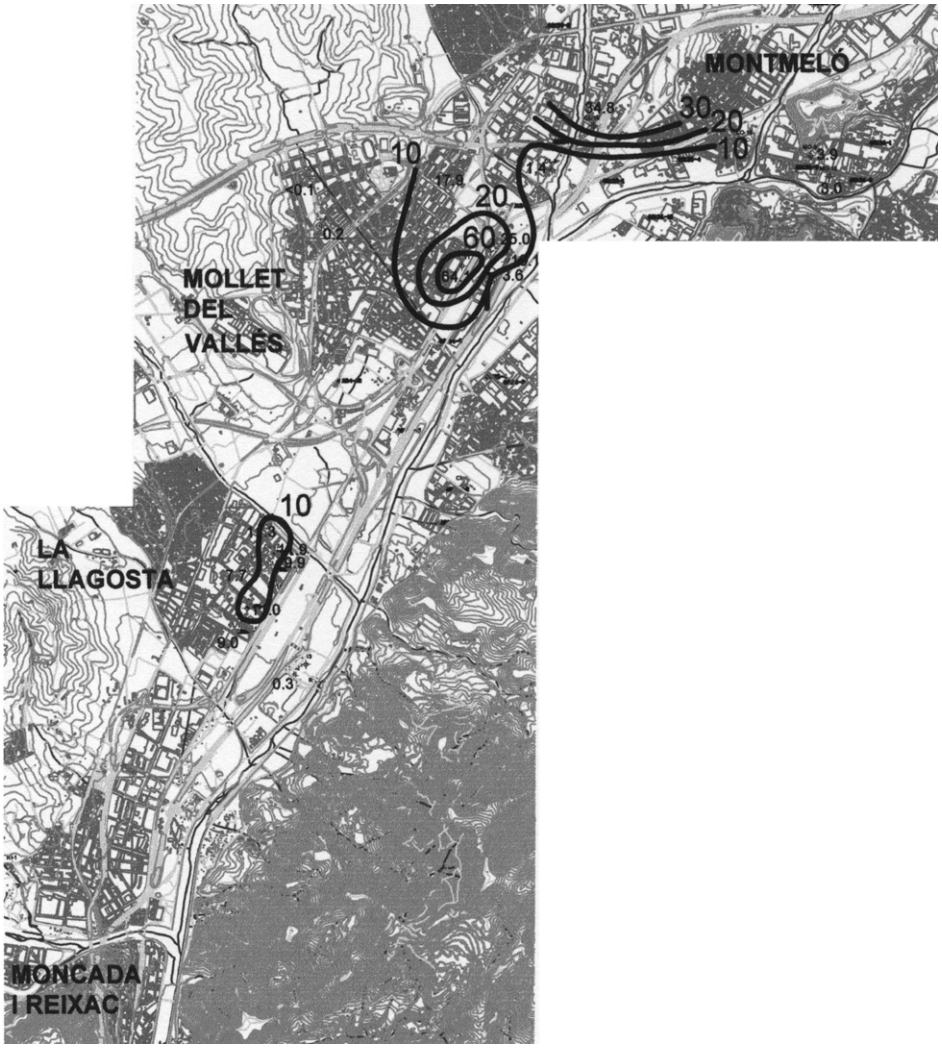

Fig. 6. Iso PCE + TCE concentration map of the La Llagosta alluvial aquifer unit (values in ppb) and location of sampling points with high amounts of dense chlorinated solvents.

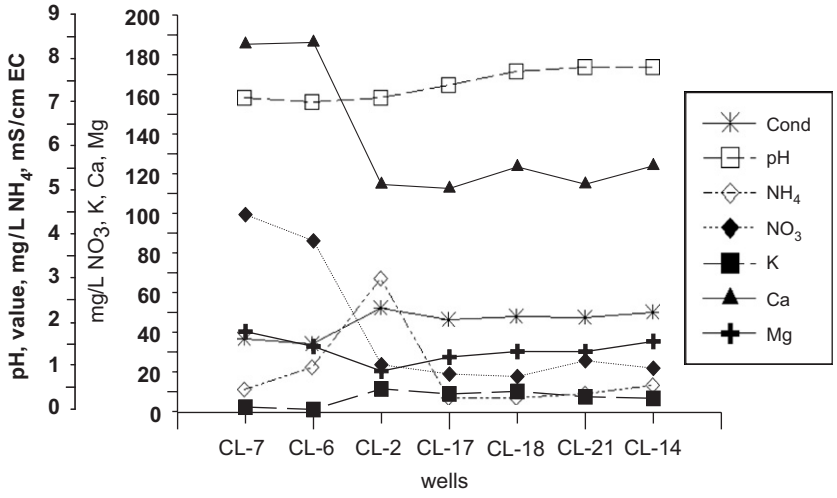

Fig. 7. Evolution of electrical conductivity, pH, NH_4, NO_3^-, K, Ca and Mg in the flow path beneath the urban (CL7-CL2) and industrial area (CL17-CL14) in the La Llagosta alluvial unit.

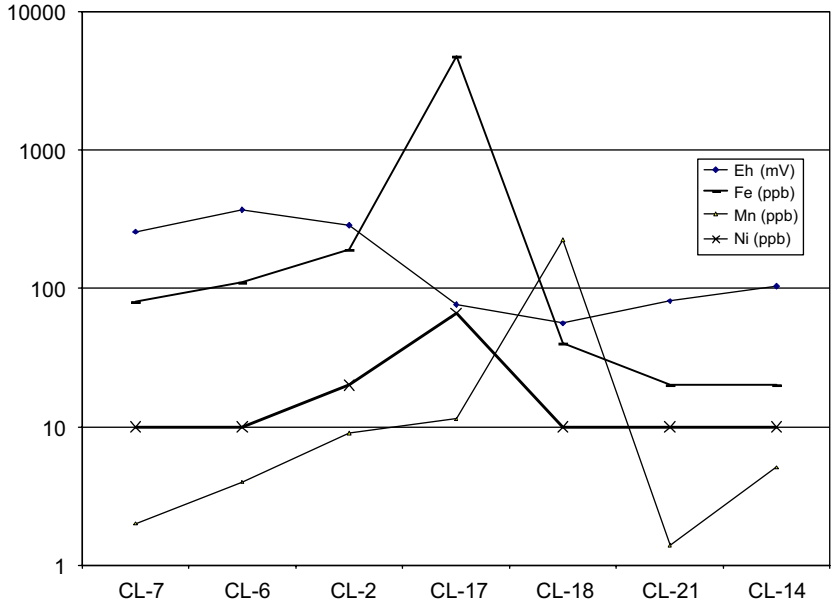

Fig. 8. Evolution of Eh, Fe, Mn and Ni in the flow path beneath the urban (CL7-CL2) and industrial area (CL17-CL14) in the La Llagosta alluvial unit.

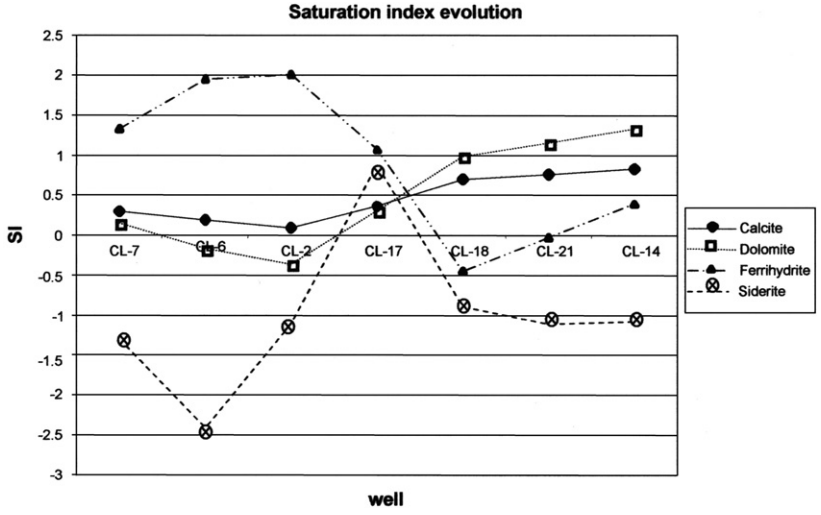

Fig. 9. Saturation index evolution of calcite, dolomite, ferrihydrite and siderite in the flow path beneath the urban (CL7-CL2) and industrial area (CL17-CL14) in the La Llagosta alluvial unit.

reduction–dissolution of Mn and Fe oxyhydroxides, caused by an important contribution of organic matter below the broken pipelines.

The presence of Ni, Pb and Zn in the groundwater near industrial facilities may be caused by the infiltration of wastewater in which these metals are present.

The trend in the saturation indices of different phase minerals was calculated using the PHREEQC code (Parkhurst and Appelo, 1999) for the samples taken along the flow line (Fig. 9). Thus, we can observe that calcite is oversaturated along the entire flow line, which is consistent with the presence of carbonates in the alluvial sediments of the aquifer. In contrast, dolomite is undersaturated under the urban area and oversaturated under the industrial area, which may suggest that the dolomite is dissolved in the urban wastewater infiltration area due to the increase in the partial pressure of CO_2 .

In the case of siderite (Fig. 9), oversaturation only occurs in the area containing a higher amount of dissolved Fe (well CL-17), which may indicate that this carbonated phase controls the concentration of dissolved Fe, as demonstrated in similar cases (Ptacek, 1998). The hydrogeochemical speciation and the calculations performed also indicate that the groundwater is saturated with respect to ferrihydrite, except in the area downstream from the area rich in dissolved Fe. This may imply that this phase or another Fe (III) oxyhydroxide is present in the sediments of the aquifer, and that the lower Eh values detected may be

controlled by near-equilibrium conditions with respect to siderite and ferrihydrite. Moreover, we cannot disregard the possibility that the mobilization of Ni and Zn is caused by the dissolution of the Fe oxyhydroxides, in the event of these metals being adsorbed on them.

4. Conclusions

The contamination of groundwater in the urban areas of the La Llagosta aquifer may originate in the infiltration of wastewater from septic tanks in urban areas, the infiltration of domestic and industrial wastewater from sewage networks, septic tanks and industrial activities.

The infiltration of domestic wastewater in urban areas resulted in the appearance of areas of high salinity and total hardness with a high nitrate content. Furthermore, at some points, contaminants such as Ni, Pb, Zn and organic micropollutants (basically PCE and TCE) were detected.

The study of the hydrogeochemistry along a groundwater flow line of the La Llagosta aquifer beneath the urban areas and near industrial areas suggests progressive hydrogeochemical changes resulting from water-rock-wastewater interactions along the flow path. The evolution of the main cations (K^+, Ca^{2+} and Mg^{2+}) and the ion nitrate shows a possible nitrification of the ammonium and the oxidization of the dissolved organic matter, which gives rise to increased concentrations of NO_3^-, CO_2 and H^+ and other dissolved constituents. Thus, the evolution of the groundwater shows an increase in the concentrations of Ca^{2+} and Mg^{2+} in the urban area, which coincides with a decrease in pH which is accompanied by the possible dissolution of the carbonate minerals and therefore by an increase in dissolved Ca^{2+} and Mg^{2+}.

The evolution of Eh indicates that the industrial zone coincides with the lowest Eh value and the highest concentrations of dissolved Fe and Mn, which reached 4.7 mg/L for Fe and 0.22 mg/L for Mn.

Mineral saturation indices were calculated using the PHREEQC code for groundwater samples collected at the sampling points along the CL7-CL14 flow path. The groundwater is near saturation or slightly saturated with respect to the calcite at all the sampling points, and the dolomite is subsaturated beneath the urban area and saturated beneath the industrial area. The ferrihydrite is supersaturated in the urban area and slightly subsaturated beneath the industrial area, which suggests a possible dissolution of Fe-oxyhydroxides.

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