Hydrochemistry and isotope geochemistry as tools for groundwater hydrodynamic investigation in multilayer aquifers: a case study from Lomellina, Po plain, South-Western Lombardy, Italy

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Abstract A multicriteria approach in studying hydrodynamics of a multilayer aquifer system has been used in the Lomellina region (Northern Italy). It involves the reconstruction of the hydrogeological framework coupled to the definition of the hydrochemical and isotopic features of the aquifers. A shallow phreatic aquifer, reaching depths of about 60–80 m from the surface, and deeper aquifers containing confined groundwater, were distinguished.

Groundwater generally shows mineralisation decreasing with depth; dissolved ions depict calcium-bicarbonate hydrochemical facies and stable isotopes define the recharge mechanisms, the origin of groundwater, and the hydraulic confinement of deep aquifers. The phreatic aquifer is fed by local infiltration and by streams and irrigation channels. Tritium and Carbon-14 groundwater dating indicate long residence times (on the order of thousands of years) for confined aquifers.

The confined aquifers show essentially passive hydrodynamic conditions and maintain a higher piezometric level than the phreatic aquifer. This inhibits the possibility of recent water penetrating far below the surface. The hydrogeological setting of the Lomellina region displays features which are common to other sectors of the Po plain. As a consequence, the results of this study, although conducted on a restricted area, are highly illustrative of groundwater hydrodynamics in large sedimentary aquifers.

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Résumé Une approche multicritère pour l'étude hydrodynamique d'un aquifère multi-couche a été appliquée à la Région de Lomellina dans le Nord de l'Italie. Elle implique la reconstruction du cadre hydrogéologique, couplée à la définition des données hydrochimiques et isotopiques des aquifères. Un aquifère phréatique, atteignant des profondeurs comprises entre 60 et 80 mètres sous la surface, et les aquifères profonds et captifs sont distingués. Les eaux souterraines montrent généralement une minéralisation décroissante avec la profondeur; les ions dissouts représentent les facièes hydrochimiques bicarbonaté-calcique, tandis que les isotopes définissent les mécanismes de recharge, l'origine des eaux souterraines, et le confinement hydraulique des aquifères pronfonds. L'aquifère phréatique est alimenté par une infiltration locale, par les cours d'eau et les canaux d'irrigation. Les datations au tritium et au Carbone 14 des eaux souterraines, indiquent des temps de résidence longs (plusieurs centaines d'années) pour les aquifères captifs. Les aquifères captifs montrent des conditions hydrodynamiques essentiellement passives, et maintiennent un niveau piézométrique plus élevé que celui des nappes phréatiques. Ceci inhibe la possibilité des eaux de surface de pénétrer les aquifères profonds. La région de Lomellina montre des similitudes hydrogéologiques avec les autres régions de la plaine du Po. Par conséquence, les résultats de cette étude, bien que conduite sur une zone restreinte, est grandement illustrative de l'hydrodynamique des eaux souterraines dans les grands aquifères sédimentaires.

Resumen Se ha utilizado un enfoque de multicriterios para estudiar la hidrodinámica de un sistema de acuíferos de capas múltiples en la región Lomelina del norte de Italia. El enfoque involucra la reconstrucción del marco hidrogeológico a la par de definir las características isotópicas e hidroquímicas de los acuíferos. Se distinguieron un acuífero freático somero, que alcanza profundidades de casi 60–80 m de la superficie, y acuíferos más profundos que contienen agua subterránea confinada. El agua subterránea muestra generalmente mineralización que disminuye con la profundidad; los iones disueltos muestran facies hidroquímicas de calcio-bicarbonato y los isótopos estables definen los mecanismos de recarga, el origen del agua subterránea, y el confinamiento hidráulico de acuíferos

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profundos. El acuífero freático es alimentado por infiltración local y por arroyos y canales de riego. La datación de aguas subterráneas con tritio y carbono-14 indica tiempos de residencia largos (en el orden de miles de años) para los acuíferos confinados. Los acuíferos confinados muestran esencialmente condiciones hidrodinámicas pasivas y mantienen un nivel piezométrico más alto que los acuíferos freáticos. Esta situación inhibe la posibilidad de que agua reciente penetre muy por debajo de la superficie. El marco hidrogeológico de la región de Lomelina ilustra características que son comunes a otros sectores de la planicie Po. Por lo tanto, los resultados de este estudio, aunque realizados en un área restringida, son altamente ilustrativos de la hidrodinámica de aguas subterráneas en acuíferos sedimentarios grandes.

Keywords Hydrochemistry · Stable isotopes · Groundwater age · Alluvial aquifers · Northern Italy

Introduction

The Po plain, located in Northern Italy, hosts a multilayer alluvial aquifer of Plio-Quaternary age, composed of gravels and sands interbedded with clays. The plain supports most of the agricultural and industrial activities of Northern Italy, which are associated with groundwater exploitation and pollution mainly in the shallower aquifers. The increasing demand of water for industrial and domestic use has led to the exploitation of deeper aquifers, without rational management plans for this resource. Only in the last decade, have local water authorities begun an evaluation at the basin scale of the quality standards of pumped groundwater, driven by the increasing need for clean water for domestic use. The task is particularly difficult because of missing, or approximated well information, as well as the presence of multifilter wells tapping different aquifers.

In this paper, the use of water chemistry and isotopic composition analysis is illustrated along the local direction of groundwater flow towards the regional drainage axis, considering also the potential of vertical inflow components. The specific goals are to:

- define the lateral extension and depth of the main aquifers of the Lomellina region;
- use trace elements, stable isotopes and radiocarbon to determine the recharge areas, groundwater evolution and age;
- estimate the hydrodynamic characteristics of aquifer systems;
- determine the predominant geochemical processes taking place along the inferred horizontal groundwater flow lines;
- detect the extent of any contaminant inputs from the surface.

With a better knowledge of the groundwater geochemistry, the prospects for improved management of the resource are highlighted.

Geological and hydrogeological setting

The Lomellina region represents a limited portion of the Po plain, of approximately 900 km^2. The region is bound by the Po River to the South, by the Sesia and the Ticino Rivers to the East and West respectively, and by the administrative boundary to the North (Fig. 1).

The aquifers are composed of sediments belonging to the continental depositional system of Plio-Pleistocenic age (IRSA-CNR 1981; Regione Lombardia and ENI Divisione AGIP 2002), overlying the marine depositional sequence. Aquifers are separated by aquicludes, which are discontinuous at the regional scale, preventing groundwater admixture.

These Plio-Pleistocenic sediments may be subdivided into two formations (Fig. 2):

- the upper alluvial sequence made of gravels and sands with interbedded clay layers, and;
- the lower “Villafranchiano” sequence of lacustrine-marsh origin, made of clays with interbedded sand layers.

The thickness of the sedimentary sequence is heavily determined by the presence of buried structures of the marine basement (Braga and Cerro 1988; Regione Lombardia and ENI Divisione AGIP 2002), which are dislocated and influenced by Apennine thrusts.

The upper formation, reaching a depth of 150–200 m, creates a multilayer aquifer system with a water table a few metres deep; it is an aquifer of great importance because of the lateral extension and the high transmissivity, of about 10^{-2} m^{2}s^{-1}, equivalent to a hydraulic conductivity of about 10^{-3} ms^{-1}. Two units can be locally recognised due to the presence of a discontinuous, impervious, silt and clay layer to a depth of 60–80 m (Fig. 3). Groundwater flow direction is roughly oriented N to S, but, in the phreatic aquifer, is strongly controlled by draining action of the Po, Sesia and Ticino rivers (Fig. 4). The Lomellina region is characterised by an elevated potential infiltration (Associazione Irrigazione Est-Sesia 1984) and is intensively cultivated with, mainly, rice and corn fields. The recharge areas for the multilayer aquifer are located in the Alpine piedmont, but significant recharge takes place from seepages of the channel networks and from rice ponds.

The lower sequence (“Villafranchiano”) is composed of a silty-clay sequence of great thickness containing discontinuous sandy aquifer bodies. The groundwater direction is again oriented N-S, although not well defined, being strongly controlled by the buried structures of the Apenninc thrust front (Braga and Cerro 1988). Hydraulic conductivity of the silty-clay sequence is about 10^{-8} ms^{-1}, thus about 5 orders of magnitude lower than that of the alluvial aquifer. Finally the Pliocene clayey marine sequences, characterised by a low permeability coefficient (around 10^{-10} ms^{-1}) and containing saline waters (Conti et al. 2000), forms the aquifer system basement.

A detailed reconstruction of the hydrogeological setting was completed through the analysis and re-interpretation of the stratigraphic data from 102 municipal wells, according

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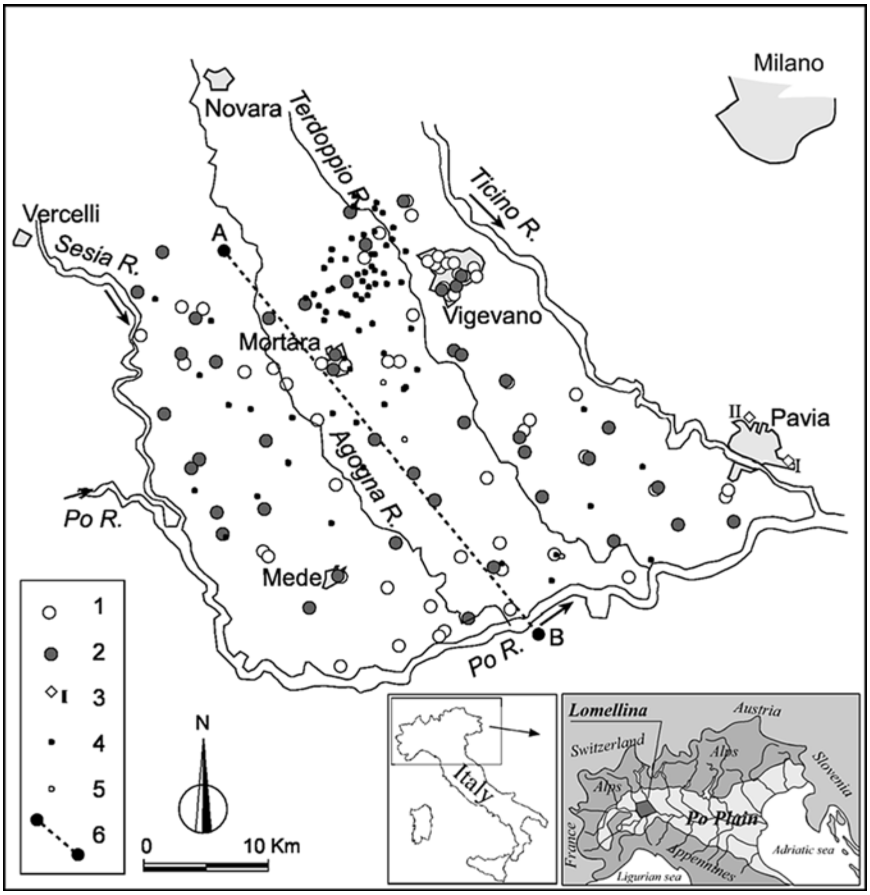

Fig. 1 Geographic settings of the Lomellina region and location of municipal wells for domestic use. 1 = well; 2 = sampled well; 3 = Pavia experimental wells; 4 = springs and natural outflows; 5 = sampled springs and natural outflows; 6 = A–B cross section of Fig. 4

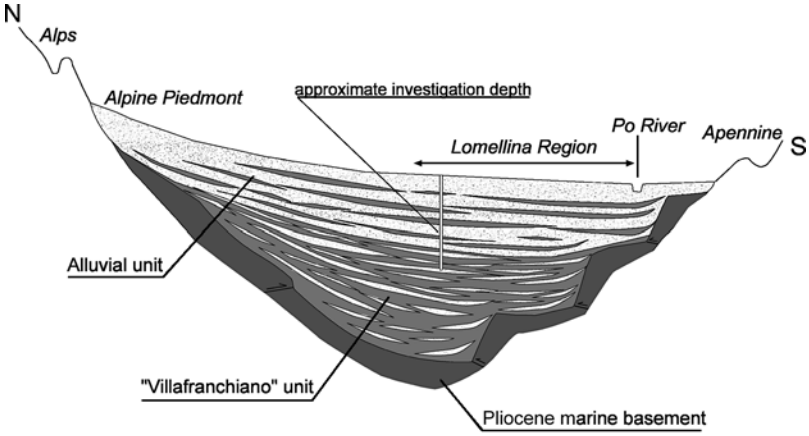

Fig. 2 Outlined cross-section of the Po plain showing the hydrogeological features of the Plio-Pleistocene continental sedimentary cover and the pattern of the main buried structures, shaped in the Pliocene marine formations (modified after Regione Lombardia and ENI Divisione AGIP 2002, Braga and Cerro 1988)

to their estimated porosity and classified as gravel and sand dominated (aquifers), silt dominated (aquitard) and clay dominated (aquiclude). An example of the reconstruction is given in Fig. 3.

Methods of investigation

Two experimental wells were drilled in 1995 near Pavia (Fig. 1), to a depth of 200 m. During the excavation, each individual productive layer was systematically isolated with packers to allow hydrodynamic measurements (Pilla 1998) and groundwater sampling (Fig. 5). This rather unique and costly procedure ensures representativity and constitutes a sound basis for the regional interpretation of groundwater data. Groundwater analyses included major ions, trace elements (NH_4^+, Sr^{2+}, Fe, Mn, see Table 1), stable isotopes of the water molecule, ^{13}C and ^{14}C of dissolved inorganic carbon, and tritium (Table 2).

In addition, 38 municipal wells and 8 natural outflows or very shallow wells were selected for the groundwater hydrochemical and isotopic depiction, which cover the

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Table 1 Chemical composition of groundwater from the two Pavia experimental wells. Aquifer P = phreatic, SC = shallow confined, DC = deep confined, MF = multifilter well

	Depth (m)	Aquifer	Cond (μS/cm)	Temp (°C)	pH	Ca^{2+} (mg/l)	Mg^{2+} (mg/l)	Na^{+} (mg/l)	K^{+} (mg/l)	Alk (mg/l)	Cl^{-} (mg/l)	SO_4^{2-} (mg/l)	NO_3^{-} (mg/l)	NH_4^{+} (mg/l)	Sr^{2+} (mg/l)	Fe (mg/l)	Mn (mg/l)
Well I	11	P	547	16	7.7	93.6	3.4	8.9	0.5	287	10.7	44.9	31.3	0.02	0.4	0.04	0.04
	17	P	352	17.2	8.0	57.2	8.6	7.1	0.8	183	13	23	1.4	0.02	0.3	N.D	<0.01
	31	P	348	14	8.2	63.2	11	4.4	0.8	250	6.5	<1	<1	0.3	0.2	0.87	0.15
	70	P	330	14	7.8	49.2	10.6	6.6	0.8	214	2.1	6.8	<1	0.1	0.2	0.32	0.11
	112	SC	237	15	7.8	39.6	11.3	8.6	0.7	189	0.7	1.5	<1	0.03	0.2	0.05	0.18
	140	DC	243	17	8.1	40.4	5.8	7.6	0.7	183	1.1	3.2	<1	0.06	0.2	0.01	0.10
	169	DC	202	18	8.2	35.6	5.8	7.6	0.7	159	1.2	2.9	<1	0.1	0.1	0.03	0.12
Well II	8.5	P	441	17.2	7.0	65.5	10.2	12.5	2.5	235	13.3	36.1	16.1	0.07	0.4	0.02	0.04
	20	P	310	14.8	7.4	44.3	8.4	10.7	2.7	189	9.0	19.2	2.3	0.07	0.34	0.04	0.02
	51	P	278	13.6	7.5	36.0	8.2	12	1.8	165	11.0	13	4	0.07	0.17	0.04	0.04
	91	SC	296	14.2	7.3	55.2	12.0	10.2	2.7	256	2.0	7.3	<1	<0.05	0.19	0.06	0.11
	110	SC	300	14.5	8.0	53.0	12.1	9.4	2.4	240	1.8	7.2	0.3	<0.05	0.24	0.03	0.10
	133	DC	248	13.7	8.5	42.1	9.1	10.0	2.4	195	2.6	6.2	<1	<0.05	0.21	0.16	0.07
	178	DC	192	14.4	8.5	30.2	6.5	12.8	1.8	149	1.3	6.0	<1	<0.05	0.28	0.01	0.04

Lomellina region homogenously both in terms of aquifer extension and depth. Analyses included: major ions, trace elements (NH_4^+, Sr^{2+}, Fe, Mn, As, see Table 3), pesticides (not discussed here), stable isotopes of the water molecule, ^{13}C and ^{14}C of Dissolved Inorganic Carbon (DIC) (Table 4). Shallow waters containing high levels of dissolved nitrates were considered for isotopic analysis ($^{15}N_{NO3-}$ and $^{18}O_{NO3-}$) (Table 5).

The pH, redox potential, alkalinity (by HCl titration) and conductivity were in most cases measured in situ. Samples were subsequently filtered at 0.45 μm and collected in pre-cleaned bottles. A sample aliquot was acidified to 1% HNO_3 for the analysis of cations and metals. Chemical analyses were done by the local groundwater control agency (ARPA) and by the Dipartimento di Scienze della Terra, University of Pavia. Anions were determined by ion chromatography, whilst cations and trace elements were determined by atomic absorption, ion chromatography and inductively coupled plasma source-atomic emission spectroscopy (ICPS-AES). All reported values have an ionic balance within 5%. Pesticides were determined by ARPA using GC or HPLC.

Samples for stable isotope analysis were collected according to the procedures described by Clark and Fritz (1997). Hydrogen isotope composition was measured by water reduction over metallic zinc (Coleman et al. 1982), while $\delta^{18}O$ was analysed by water-CO_2 equilibration at 25 °C (Epstein and Mayeda 1953); both results are expressed in δ‰V-SMOW (IAEA 1995). The analytical errors are ±1 and ±0.1‰respectively. The $\delta^{13}C$ of DIC was analysed by direct acidification of the water sample with phosphoric acid (Kroopnick 1974). These results are expressed in δ‰V-PDB (IAEA 1995). The analytical error is ±0.2 ‰. $\delta^{15}N_{NO3}$ and $\delta^{18}O_{NO3}$ of dissolved nitrates were analysed following the procedure described by Silva et al. 2000 and refer to AIR (IAEA 1995). The analytical error is ±0.5 ‰and ±1 ‰respectively. All gases were analysed on a Finnigan MAT 250 Mass Spectrometer at ISO4 s.s., Turin, Italy.

^{14}C analyses were performed at Hydroisotop GmbH, Germany, by conventional beta-counting or by accelerator mass spectrometry (AMS), depending on sample availability. The results are reported in Percent Modern Carbon (pmc) along with the analytical error. Tritium concentration was also determined at the Hydroisotop laboratory, by a scintillation counter following electrolytic enrichment (±0.1 to 0.2 T.U. at 1σ).

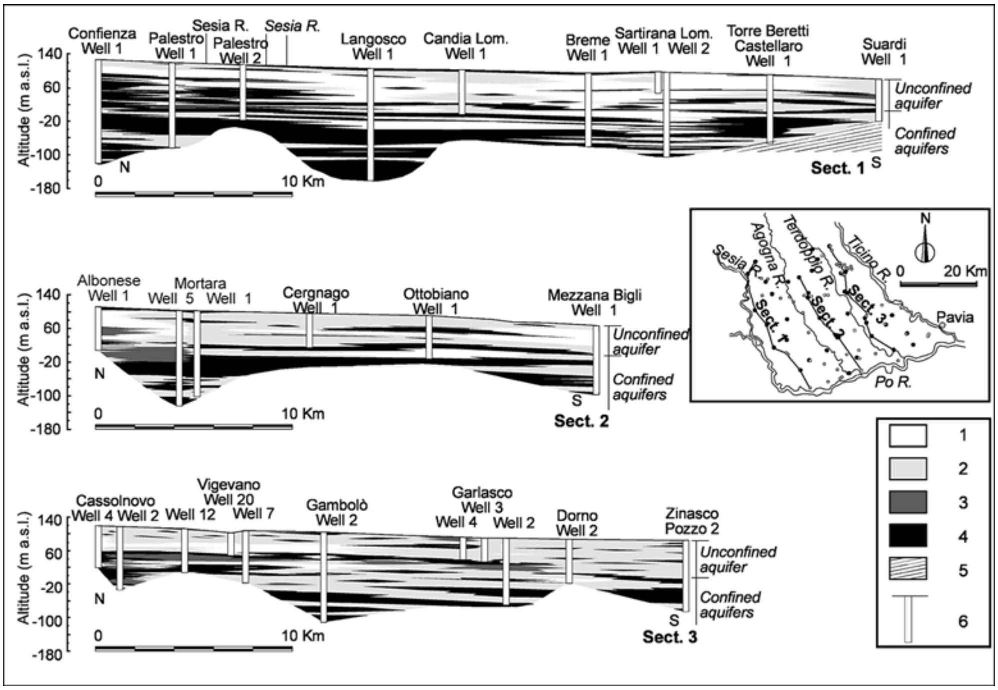
Results

Experimental wells

Results of the hydrochemical and isotopic analyses as a function of depth are reported in Tables 1 and 2 respectively, and shown in Figs. 5, 6, 8 and 9.

Groundwaters generally show a decrease in conductivity and mineralisation with depth, while pH increases from neutrality to 8.5. The hydrochemical facies for all samples is calcium-bicarbonate.

Fig. 3 Examples of cross sections obtained in this study. 1 = gravel dominated lithofacies (aquifer); 2 = sand dominated lithofacies (aquifer); 3 = silt dominated lithofacies (aquitard); 4 = clay dominated lithofacies (aquiclude); 5 = marine basement; 6 = well with stratigraphic information



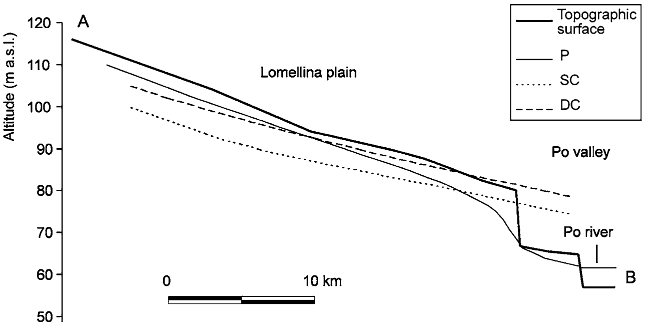


Fig. 4 Schematic cross section of the Lomellina plain showing the mean piezometric levels measured in the different aquifers. The location of the cross section A-B is shown on Fig.1. P = phreatic aquifer; SC = shallow confined aquifer; DC = deep confined aquifer. Unpublished data from ARPA (Agenzia Regionale per la Protezione dell'Ambiente) Lombardia, Settore Risorse Idriche

Stable isotopes of the water molecule range from −8.02‰ to − 8.94‰ and from −53.5‰ to −57.9‰ V-SMOW for δ^{18}O and δ^{2}H respectively. The isotopic analysis shows a discontinuous trend with a more enriched unit located at approximately 100 m below surface (Fig. 5).

δ^{13}C values for dissolved inorganic carbon range from −9.84‰to −12.69 δ ‰V-PDB, the more enriched values belonging to the unconfined aquifers. ^{14}C activities range from 73.0 to 39.8 pmc, displaying a regular decrease with depth. Samples from the deep confined aquifers display low Tritium content, near the detection limit, whereas the sample from the phreatic aquifer has 3 T.U.

The definition of aquitype, i.e. the chemical and isotopic characteristic composition of water in well-defined depth and aquifer (Kilchmann et al. 2004), provides an excellent tool for the data interpretation of groundwater collected in the municipal wells of the Lomellina region.

Fig. 5 Hydrostratigraphy of the experimental wells, coupled to electric conductivity and δ^{18}O profiles. Modified after Pilla 1998

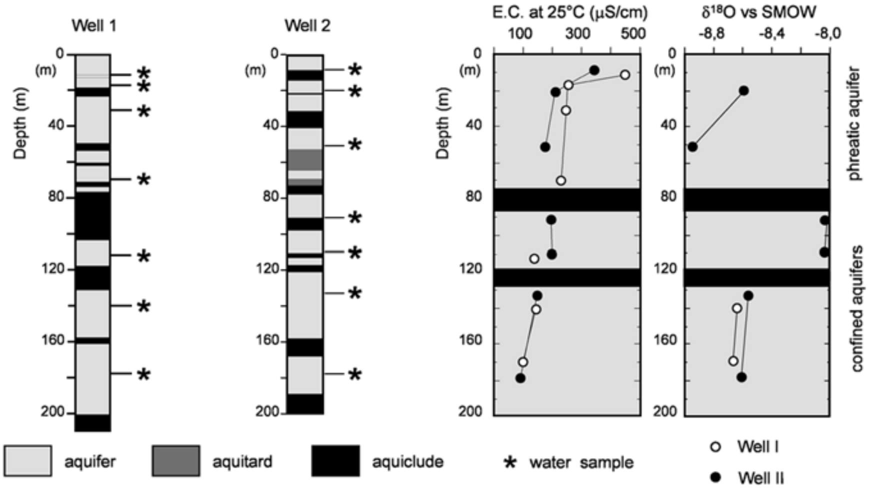


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Table 2 Isotopic composition of selected groundwater samples from the two Pavia experimental wells. Aquifer P = phreatic, SC = shallow confined, DC = deep confined, MF = multifilter well

	Depth (m)	Aquifer	δ^{18}O V-SMOW	δ^{2}H V-SMOW	δ^{13}C V-PDB	A^{14}C pmc	Tritium (T.U.)
Well I	140	DC	−8.64	−55.1	−12.06	46.8 ± 0.6	N.D
	169	DC	−8.67	−55.0	−12.25	42.6 ± 0.5	0.2
Well II	20	P	−8.59	−56.7	−9.84	N.D	N.D
	51	P	−8.94	−57.9	−11.79	N.D	3
	91	SC	−8.02	−53.5	−11.87	70.2 ± 0.6	N.D
	110	SC	−8.04	−54.0	−12.69	73.0 ± 0.4	N.D
	133	DC	−8.56	−55.6	−12.22	64.7 ± 0.5	N.D
	178	DC	−8.61	−56.0	−12.67	39.8 ± 0.4	1

Lomellina wells

Results of the hydrochemical and isotopic analyses of the Lomellina wells are reported in Tables 3 and 4 respectively.

Wells are classified according to their respective aquifer; multiple filter wells are classified separately but an indication of the filter depth is given. Although this classification, if based essentially on well logs, is questionable, the chemical and isotopic composition of groundwater provides additional support to this interpretation. Most of the wells withdraw water from the alluvial aquifer, although the deepest wells may reach sandy layers in the "Villafranchiano" sequence. The evolution of groundwater chemistry with depth is reported in Fig. 6. As for the two experimental wells, a decrease in conductivity and mineralisation, and a parallel increase of pH with depth can be observed.

The stable isotope composition of the different aquifers shows a wider range of values: from −10.64‰ to −8.32‰ and from −75.6‰ to − 58.0‰ V-SMOW for δ^{18}O and δ^{2}H respectively, and from −18.30‰to −9.60‰δ V-PDB for δ^{13}C. ^{14}C activities range from 71.7 to 13.2 pmc. Given the low levels of tritium found in the experimental wells, tritium analyses were not conducted on these samples.

Water samples from outflows and shallow wells showing high levels of nitrates were selected for isotopic analysis ($^{15}N_{NO3-}$ and $^{18}O_{NO3-}$). Results (Table 5) range from −7.39‰to 0.98 ‰AIR and from 3.4‰to 16.9‰V-SMOW for δ^{15}N and δ^{18}O respectively, corresponding to the compositional range of the nitrification of synthetic fertilisers (Clark and Fritz 1997).

Discussion

Origin and age of groundwater

A linear regression performed on groundwater stable isotope composition (Fig. 7) provides the following result:

$$\delta^{2}H = 7.78\,\delta^{18}O + 8.9$$

rather similar to that obtained by Bortolami et al. (1983) ($\delta^{2}H = 8.03\ \delta^{18}O+11.3$) and Avanzini et al. (1994) ($\delta^{2}H = 7.58\ \delta^{18}O+7.54$) in adjacent sectors of the Po plain (Novara and Vercelli).

The mean annual weighted isotopic composition of precipitation over the investigated area has a δ^{18}O ranging between −7.70‰and −7.13‰(Longinelli and Selmo 2003). Moreover, the influence of atmospheric circulation on the precipitation of isotopic compositions has been recognised at the regional scale. Dray et al. (1997) and more recently Longinelli and Selmo (2003) have found isotopically enriched waters on the southern side of the Po valley (Apennines), as compared to isotopically depleted waters in the northern side (Alps). This fact reflects the lower altitude of the aquifer replenishment processes in the Apennines sector, as compared to the altitude of "alpine aquifers" recharge areas. Even though the origin of precipitation water was similar to the present as indicated by deuterium excess numbers (Zuppi and Sacchi 2004a), the aquifer recharge processes changed during the Holocene with varying temperature regimes. In other words, on a millennia time scale, the influence of differential cooling or warming between the chains could be considered negligible, as the orographic effects on the precipitation isotopic composition remain the same. Because the isotopic content of precipitation distinguishes clearly between the two main recharge sectors, the hydraulic characteristics of aquifers can be pointed out. In addition, stable isotopes confirm the hydraulic confinement of deeper aquifers, and verify the inadequate drilling operation and the scarce maintenance of wells. The five groups (Fig. 8) summarise the following frame:

- group A shows depleted values (δ^{18}O ∼ −10.4‰± 0.3) corresponding to the isotopic composition of major rivers, which are used for irrigation through a dense network of channels (Associazione Irrigazione Est-Sesia 1984). The isotopic composition of major Alpine rivers (Po, Sesia, Ticino, Dora Baltea), show different values according to the mean altitude of their drainage basin: for instance the Dora Baltea River shows very low values (δ^{18}O = −13.34‰), while the Po, Sesia and Ticino rivers range from −10‰to −11‰(Bortolami et al. 1983).
- group B shows more enriched values (δ^{18}O ∼ −9.0‰± 0.5) corresponding to a mixing between the isotopic composition of local precipitation (Longinelli and Selmo 2003) and group A, suggesting the participation of the canals network to the aquifer recharge.
- group C shows, again, more enriched isotopic compositions (δ^{18}O ∼ −8.5‰± 0.5). These values are in agreement with deep confined waters sampled in the Milano

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Table 3 Chemical composition of groundwater from the Lomellina region. Aquifer P = phreatic, SC = shallow confined, DC = deep confined, MF = multifilter well. N.D. = not determined

Sample	Filter depth (m)	Aquifer	Cond. (µS/cm)	Temp. (°C)	pH	O_2 (mg/l)	Ca^{2+} (mg/l)	Mg^{2+} (mg/l)	Na^+ (mg/l)	K^+ (mg/l)	Alk. (mg/l)	Cl^- (mg/l)	$SO_4{}^{2-}$ (mg/l)	$NO_3{}^-$ (mg/l)	$NH_4{}^+$ (mg/l)	Sr^{2+} (mg/l)	SiO_2 (mg/l)	Fe (mg/l)	Mn (mg/l)	As (mg/l)
ALBONESE 1	90	P	387	15.1	7.7	1.46	48	13	7	1.3	213	3	24	<1	0.14	0.16	28.5	1.1	0.37	1.5
BORGO S. SIRO 1	46	P	498	16.5	7.6	N.D	69	16	8.7	2.8	226	11	45	6	<0.05	0.2	14.3	0.36	0.01	1.3
BREME 1	155	DC	294	15.7	8.1	N.D	33	8	23	1.1	165	10	<1	<1	0.19	0.14	16.9	0.09	0.1	<1
CANDIA 1	92	SC	325	14.7	8	N.D	46	10	5.3	0.9	165	3	22	<1	<0.05	0.16	22.3	<0.05	<0.01	2.3
CASSOLNOVO 4	36	P	318	14.4	6.6	N.D	37	11	7.8	1.9	116	8	35	11	<0.05	0.12	17.5	<0.05	<0.01	<1
CASTELNOVETTO 1	85–135	MF	380	15.7	7.9	N.D	58	12	5.8	1.3	201	3	21	<1	0.09	0.17	23.3	0.19	0.2	<1
CERGNAGO 1	70	P	381	13.8	7.8	N.D	59	11	6.9	1.3	214	3	27	<1	0.16	0.13	22.9	0.6	0.34	8.4
CILAVEGNA 1	60	P	461	12.9	7.8	N.D	60	20	7	2.6	220	6	54	<1	<0.05	0.15	16.9	0.36	0.27	4.4
CILAVEGNA 2	44	P	465	12.9	7.8	N.D	59	21	7.5	3.1	220	6	52	<1	<0.05	0.14	17.3	1.4	0.24	4.3
CONFIENZA 1	115–235	MF	194	15.9	8.1	1.88	21	4	13	0.5	116	1	<1	1	0.56	0.09	20.5	<0.05	0.1	3.7
DORNO 2	93	SC	439	14.2	7.4	N.D	55	19	5.9	2.2	214	6	44	<1	<0.05	0.18	21.4	3.2	1.7	<1
GAMBOLO' 1	80.5	SC	285	14.4	8	N.D	37	10	5.3	1.8	122	3	30	<1	0.09	0.08	21.4	0.35	0.12	<1
GAMBOLO' 2	185	DC	243	14.6	8	N.D	33	8	4.5	1.6	122	2	23	<1	0.1	0.07	21.4	0.16	0.1	1.2
GARLASCO 2	149	SC	213	16	8.2	1	27	5	6.4	1.2	122	2	8	<1	0.21	0.08	20.8	0.06	0.1	3.3
GARLASCO 3	40	P	448	17	7.7	N.D	64	12	7.4	2.1	183	6	40	14	<0.05	0.23	15.8	<0.05	<0.01	1.1
GRAVELLONA 1	80–150	MF	192	13.9	7.5	1.3	21	7	6.7	0.9	98	1	8	<1	0.05	0.08	25	0.37	0.23	1.4
LANGOSCO 1	130	SC	398	15	7.9	N.D	61	12	5.6	1.3	189	6	37	<1	<0.05	0.19	23.7	<0.05	0.03	1.5
LOMELLO 1	120	DC	279	15.1	8.1	N.D	42	8	11	1.2	183	3	<1	<1	0.24	0.12	19.9	0.14	0.14	4.6
MEDE 3	130	SC	313	14.5	8.1	N.D	61	10	5	1.1	183	2	13	<1	0.11	0.17	18.4	0.28	0.12	2.6
MEZZANA BIGLI 2	160	DC	229	16.2	8.1	N.D	31	6	13	0.9	153	3	<1	<1	0.24	0.11	18.6	0.13	0.08	<1
MORTARA 1	175	DC	171	15.4	7.9	1.83	18	3	12.3	<0.5	110	1	<1	<1	0.68	0.07	19	<0.05	0.08	13
MORTARA 5	110–185	MF	213	14.1	7.9	1.67	24	6	8	0.7	122	1	1	<1	0.38	0.09	21	<0.05	0.13	9.3
NICORVO 1	160	DC	150	15.8	8.2	1.52	18	3	8.6	<0.5	98	1	<1	<1	0.44	0.08	19	<0.05	0.09	5.6
OTTOBIANO 1	90	SC	263	15.3	8.3	N.D	19	4	33	0.5	153	9	<1	<1	0.77	0.08	17.2	0.07	0.06	9
PALESTRO 1	185	DC	167	15.5	8.3	1.47	19	5	7.8	0.5	104	1	<1	<1	0.28	0.07	19.5	<0.05	0.09	<1
ROBBIO 5	100–145	MF	185	15.6	8.2	1.65	22	5	8.2	0.5	110	1	1	<1	0.33	0.09	19.7	<0.05	0.11	3
SANNAZZARO 2	95–140	MF	205	14.8	8.1	N.D	28	5	6.3	0.9	128	1	6	<1	0.17	0.08	20.1	0.07	0.12	<1
SOMMO 2	160	DC	198	16	8.3	N.D	22	5	9.8	0.6	122	2	<1	<1	0.51	0.09	19.9	<0.05	0.22	1.9
TORRE BERETTI 1	90	SC	343	15.5	8	N.D	50	11	6.2	1.1	195	2	14	<1	0.11	0.21	18.8	0.1	0.11	1
TROMELLO 1	110	SC	229	15.8	8	0.6	31	6	5.1	1.2	122	1	14	<1	0.12	0.08	22	0.21	0.18	<1
VALLE LOMELLINA 1	120	SC	444	15.5	7.6	N.D	72	15	4.5	1.4	226	2	38	3	<0.05	0.24	25.5	<0.05	0.01	1.2
VIGEVANO 17	60–110	MF	341	14.6	7.6	N.D	36	12	7.8	2.2	122	10	42	13	<0.05	0.14	18.4	<0.05	<0.01	<1
VIGEVANO 20	35	P	357	14.9	7.2	N.D	40	12	10.3	2.3	116	12	44	23	<0.05	0.18	18.4	<0.05	<0.01	<1
VIGEVANO 04	120	SC	153	14.5	8.3	N.D	16	4	7.3	0.7	98	1	<1	<1	0.15	0.12	23.5	<0.05	0.1	<1
VIGEVANO 09	175	DC	161	15.6	8.4	N.D	12	3	19	0.4	110	2	<1	<1	0.41	0.12	19.3	<0.05	0.06	3.1
ZEME 1	184	DC	192	17.2	8.4	N.D	20	5	12.9	0.5	122	2	<1	<1	0.47	0.08	18.2	<0.05	0.06	<1
ZERBOLO' 1	79	P	369	16.3	8.1	N.D	51	10	6.9	1.6	195	2	24	<1	0.23	0.2	21.4	0.15	0.12	<1
ZINASCO 2	125	SC	329	15.8	8.2	0.8	45	9	5.8	0.9	165	4	23	<1	0.22	0.14	21.2	0.07	0.15	<1

Table 4 Isotopic composition of groundwater from the Lomellina region. Aquifer P = phreatic, SC = shallow confined, DC = deep confined, MF = multifilter well. N.D. = not determined

Sample	Aquifer	δ^{18}O V-SMOW	δ^{2}H V-SMOW	δ^{13}C V-PDB	A^{14}C pmc
ALBONESE 1	P	−10.05	−70.6	−13.50	71.7 ± 3.2
BORGO S. SIRO 1	P	−8.42	−60.0	−11.78	N.D
BREME 1	DC	−9.84	−68.0	−14.00	13.2 ± 2.1
CANDIA 1	SC	−9.81	−66.9	−12.90	67.3 ± 3.2
CASSOLNOVO 1	P	−8.43	−58.0	−15.07	N.D
CASSOLNOVO 4	P	−8.91	−63.7	−15.22	N.D
CASTELNOVETTO 1	MF	−9.56	−66.3	−14.81	N.D
CERGNAGO 1	P	−10.64	−73.7	−13.02	N.D
CILAVEGNA 1	P	−10.64	−71.7	−12.33	N.D
CILAVEGNA 2	P	−10.51	−75.6	−13.46	N.D
CONFIENZA 1	MF	−9.08	−59.3	−13.69	N.D
DORNO 2	SC	−9.17	−63.3	−11.57	N.D
GAMBOLO' 1	SC	−9.63	−63.8	−13.87	N.D
GAMBOLO' 2	DC	−9.66	−65.6	−11.20	66.6 ± 3.2
GARLASCO 2	SC	−9.55	−64.2	−13.30	65.9 ± 0.8
GARLASCO 3	P	−9.51	−66.0	−11.87	N.D
GRAVELLONA 1	MF	−9.28	−65.5	−18.14	N.D
LANGOSCO 1	SC	−9.97	−70.9	−12.60	69.1 ± 4.5
LOMELLO 1	DC	−8.32	−58.6	−14.50	55.7 ± 0.8
MEDE 1	P	−9.27	−66.7	−12.31	N.D
MEDE 3	SC	−9.32	−66.2	−12.70	56.9 ± 2.5
MEZZANA BIGLI 2	DC	−8.76	−58.5	−14.80	31.4 ± 2.4
MORTARA 1	DC	−8.70	−56.6	−14.60	28.9 ± 0.6
MORTARA 5	MF	−8.71	−57.6	−12.89	N.D
NICORVO 1	DC	−8.74	−58.0	−17.30	37.4 ± 0.6
OTTOBIANO 1	SC	−9.31	−62.7	−12.09	N.D
PALESTRO 1	DC	−8.88	−57.1	N.D	42.7 ± 0.6
ROBBIO 5	MF	−8.78	−59.0	N.D	49.8 ± 0.7
SANNAZZARO 2	MF	−9.26	−60.9	−15.28	N.D
SOMMO 2	DC	−8.99	−59.0	N.D	47.2 ± 0.6
TORRE BERETTI 1	SC	−9.47	−65.4	−11.80	56.4 ± 2.3
TROMELLO 1	SC	−9.67	−67.0	−12.40	66.9 ± 0.8
VALLE LOMELLINA 1	SC	−10.25	−71.4	−11.70	71.0 ± 2.8
VIGEVANO 17	MF	−8.85	−59.9	−18.30	N.D
VIGEVANO 20	P	−8.72	−57.8	−9.60	N.D
VIGEVANO 04	SC	−9.46	−64.8	−13.71	68.8 ± 1.0
VIGEVANO 09	DC	−9.13	−61.7	−14.16	22.7 ± 4.2
ZEME 1	DC	−8.89	−56.8	−16.20	33.5 ± 0.8
ZERBOLO' 1	P	−10.63	−71.8	−11.56	N.D
ZINASCO 2	SC	−9.53	−67.1	−13.90	N.D

region (Avanzini et al. 1994), confirming the aquifer continuity northward. The recharge area of this waters is likely located at the foothills of the Alps.

- group D, formed by waters collected in the shallow confined and in multifilter wells show intermediate isotopic compositions. (δ^{18}O ∼ −9.5 ‰± 1.0). This is due to mixing processes inside the aquifer, which is a consequence of high withdrawal rates.

Generally, the DIC δ^{13}C varies between −14‰and −10‰(Fig. 9), corresponding to a system, where the soil derived CO_2 mixes with a dead dissolved carbon from the aquifer matrix (Clark and Fritz 1997). Nevertheless, some groundwater samples, displaying lower δ^{13}C (group A), require another more depleted carbon source to be considered. It corresponds to the degradation of organic matter present in the aquifer matrix (Zuppi and Sacchi 2004a,b). Indeed, organic matter participated and still participates in sedimentation giving origin to lignite, peat and organic clay deposits which often form aquicludes in the whole Po valley (Regione Lombardia and ENI Divisione AGIP 2002).

In the phreatic aquifer, the continuous mixing of different hydraulic components and the generalised anthropogenic perturbation which homogenises tracers, do not allow evaluation of the transit time. Instead, water in the confined aquifers flows essentially following a piston model, as indicated in Fig. 10, which shows the radiometric decay of ^{14}C and by the constant values of δ^{13}C (around –15‰).

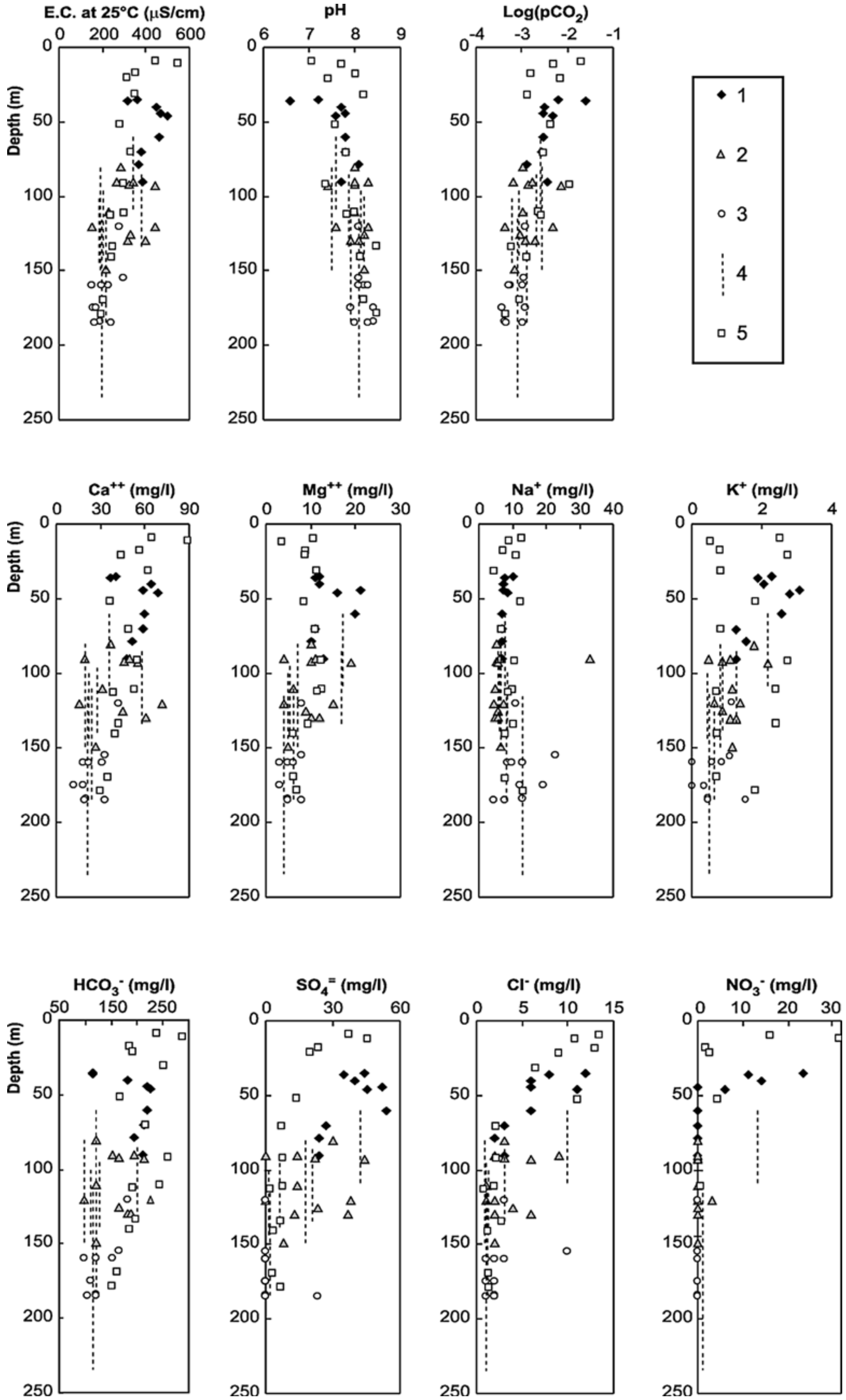

Fig. 6 Evolution of hydrochemical parameters with depth. 1 = phreatic aquifers; 2 = shallow confined aquifers; 3 = deep confined aquifers; 4 = multifilter wells; 5 = Pavia experimental wells

Table 5 Chemical and isotopic composition (nitrogen and oxygen of dissolved nitrates) from springs, natural outflows and very shallow wells

Sample	Depth (m)	Cond. (μS/cm)	Temp. (°C)	Ca^{2+} (mg/l)	Mg^{2+} (mg/l)	Na^{+} (mg/l)	K^{+} (mg/l)	Cl^{-} (mg/l)	SO$_4^{2-}$ (mg/l)	HCO$_3^{-}$ (mg/l)	NO$_3^{-}$ (mg/l)	δ^{15}N$_{NO3}$ AIR	δ^{18}O$_{NO3}$ V-SMOW
Fontanile 52	0	380	16.8	44.5	10.1	9.4	1.8	12.4	48.6	134	20.3	−2.75	10.0
Fontanile 39	0	312	15.5	39.3	7.3	9.6	2.6	17.3	39.1	100	33.4	0.98	12.9
Garlasco 3	40	448	17.0	64	12	7.4	2.1	6	40	183	14	−7.39	10.4
Travacó Sicc. (fraz. Colonne)	8	455	20.6	73.2	9.1	8.5	2.3	11.0	38.1	224	26.6	−2.27	8.4
Pieve Albignola (spring)	0	380	16.2	45.3	12.3	9.4	2.9	< 1	< 1	100	49.7	1.67	3.4
Candia (C.Fornace)	12	657	15.9	107.2	17.9	10.8	4.6	< 1	< 1	349	18.5	−2.05	9.0
Breme (C.Dallone)	10	439	13.9	65.6	10.9	8.6	8.5	< 1	< 1	76	17.2	−2.25	7.1
Rosasco (Aia di Biana)	14	660	14.9	63.5	40.5	14.4	1.9	< 1	< 1	266	12.4	−0.55	13.5
Ottobiano (C.Rotorta)	30	359	16.6	51.5	11.9	8.2	1.3	< 1	< 1	168	12.8	−7.84	10.9
Cassolnovo 1	39	N.D	N.D	40.9	12.6	14.1	2.3	12.7	45.4	142	9.8	−3.09	16.9

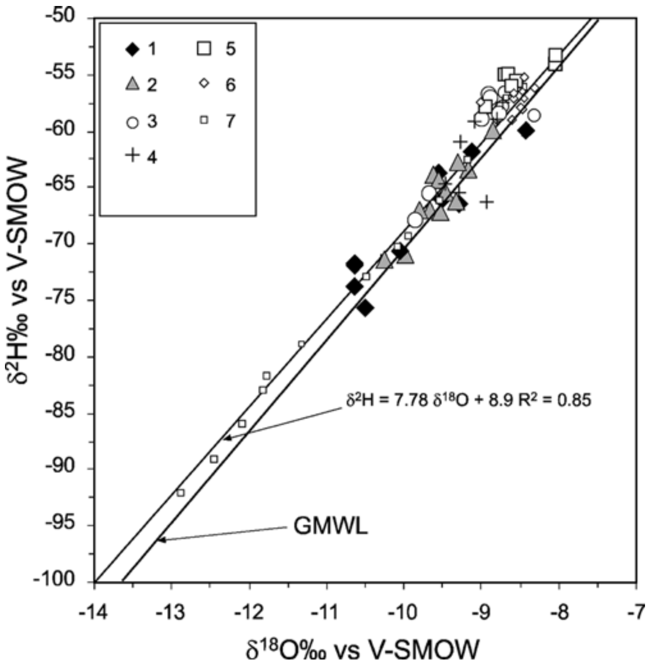

Fig. 7 δ^{2}H vs. δ^{18}O diagram. 1 = phreatic aquifers; 2 = shallow confined aquifers; 3 = deep confined aquifers; 4 = multifilter wells; 5 = Pavia experimental wells; 6 = Milano plain (Avanzini et al. 1994); 7 = Novara and Vercelli plain (Bortolami et al. 1983). *Full line*: linear regression, this study data. *Dashed line*: Global Meteoric Water Line (GMWL) (Rozanski et al. 1993)

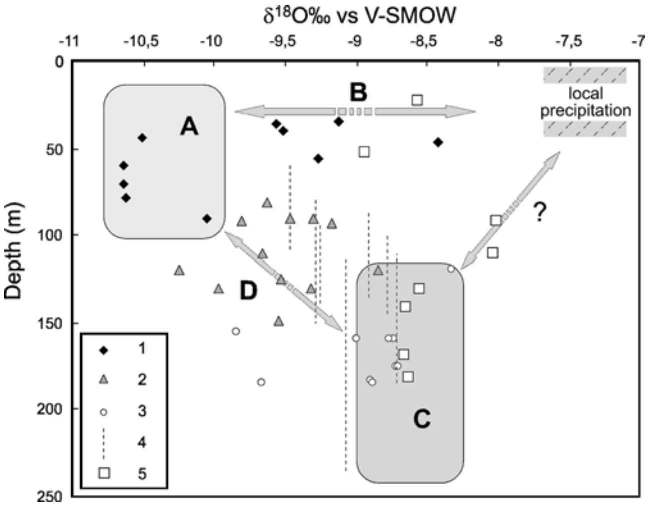

Fig. 8 Evolution of δ^{18}O with depth. 1 = phreatic aquifers; 2 = shallow confined aquifers; 3 = deep confined aquifers; 4 = multifilter wells; 5 = Pavia experimental wells. A, B, C and D, see text for explanation

Moreover, from recharge and discharge areas, the water velocity can not be easily evaluated because of the variable aquifer sections as a consequence of buried structures of the Apennine thrust front (Braga and Cerro 1988).

The presence of an organic source of "dead" carbon affects the ^{14}C activity correction, thus precluding precise dating. Nevertheless, residence times have been calculated using the model, described by Pearson (1965), which is the most suitable model for terrigenous aquifers (Table 6). The following values have been used in age calculation: the activity of soil CO$_2$, which is equal to 100 pmc, −25‰as δ^{13}C; the activity of inorganic carbonates within the aquifer matrix, which are equal to 0 pmc and δ^{13}C = 0‰.

Water age indicates that recharge took place in different periods: the present for the phreatic aquifer, while for the confined aquifers recharge occurred in the Holocene between 5 and 7 Ka BP and in the late Wurm Pluvial (MIS 2) lasting from about 18 to 11 Ka BP (Zuppi and Sacchi 2004a). This information, coupled with the high quality standards of deep confined groundwater, raises some concern about their exploitation for use other than domestic.

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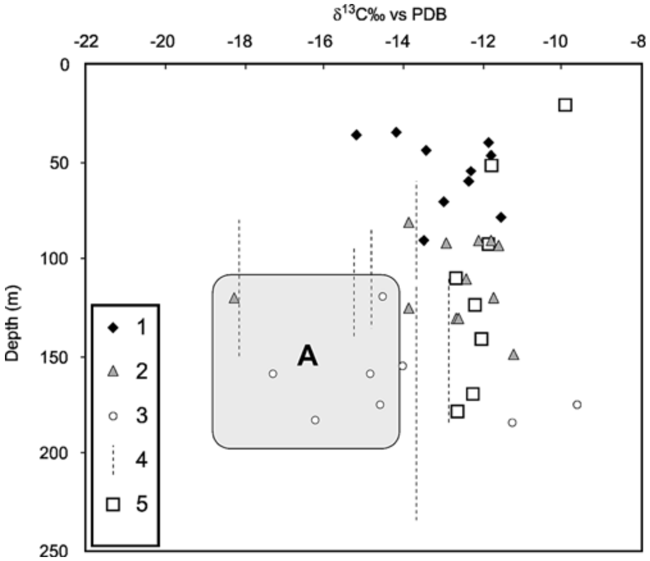

Fig. 9 Evolution of $\delta^{13}C$ in DIC with depth. 1 = phreatic aquifers; 2 = shallow confined aquifers; 3 = deep confined aquifers; 4 = multifilter wells; 5 = Pavia experimental wells. *Box A*, see text for explanation

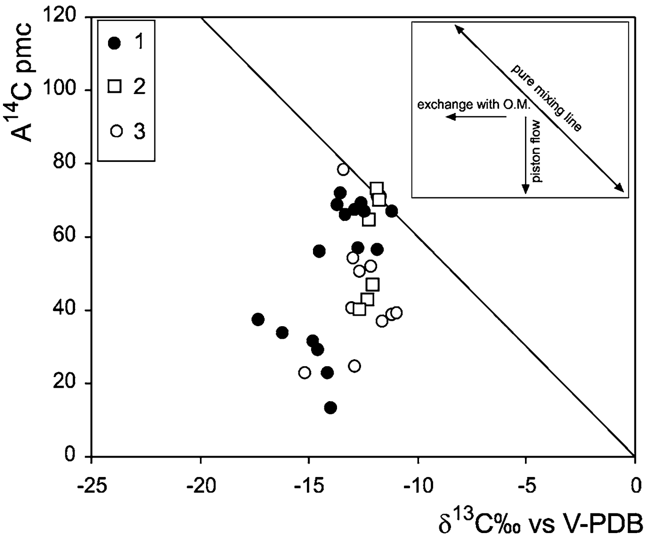

Fig. 10 $\delta^{13}C$ vs. ^{14}C activity in DIC. 1 = Lomellina plain; 2 = Pavia experimental wells; 3 = Milano plain

Table 6 Radiometric ages of groundwater calculated according to the Pearson (1965) model. *R* = recent waters, recharged after 1952

Sample	Residence time Uncorrected Ao = 100	Residence time Corrected Pearson model
Pavia experimental wells		
Well I (140 m)	6277	251
Well I (169 m)	7054	1157
Well II (91 m)	2925	R
Well II (110 m)	2602	R
Well II (133 m)	3599	R
Well II (178 m)	7616	1961
Lomellina wells		
Albonese 1	2750	R
Palestro 1	7035	R
Sommo 2	6206	R
Robbio 5	5763	R
Nicorvo 1	8130	5087
Mortara 1	10262	5815
Mede 3	4661	R
Breme 1	16740	11946
Lomello 1	4838	334
Mezzana Bigli 2	9576	5242
Gambolo 2	3360	R
Garlasco 2	3447	R
Tromello 1	3323	R
Torre Beretti 1	4734	R
Valle Lomell 1	2831	R
Zeme 1	9041	5454
Candia 1	3274	R
Langosco 1	3055	R
Vigevano 04	3091	512
Vigevano 09	12258	4346

Origin of groundwater mineralisation

According to recently published data, silicates from the dismantling of the mountain chains constitute, essentially, the deposits which have filled the Po valley, during the Late Alpine orogenesis (Dinelli et al. 1999; Regione Lombardia and ENI Divisione AGIP 2002; Di Giulio et al. 2003). Aquifers do not differ significantly in their mineralogical and petrographic composition of matrixes, and, therefore, it is not surprising that groundwater chemical composition is consequently very similar. Meanwhile, sediments filled the Adriatic palaeo–gulf under different environmental conditions. Indeed, biomass accumulated with and inside terrigenous sediments that evolved with a different maturity degree (gas, coal, lignite, peat), and control the redox behaviours of aqueous phases in aquifers and aquicludes. The alteration state of silicates indicates, primarily, the hydrogeological characteristics of the shallow hydrological system. When there is aqueous CO_2 no longer available, and the second unit becomes confined, the pH increases. The hydrolysis is more active in the first unit where the systems, either hydrogeological or geochemical, are open.

Deep waters show higher pH (around 8.1) as well as the absence of nitrates and sulphates, likely corresponding to larger CO_2 and dissolved O_2 consumption with respect to shallow waters. As a consequence, As and NH_4^+ are significantly present, thus confirming the hydrogeological and geochemical captivity of the deep aquifer (Conti et al. 2000).

Ion activities and saturation indexes for groundwater were calculated using the WATEQ code (Truesdell and Jones 1974). Even waters circulating in the phreatic aquifer reach calcite saturation. Exception is given to water samples collected in nearby rivers or canals and infiltrated by direct seepage. This prevents the use of the calcite saturation index to depict the progress of the water–rock interaction along the flow lines.

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Activity diagrams (Fig. 11) demonstrate the control of the aquifer matrixes on the dissolved Ca and Na, either in phreatic aquifer or in the confined sands. Although the lack of Al data does not allow a complete thermodynamic modelling of groundwater evolution, a geochemical-evolutionary trend can be seen for waters of increasing depth (Helgeson et al. 1976; Appelo and Postma 1994; Michard et al. 1996). In fact a clear distinction appears between waters of the phreatic and those of confined aquifers. Water from all aquifers are largely in equilibrium with respect to the weathered phases of silicates such as kaolinite. The requested time for water to reach the kinetic equilibrium with kaolinite during silicate interaction is in agreement with isotopic chronometers (Tritium Units and Modern Carbon). While water is far from feldspar equilibrium, they account for a relatively long interaction time with the aquifer matrix (Lasaga 1984).

Also, water samples from the confined aquifer are in equilibrium with calcite; pH close to 8.1 is controlled by the incongruent dissolution of silicates. The constant values depicted by the ratio of Ca and H activities suggest that precipitation of secondary mineral is equilibrated by dissolution of Ca^{+2}-bearing primary minerals. In this system kaolinite is initially the stable clay mineral, but in deep groundwater the more complex leonhardite could be stable.

The geochemical evolution described would no longer concern only water masses with similar origin, but would reflect mixing with surface waters. An increasing chemical load would then not necessarily reflect increasing water ages or residence times. In fact, the deep confined aquifer, although there is a presence of As and NH_4^+ ions, contains groundwater which is, generally of excellent quality. On the contrary the phreatic aquifer displays waters of poor quality: higher mineralisation, high nitrate, sulphate and chloride contents and, locally, detectable amounts of pesticides. Anthropogenic influence on water quality sampled in the shallow aquifer is also highlighted by the isotopic composition of dissolved nitrates. $\delta^{15}N$ (Fig. 12) confirms for most samples an agricultural origin of contaminants due to the nitrification of synthetic fertilisers (Clark and Fritz 1997; Kendall 1998). Two samples show further negative values in $\delta^{15}N$. The depleted composition may be due to the presence of a biogenic NH_4^+, which is oxidised during water movement. Biological ammonium indicates the large contribution of ditches to the aquifer recharge, through the contemporaneous presence of other organic compounds (pesticides).

A correlation of isotopic composition with nitrate concentrations (and consequently with depth) is also observed (Fig. 12). The progressive increase of $\delta^{15}N$ with concentration may be due to the constant buildup of nitrates in groundwater, continuously added by the transport and nitrification of fertilisers. Conversely, the decrease in $\delta^{18}O$ indicates the progressive equilibration with the isotopic composition of groundwater and the closing of the system to atmospheric oxygen.

The limit of high nitrate waters may mark the maximum penetration of groundwater from the surface. Beyond this, waters with low nitrate but still in aerobic conditions, may

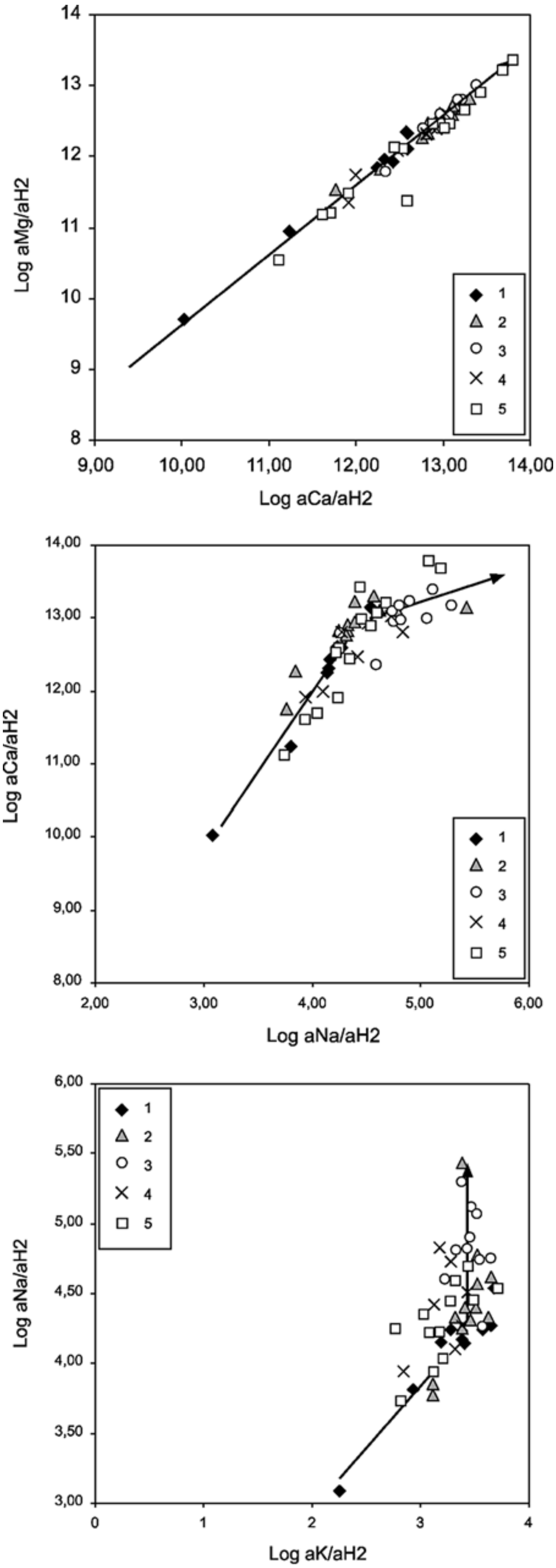

Fig. 11 Activity diagrams for Ca, Mg, Na and K. 1 = phreatic aquifers; 2 = shallow confined aquifers; 3 = deep confined aquifers; 4 = multifilter wells; 5 = Pavia experimental wells

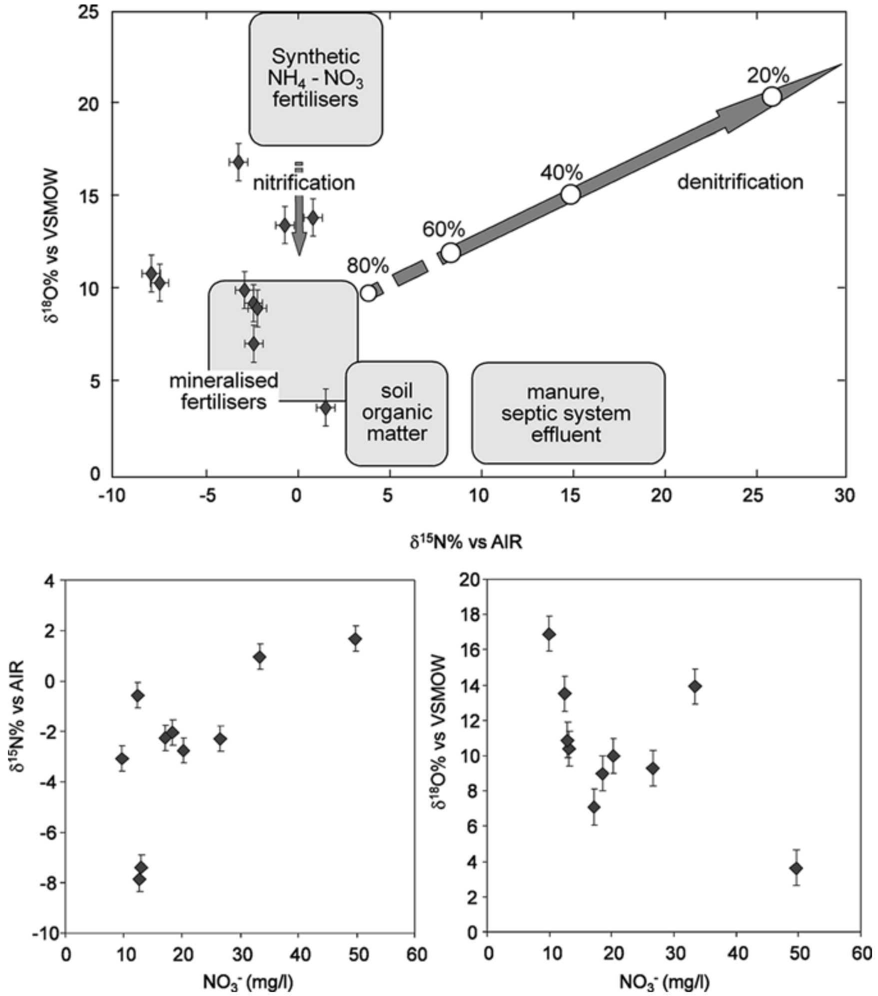

Fig. 12 **a** δ^{15}N and δ^{18}O of dissolved nitrates. Compositional ranges and processes after Kendall 1998, Clark and Fritz 1997; **b** δ^{15}N vs. nitrate concentration; **c** δ^{18}O vs. nitrate concentration

reflect low total nitrogen input from pre-industrial times rather than denitrification. The redox boundary, which must coincide with the complete reaction of oxygen is found in the depth range of 100–150 m.

Summary and conclusion

This study reconstructs the hydrogeological framework of the Po plain in the Lomellina region and defines the hydrochemical and isotopic features of the aquifers. A shallow phreatic aquifer, reaching depths of 60–80 m, and two groups of confined aquifers, one in the alluvial sequence and one in the “Villafranchiano” lacustrine sequence, have been identified.

The hydrogeological conceptual model could be as follows. Oldest water is found in the confined aquifers, where the presence of buried structures hinders natural discharge. In other words, the water is practically stagnant (Mazor et al. 1995). This water infiltrated at the end of the cold dry climatic period of the last glacial maximum (LGM), when discharge from the Po River increased simultaneously with the melting phase of glaciers in the Alps and Apennines. Anthropogenically induced perturbations in deep aquifers favour the slow movement of younger waters (early Holocene) coming from the Alpine piedmont recharge area.

The confined aquifers show essentially passive hydrodynamic conditions and pressure heads maintain a higher piezometric level than the phreatic aquifer (Fig. 4). This inhibits the possibility of recent water penetrating far below the surface. In other words, the oldest waters act as a piston through the lithological and granulometric discontinuities of aquicludes and aquitards; the upward pressure transfer of deep groundwater avoids the downward mass transfer of polluted shallow groundwater. The interface between passive and active waters is highlighted by the, so called, mixed water from Fig. 8 (group D).The differences in mixing rates, as well as the ambiguous interface, are the consequence of anthropogenic artefacts such as high withdrawal rates. Data suggest that, at the present time, water pumped in the shallow aquifer even throughout monofilter wells are, in fact, mixed and thus waters are older than the results show. In fact, using chronometers, the mixing between old and recent waters is an exponential function. Furthermore, the pressure heads move the deepest water upward continuously, following, slowly, the depletion of the shallow aquifer. The long time-response of pressure heads does not facilitate, over a short period, the ability to

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recognise the fact that the exploited resources are partially from deep aquifers.

The hydrogeological setting of the Lomellina region displays features which are common to other sectors of the Po plain. As a consequence, the results of this study, although conducted on a restricted area, are highly illustrative of groundwater hydrodynamics in similar sedimentary aquifers. The integration of all data available on the municipal wells from the Lomellina in a GIS database provides the local administration with a leading management tool for monitoring groundwater quality, enforce better agricultural practices, implement remedial actions for local pollution problems and plan a rational development of the groundwater exploitation.

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