Nitrates in Groundwater (Northern Italy): isotopic prospection in high vulnerability area

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Abstract A hydrogeochemical prospection has been carried out in the Milano province with the purpose to better identify and characterize Nitrogen pollution sources. A network of 90 wells has been considered for geochemical prospection and 37 wells were also considered for isotopic survey. A geochemical stratification both in chemical characters and in isotopic ones has been identified and related to local pollution phenomena. The organic character of Nitrogen pollution phenomena has been identified and related to vulnerability characters of surveyed area. The obtained results allow to improve previous vulnerability mapping methods.

Keywords: Hydrochemistry - Stable isotopes - Diffuse pollution - nitrate - Northern Italy

1. Introduction

Diffuse and localized pollution phenomena characterize many aquifers located at foothills of Alps. In particular in the Milano province high vulnerability values of local sediments are accompanied by intense anthropic impact due to industrial and agricultural activities. Detailed researches on environmental impact of anthropic activities started in the second half of past century. In particular Martinis et al. (1976) described the hydrological characteristics of the Po plain between the Ticino and Oglio rivers and identified main physical and chemical characteristics of phreatic nappe, of second semi-confined aquifer and of deep local aquifer. Francani (1978) discussed pollution dispersion phenomena in different sedimentary conditions of the Milano plain. Francani (1980) furtherly discussed feeding characteristics of aquifers in the Milano area. Avanzini et al. (1995) preliminarly described main isotopic features of the Milano province. Colombo et al.(1996) discussed groundwatwer exploitation features in the highly industrialized area of Milano. Gorla (2001) described hydrologic conditions of deep aquifers in the Milano area. Carcano and Piccin (2002) described all aquifers of Lombardy Region and payed attention to hydrostratigraphic features. In particular three main aquifers are widely present in the Milano province. The first aquifer is phreatic and is constituted by gravels and sands derived from carbonatic Pre-Alpine hills. Semi confined and confined deepest aquifers are characterized by more siliceous components attributable to alpine petrofacies (Carcano and Piccin, 2002). The contemporary existence of high permeability aquifers and highly polluting human activities caused matter of concern about vulnerability of aquifers in past decades.

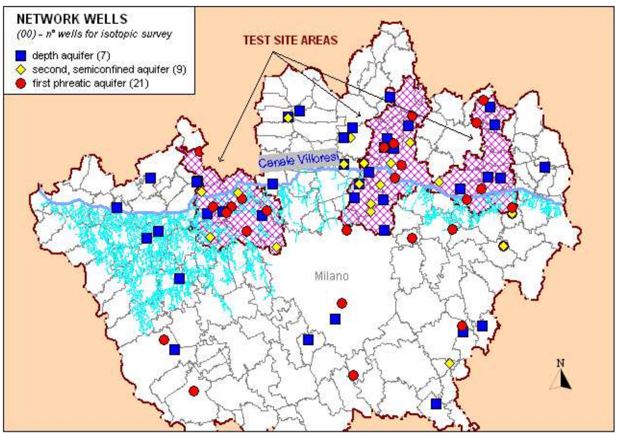

Fig. 1. Province of Milano - Sampling point area

Porto et al. (2006) summarized information coming from different sources with the purpose to compile a new vulnerability map of the Milano province. Nitrate concentration increased during past three decades inducing research Agencies and local Authorities to promote further researches on pollution diffusion features of the area. With the purpose to better highlight nitrate increasing in groundwaters a geochemical and isotopic prospection was recently launched by the Province of Milano (Fig. 1) in the frame of “Progetto Nitrati”.

2. Sampling and analytical methods

Three test site areas (Fig. 1) were selected within the Milano province territory. In test site areas groundwaters were sampled from wells characterized by depth in the range 20÷220 m.
In particular a group of wells was chosen in the first phreatic aquifer, while a second group was chosen in the second, semiconfined aquifer in wells characterized by a depth of 40÷100 m. Some samples were chosen in the deep aquifer in wells characterized by a depth of 100÷250 m.
All samples were collected in polyethylene 500 cc. bottles and stored in a refrigerator. Electric conductivity, temperature and HCO_3 were analyzed in the field. Cl, SO_4, NO_3, were measured by Liquid Chromatography, while Ca, Mg, Na, K were analyzed by Atomic Absorption Spectroscopy. Analytical error has been estimated <5%.
Oxygen and Hydrogen isotopes were analyzed by means of THERMO DELTA^{plus} mass spectrometer according to equilibration method. Nitrogen and Oxygen in NO_3 were analyzed according to Fukada et al. (2003).

3. Geochemical features of groundwaters

Main geochemical characters of analyzed samples are summarized in the Table 1 and in the Piper diagram showed in Fig. 2. Ca-HCO_3 ionic couple prevailed in all samples.

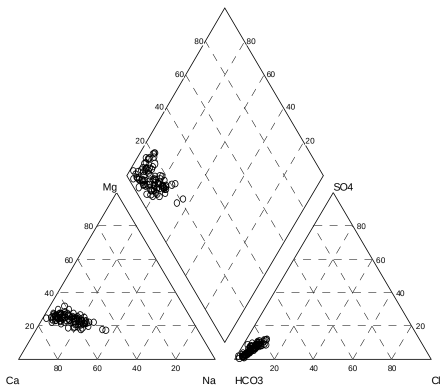

Fig. 2. Piper diagram of all sampled groundwaters.

Electric Conductivity values range between 200 and 800 µS/cm (Fig. 3).

Fig. 3. Regression line of Electric Conductivity vs HCO_3 in Milano province's aquifers (R^2=0.85).

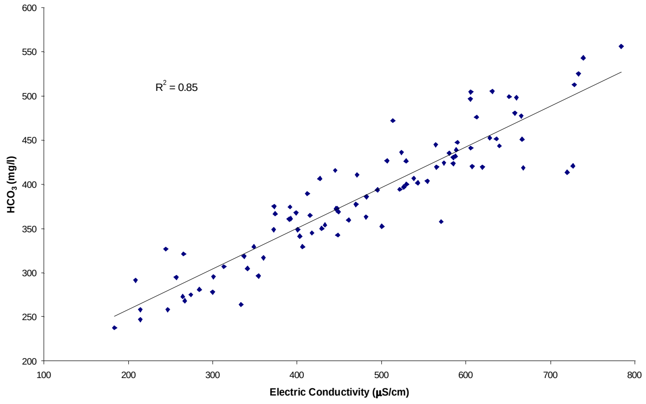

Table 1
Chemical and isotopic composition of sampled groundwater

ID	Municipality	Depth	Sampling date	EC	NO3	SO4	Cl	HCO3	SiO2	Ca	Mg	Na	K	δ18O-H2O	δD-H2O	δ15N-NO3	δ18O-NO3
1	Agrate Brianza	40.0	05/12/06	726.8	22.3	36.0	35.0	420.5	18.1	114.2	29.6	13.6	1.2			9.8	9.1
2	Bernareggio	95.0	22/11/06	605.1	42.1	34.0	13.0	496.4	17.8	114.2	28.3	37.3	3.8	-8.06	-52.0	6.6	6.9
3	Biassono	57.3	11/12/06	445.0	0.5	7.0	2.0	415.7	15.0	91.0	19.3	14.7	1.4	-8.32	-53.8	7.7	
4	Biassono	144.9	11/12/06	482.0	3.9	6.0	7.0	386.1	14.7	95.2	22.7	9.7	1.0	-8.40	-56.0		
5	Cambiago	33.5	22/11/06	628.0	41.8	25.0	11.0	452.6	15.4	114.9	28.3	14.8	1.4			5.3	
6	Cambiago	77.1	22/11/06	605.7	0.5	16.0	7.0	504.5	15.1	118.6	27.0	13.2	1.4	-8.40	-55.8		
7	Cavenago di Brianza	89.0	22/11/06	666.5	54.2	32.0	12.0	450.8	15.9	119.7	27.3	21.4	2.0			8.1	6.4
8	Cerro Maggiore	42.0	08/11/06	529.6	46.8	13.0	13.0	399.9	12.0	101.3	23.4	14.9	1.5	-8.19	-53.8	8.5	10.3
9	Cinisello Balsamo	46.0	24/11/06	523.7	37.8	36.0	18.0	436.1	11.4	105.6	22.2	36.9	3.7	-8.14	-53.2	6.9	
10	Cinisello Balsamo	79.7	24/11/06	639.4	39.9	37.0	20.0	443.5	14.5	127.0	28.7	9.0	0.8	-7.99	-53.6	4.7	
11	Cinisello Balsamo	55.0	24/11/06	543.0	35.0	31.0	18.0	401.6	17.2	108.7	21.1	19.7	2.0			7.7	
12	Gessate	45.5	13/12/06	506.3	49.2	30.0	14.0	426.6	12.5	111.0	31.0	10.2	1.1	-8.35	-54.6	5.7	
13	Lainate	80.0	13/11/06	398.6	44.6	27.0	15.0	367.8	22.2	102.3	23.1	9.6	1.0	-8.25	-54.0	7.4	2.4
14	Lesmo	55.0	05/12/06	513.4	20.2	21.0	14.0	472.0	16.7	108.3	20.2	36.2	3.5	-8.02	-51.2	7.6	
15	Lissone	61.3	22/11/06	667.7	45.5	32.0	24.0	418.5	13.5	118.6	27.6	12.8	1.2	-7.69	-50.6	7.4	4.6
16	Monza	51.5	22/11/06	471.0	15.6	10.0	6.0	410.5	13.1	100.3	21.2	11.6	1.2			6.2	4.7
17	Monza	48.0	22/11/06	720.1	45.3	38.0	31.0	413.4	11.9	118.5	30.2	16.8	1.6			7.8	4.7
18	Monza	38.0	22/11/06	495.2	11.1	13.0	14.0	393.6	18.4	100.1	20.7	8.6	0.7	-8.21	-54.5	5.7	7.2
19	Monza	60.0	30/11/06	570.6	48.0	42.0	24.0	357.7	16.6	111.3	22.6	12.8	1.2	-7.38	-48.1	8.6	
20	Monza	37.0	21/11/06	526.3	46.9	32.0	26.0	396.9	16.1	80.4	18.2	63.9	6.3	-7.36	-48.5	8.4	
21	Muggiò	126.0	01/12/06	580.0	27.7	27.0	17.0	435.4	13.2	114.4	25.7	14.7	1.3			7.8	3.7
22	Nerviano	103.5	08/11/06	589.8	41.2	41.0	12.0	447.4	12.0	115.7	27.2	18.6	1.9			7.0	7.6
23	Nerviano	22.0	07/11/06	636.0	35.7	26.0	19.0	451.4	17.1	114.9	28.4	19.5	2.0			5.7	2.4
24	Pero	67.0	13/11/06	500.3	35.4	41.0	26.0	352.5	18.6	103.6	23.4	13.0	1.4	-8.96	-60.7	6.2	6.5
25	Pessano con Bornago	40.8	13/12/06	733.2	31.1	43.0	32.0	524.9	15.9	115.6	28.9	54.3	5.4			7.8	6.4
26	Pogliano Milanese	14.0	06/11/06	728.2	52.3	32.0	25.0	512.6	15.8	121.5	26.4	42.8	4.2			8.2	2.8
27	Rho	59.3	13/11/06	448.7	42.0	38.0	16.0	368.7	13.0	107.9	20.4	10.0	1.0	-8.59	-56.5	7.1	4.9
28	Rho	22.5	06/11/06	587.2	49.7	52.0	32.0	431.8	17.0	86.7	19.9	75.3	7.5	-8.28	-55.2	8.9	4.5
29	Rho	23.0	06/11/06	584.9	35.2	34.0	29.0	430.5	16.4	97.5	24.5	40.5	4.0			6.2	3.8
30	Ronco Briantino	32.7	21/11/06	565.2	56.9	45.0	20.0	419.2	19.0	114.5	26.5	21.2	2.1			9.2	7.7
31	Sesto San Giovanni	78.0	24/11/06	605.6	43.0	44.0	23.0	440.9	15.6	101.3	29.4	37.8	3.8			7.1	4.7
32	Sesto San Giovanni	86.0	24/11/06	432.8	28.5	26.0	10.0	353.8	16.4	93.2	20.5	12.6	1.3	-8.50	-55.3	4.2	
33	Sulbiate	58.0	22/11/06	607.2	61.5	39.0	18.0	420.1	19.6	118.2	27.9	10.9	1.0			8.1	6.4
34	Triuggio	90.0	01/12/06	426.8	28.3	28.0	17.0	406.4	15.0	95.1	24.1	28.9	2.9	-7.85	-50.9	6.7	
35	Vanzago	52.0	13/11/06	521.5	35.2	39.0	18.0	394.1	15.7	92.7	18.2	42.3	4.2	-8.61	-58.3	6.6	
36	Vedano al Lambro	126.0	22/11/06	564.0	35.1	35.0	22.0	444.7	14.3	106.3	24.6	49.1	4.9	-7.56	-50.1		
37	Vedano al Lambro	45.0	21/11/06	573.9	11.1	27.0	14.0	424.2	13.9	95.4	18.2	33.2	3.3			7.0	
38	castiglione stiviere	23.0	07/11/06	784.0	20.0	39.0	15.0	556.0	16.1	126.5	40.9	17.5	1.7			7.1	
39	guidizzolo	49.0	27/11/06	739.0	55.0	44.0	29.0	543.1	10.7	133.9	41.1	26.9	2.7			6.5	
40	merate	39.5	21/11/06	588.4	28.7	25.8	12.6	438.8	15.2	107.9	27.9	14.7	1.4	-7.97	-51.6	6.4	
41	Abbiategrasso	102.0	20/12/04	391.6	16.8	26.8	19.1	374.4	14.7	93.1	18.2	36.8	3.6				
42	Abbiategrasso	187.0	22/04/04	417.3	29.5	37.5	23.7	345.0	11.1	84.5	18.7	45.3	4.4				
43	Arconate	206.0	03/11/04	333.4	6.0	21.0	3.5	263.8	14.1	71.2	16.4	6.6	0.5				
44	Assago	170.0	11/10/04	246.4	6.1	4.6	4.8	258.0	14.0	70.1	14.2	1.8	0.2				
45	Barlassina	140.0	06/10/04	392.4	22.8	12.4	9.2	361.1	16.7	83.2	19.1	26.6	2.7				
46	Barlassina	198.6	06/12/01	264.3	4.9	12.9	12.5	273.1	16.0	71.0	14.8	14.9	1.5				
47	Bellinzago Lombardo	32.0	05/05/04	658.0	36.2	29.4	20.8	480.5	15.0	110.5	27.7	46.5	4.6				
48	Bellinzago Lombardo	54.0	12/05/04	585.0	31.2	19.2	15.9	423.3	13.8	98.4	22.7	31.8	3.0				
49	Bellinzago Lombardo	92.0	22/04/04	429.0	8.4	9.0	7.6	349.9	14.2	88.8	18.2	14.9	1.4				
50	Caponago	59.0	16/09/03	659.7	24.0	33.7	23.6	497.8	14.1	104.1	26.8	55.7	5.4				
51	Caponago	150.0	16/09/03	412.0	4.0	14.7	12.5	389.5	14.6	92.6	20.9	24.5	2.4				
52	Casorezzo	210.0	05/10/04	340.8	11.6	14.0	10.6	304.8	14.1	69.9	12.9	30.6	3.0				
53	Cernusco sul Navigl	45.0	16/12/04	612.3	24.5	36.5	24.6	475.9	13.3	114.1	26.5	50.6	5.0				
54	Cerro al Lambro	180.0	15/07/04	266.7	1.0	5.9	7.4	268.1	17.9	60.4	16.9	10.2	1.0				
55	Cinisello Balsamo	76.0	15/07/03	631.0	39.9	38.6	23.3	505.2	15.0	122.7	27.0	52.4	5.2				
56	Cinisello Balsamo	149.0	14/01/03	284.0	5.0	3.0	7.1	280.8	15.3	67.6	17.4	8.6	0.7				

Table 1 (continued)

ID	Municipality	Depth	Sampling date	EC	NO3	SO4	Cl	HCO3	SiO2	Ca	Mg	Na	K	δ18O-H2O	δD-H2O	δ15N-NO3	δ18O-NO3
57	Cinisello Balsamo	180.0	14/01/03	214.0	2.0	3.0	4.8	246.8	17.3	60.9	12.4	5.2	0.4				
58	Cogliate	165.0	15/12/04	337.0	26.3	12.6	11.0	318.4	18.9	71.6	18.8	29.1	2.8				
59	Colturano	115.0	09/06/04	403.1	4.8	10.8	9.4	341.1	15.7	80.2	20.7	15.1	1.4				
60	Corbetta	133.5	09/11/04	529.0	23.0	35.5	21.8	426.1	15.0	99.1	24.2	49.8	5.0				
61	Corbetta	186.0	09/11/04	406.4	21.0	20.0	15.6	329.2	14.3	78.8	20.8	29.0	2.9				
62	Desio	109.0	20/08/03	538.3	41.3	32.8	19.7	406.6	15.8	100.2	24.4	42.7	4.2				
63	Desio	148.0	16/07/03	265.3	14.0	11.0	8.4	321.2	16.1	76.7	16.8	23.4	2.2				
64	Desio	63.0	12/11/03	461.0	26.5	21.0	17.1	359.5	16.1	90.5	22.3	27.6	2.7				
65	Garbagnate Milanese	176.0	17/11/04	183.6	7.1	4.8	6.4	237.7	18.7	56.3	14.6	9.2	0.9				
66	Grezzago	100.0	16/12/03	372.0	2.0	16.0	10.8	348.7	16.0	84.2	19.8	19.9	2.0				
67	Grezzago	160.0	17/12/03	354.0	2.0	2.0	3.5	296.1	15.7	75.7	16.3	5.1	0.8				
68	Inveruno	150.0	03/11/04	372.7	9.5	10.0	8.3	374.7	12.0	88.4	19.8	19.9	2.0				
69	Inveruno	178.0	03/11/04	360.0	4.0	7.0	6.9	316.9	17.6	70.6	19.5	14.3	1.3				
70	Legnano	125.0	14/10/04	415.3	5.1	16.5	11.9	364.8	11.6	74.9	21.0	32.7	3.3				
71	Legnano	153.0	14/10/04	300.7	10.0	7.5	7.7	295.3	14.8	74.1	17.8	5.4	0.5				
72	Lissone	136.0	19/04/04	554.0	13.8	50.0	31.1	403.4	18.0	91.8	24.9	55.9	5.6				
73	Lissone	70.0	15/11/04	665.6	45.0	39.3	24.7	477.3	19.7	123.9	28.0	42.0	4.1				
74	Melzo	90.0	13/05/04	448.0	15.8	23.5	15.9	342.5	14.4	83.4	21.9	23.1	2.4				
75	Melzo	87.0	31/05/04	447.3	14.7	27.1	18.7	372.7	12.9	84.2	21.9	40.1	4.0				
76	Muggiò	80.0	10/09/03	651.0	42.0	39.0	24.5	499.0	14.4	116.9	27.6	55.8	5.6				
77	Muggiò	151.0	10/09/03	390.5	17.5	19.0	13.1	360.5	14.9	84.1	20.3	31.8	3.2				
78	Nerviano	164.0	20/09/04	214.0	1.9	3.0	6.2	258.1	13.1	63.0	15.4	3.9	0.3				
80	Nova Milanese	70.0	10/11/04	619.5	41.6	37.5	22.5	419.3	15.3	107.8	26.7	35.2	3.4				
81	Parabiago	100.0	29/11/04	481.4	40.7	23.0	16.8	363.0	17.1	90.6	22.8	32.0	3.2				
82	Parabiago	164.0	29/11/04	299.7	15.4	9.4	9.0	278.2	14.4	61.3	17.8	16.8	1.7				
83	Parabiago	100.0	29/11/04	446.0	29.7	15.6	12.4	372.2	15.8	85.2	21.9	29.1	3.0				
84	Parabiago	200.0	20/10/03	256.6	9.1	16.0	12.0	294.8	17.8	71.9	16.6	18.6	1.8				
85	Paullo	118.5	26/05/04	400.7	5.2	8.3	9.1	348.8	16.5	78.8	20.6	17.2	1.6				
86	Pogliano Milanese	170.0	14/09/04	313.0	11.2	7.5	9.8	306.8	18.0	71.9	18.2	17.5	1.8				
87	Pogliano Milanese	200.0	11/05/04	348.6	3.4	10.5	10.5	329.2	13.3	69.8	19.1	24.0	2.4				
88	Rho	152.0	14/12/04	244.2	2.5	8.0	9.2	326.6	15.8	66.8	16.2	25.6	2.5				
89	Rho	184.0	14/12/04	208.4	2.0	7.0	7.0	291.6	17.8	59.9	15.3	21.2	2.0				
90	Tribiano	90.0	09/06/04	469.5	9.6	25.1	15.3	377.2	15.9	88.9	22.5	24.9	2.6				
91	Tribiano	143.0	09/06/04	374.0	4.1	6.4	8.3	366.5	16.0	82.2	19.9	16.4	1.6				

HCO_3 highest values are found in the first phreatic aquifer, due to prevalence of pre alpine calcareous rocks in aquifer. Lowest HCO_3 values are found in the second semiconfined aquifer. Siliceous matrix is characterized by limited release of salts during water interaction processes, thus upper aquifers are relatively enriched in HCO_3 compared to second and deep aquifers (Fig. 4).

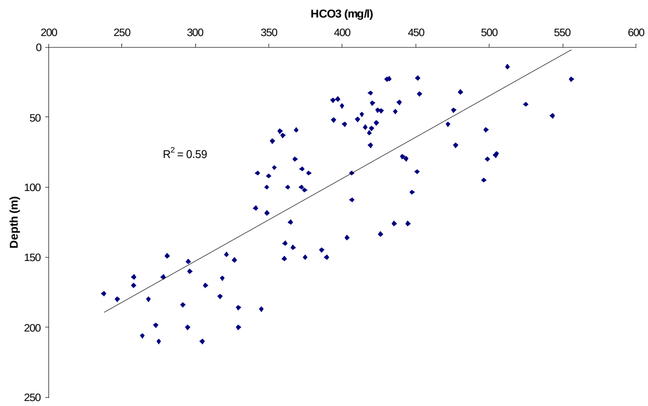

Fig. 4. Regression line of HCO_3 vs depth in Milano province's aquifers (R^2=0.59).

Nitrate are particularly present in the north of the Milano province and are related to the existence of towns sewages, of cattle-breadings and to the wide utilizations of inorganic fertilizers, thus isotope techniques were utilized to better understand groundwaters origin and to discriminate the exact origin of Nitrogen.

4. Isotopic characteristics

Isotopic values are summarized in Table 1. The obtained isotopic water line (Fig. 5) is very similar to the line obtained by Longinelli and Selmo (2003) utilizing precipitation samples collected in Northern Italy ($\delta D = 7.7\ \delta^{18}O + 9.4$).

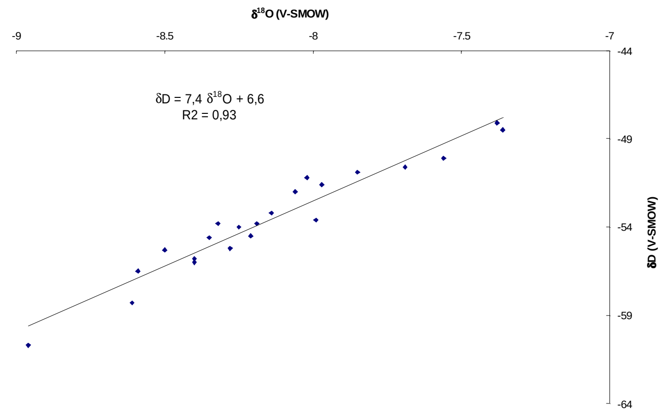

Fig. 5. Regression line of $\delta^{18}O$ vs δD isotopic groundwater composition in Milano province's aquifers.

Values in the interval -7 ÷ -8 were found in the upper aquifer and evidence local recharge processes (Longinelli and Selmo, 2003). More depleted samples were found in the second and third aquifer. They evidence that deeper aquifer are feeded by waters precipitated on Pre-Alpine and Alpine mountains.

Some samples collected in wells characterized by shallow depth were also characterized by relatively depleted values in Oxygen and Hydrogen isotopes due to the feeding effects of the close Villoresi Channel (Fig. 6).

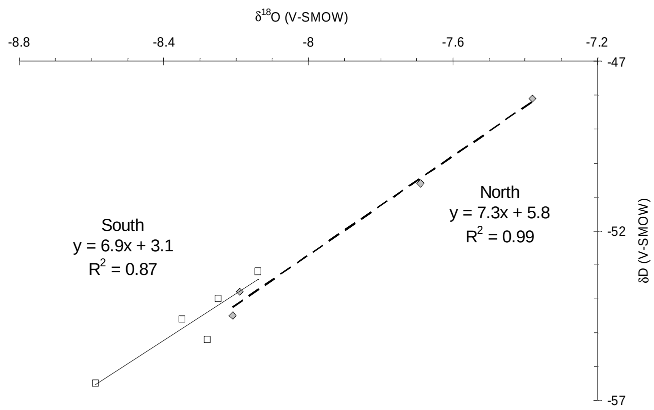

Fig. 6. Regression lines of $\delta^{18}O$ vs δD composition in selected wells near Villoresi Channel

Nitrogen isotopic values were found in the range +4.5 ÷ +10 (Fig. 7). All samples are in the typical range of organic derived Nitrogen (Clark and Fritz, 1997; Kendall, 1998).

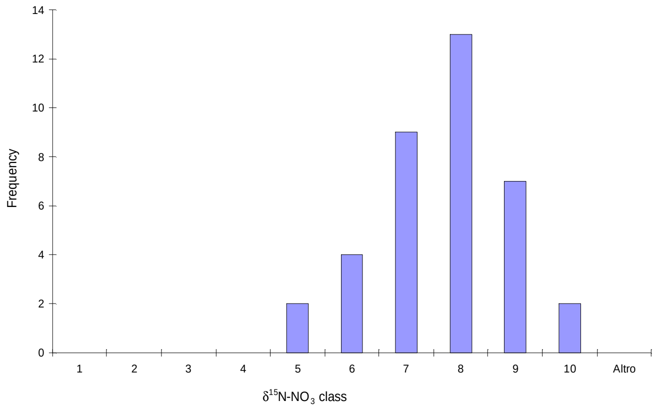

Fig. 7. Frequency distribution of $\delta^{15}N$ in nitrate coumpound of sampled groundwaters

Although all samples were found, in principle, originated by organic processes a significant dispersion of values is noticeable (Fig. 8). Obtained values (Fig. 9) allow to confirm the organic origin of Nitrogen compounds collected in considered wells. Similar values were collected by Dadomo et al. (2005), Pilla et al. (2005).

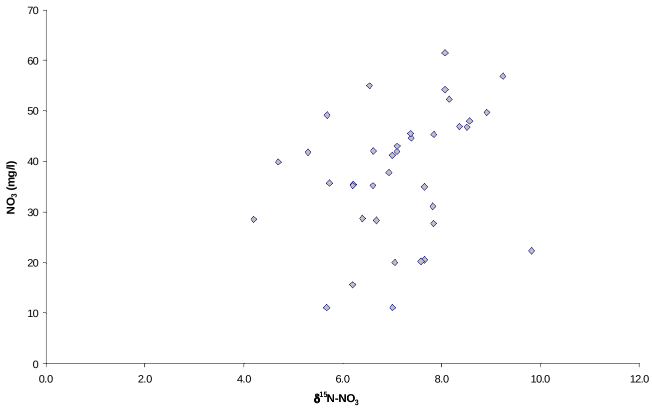

Fig. 8. $\delta^{15}N$ vs NO_3 in sampled groundwaters

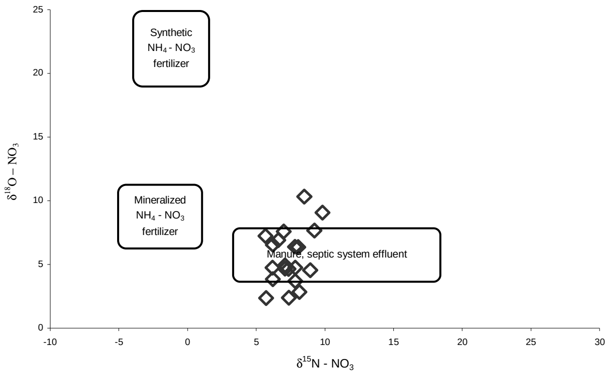

Fig. 9. $\delta^{15}N$ vs $\delta^{18}O$ in sampled wells

In the centre-north area of the Milano province a nitrate dilution process as been evidenced: high nitrate content waters characterized by a $\delta^{18}O$ typical of rains (Longinelli and Selmo, 2003) are diluted with isotopically depleted waters typical of deeper aquifers feeded by northern areas (Fig. 10).

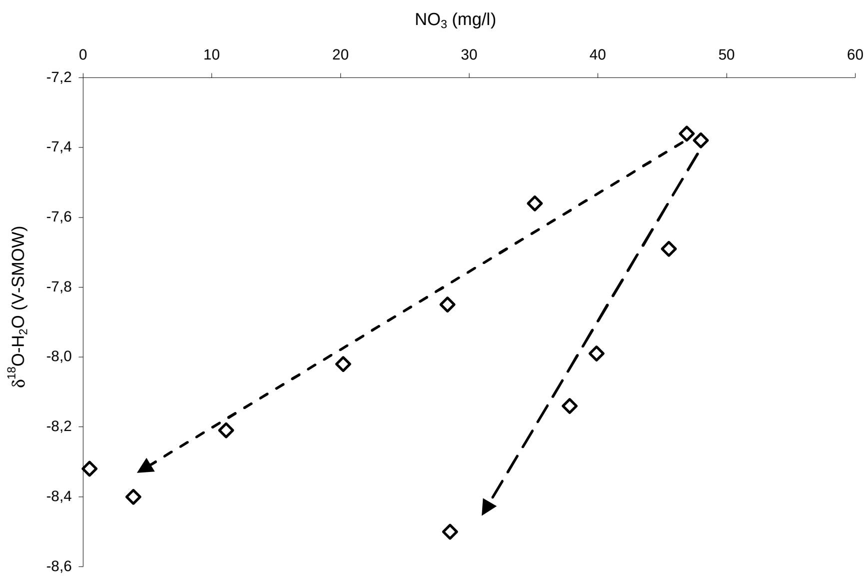

Fig. 10. Different dilution processes evidenced by NO_3 and $\delta^{18}O$-H_2O in sampled groundwaters

5. Vulnerability implications

Highest organic Nitrogen values were found in some hot spot areas of the Milano province. Not all identified areas are affected by cattle-breadings areas, thus urban sewages originated by towns can be considered responsible for observed pollution phenomena. Available vulnerability map (Porto et al., 2006) allows a general description of potentially vulnerable areas obtained by superimposition of informative layers related to water depth, aquifer permeability, slope, etc. No informative layers related to processes originating Nitrogen compounds is considered and obtained data on Nitrogen isotopes should be considered as an additional parameter useful to better constraint vulnerability characteristics of the Milano province.

In particular intrinsic vulnerability evaluated by means of SINTACS methodology (Civita, 1994) considers phreatic aquifer. In the considered area aquifer setting is relatively heterogeneous and aquifers located in the Northern side of the Milano province are characterized by gravel and sands and exploited both at shallow and highest depths. In the Southern side aquifers are multilayered and exploited only at depth > 30 m characterized by low vertical permeability. Usual hydrochemical monitoring techniques don't allow to effectively detect pollution phenomena, while isotopic techniques allowed the detection of more detailed pollution phenomena processes.

However an isoconcentration map for nitrates is useful to identify a local criticality. A critical small zone (pilot area) in north of Milan Province has been analyzed in order to estimate trends about nitrate concentrations in groundwater (complying the Directive 2006/118/EC).

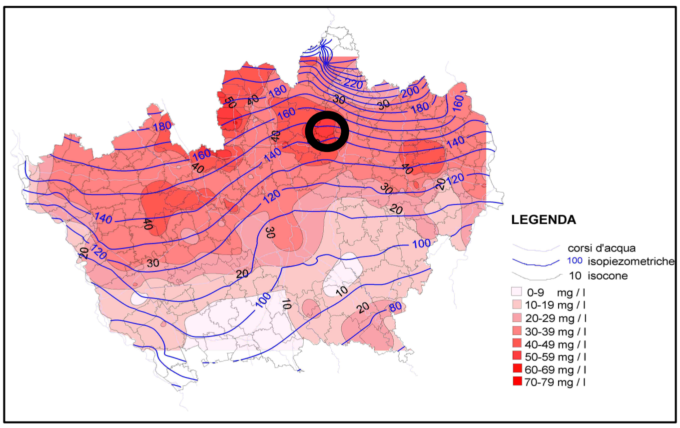

Fig. 11. Isoconcentration Map for Nitrate in Milano Province – 2004

23 wells have been analyzed in such area: 90% of distributed water exceed 37,5 mg/l (75% of the CMA, Concentration Maximum Admissible. Fig.12).

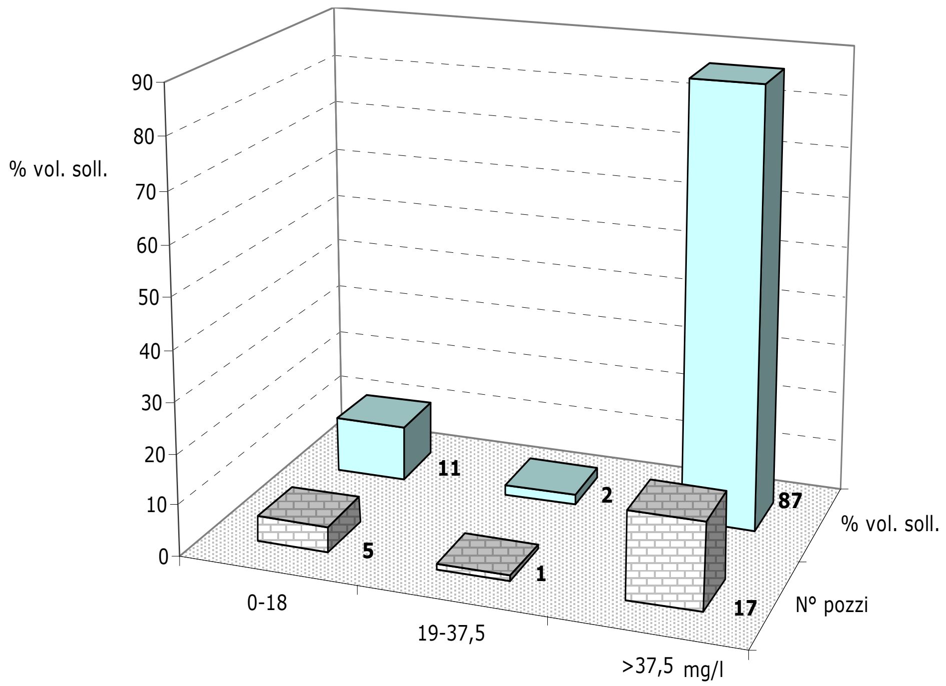

Fig. 12. Distribution of water withdrawn from some public wells in the critical area. Water amounts are divided into three concentration classes which reflect quality of resource.

6. Conclusions

Exploitation of groundwater resources has risen because demand and uses had risen in recent years (drinking water, industrial, geothermal etc.). Generally quality of resource is getting worse and concentrations of such pollutants (in particular nitrates) increased in last decades.

The Province of Milano, as a control agency, has the task to protect and monitor water resources and must promote an integrated policy to planning a sustainable management in the long time (complying the Regional Law of Lombardia 26/2003).

From a hydrogeological point of view water resource of superficial layers of the subsoil (Traditional Acquifer - A + B) ensure high productivity in this area; nevertheless the gradual deterioration of these layers led authorities to the treatment of resource as well as a gradual deepening of the filters, in order to intercept the deeper waters, characterized by limited productivity but by a discrete quality.

Nowadays a great number of wells are digged next to the towns and scattered without sustainable criteria.

Yet water demand will not be satisfied by contribute of deep acquifers alone and, at the same time, employment of higher acquifers has considerably increased to generate energy (heat pumps).

Obtained values allow to confirm highly vulnerable characteristics of explored aquifers. Oxygen and Hydrogen isotopic ratios of sampled waters evidenced that shallow aquifers are feeded by local precipitations. This feature confirm that most local pollution phenomena are characterized by short paths and short time duration processes. Longer times allows dilution processes of pollutants able to affect the deeper aquifers. Nitrogen isotopic values and Oxygen isotopic ratio in Nitrate allowed to identify the organic origin of Nitrogen.

However, in areas where anthropic impact is lower, short time recharging allows a good regeneration of groundwater in higher acquifers. This hypothesis would explain worst quality of deep waters in such areas, which require a longer recharging time.

Previous studies on isotopic features of the Milano area were carried out by the University (Politecnico di Milano) and by the Drinking Water Consortium (CAP), outlined the average residence time of local groundwaters by means of Tritium and Carbon 14 data. Deep aquifers are characterized

by relatively short residence times and their pollution could be consistent with the impact caused by industrial waste during the maximum period of industrialization.
The exploitation of deep aquifers could be uncorrect in the medium-long term. Overexploitation for irrigation or for geothermal purposes could irreparebly deplete strategic water resources useful for civil and industrial utilizations.
Planning activities should consider both quantitative and qualitative features of groundwaters and isotopic techniques, monitoring techniques and tridimensional modeling will allow to:

1. upgrade water withdrawal permits criteria
2. localize strategic aquifers whose exploitation should be allowed in monitored and planned conditions
3. recovery polluted aquifers
4. reduce industrial and agricultural pollution
5. localize areas characterized by polluting sewages systems in order to refurbish them

Infact a significant amount of Nitrogen is generated by local sewages and local Authorities should avoid further environmental worsening.
Deeper isotopic prospection studies are possible in specific areas in Milan in order to:

- better census of critical area
- definition of critical points
- improvement of monitoring methods

Next steps are necessary to deepen local criticalness:

1. defining new isotopic and hydro-chemical analyses
2. achieving even geo-physical investigation if necessary
3. defining a mathematical model.

This method would improve groundwaters management in order to better exploit water-resource for human hydro-potable uses in the future.

The Province of Milano would develop an instrument of resource management based on the revision of the existing monitoring networks with geostatistical criteria, divided into homogeneous aquifers, which will allow, together with the use of modeling system, to locate the existing qualitative/quantitative criticities, and to plan both waters resources management activities and the actions having an evident impact on it:

- planning of new wells for hydro-potable use and renovation of the existing ones,
- location of contamination sources, either spread or punctual,
- renovation of sewer systems

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References

Avanzini M., Beretta G.P., Francani V., Nespoli M. (1995) - "Indagine preliminare sull'uso sostenibile delle falde profonde nella provincia di Milano". Ed. CAP Milano

Colombo F., Raffaelli L., Raimondi P., Rosti G. (1996) - "Le problematiche idrogeologiche delle aree altamente industrializzate: l'esempio di Milano"C.N.R. - G.N.D.C.I., Pubblicazione n°1351

Dadomo A, Fava A, Martinelli G, Russo E, Sogni R (2005) Nitrogen sources identification by hydrogeochemical and isotopic survey in aquifers of the Piacenza plain. “Aquifer Vulnerability and Risk”, 2nd International Workshop, 4th Congress on the Protection and Management of Groundwater, CD Edition, ID220. Colorno, 21-22-23 Settembre 2005.

Fukada T, Hiscocka K M, Dennisa P F, Grischek T (2003) A dual isotope approach to identify denitrification in groundwater at a river-bank infiltration site. Water Research Vol. 37:3070–3078.

Gorla M. (2001) - "Acquiferi confinati profondi della Provincia di Milano: sviluppi delle conoscenze idrogeologiche e idrochimiche ai fini di un loro uso sostenibile". Acque Sotterranee, 73, 9-27.

Kendall C (1998) Tracing nitrogen sources and cycles in catchments. In: Kendall C and McDonnel JJ (eds.) Isotope tracers in catchment hydrology. Elsevier, 519-576

Clark I, Fritz P (1997) Environmental isotopes in hydrogeology. Lewis Publishers, Boca Raton, New York, 328 pp.

Carcano C, Piccin B (2002) Geologia degli acquiferi Padani della Regione Lombardia. In: Regione Lombardia, ENI-AGIP. S.EL.CA, Firenze, 130 pp.

Civita M. (1994) Le carte della vulnerabilità degli acquiferi all’inquinamento. Quaderni di tecniche di protezione ambientale Vol. 7:229-240

Francani V (1978) I metodi idrogeologici per lo studio della evoluzione degli inquinamenti delle acque sotterranee nella pianura Milanese. Quaderni dell’Istituto di Ricerca sulle Acque Vol. 34:229-239.

Francani V (1980) Le condizioni di alimentazione delle falde della regione Milanese. Quaderni dell’Istituto di Ricerca sulle Acque Vol. 51:33-55.

Longinelli A, Selmo E (2003) Isotopic composition of precipitation in Italy: a first overall map. Journal of Hydrology Vol. 270:75-88.

Martinis B, Pozzi R, Cavallin A, Mancuso M (1976) Indagine sugli acquiferi della Lombardia centro settentrionale. Quaderni dell’Istituto di Ricerca sulle Acque Vol. 28:97-134

Pilla G, Sacchi E, Zuppi G, Braga G, Ciancetti G (2005) Hydrochemistry and isotope geochemistry as tools for groundwater hydrodynamic investigation in multilayer aquifers: a case study from Lomellina, Po plain, South-Western Lombardy, Italy. Hydrogeology Journal Vol. 14:795-808

Rosti G., Arduini C., Zelioli A., Porto G. (1997). Nitrati in falda – Anni 1990/95. Provincia di Milano, Comune di Milano, Azienda Consorzio Acqua Potabile, Azienda USSL – PMIP (Milano, Parabiago, Lodi, Monza). Quaderno n. 1 – Sistema Informativo Falda, Provincia di Milano.

Porto G, Mauri S, Arduini C. (2006) Nuova carta della vulnerabilità ai Nitrati come strumento per la pianificazione delle risorse idriche e gestione delle emergenze. 10[a] Conferenza Nazionale ASITA, CD Edition,, Fiera di Bolzano, Bolzano, Bolzano, 14 - 17 novembre 2006

Arduini C, Dadomo A, Martinelli G, Porto G, Sogni R, Zelioli A (2007) Isotopic prospection in high vulnerability area of the Milano Province (Northern Italy) IAH Congress, Groundwater and Ecosystem, Lisbona, Settembre 2007.