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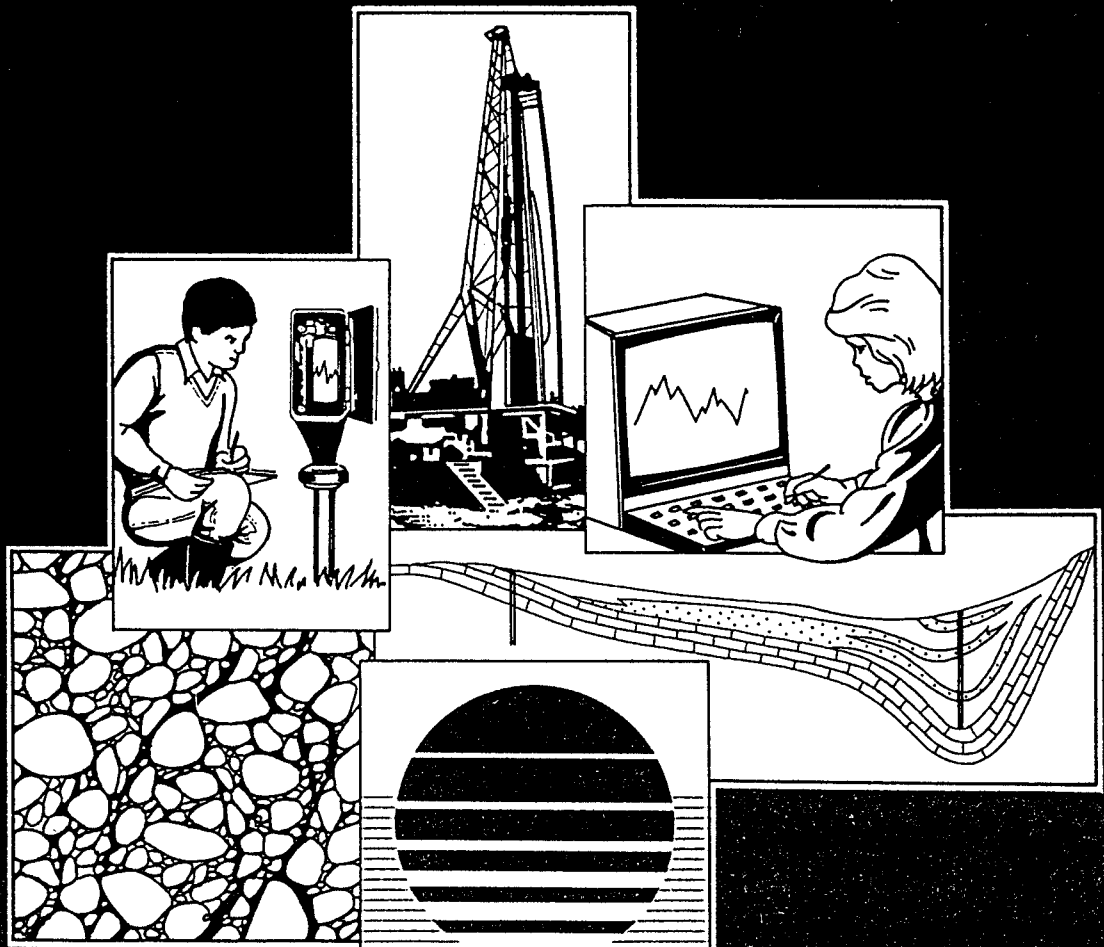
A case of groundwater contamination by organo-chlorine compounds

Un exemple de pollution des eaux souterraines par des composés organo-chlorurés

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Abstract

Over the last 15 years, 25 cases of groundwater pollution by chlorinated hydrocarbon compounds have been discovered in the Venetian Plain. The pollution originates in the upper Venetian Plain in an unconfined aquifer and often reaches confined aquifers located downstream.

These are point source pollutions and the pollutants are transported by groundwater flow with very little dispersion. The distance covered can reach 20 km with a residence time in some place of more than 10 years.

A pollution lasting 4 years, recognised in 1986 near Cittadella (Padova, Northeastern Italy), was investigated in detail. The spatial and temporal evolution of the pollution process was studied following chemical analysis of 490 monitoring wells. The points farthest from the source of the pollution to be affected were springs 6 km downstream.

The temporal evolution is characterised by a relatively rapide decrease in the concentration, linked to the rapid flow rate of the aquifer (10 to 20 m/day).

In wells located nearest the source of pollution (1 to 2 km), sudden increases in concentration, very marked and of short duration (1 to 2 months) are related to a rise of the water table of the unconfined aquifer. This phenomena can be explained by the periodic leaching of pollutants, during infiltration into the unsaturated zone.

Résumé

Au cours des 15 dernières années, 25 cas de pollution des eaux souterraines ont été relevés, dans la plaine vénitienne. Il s'agit de pollution d'organo-halogénés.

Ces processus de pollution ont commencé en haute plaine vénitienne, dans un aquifère à nappe libre. Ils ont souvent atteint les nappes captives situées plus au sud. Les sources de pollution sont ponctuelles et les polluants se transfèrent avec l'eau souterraine selon la direction d'écoulement de la nappe, avec une dispersion très limitée. La distance parcourue peut atteindre 20 km, avec une persistance en certains cas supérieure à dix ans.

Il a été étudié avec précision un cas reconnu en 1986 d'une durée de 4 ans, dans la zone de Cittadella (Padova, Nord-Est Italie). Des analyses chimiques initiales de 490 puits de surveillance ont permis d'étudier l'évolution spatiale et temporelle du processus de pollution.

La pollution s'est déplacée sur une distance de 6 km, jusqu'aux « résurgences », qui furent les points les plus lointains atteints.

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L'évolution temporelle est caractérisée par une tendance à une rapide diminution de concentration, liée à l'écoulement rapide de la nappe (10-20 m/jour).

Dans les puits les plus près de la source (1-2 km) de rapides augmentations de la concentration, très nettes et limitées dans le temps (1-2 mois) sont en relation avec la remontée de la surface piézométrique de l'aquifère à nappe libre. Ce phénomène s'explique par l'entraînement des polluants, lors des épisodes d'infiltration, dans la zone non saturée.

Introduction

Aquifer contaminations by organo-chlorine compounds are detected in many industralized countries, nevertheless there are a few systematic analytical data on cases of groundwater contamination. This study concerns a case occurred in the Venetian Plain (Fig. 2). The contamination evolution of organochlorine compounds by means of numerous chemical groundwater analyses has been studied.

The hydrogeological situation of Venetian Plain [Bortolami et al., 1976] is schematically illustrated in figure 1. The subsoil of the high Venetian Plain is made of gravels depositated by the rivers Leogra, Astico, Brenta and Piave. These deposits form an unconfined aquifer. Its watertable is 50-100 metres deep along a belt at the foot of the mountains while it becomes shallower, going South, until it outdrops spontaneously in the lowest parts along a continuous E-W belt in the middle plain (« risorgive »). Here,

the subsoil, composed of alternating gravel beds and silty-clayey layers, forms a multistratum confined system. The natural feed factors of this aquifer are mainly the dispersion from watercourses and secondary the direct infiltration of rainwater.

Groundwater regime of high Venetian Plain is characterized by one high level period (usually September), and one low level period (usually April). Figure 4 shows the groundwater regime since 1986 in a well near Cittadella (Padova, North-East Italy) (fig. 2). This case of contamination is located in the transition zone from high plain to middle plain, near the belt of « risorgive » (Fig. 1 and 2). Watertable depth is more than 10 m near the pollution source and less than 1 m near the « risorgive ». An example of stratigraphic situation is reported in Figure 3.

In July 1986 the contamination was detected during routine analyses of groundwater quality. Trichloroethylene was the main contaminant while tetrachloroethylene and 1,1,1 trichloroethane were of minor importance.
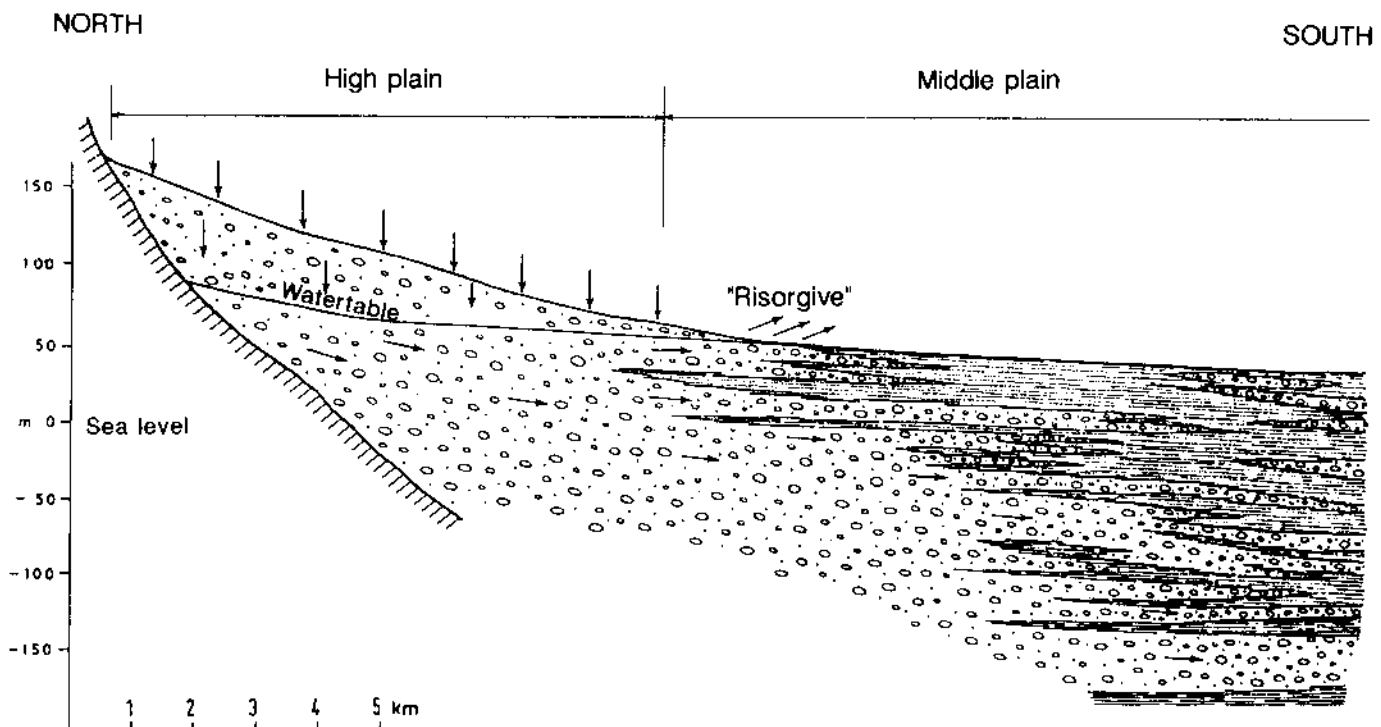

Fig. 1. - *Hydrogeological model of high and middle Venetian Plain* (Modèle hydrogéologique de la haute et de la moyenne Plaine vénitienne)

Between July and August 490 groundwater wells were analysed to characterize both the plume of contamination and the spatial concentration distribution and, finally, to identify the contamination source (industrial wastes).

When contamination was detected, the plume was already 6 km long and 0.7 km wide. It coincided with a paleochannel of Brenta river as shown in aereal photographs.

Downstream the contamination source the maximum concentration recorded was 1074 µg/l.

The pollution time-evolution was studied using fortnightly chemical analyses on 14 monitoring wells (Fig. 2).

Between 1986 and 1987 the water of 126 private wells was declared unpotable because it exceeded the limit of potability (100 µg/l). Today the contamination is almost exausted.

Chemical water analyses were made by gas-cromatographic methods.

1. - Analysis of contaminant introduction in groundwater

Figure 4 shows the groundwater regime and the organo-chlorine compounds concentration observed in well 83; this well is 150 m downstream the pollution source. There is an evident relation between watertable depth and contaminant concentration : the raising of watertable washes away contaminants from the unsatured zone.

Yearly the groundwater regime (Fig. 4) is characterized by only one maximum. Therefore there is a sequence of « contamination peaks » with annual period and decreasing intensity.

Contamination peaks decrease exponentially as shown in wells 74, 80 and 81 downstream well 83 (Fig. 5).

It's important to remember that there has been no introduction of other contaminants after discovering of this contamination.
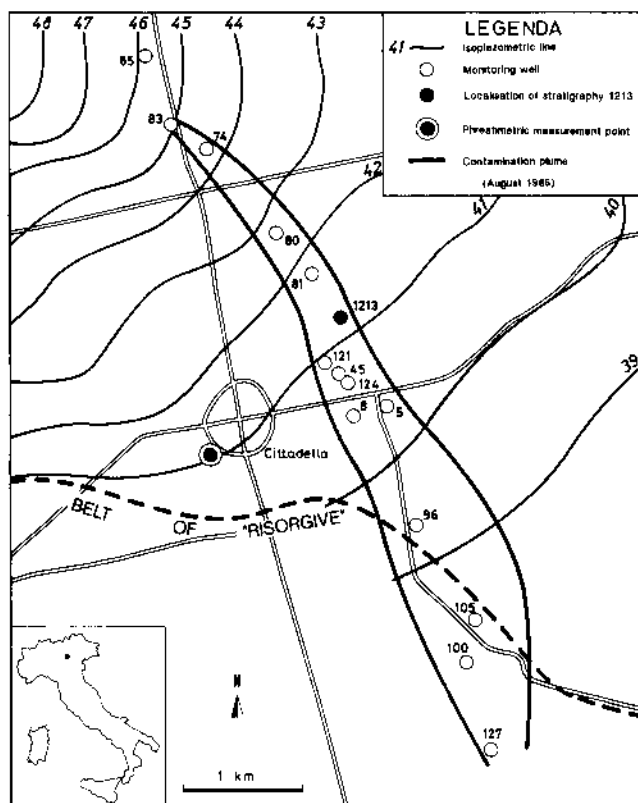

Fig. 2. - Localisation of monitoring wells and of contamination plume (Localisation des puits de surveillance et du panache de pollution)
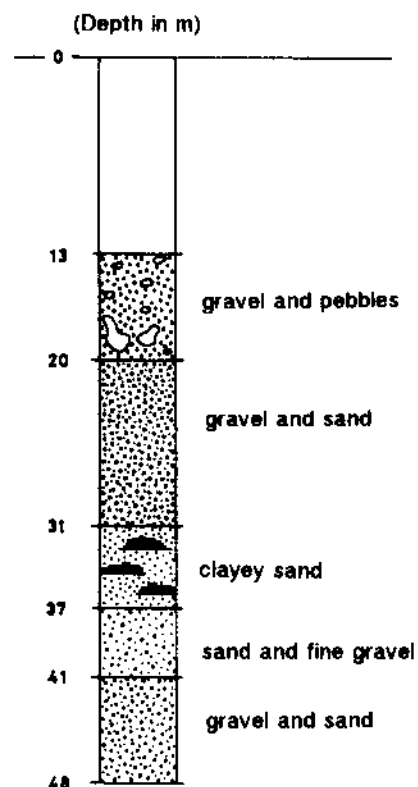

Fig. 3. - Stratigraphy of well 1213 (Coupe stratigraphique du puits 1213)

2. - Analysis of contaminant propagation in groundwater

Analysis of concentration-time diagrams of monitored wells permits to divide them in two groups.

The first group includes those wells (74, 80 and 81) located more than 1,5 km downstream the contamination source (Fig. 5) ; the second group includes wells located further (121, 124, 8, 96, 105, 100 and 127) (Fig. 6).

The depth of all these wells ranges from 20 and 30 m. Well 45 is discussed later, because its depth is more than 50 m.

2.1. - The first group of wells

The main characteristics of these wells are :

a) time-concentration curve decreasing ;

b) a series of « contamination peaks » with yearly period.

Well 83, located close to the pollution source, shows two « principal peaks » (A = 1074 μg/l and B = 600 μg/l) and one « secondary peak » (A1 620 μg/l) (Fig. 4).

The « principal peak » A is very evident in the first group of wells (Fig. 5). As previously observed at well 83, the arrival of the contamination peak is recognizable in all wells belonging to the first group. Besides there are other less evident contaminant peaks spaced one year between them.

Knowing the distance between wells, the arrival times of the contaminant peak (with a precision of

15 days depending on monitoring frequency) and well location (they are along the same stream line), it's possible to calculate the contaminant propagation velocity through the arrival of « contaminant peaks » in wells 74, 80 and 81 (Tabl. 1).
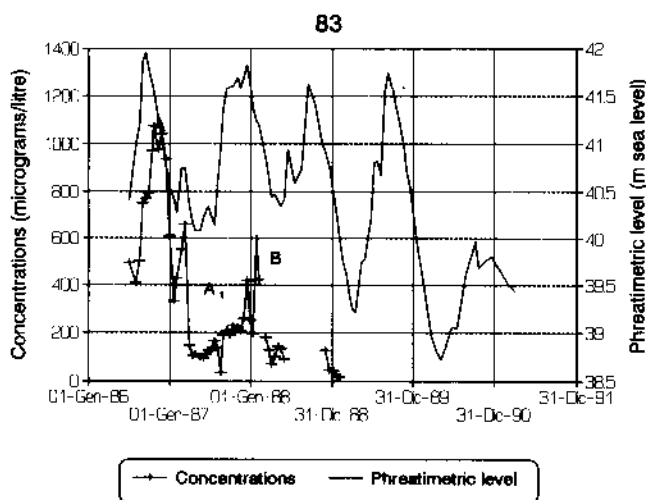

Fig. 4. - *Concentration-time diagram and groundwater regime in well 83* (Diagramme et régime de l'eau souterraine dans le puits 83)
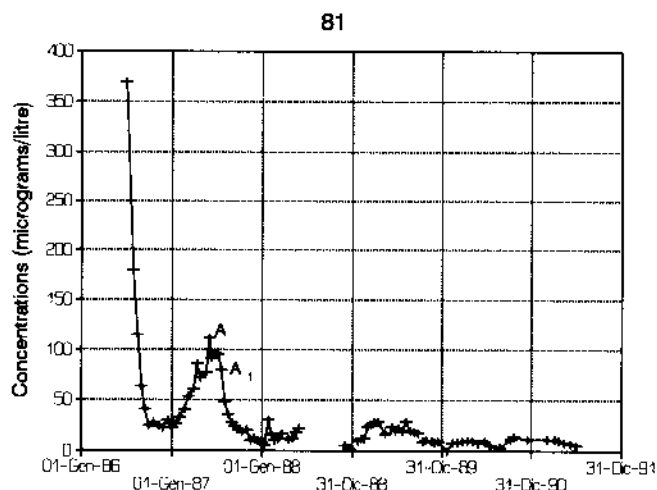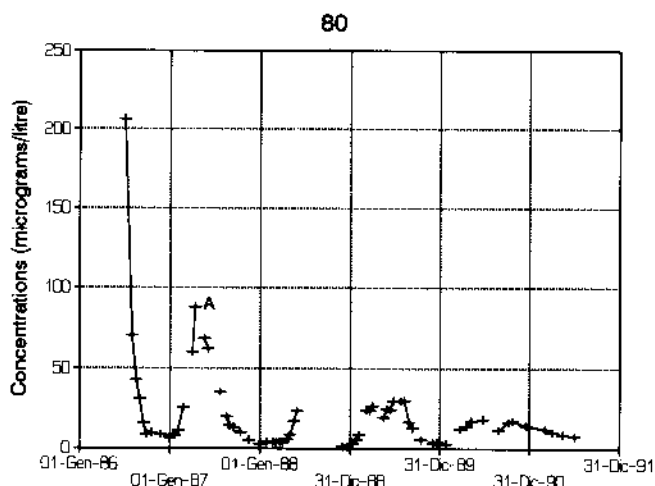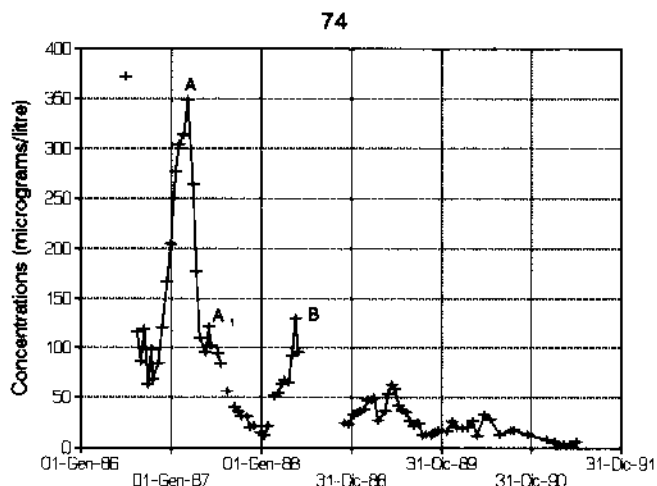

Fig. 5. - *Concentration-time diagrams of the first group of wells* (Diagramme du premier groupe de puits)

Tabl. 1. - Contaminant velocity
(Vitesse du polluant)

v_{avg} = dist./time = average velocity of contaminant (m/day);
v_{min} = dist./(time-15) = minimum velocity of contaminant (m/day);
v_{max} = dist./(time+15) = maximum velocity of contaminant (m/day);

Wells	Peak	Dist. (m)	Time (day)	v_{avg} (m/day)	v_{min} (m/day)	v_{max} (m/day)
83-74	A	350	122	2.87	2.55	3.27
83-74	A1	350	83	4.22	3.57	5.15
83-74	B	350	110	3.18	2.80	3.68
74-80	A	900	49	18.37	14.06	26.47
80-81	A	450	32	14.06	9.57	26.47
74-81	A	1350	83	16.27	13.78	19.85
74-81	A1	1350	86	15.70	13.37	19.01
74-8	A	2550	190	13.42	12.44	14.57
74-127	A	5500	335	16.42	15.71	17.19

Well 83 is out of paleochannel while well 74 is within paleochannel : the arrival at well 74 is slow (average velocity = 3.4 m/day). In those wells located within paleochannel the contaminant velocity is higher, that is to say average velocity is 16,1 m/day (tabl. 1).

In the concentration-time diagrams of wells 80 and 81 there is a very high peak (named « 0 » in Figure 5), which indicates the presence of a peak older than « A ». This observation is more evident in the concentration-time diagrams of the second group of wells, where the peak « A » is not clearly recognizable except in wells 8 and 127 with uncertainty (the calculated velocities are 13 and 17 m/day).

Is should be noted that the groundwater velocity is higher or equal to contaminant velocity. In fact, during transport organic contaminants can be absorbed and desorbed by organic material of the solid phase aquifer.

having :
$v_f = R^* v_i$
Where :
v_f = groundwater velocity;
R = retardation factor;
v_i = contaminant velocity.
According to Mc Carty *et al.* [1981] :
$R = 1 + 0.63 \, (f_{oc}) \, (k_{ow}) \, (\delta/n)$
Where :
f_{oc} = organic matter content in the solid phase
k_{ow} = distribution coefficient n-octanole/water
δ = density of solid phase
n = porosity

Groundwater velocity is about 30 m/day, considering $R = 2$, in our hydrogeological situation for trichloroethylene [Mc Carthy *et al.*, 1981 ; Berretta, 1992]. The value thus calculated is very high ; generally, in these areas, groundwater velocity ranges few metres/day. The high velocity can be related to the presence of paleochannel and to the drainage effect due to « risorgive ».

2.2. - The second group of wells

The specific characteristics of this second group of wells (Fig. 6) can be thus synthetized :

a) concentration-time curve exponentially decreasing;

b) the present of « principal peak » (called 0) only slightly evident in the first group of wells.

The above-mentioned behaviour (see point a) is connected to a distance higher than 1,5 km between the second group of wells and the source.

In these conditions the following physical and chemical phenomena are important :

— hydrodispersion;
— interaction between aquifer solid phase and contaminant;
— differential filtration velocity at different depth (hydrodynamic dispersion by fingering);

Considering the effect of these three factors, the observation made above a) is explainable as intersection and superimposition of single contaminant peaks. The result of this phenomenum is a « discharge exponential curve ». This curve is not a discensional phase of a single « contaminant peak » but a « not real » discharge peak deriving from the fusion of single peaks.

The contaminant input mechanism in the aquifer is shown in figure 7A (comparable to well 83); figure 7B (wells situated 1,5 km downstream) and figure 7C (wells situated downstream).

In the first and in the second group of wells, in the final part of their concentration-time diagrams (starting from November 1990), it can be observed a contemporaneous increase in concentration values (10-20 µg/l). Such increment of contaminant values coincides with phreatimetric level increment. Therefore it can be supposed that the increase in phreatimetric level washes away contaminants adsorbed in the fluctuation aquifer zone. This phenomenum, common in the all area concerned by contaminant
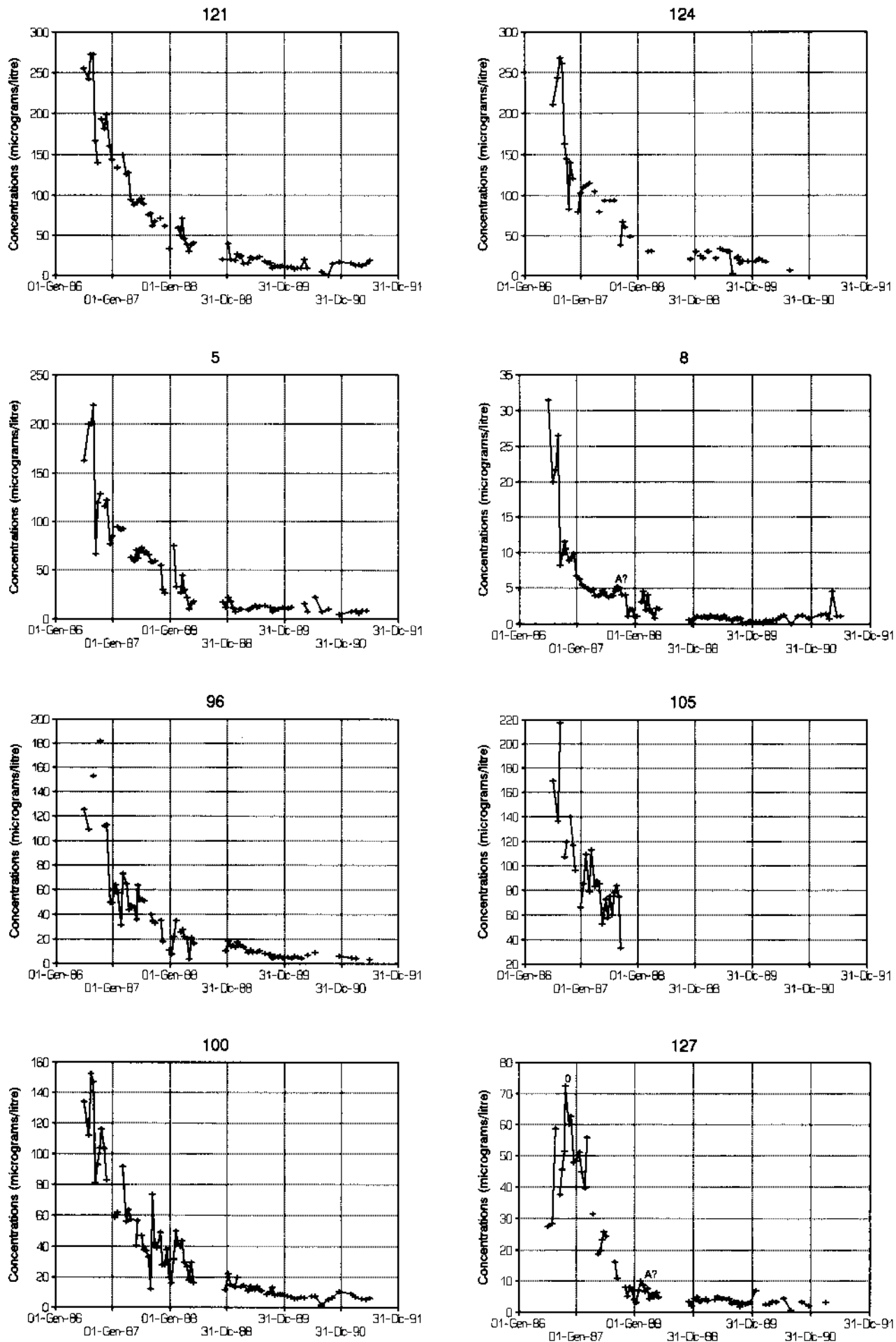
Fig. 6. - Concentration-time diagrams of the second group of wells (Diagramme du deuxième groupe de puits)

event, happens probably throughout the analysed period. During initial stages the concentration values are so high that the concentration level increament is visible only in the final part of all diagrams.

Finally, in the second group of wells the contaminant peaks are difficult to recognize. In this case, fortnightly sampling interval can lead to the loss of the single peak culmination.

The different factors above-listed interact with the concentration course during time. Unfortunately it is difficult to quantify exactly the different factors and their variation during time.

As reported in point b), in the second group of wells there is a peak 0, which is not so evident in the diagrams of first group of wells. Considering a contaminant propagation average velocity of about 16 m/day (tabl. 1), it can be calculated that peak 0 started in September 1985 and arrived at well 127 (situated about 6 km from source) in October 1986.

In September 1985 there was the annual phreatimetric level culmination.

It is possible that this peak was too produced by the same mechanism previously described : the washing away of the pollutant present in the unsaturated zone of source area.
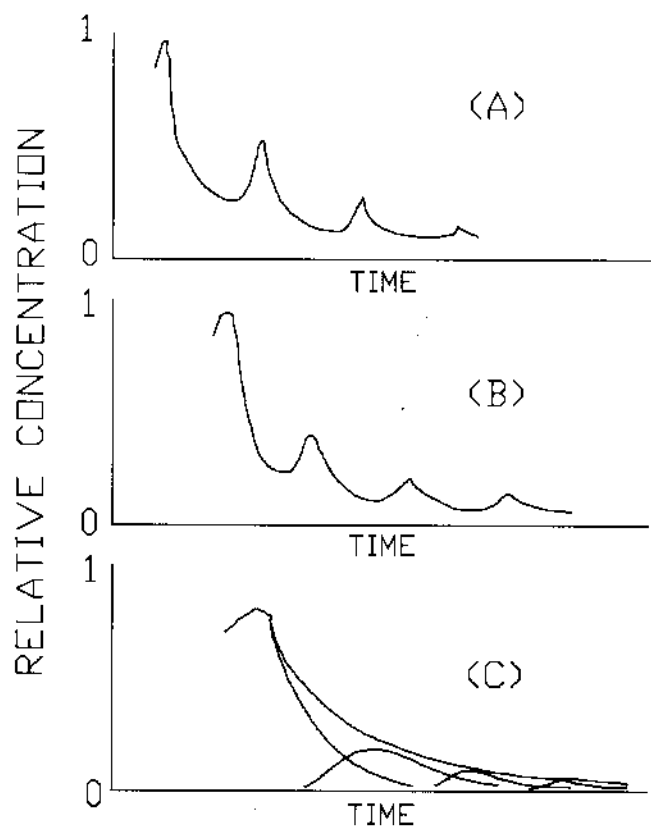

Fig. 7. - A) Schematic representation of time-concentration near the source; B) in the first group of wells; C) in the second group of wells. (A) Représentation schématique des variations de concentration près de la source ; B) dans le premier groupe de puits ; C) dans le deuxième groupe de puits)

In well 83 this peak 0 must have a higher concentration (some thousands of μg/l) than the highest measured value.

2.3. - Analysis of the contaminant depletion phase in the second group of wells

Analysis of concentration-time diagrams of the second group of wells (Fig. 6) shows that contaminant depletion follows an exponential equation :

$$C_t = C_0 \cdot e^{-at}$$

where :

C_t = concentration at time t (μg/l) ;
C_0 = highest concentration calculated (μg/l) ;
a = depletion coefficient ;
t = time from the start of the depletion phase (days).

The exponential equation can be simply transformed in :

$$Log\ C_t = Log\ C_0 - a \cdot t \cdot Log(e)$$

Data used in elaborations have been thus treated :

— « Pollution culmination » was considered the start point.

In almost all the second group of wells, when pollution was determined (July 1986) the culmination phase which is before the « depletion phase », was already over. Therefore July 1986 was chosen as depletion start phase. Only in the most southern well (well 127) values before October 1986 were excluded.

— Values after October 1990 were excluded. In fact these excluded values individualize concentrations still rising, coming from a raising of the aquifer, (par. 3.2). The excluded values represent low pollution concentration, mostly influenced by strumental errors.

An example of elaboration results related to well 121 is shown in the figure 8.

The values of « a » was calculated for the second group of wells. These values are shown in table 2.

Tabl. 2. - Values of « a » of the second group of wells
(Valeurs de « a » dans le deuxième groupe de puits)

Well	a•(10⁻³)
5	2.12
8	2.58
96	2.16
100	2.10
121	2.35
124	1.82
127	2.26
Average	2.19

It can be observed that value « a » is similar in all wells suggesting therefore similar time and velocity conditions of the pollution depletion.

Parameter « a » like depletion coefficients used in hydraulic and hydrogeological problems (i.e. depletion spring curve), shows the depletion rapidity.

In the cases of pollution depletion values of « a » depend on source characteristics, contaminant types and hydrogeological characteristics of aquifer.

It could be interesting to compare different contaminant situations during depletion phase ; generally there are not many data about evolution of the pollution depletion.

2.4. - Observations about well 45

Well 45 is the deepest well considered (60 m deep compared to 20-30 m deep of the other wells) and it was screened only in the last 6 m. It is situated between the unconfined aquifer and the first confined aquifer.

Comparing the concentration-time curve of well 45 (Fig. 9) 121 and 124 (Fig. 6), these last two are from 20 to 30 metres far from well 45, it can be noted that pollution arrives to all three wells but with very different time and concentration.

In well 45 the maximum concentration measured has a delay time of one year and half compared to wells 121 and 124 ; besides its value is three time lower than the one measured in wells 121 and 124.

This behaviour can be thus explained :

— organo-chlorine compounds in aquifer tend to go down ;

— effective velocity changes with the depth ;

— greater retardation factor.

Depletion coefficient « a » was calculated also for well 45. This value $(1.68 \cdot 10\text{-}3)$ is comparable to the ones of the second group of wells. In fact it represents the same pollution event in hydrogeological condition partially different.

Well 45 is the only one deep 60 m, so other observations are not possible.

It is clear that pollutions involving the unconfined aquifer can spread dangerously, in relatively long-time, in a confined aquifer, as already occurred in other pollution events in the Venetian Plain [Altissimo et al., 1990 ; Altissimo et al., 1991].

Finally, it is essential remember the importance of geological structure in the contaminant propagation control.

Conclusions

In groundwater contamination studies it is fundamental the analysis of space-temporal evolution.

An example of organo-chlorine pollution selected among the numerous happened in the Venetian plain is reported in this paper [Altissimo et al., 1991]. The analysis has been made comparing hydrochemical data (fortnightly analyses made by U.L.S.S. 19) with hydrogeological data (phreatimetric level, pluviometric heads and lithostratigraphy).

The distance between contaminant source and monitoring wells, the particular hydrogeological structure in which the phenomenum took place, have been considered in the analysis.
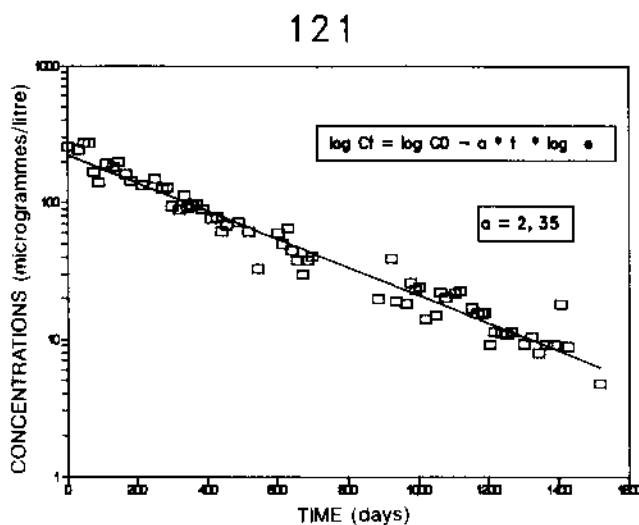

Fig. 8. - Depletion curve of well 121 (Courbe de tarissement du puits 121)
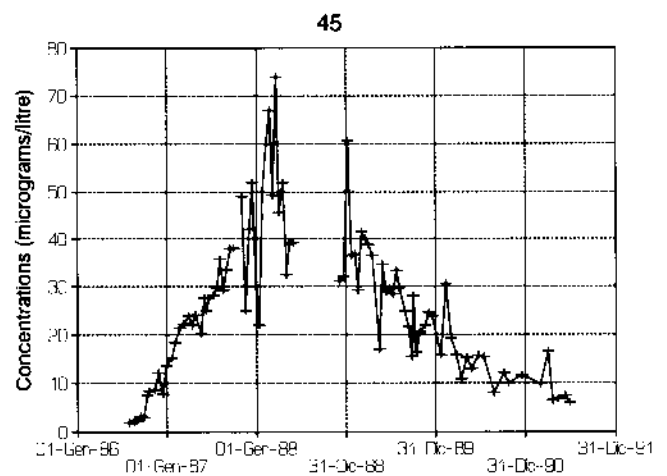

Fig. 9. - Concentration-time diagram of well 45. (Diagramme de variation de concentration du puits 45)

According to the recorded data it is possible to make thes general considerations :

— Evolution of space-temporal contaminant phenomena is a function of hydrogeological structure, contaminant type and input mechanism to the aquifer.

— Presence of paleochannels in this area confirm that these morphological features have a high intrinsic vulnerability. Such features act as drainage axis and draw around the contaminants. It is noted that this hydrogeological situation allows a quick evolution of contaminant depletion.

This is an advantage for the pollution natural exhaustion and permits to study its evolution during time ;

— to compare hydrogeological and hydrochimical data is very important in order to understand the contaminant input mechanism to the aquifer ;

Particularly in this studied case it has been possible :

— to identify the contaminant input mechanism to the aquifer, which is controlled by phreatic regime ;

— to distinguish single contaminant peaks in a distance of about 1,5 km and to calculate propagation contaminant velocity ;

— to individuate the « contaminant peak » presence (peak 0) preceding peak A, which is the maximum concentration found ;

— to quantify approximately depletion time of this pollution, induced by an intermittent source with decreasing intensity.

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