THE USE OF SOIL-GAS SAMPLING IN THE STUDY OF GROUNDWATER POLLUTION BY VOLATILE SOLVENTS (VOC): THE EXAMPLE OF THE PORTO FELIZ (SÃO PAULO, BRASIL) CASE.

R. C. A. Hirata* and R. W. Cleary**

*Instituto Geológico - Secretaria do Meio Ambiente do Estado de São Paulo. Caixa Postal 8772, CEP: 04301, São Paulo(SP) Brasil
**Insituto de Geociências - Universidade de São Paulo
Caixa Postal 20899, CEP: 05508, São Paulo(SP) Brasil

ABSTRACT

In 1983, a serious accident occurred in Porto Feliz, São Paulo, Brasil when the rupture of a storage tank released 400,000 liters of volatile organic solvents. A large portion of the underlying aquifer was contaminated including some deep wells and shallow hand-dug wells.
Soil-gas sampling was the technique used to evaluate the degree and extent of contamination. The method is based on the analysis of small quantities of soil vapors extracted at shallow depths. The origin of these vapors is the underlying contaminated groundwater and the vapor concentration distribution reflects the degree and extent of aquifer contamination. Other techniques were rejected since the physico-chemical characteristics of the pollutants did not allow their detection by traditional geophysical methods and the thick unsaturated zone and difficult geology would have resulted in exorbitant driling costs for monitoring wells.

The use of soil-gas sampling allowed mapping of the pollution plume, defining its two-dimensional shape and location. Vapor analyses at different depths permitted the establishment of concentration gradients and an estimation of vertical vapor flow behavior in the unsaturated zone as well as surface losses by volatilization.

Water levels in existing wells made it possible to construct potentiometric surface maps, defining the groundwater flow pattern. Periodic groundwater quality monitoring furnished data for the evaluation of the plume migration velocity and the influence of rainfall on the increase of pollutant concentrations in the aquifer.

The groundwater pollutant concentrations obtained gave a good correlation between the two means.

KEYWORDS

Groundwater; soil-gas sampling; contamination; volatile organic compounds; VOCs; DNAPLs; geophysical methods; Porto Feliz (São Paulo, Brasil).

INTRODUCTION

In 1983, a serious accident occurred in Porto Feliz, São Paulo, Brasil where the rupture of a storage tank released 400,000 liters of volatile organic solvents. A large portion of the underlying aquifer was contaminated including deep wells and shallow hand-dug boreholes.

Soil-gas sampling was the technique used to evaluate the degree and extent of groundwater contamination. This method is applied for the first time in Brasil. It is based on the analysis of small quantities of soil vapors extracted at shallow depths. The origin of these vapors is the underlying contaminated groundwater and the vapor concentration distribution reflects the degree and extent of aquifer contamination. In many cases, this upward flux of vapors creates a gaseous "shadow" of the underlying plume as Fig. 1 illustrates.

This study developed a soil gas sampling technique which is innovative in the way pollutant vapors are captured through the use of double activated carbon columns and their subsequent analysis and identification using gas chromatography.

The technique allowed the rapid and inexpensive mapping of the contaminant plume, characterizing it as to its shape and areal extent as well as establishing three distinct contamination zones. Analyses of vapors taken at different depths allowed the calculation of concentration gradients which made it possible to define the vertical flux of the vapors and consequent losses by volatilization to the atmosphere.

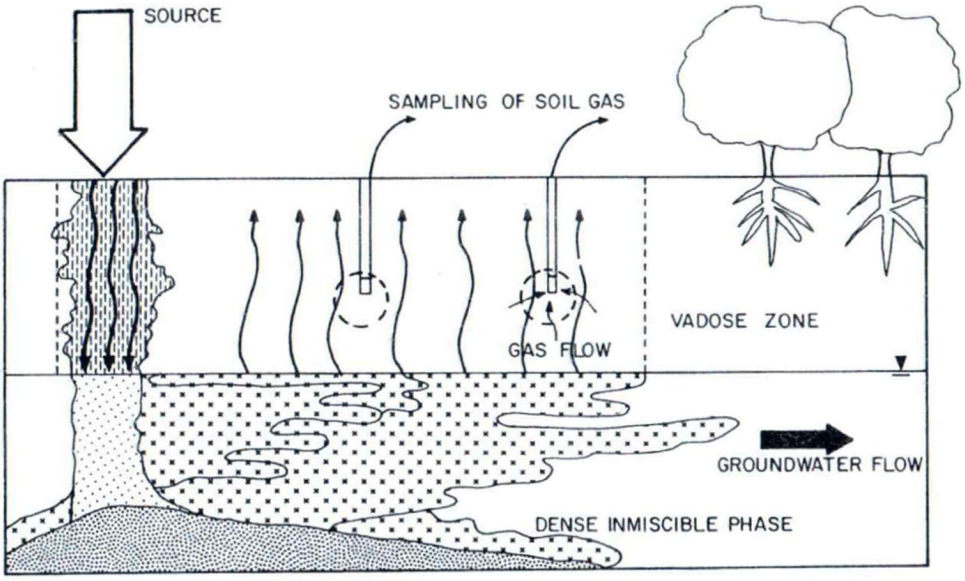

Fig. 1. Principle of soil-gas sampling and vapor/gas movement in vadose zone (after Hirata et al. ,1988)

LOCAL HYDROGEOLOGY

Porto Feliz is a city of approximately 30,000 inhabitants, located in the Valley of Tietê River, 110 km northwest of the city of São Paulo. In the study area, south of the city, outcrops can be seen of the sedimentary permo-carboniferous rocks of the Itararé Subgroup associated with the Serra Geral event of Cretaceous age (IPT, 1981).

The sediments of the Itararé Subgroup make up a low yielding aquifer which is highly heterogeneous in vertical and horizontal extent. It is found to be phreatic in some areas while semi-confined in other locations.

According to DAEE (1982), the Tubarão Aquifer (Itararé and Tatui) has a specific capacity which ranges from 0.02 to 0.5 $m^3/hr/m$ with the majority of values between 0.08 and 0.2 m /hr/m^3; the transmissivity varies between 1 and 10 m^2/day. The natural groundwater quality is normaly good although hard in some areas. The total dissolved solids content is relatively low with the water being classified as mixed bicarbonate or sodium or calcium bicarbonate.

In the study area, well log data was collected on 8 drilled wells of various depths (80 to 250 m), 5 dug wells and 3 springs (Fig. 2). Pumping tests resulted in specific capacities ranging from 0.04 to 1.9 m /hr/m and very low transmissivities varving from 0.04 to 0.3 m^2/day.

Fig. 2 is a potenciometric map of the area. The equipotential lines show the USA Chemical installation is located close to a groundwater divide and on top of a local recharge area. The groundwater flux is in the SSW-NNE direction following the local topography.

With respect to the unsaturated zone, it is worth noting two important observations at this point. First, there are suspended aquifers in the study area due to the highly heterogeneous geology in the aquifer. Second, the aquifer is characterized by intense fracturing caused by weathering of the lutaceous material. Such fracturing, given the associated increase in rock hydraulic conductivity, allows liquids to easily infiltrate vertically.

The presence of less permeable layers makes it difficult to predict contaminant plume movement and direction. Besides causing greater lateral dispersion, these layers are sometimes inclined in such a way that the denser phase (pure solvent) can to move by gravity against the general direction of groundwater flow.

THE SOIL GAS SAMPLING TECHNIQUE

The apparatus used in this study was especially developed for the Porto Feliz case. With respect to other soil gas sampling techniques, its double-tube activated carbon configuration for capturing soil vapors is innovative. Construction details, collection procedures and methods of analysis may be found in Hirata et al. (1988) and Hirata (1990).

The technical literature on soil-gas sampling until the middle of the eighties, restricted itself to describing the technique and the results obtained. After 1985, researchers began to show a larger concern for the physico-chemical characteristics of the contaminants, the porous medium and the applicability of soil-gas sampling. The publications of Devitt et al. (1987), Thompson and Marrin (1987), Pitchford et al. (1988) and Hirata (1990), among others, are good examples of studies concerned with these important aspects of soil-gas sampling.

As analysis of the applicability of soil-gas sampling and its limitations should take into account the following (Hirata, 1990):
- physico-chemical aspects of the contaminants (in order of priority: Henry's Law constant, partial pressure, concentration and solubility, solid-liquid partition coefficient and resistance to biodegradation);

- properties of the unsaturated zone (texture analyzed as to air porosity, size, shape and continuity of the pores and the thickness of the unsaturated zone);

- hydrodynamic properties of the aquifer (groundwater velocity, water table fluctuations and lithology),

- characteristics of the spill or accident,

- climatic consideration.

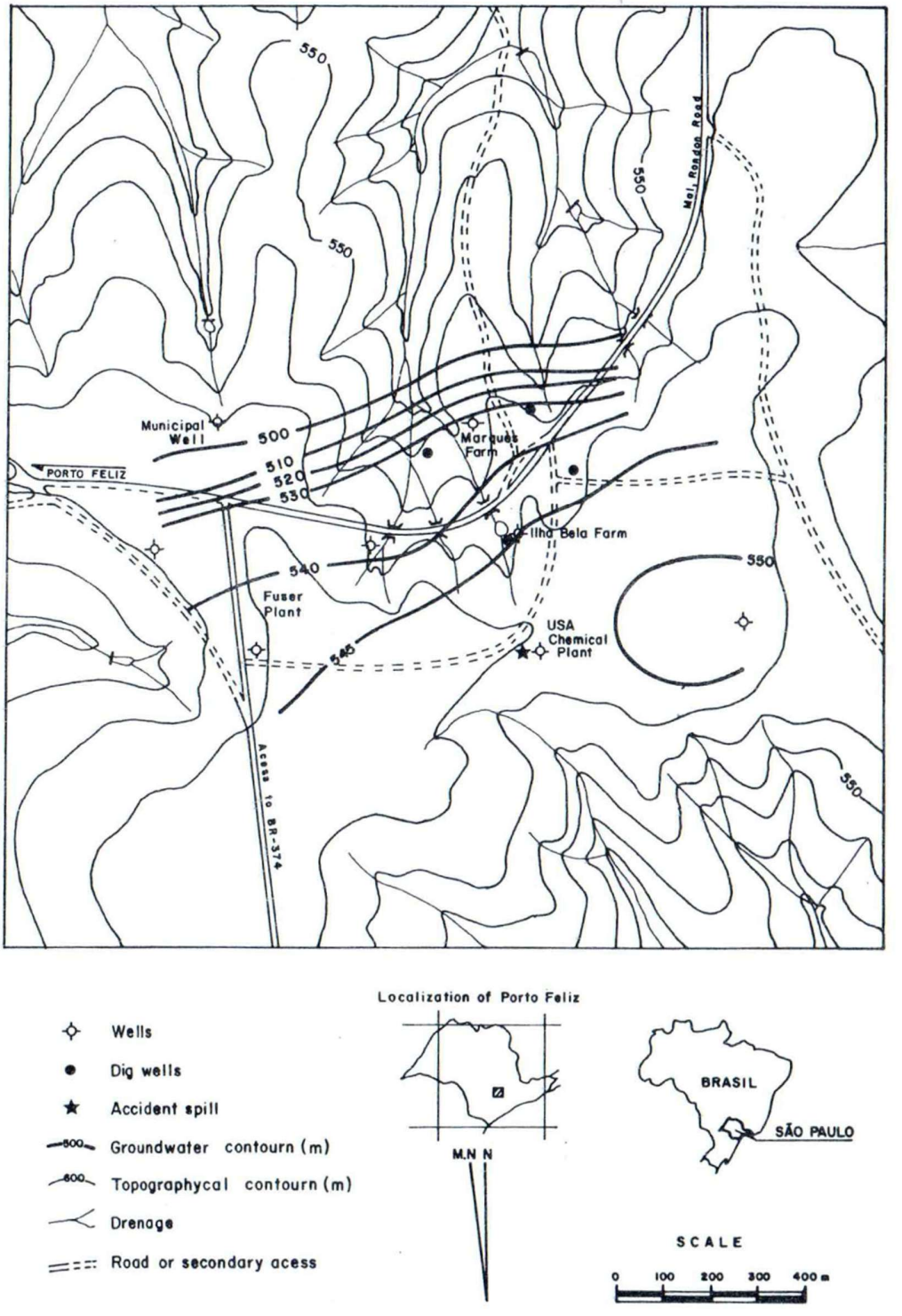

Fig. 2 - Location of the study area and groundwater equipotencial lines

PRESENTATION AND DISCUSSION OR RESULTS

Soil-gas Samplers

The results of sampling soil organic vapors demonstrate the validity of the method for the area under study. The results obtained in five sampling studies show halogenated solvents in the form of vapors in the unsaturated zone layers and also a relationship between concentrations in the soil gases and concentrations in the groundwater (log-log). A GC-MS analysis of soil gases collected with an adsorption column at USA Chemical Ltda. resulted in the positive identification of several organic chemicals inclunding: chloroform, carbon tetrachloride, 1,2 - dichloroethane (DCA), benzene, trichloroethene (TCE), and 1.1.2 - trichloroethane. Besides these aliphatics, some aromatics and a few unknown peaks were observed. Among these aliphatics, chloroform and carbon tetrachoride were the species most consistently seen in analyses of soil gases taken downgradient from the accident site. Organic vapor concentrations varied over six orders of magnitude from traces (< 0.001ug/l) to 1625ug/l. Trace concentrations at the parts per trillion level were calculated based on knowing the volume of air extracted and the mass quantity of contaminant detected.

The consistent detection of carbon tetrachloride and chloroform at a large number of sampling points is not only due to their frequent presence in the groundwater but also to their physico-chemical characteristics.

With the idea of studing how soil gas concentrations change with space and time, a special sampling plan was devised. The variation of vapor concentrations as a function of time was demonstrated in a comparative analysis of data collected on different dates at the same location. For example, at location 5, on the Ilha Bela farm, four samples were taken with the following carbon tetrachloride concentrations and dates: 0.006ug/l (11/27/85), trace amounts (1/22/87), not-detected (3/25/87) and 0.01ug/l (5/27/87). Chloroform varied similary with time as the following data illustrate: 0.069 g/l (11/27/85), not-detected (1/22/87), 0.66ug/l (3/25/87) and 0.03 ug/l (5/27/87). It is obvious from these data that if one wants to correlate spatial concentration data, sampling must take place at all points on the same day or within a short period of time.

The results of samples taken from two locations separated 3 and 5 m from a third point, show variations of chloroform concentration of 50% and 90% respectively. These large differences could reflect horizontal variations in the geology, or the imprecision of the method and/or instrument.

The hydrogeologic heterogeneity in the study area could affect the rise of the contaminant vapors to the land surface. Factors such as the presence of suspended aquifers, pronounced lithologic variations, clay content variability and different moisture contents could be responsible for the wide variation in sampled concentrations and the appearance of horizontal vapor fluxes below the land surface.

The high level of fracturing of siltstones, shales and some sandstones observed in many outcrops in the study area, provide excellent hydrogeologic conditions for upward movement of vapors and downward movement of liquid contaminants.

Such results and observations make one conclude that the analysis of soil gases taken at isolated points means very little from a practical viewpoint. Soil-gas sampling studies should be done with a reasonable number of points and the data must be analyzed conjunctively.

In areas where groundwater is most vulnerable to pollution, defined as accessibility of a given contaminant loading to an aquifer (Foster and Hirata, 1988), soil-gas sampling has the highest chances of succeeding in the detection and mapping of a pollutant plume, since upward vertical fluxes of vapors in these areas will encounter no problems.

The Vertical Flux of Vapors and Losses To The Atmosphere

With the objective of calculating the vapor emission flux of contaminants lost to the atmosphere, six small vapor/gas collection wells at different depths were constructed on the Ilha Bela farm near its water well. To establish a vertical gradient, the vapor wells were placed two to a location with a shallow well at 1 m depth and a deeper well at 2 m. The three groups of two wells each were separated from each other by distances from 10 to 15 meters and the differences in measured vapor concentrations were used to calculate vertical gradients.

The principal transport mechanism for gases in the subsurface, including halogenated solvent vapors, is molecular diffusion. Assuming convective and turbulent processes are insignificant in the unsaturated zone, it is reasonable to suppose that vapor emission flux calculations should be based on Fick's first law. To calculate the effective gas diffusion coefficient, D', used in this law, the equation of Penman (1940, apud Marrin, 1984) was employed. To estimate the diffusivity or the coefficient of air diffusion, the empirical relation of O'Connor et al. (1987) was used. The vapor flux is then calculated using:

$$q = D' \frac{C_2 - C_1}{Z_2 - Z_1}$$

where C_2 and C_1 are the vapor concentrations measured at the 1 and 2 meter depths, Z_2 and Z_1 and D' is the effective gas diffusion coefficient, defined by the following relationship:

$$D' = D.0.66\ fa$$

where fa is the air-filled porosity (L^o) and D is the air diffusion coefficient or diffusivity (cm^2/s), defined according to the following relationship:

$$D = 1.9\ M^{-2/3}$$

where M is the molecular weight of the contaminant.

The calculated values at the three locations show an average vapor emission rate for carbon tetrachloride of $0.86 \pm 0.06 ug/m^2/day$, while chloroform is $5.49 \pm 1.47 ug/m^2/day$. The correlations among the ratios of the emission flux rates of the emission flux rates for the first, second and third group of vapor wells were approximately 1.08, 1.05 and 1.14 for carbon tetrachloride and 0.7, 0.9 and 1.7 for chloroform. The higher emission flux rates for chloroform compared to carbon tetrachloride were expected, given the physico-chemical characteristics of the two products.

Beginning with these emission flux data and keeping the same assumptions and restrictions discussed earlier, it is possible to establish a total loss of volatile organics to the atmosphere over the study area. This is, of course, further assuming the contaminated groundwater has the same concentration over the entire area. Considering the contaminant plume occupies an area 113,000 m^2 (based on horizontal mapping) and the average emission fluxes for carbon tetrachloride and chloroform are $0.86 ug/m^2/day$ and $5.49 ug/m^2/day$ respectively, the volatilization losses over the whole area are 97.2 and 620.4 mg/day respectively. These values are overestimate, because the points of gradients calculation are the highest of this contamination area.

Mapping The Plume In The Areal Plane Through Soil-Gas Sampling

To establish the horizontal movement and dimensions of the plume, a network of 34 points was installed of which 26 were analyzed. The 26 samples were removed from the unsaturated zone at a depth of 1.14 meters and an average distance between points of 25 to 30 meters.

In locating the sampling points, the following factors were considered, which when analyzed conjunctively explain the network configuration selected:
- pathways on the land surface selected by the liquid contaminants at the time of the accident;

- nearness of vapor sampling points to the underlying groundwater;

- probable regional groundwater direction in the area;

- area topography.

With respect to sampling point spacing, little is written in the literature. It seems clear that the denser the network of sampling points, the better one can define the plume configuration. Of course, how dense the network will be is a compromise between the costs for constructing, maintaining and sampling a large network on the one hand an the desire for representative data on the other. It was clear in this study that samples taken very close to each other can generate very different results due to the effects of lateral diffusion and porous medium heterogeneity. For this reason, each soil-gas sampling results should be analyzed comparatively with the others.

The difficulty of mapping the contaminant plume in the study area is owed, among other factors, to the wide dispersal of the spilled liquid contaminants which did not restrict themselves to the perimeter of USA Chemical Ltda. They flowed along the land surface in the direction os neighboring drainage ditches (Hirata, 1990). In this way, each small drainage segment affected became a new contaminant distribution point or source. This problem is not restricted to the time of the spill, as analyses of waters collected in drainage ditchess close to the tanks, which earlier served as principal pathways for the liquid contaminants, showed concentrations of 29ug/l for chloroform and 6.4ug/l for carbon tetracloride, even four years after the accident.

Vapor concentrations obtained at each sampling point by this method, when plotted on a map, can be used to establish areas where the relative presence of chloroform and carbon tetracloride can be defined as high, present and absent (Fig. 3).

The zone of highest detected concentration is clearly in the vicinity of the accident and its adjoining areas. The results show also the clear presence of high concentrations of contaminants near the surface drainage ditches that were used by the pollutants for surface runoff. It is very likely that these runoff contaminants influence the soil-gas sampling points near the drainage ditches.

The organic vapors moving upward through the unsaturated zone experience lateral dispersive effects resulting in a spreading out of the soil gases in the areal plane. The resulting "gas plume" defined by soil-gas sampling probes is laterally larger than the underlying groundwater plume. There are several possible explanations for this lateral dispersive spreading inclunding: a heterogeneous horizontal hydraulic conductivity distribution, suspended aquifers composed of lutaceous materials and variable moisture content throughout the heterogeneous unsaturated zone. Several authors have noted that lateral spreading of soil gas can result in "false positive" readings (Hirata, 1990). A careful analysis of the case histories cited in Pitchford et al. (1988) shows a lateral dispersion of tens of meters. Nazaroff et al. (1987, apud Silka, 1988) describe subsurface pressure and temperature gradients which induce advective transport up to 6 meters in the horizontal direction. The plume obtained by horizontal mapping in the present study showed a similitude for the two products traced: carbon tetrachloride and chloroform.

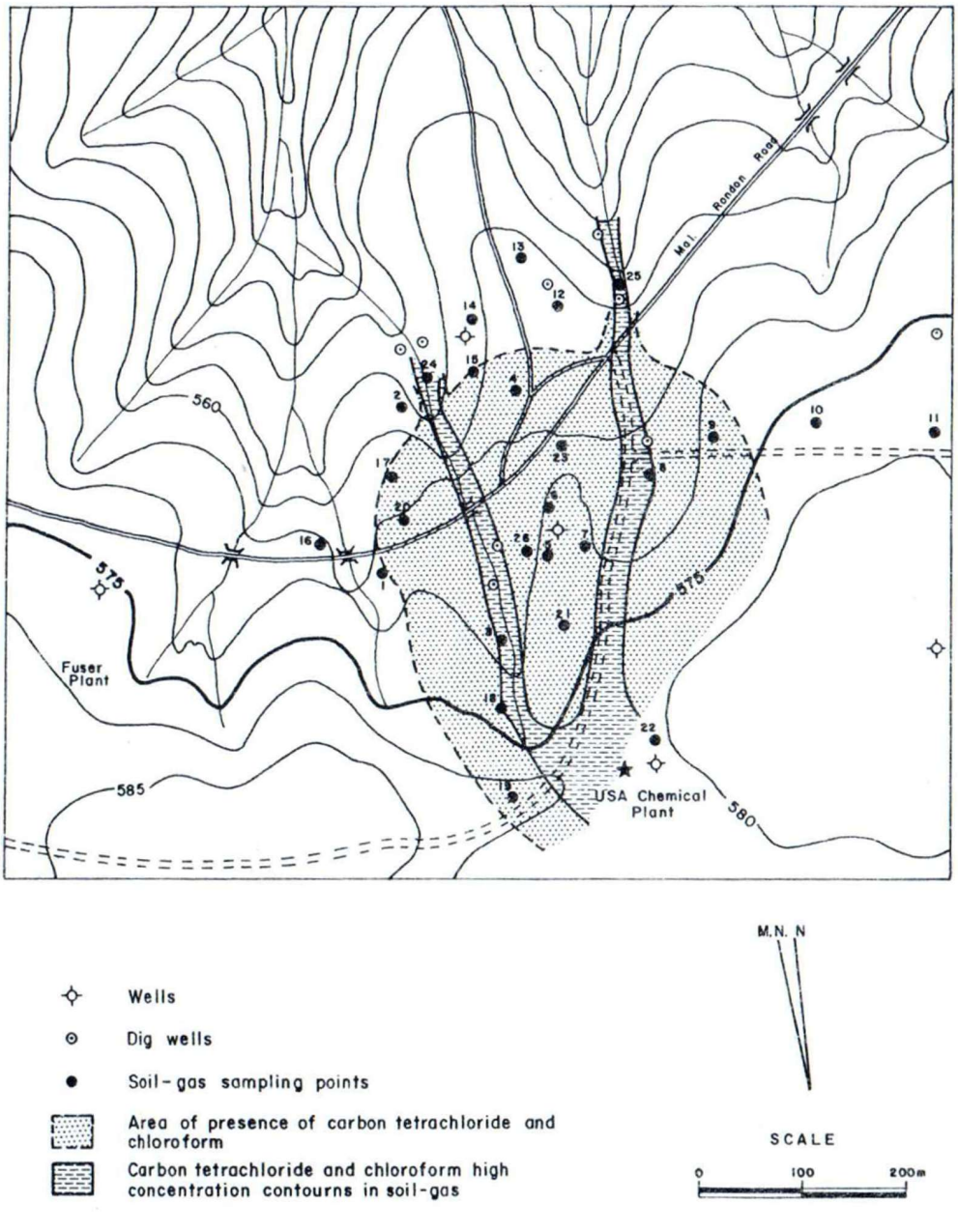

Fig. 3 - Vapor concentration obtained by soil-gas sampling method

Finally, the results of such soil-gas mapping show a relationship with groundwater sampling results. The presence of the contaminants in the groundwater of the Ilha Bela farm well (point B) and the absence of the two organics in the Marques farm well (point C) and the dug well of the Paula farm (point L) showed that the delineation of the body of contaminated groundwater is between these points which is supported by the soil-gas sampling concentrations.

Groundwater

After accident occurred at USA Chemical Ltda. several water collection efforts were made to sample deep and shallow wells as well as springs and surface drains. These sampling locations are identified in Fig. 2.

With the goal of identifying the compounds present, a water sample was analyzed using a Hewlett-Packard GC-MS and the results indicated the presence of the same volatile organics found in the soil vapors.

Analysing the concentrations of carbon tetrachloride and chloroform in a sample from a well on the Ilha Bela farm property (point B), one notes a variation of three orders of magnitude from 1983 to 1987. During this period, the concentrations of these volatiles reached four distinct peaks, principally in the period from 1983 to 1985 when the region experienced the highest amount of rainfall. This seems to suggest a relationship between the rising organic concentrations and the increase in rainfall.

An analysis of the organic vapor concentrations taken at the Ilha Bela farm shows the highest values at the end of 1988. These peaks seem to reflect the presence of the center of mass of the contaminant plume. The apparent inversion in concentration values between chloroform and carbon tetrachloride could indicate that the center of mass of the chloroform has already passed. Unfortunately, sampling was not done at the appropriate time to establish this fact. Chloroform, however, has a much lower organic carbon partition coefficient than carbon tetrachloride and so one would expect its retarded seepage velocity to be significantly higher than carbon tetrachoride.

Assuming the above to be valid, the contamination at the Ilha Bela well (point B) could be explained in the following way: the initial concentration originated either with the runoff of the liquid pollutants along the dirt road and drainage ditches near the farm's well (and thus would appear sooner than one would expect based on the date of the accident) or there were other releases which occured before the major accident, as one of the employees of USA Chemical Ltda. claimed. The appearance of the highest concentrations, at the end of 1988, is most likely related to the vertical infiltration which occured at the USA Chemical Ltda. location.

Considering the December 7, 1988 sampling date as corresponding to the center of mass of the contaminant plume at the Ilha Bela farm and the starting location as being USA Chemical Ltda., the real velocity would be 0.12 m/day. Using this result and hydrogeologic data in the literature for estimating the effective porosity, one can calculate an average hydraulic conductivity for the aquifer of 1.7 m/day. In a similar way, if the above analysis is correct, the center of mass of the contaminant plume should reach the Marques farm in 1995.

Correlation of Results of Soil-Gas Sampling With Groundwater Concentrations

Beginning with the principal that volatile organics in the unsaturated zone originated in the contamined groundwater plume, one expects to find a relationship between soil-gas concentration of a given volatile organic and groundwater concentrations of the same chemical, taking into account, of course, geologic and hydrogeologic variability (Fig. 5).

A comparison of concentrations of chloroform and carbon tetrachloride in groundwater and corresponding soil vapor samples taken within a horizontal

distance of 25 meters from the groundwater well, showed excellent coefficients of 0.9 and 0.8 respectively. It is true that the number of observation points was reduced in order to confirm this correlation but the procedure nevertheless shows that one can securely estimate the groundwater concentration at a given location within one or two order of magnitude based on the soil-gas concentration directly above and ar the same areal position.

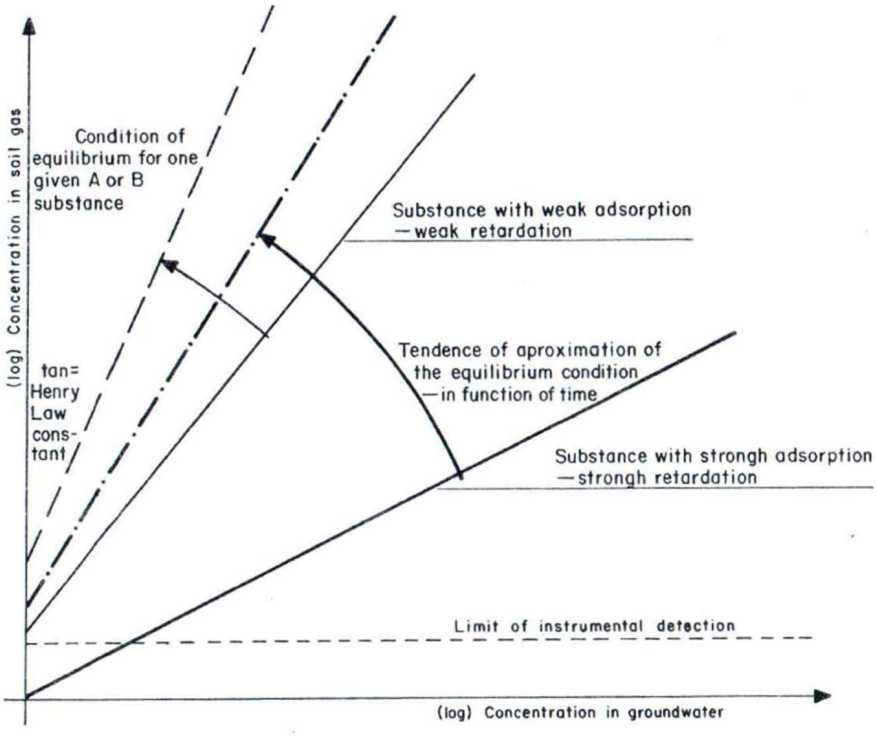

Fig. 4. Theoretical relationship between groundwater and soil-gas concentration (after Hirata, 1990)

The behavior of volatile organics in the unsaturated zone is a function of the physico-chemical characteristics of the substance involved, the porous medium, and the interaction of the organics with this medium. Each organic chemical behaves uniquely with respect to volabilization, adsorption and biodegradation. Organic vapors moving vertically upward suffer adsorption (solid-liquid partitioning) similar to the same process in the saturated zone. The unsaturated zone, however, has and additional partitioning process between the liquid and the vapor which is described by Henry's law. This results in an unsaturated zone retardation factor which is a function of Henry's law constant, the partition coefficient for solids/liquids and the water and air contents of the soil pores. The net result is a slower velocity and a higher residence time in the unsaturated zone with the possibility of increased biodegradation. Adsorption between solids and liquids can be quantified by the partition coefficient which is a function of the fraction of organic carbon in the soil (oxides and fine sediments can also play a role). Although not completely understood, the phenomenon basically involves the interaction of electrostatic forces, hydrogen bridging and Van der Wall's forces. Fig. 5 shows correlation curves between concentrations in the vapor and the groundwater for different degrees of adsorption. In a non-equilibrium situation, the larger the degree of adsorption, the larger is the retardation with a consequent tendency of the curve to lean in the direction of the

groundwater axis. In the end, the curve of a given chemical will tend to line itself up with its specific equilibrium curve whose slope is a function of its Henry's law constant. Consequently, one would expect the equilibrium curve for carbon tetrachloride to be less inclined than the curve for chloroform since Henry's law constant for the former is 0.38 ± 0.03 $kPam^2/mol$ while for the latter it is 2.0 ± 0.4 $kPam^2$ /mol. The behavior of the volatile organics in this study, however, does not follow this theory. This could indicate that equilibrium conditions have not been attained yet with the volatile organics still under the influence of adsorption, resulting in retardation of the arrival of carbon tetrachloride. The lowest estimative concentration in groundwater using the method of soil-gas sampling and a correlation curve will be a function of the laboratory instrument lower detection limit for the vapors of interest. Soil bacteria can consume biodegradable organics in the unsaturated zone resulting in non-detectable concentrations using soil-gas sampling methods at the land surface. This is commonly seen, for example, in gasoline contamination cases when upwardly moving benzene is consumed before it reaches the land surface. In some cases, soil bacteria may convert an organic volatilizing from the groundwater surface into another product, resulting in the measurement at the land surface of substances which do not exist in the groundwater. Examples of this are the conversion of carbon tetrachoride to methylene chloride and the reduction of trichloroethylene to the carcinogen, vinyl chloride.

CONCLUSIONS

Soil-gas sampling is a new technique developed to indirectly define the contamination of aquifers by volatile organic solvents. It involves the shallow-depth extraction of small quantities of soil-gases. The gases are analyzed in the field or in the laboratory for volatile organic compounds which originated in the underlying groundwater. The physico-chemical processes behind the detection of soil-gases involve the volatilization of organics from the groundwater plume with subsequent upward movement by molecular diffusion, establishing a concentration gradient which results in measurable concentrations at the land surface. One objective is to correlate the concentrations found in the gases with concentrations found in the groundwater. If a correlation can be established, one can use the soil-gas technique to inexpensively map out the longitudinal and lateral extent of a contaminated groundwater plume. The cost savings in fewer monitoring wells can be substantial. The technique is also used to indicate where one migth want to place future groundwater monitoring wells to maximize information obtained.

After researching and testing in the laboratory and the field, it was possible develop a soil-gas sampling methodology involving the design of an apparatus to collect soil-gases, establishment of sampling protocols and the adaptation of laboratory analysis techniques. The method developed in this study is innovative in its use of double activated carbon columns for the capturing and concentration of organic soil vapors.

Soil-gas sampling was used for the first time in Brasil in this study of the environmental accident which occured in Porto Feliz. The results of evaluating the quality of the aquifer with the method showed good results. The technique allowed the evaluation of the extent of the accident with respect to groundwater pollution by helping to define the shape of the groundwater plume.

The use of this method permitted the definition of three concentration zones in the sampled vapors: high, present and absent. It is important to remember that the areas of highest concentrations were in the vicinity of the drainage ditches and the land near the ruptured tank where the spilled liquids ran off and infiltrated on the day of the accident.

It was possible, with a precision conditioned on the number of groundwater samples, to correlate the concentrations of chloroform and carbon tetrachloride in groundwater with concentrations found in soil-gases taken from a radius of less than 15 m from the groundwater sampling well. The correlation coefficients were 0.9 and 0.8 respectively for chloroform and

carbon tetrachoride. Such excellent correlation indicates a smaller role was played by geologic heterogeneities than was expected.

From the data obtained, it is concluded that the pollutants are moving in a prefential direction from SSE to NNW, accompanying the regional grounwater flow direction. An analysis of groundwater collected at the Ilha Bela farm gives a seepage groundwater velocity for the center of mass of the plume of 0.12 m/day.

The results of sampling soil-gases in vapor wells at 1 and 2 m depths can be used to establish vapor flux emission rates for the area, assuming molecular diffusion is the principal mechanism of transport in the unsaturated zone. In the area of the Ilha Bela farm, the vapor flux emission rates were 0.001 $\pm$ 0.0006ug/m^2 /day and 0.008 $\pm$ 0.002ug/m^2 /day for carbon tetrachloride and chloroform respectively. Using these values and considering an area of 113,000 m^2 for the area of the contaminated plume, there is a loss to the atmosphere of 904 and 113ug/day for chloroform and carbon tetrachloride respectively.

REFERENCES

Devitt, D.A., Evans, R.B., Jury, W.A., Starks, T.H., Eklund, B. and Gnolson, A. (1987). Soil-gas sensing for detection and mapping of volatile organics. Dublin. NWWA, 270 p.

Foster, S.S.D. and Hirata, R.C.A. (1988). Groundwater pollution risk assessment. The methodology based in available data. CEPIS Pan-American Health Organization - WHO. Lima. 79 p.

Hirata, R.C.A. (1990). Amostradores de vapores do solo (AVS): o desenvolvimento de uma técnica para a detecção de água subterrânea contaminada por solventes orgânicos voláteis. O estudo de caso de Porto Feliz (SP). Dissertation of M.S. Universidade de São Paulo. 170 p

Hirata, R.C.A., Cleary, R.W. and Bastos, C.R. (1988). Amostragem de gases da zona vadosa: uma nova técnica para o estudo da contaminação das águas subterrâneas por solventes orgânicos voláteis. Proc Congres. Bras. de águas Subterrâneas, 4 São Paulo. ABAS. p. 196-206.

INSTITUTO DE PESQUISAS TECNOLóGICAS DO ESTADO DE SÃO PAULO (1981). Mapa Geológico do Estado de São Paulo. São Paulo, Monograph Serie. (1). 2 vol.

O'Connor, D.J., Farley, K.J. and Schnoor, J.L. (1987). Modeling of fate and effects of toxic substances in surface and groundwater. New York. Manhattan College New York. p. 2-41-2-45.

Pitchford, A.M., Mazzella, A.T. and Scarbroungh, K.R. (1988) Soil-gas and geophysical techniques for detection of subsurface organic contamination. Draft Version. Las Vegas U.S. Environmental Protection Agency. 220 p.

Thompson, G.M. and Marrin, D.L. (1987) Soil-gas contaminant investigation: a dynamic approach. Ground Water Monitoring Review - Summer. p. 88-93.