

## A MULTI-LAYER SAMPLER FOR GROUNDWATER: NEW FIELD TECHNIQUE TO STUDY CHEMICAL PROCESSES AND TRANSPORT PHENOMENA IN AQUIFERS

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### ABSTRACT

A multi-layer sampler (MLS) was developed and utilized for: a) sampling detailed undisturbed groundwater chemical profiles; b) sampling gases in both the saturated and the unsaturated zone; c) deriving detailed vertical profiles of the horizontal component of the specific discharge. Sampling is based on the dialysis-cell method; the sampling volume is defined by the desired sampling interval. The MLS is portable, cheap and easy to operate.

The results of the field study conducted in Israel revealed: 1) intensive biochemical activity as reflected by the consumption of dissolved  $O_2$  with the concomitant oxidation of organic matter and the development of an anoxic layer, and the production of  $N_2O$  (up to  $400 \mu g l^{-1}$ ) and  $CO_2$  (log  $pCO_2$  from -1.7 to -1.3); 2) the presence of an almost stagnant water layer (specific discharge  $0.5 m yr^{-1}$ ) down to a depth of 60 cm below the water table; 3) the presence of microscale isothermal water parcels (characteristic vertical and horizontal length dimensions on the order of less than 1 m) which differ from each other in their chemical composition and density and are characterized by very sharp boundaries between them. It is postulated that the gases produced during the biodegradation of the organic matter accumulate as a distinct gas phase (bubbles) down to a depth of 1 m below the water table, reducing the groundwater flow. The replenishment of the aquifer by water of different chemical composition and the almost stagnant conditions prevailing at the water table region (where mechanical dispersion by advection is negligible) lead to the development of microscale parcels of water of different chemical composition. It is suggested that haline convection is a major transport and mixing mechanism at the water table region.

## INTRODUCTION

The contamination of groundwater, from a pollution source located on the replenishment area of an aquifer, is a complex and long term process which can be divided into four schematic stages: A) Surface disposal of pollutants, B) Transport through the unsaturated zone; C) Arrival at the water table surface, and D) Transport within the saturated zone.

At the present level of knowledge the quantitative relationship between the amount of a pollutant applied to the soil surface and its concentration in groundwater is still highly uncertain (Mercado, 1973; Kanfi, et. al., 1983). This is primarily due to the lack of both knowledge and scarcity of data concerning the physiochemical, biological and transport processes undergone by contaminants in the unsaturated zone and in the uppermost saturated part of the aquifer - the water table region. The water table region is here defined as a water layer of up to 3 meters just below the surface along which the hydrostatic pressure is equal to the atmospheric pressure.

So far, most of the relevant studies have dealt with processes either in the unsaturated or in the saturated zones proper (Idelovitch and Michael, 1981; Pratt and Jury, 1984; Yaron et al., 1984). Very few data exist on the water table region (Stewart et al., 1968; Krajenbrink, 1983; Trudell, 1986) and no systematic studies have been carried out to elucidate chemical and transport processes taking place in this zone. This is probably due to the lack of available methodologies and sampling procedures.

The interface between the unsaturated and saturated zones of a phreatic aquifer is characterized by the change from a three phase (rock-water-gas) system to a two phase (rock-water) system. Saturated conditions already exist at the capillary fringe, above the water table (Davis and DeWiest, 1966; Bear, 1972). In this zone, water is held by surface tension forces (at pressures lower than atmospheric) and the "real" unsaturated-saturated interface has an irregular shape (Freeze and Cherry, 1979). In the unsaturated zone, water is in close contact with the gas phase which fills the pore spaces. The moisture content increases at the capillary fringe and at the water table (or, more strictly, when the pores are totally saturated with water), groundwater is isolated from the atmosphere above.

If a solute (like  $\text{Cl}^-$ ,  $\text{NO}_3^-$ , or Dissolved Organic Carbon) originating at the top-soil is transported downwards, through the unsaturated zone, and the input concentration of the solute is higher than the background

concentration in the aquifer, (the common situation in areas with a high surface load of pollutants), it is expected that its highest concentration in groundwater will occur in the water table region. Moreover, as the chemical quality of water of different recharge events was found to be preserved in the unsaturated zone (Gvirtzman et al., 1986), a recharge of variable chemical composition will lead to a chemical heterogeneous input to the water table region.

The variation with time in the concentration of a conservative solute (e.g.  $\text{Cl}^-$ ), at the water table region, will be defined by the rate of the transport controlling processes. However, no data is available on the rate of groundwater movement at the unsaturated-saturated interface. It is not known whether water in the capillary fringe and the water table region below it flow at a similar average velocity as water in the bulk aquifer. Therefore, it is difficult to know what is the relative importance of different transport and mixing processes (advection, dispersion, diffusion). The variation of the concentration of a non-conservative component (like oxygen, nitrate and Dissolved Organic Carbon) in the water table region may also be influenced by chemical and biological processes. Since the solubility of oxygen in water is low ( $8.7 \text{ mg l}^{-1}$  at  $22^\circ\text{C}$ ) and because oxygen replenishment in subsurface environments is limited the biodegradation of only a small amount of organic matter can lead to anoxic conditions (Freeze and Cherry, 1979). Therefore, nitrogen speciation (and thus the concentration of e.g. nitrate) may be controlled by processes such as denitrification (Hendry et al., 1983; Trudell et al., 1986).

From the above arguments it is reasonable to assume that large chemical variabilities can be expected to be found at the water table region.

A major problem in hydrochemical studies is obtaining small-interval, representative groundwater samples of the undisturbed flowing system. Generally, samples are collected from pumping wells or by samplers lowered to different depths in observation boreholes. These procedures disturb chemical gradients and can yield mixed water samples from different horizons of the aquifer. Devices to obtain profile samples reported in the literature have been used primarily for shallow aquifers. In most of these devices the water sample is pumped from the surface and the sampling intervals are greater than 0.5 m (Hansen and Harris, 1974; Edworthy and Brown, 1976; Pickens et al., 1978; Harrison and Ostéerkamp, 1981; Molz et al., 1986). The problem is how to sample a flowing system with minimal perturbation either due to the introduction of the sampler or the retrieval of the sample. Moreover, the fluctuations of the water table necessitates a variable sampling system (not fixed in the aquifer) so that it

enables the adjustment of sampling depth according to variations of the water table.

In this paper we present a new multi-layer sampler developed for the study and monitoring of groundwater. Its application to the study of the water table region of polluted aquifers is also shown.

## METHODS

### 1. The multi-layer sampler (MLS).

The multi-layer sampler enables water sampling at predetermined depth intervals by use of the dialysis membrane technique (Mayer, 1976; Hesslein, 1976). The sampler can be built of different materials according to monitoring or research needs. For example, PVC may be selected for monitoring the concentration of heavy metals and major ions and Teflon® may be used for the study of trace organics.

The sampler for the study trace organics (Fig. 1) consists of a 5 cm diameter Teflon® rod 70 cm long with 12 perpendicular crisscrossed holes to accommodate the dialysis cells. The cells are spaced at 5 cm intervals and separated by flexible Teflon® -coated seals whose diameter fit loosely that of the inner diameter of the sampling well. A Teflon® ring, whose purpose is to guide the sampler through the well, is mounted at one end of the rod. The dialysis cells are secured by stainless steel screws. A nylon rope is attached to the upper segment. The sampler is built in a modular way so that several rod segments may be connected by a double-screw.



Fig. 1. Multi-layer sampler specially designed for the study of trace organics. All the components of the sampler are built of Teflon® and stainless steel.

The dialysis cells are made of stainless steel with replaceable dialysis membranes on both ends. After retrieving the sampler from the well the dialysis cells may be sealed using an impermeable Teflon® membrane thus enabling transport, storage and subsequent extraction of the sample for chemical analysis (Fig. 2).

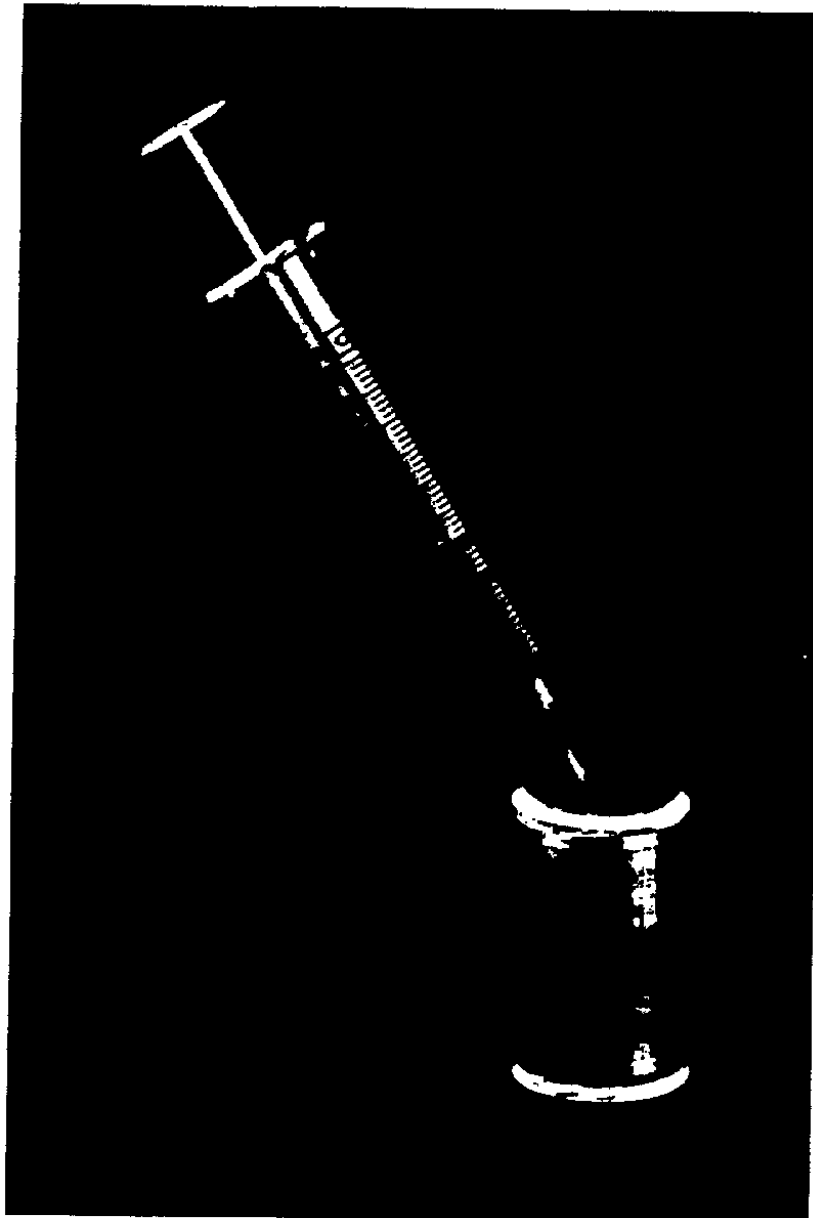


Fig. 2. Extraction of a water sampler from the stainless steel dialysis cell for analysis of trace organics. The dialysis membrane is covered in the field by a Teflon® membrane and PVC cap leaving a septum through which the water sample may be extracted in the laboratory.

## 2. The equilibration time of the dialysis cells.

The equilibration time of the dialysis cell can be calculated using Fick's second law of diffusion, given by Crank (1975) as

$$C = \left( \frac{C_0}{2} \right) \operatorname{erfc} \left( \frac{x}{2} \sqrt{Dt} \right)$$

where  $C$  = concentration;  $C_0$  = original concentration,  $D$  = ionic diffusion coefficient for a specific temperature. In order to determine empirically the equilibration time of the dialysis cells in the developed system a laboratory test was performed where pairs of dialysis cells filled with distilled water were submerged in separated baths of a 800 ml solution ( $\text{Cl}^- = 200 \text{ mg l}^{-1}$ ;  $\text{NO}_3^- = 100 \text{ mg l}^{-1}$ ;  $\text{SO}_4^{2-} = 60 \text{ mg l}^{-1}$ ). The water was continuously stirred at 126 RPM so as to eliminate spatial heterogeneities. The ambient temperature was 20 to 22°C. The test was performed for two types of dialysis membranes: a) a Cellulose Acetate membrane with a cut-off of 12,000 molecular weight (pore size about 40 Å) and a thickness of 0.040 mm (C-75, Union Carbide Corporation) and, b) a Nylon membrane composed of a non-woven nylon fabric coated by a white acrylic copolymer with a pore size of 0.2 μm (Versapor V-200, Gelman Sciences). The equilibration time of the dialysis cells is presented in Fig. 3.

The test (for Cellulose Acetate membranes, Fig. 3a) shows that for  $\text{Cl}^-$  and  $\text{NO}_3^-$  90% equilibration is obtained within 24 hours whereas only 50% equilibration is achieved for  $\text{SO}_4^{2-}$ , as expected from its lower diffusion coefficient. Total equilibration for these anions are obtained in one week. About 95% equilibration is obtained within 24 hours for all the anions using the Nylon membranes (Fig. 3b). This could be expected as advection may influence the transport of solutes through the relatively large pores of this membrane; it may be recalled that during the experiment the bath where the cells were submerged was continuously stirred. A similar diffusion experiment was conducted using dialysis cell made of Pyrex with Teflon® O-rings to test the suitability of the system to sample organic micropollutants (Fig. 4).

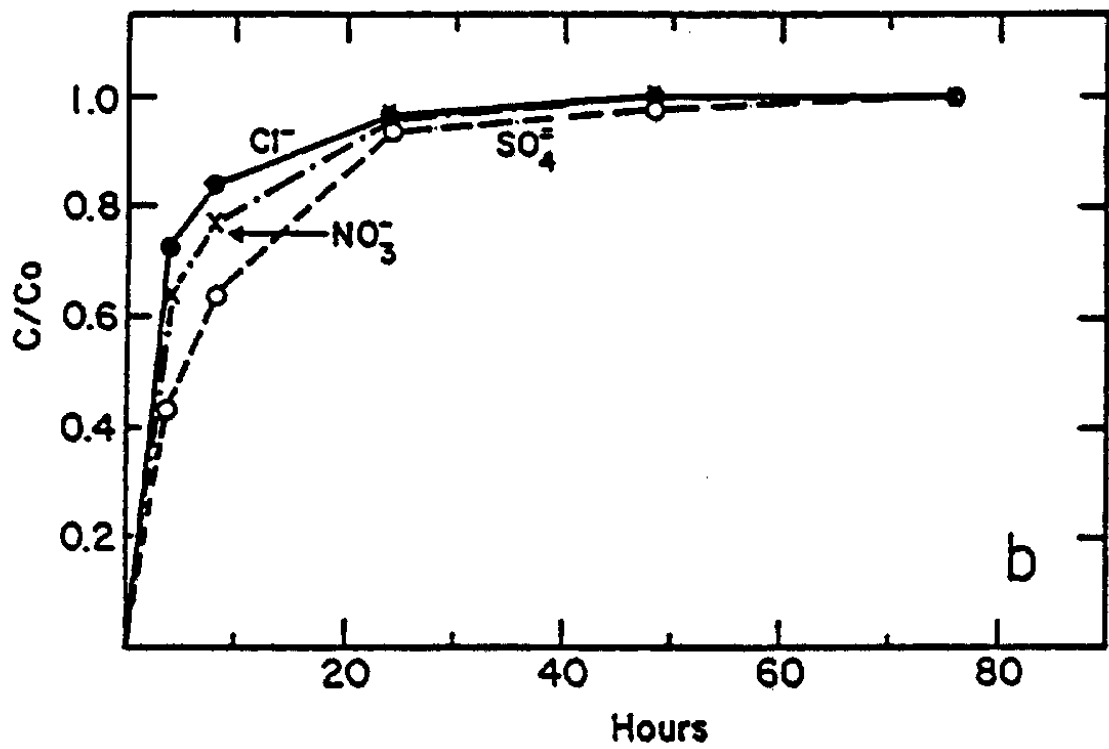
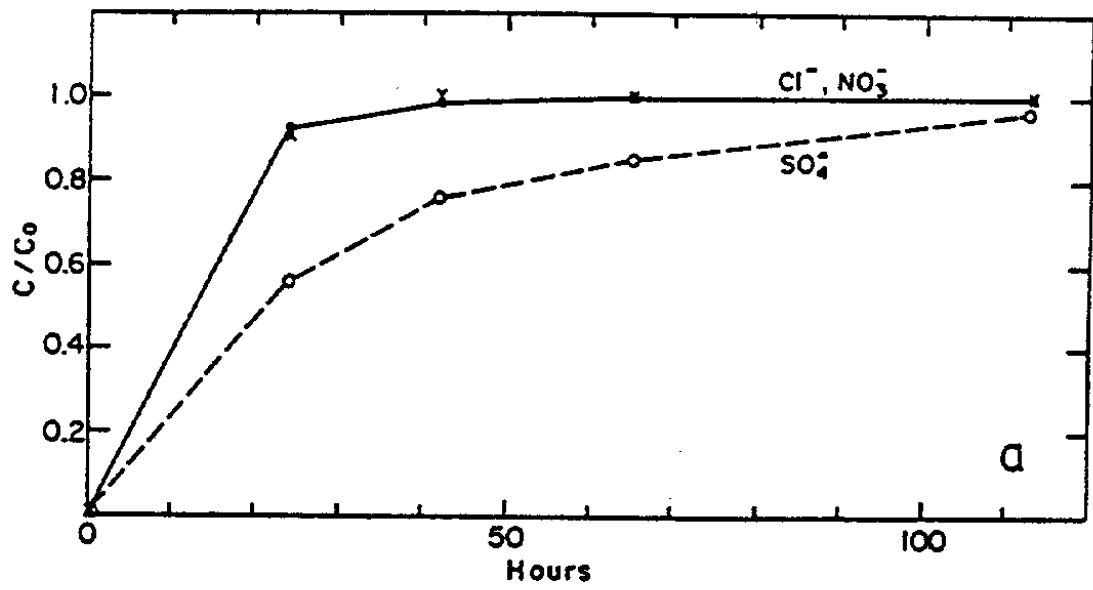


Fig. 3 Equilibration test of dialysis cells conducted at 22°C each data point represents two equilibration tests; a) cellulose acetate membranes, b) Nylon membranes.



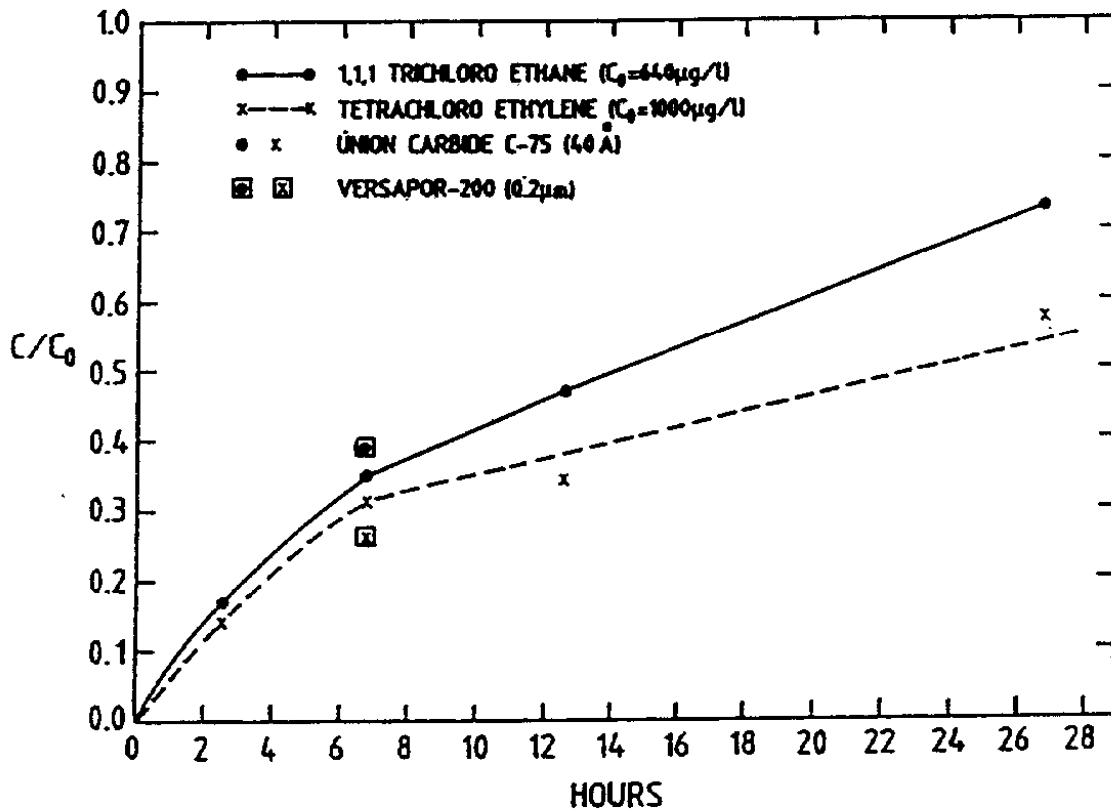


Fig. 4. Preliminary results of equilibration test with test with Pyrex dialysis cells and two different types of dialysis membranes. The dialysis cells were submerged in separate baths and continuously stirred at 22°C (the experiment was stopped after 28 hours for technical reasons).

### 3. Sampling and measurement of dissolved gases.

The sampler enables both the measurement of dissolved gases (e.g.  $O_2$ ) inside the dialysis cells in the field and also obtaining water samples for the subsequent extraction and measurement of gases (e.g.  $N_2O$ ) in the laboratory. If the research wells are equipped with screens above ground-water, this arrangement permits also the sampling of the gas composition of the unsaturated zone as it achieves equilibrium with the distilled water in the dialysis cells.

For the analysis of gases in the laboratory, water samples are obtained by introducing a needle through the dialysis membrane into two to three dialysis cells of the multilayer sampler and extracting the water under suction into a glass vessel. After filling the vessel it is closed by two vacuum stopcocks (Fig. 5). All samples are immediately transported to the laboratory for gas extraction.

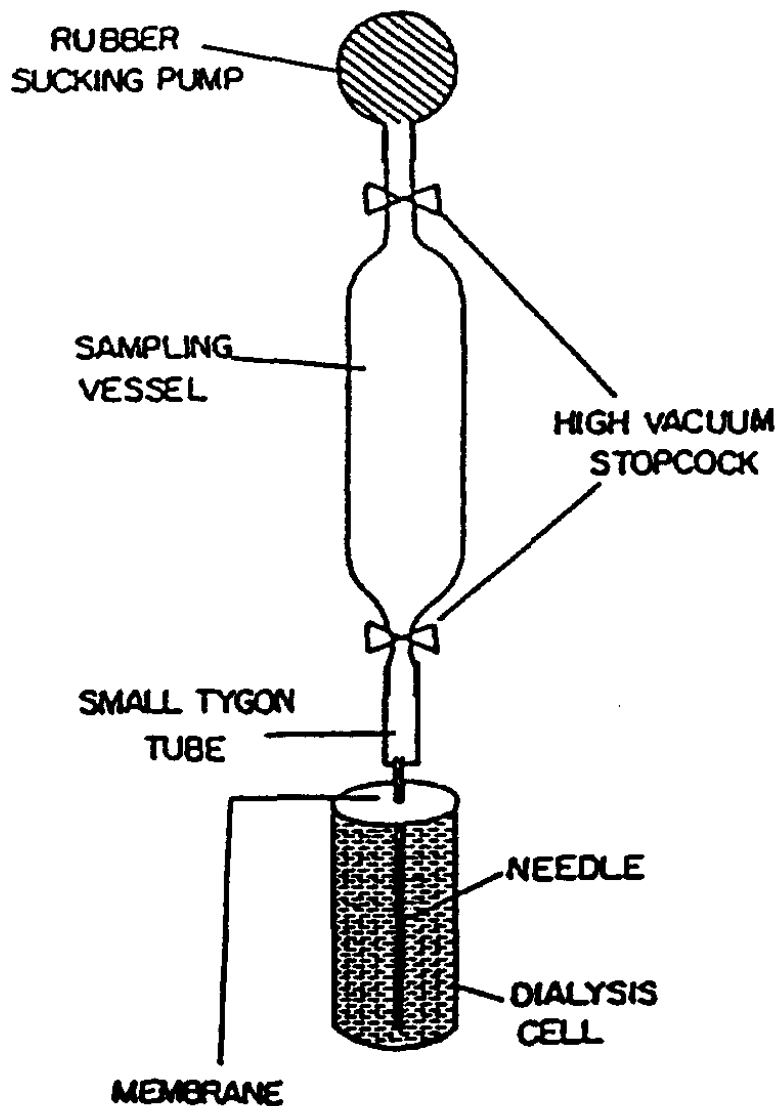


Fig. 5. Schematic representation of the method used to extract water samples for the analysis of  $N_2O$ )

#### 4. Methodology for calculating the specific discharge.

A new methodology was developed for deriving detailed vertical profiles of the horizontal component of the specific discharge. This methodology employs both a modified point dilution technique under natural flow conditions and a mathematical diffusion model (Ronen et al., 1986). The technique includes observations of the concentration of an ideal solute along the perforated section of an observation well. Water containing an initial concentration of the tracer is introduced into each dialysis cell and the  $\bar{M}LS$  is lowered into the observation well. After a given interval of time, the sampler is pulled out and the concentration of the tracer in each dialysis cell is determined. The procedure is repeated according to the desired number of data points.

## APPLICATIONS OF THE MLS

The MLS has been used continuously to study: 1) the water table region of a 30 m deep sandy aquifer in Israel (since 1984) in an agricultural area irrigated with sewage effluents; 2) the water table region in the Netherlands (since 1986) in a forest region subjected to the input of acid rain, and under fertilized pasture-land; 3) the vertical profile of the horizontal component of the specific discharge in a confined aquifer in Mobile, Alabama (in 1988), using a modified point dilution technique.

### *a. The water table region under sewage irrigated land*

The phreatic aquifer at the Glil Yam study area in Israel has been under a high organic carbon load, averaging  $140 \text{ Kg C}_{\text{org}} \text{ ha}^{-1} \text{ yr}^{-1}$ , due to the utilization of sewage effluents as irrigation water since the early 1960's (Ronen and Magaritz, 1985). Under a supply of biodegradable organic matter from the unsaturated zone, with an average DOC flux calculated to be at least  $3.1 \times 10^{-2} \text{ mg C}_{\text{org}} \text{ cm}^2 \text{ yr}^{-1}$ , the oxygen dissolved in groundwater at the water table region is consumed (Ronen et al., 1987), the average  $\text{O}_2$  decrease to  $0.78 \text{ mg l}^{-1}$  (Fig. 6). Oxygen consumption, the very high concentrations of  $\text{N}_2\text{O}$  (up to  $400 \text{ } \mu\text{g l}^{-1}$ , Fig. 7) and  $\text{CO}_2$  (log  $\text{pCO}_2$  from -1.7 - 1.3) and the large amount of bacteria (bacterial population  $10^5$  to  $10^6 \text{ ml}^{-1}$ ) at the water table region are evidence of the intensive biological activity operative at the saturated-unsaturated zone interface (Ronen et al., 1988a).

The gases produced during the biodegradation of the organic matter and/or air entrapped in the porous medium during groundwater recharge accumulate as a distinct gas phase - bubbles - down to a depth of less than 1 meter below the water table. This is the theoretical critical depth at which bubbles are most likely to be found in the study region. Large bubbles (radius  $\approx 200 \text{ } \mu\text{m}$ ) reduce volumetric water content and, hence, hydraulic conductivity. Small bubbles (radius  $\approx 50 \text{ } \mu\text{m}$ ) clog pores without significantly decreasing the volumetric water content. At a depth of less than one meter the pressure at a point in the moving fluid ( $10^{-1} \text{ atm}$ ) is at least one order of magnitude smaller than that required to both initiate the movement of bubbles through a pore space and to overcome the resistance to flow offered by detached gas bubbles and liquid drops in capillary conduits. Thus, the presence of gas bubbles significantly reduces the flow, leading to the development of an almost stagnant water layer (specific discharge  $0.5 \text{ m yr}^{-1}$ , Fig. 8) down to a depth of 60 cm below the water table. This is the depth of the almost stagnant water layer found in

the field experiments (Ronen et al., 1986). The hydraulic properties developed in the aquifer are transient and difficult to predict due to the dynamic characteristic of bubbles (production, mobility and dissolution, Ronen et al., 1989)

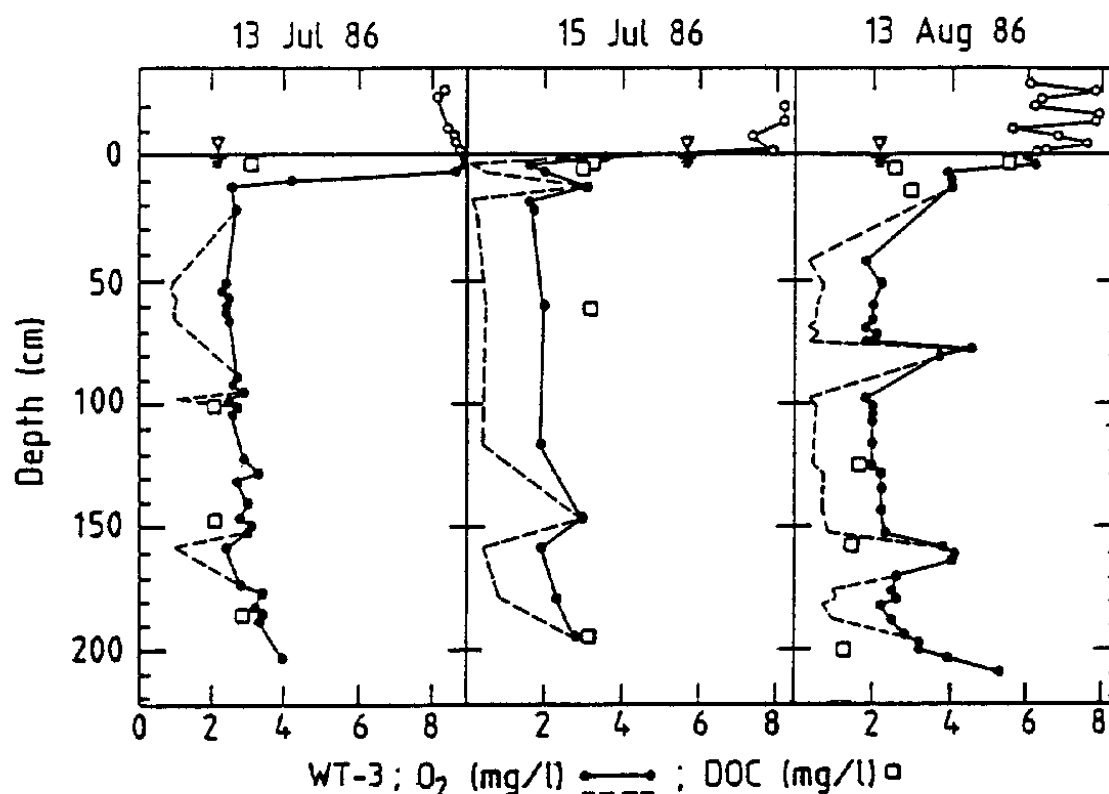


Fig. 6. Dissolved oxygen profiles and dissolved organic carbon content at the water table region under land irrigated with sewage effluents, research well WT-3, Israel. (---) Corrected values to account for the long response time of the oxygen probe (Ronen et al., 1987).

The intermittent input of rain and irrigation water of varying chemical composition (e.g.  $20 \text{ mg l}^{-1} \text{ Cl}^-$  from rain and about  $200 \text{ mg l}^{-1} \text{ Cl}^-$  from sewage effluents) along with the periodic input of other chemicals such as fertilizers creates a vertical profile composed of discrete water layers of varying composition in the unsaturated zone (Gvirtzman et al., 1986). Evapotranspiration reduces the amount of water recharge mainly during summer, thus increasing further the difference between the salinity input of sewage effluents and that of rain. The replenishment of groundwater by this influx and the almost stagnant conditions prevailing at the water table region lead to the development of microscale parcels of water, having vertical and horizontal length dimensions of less than 1 m (Fig. 9) and varying chemical composition (in some cases by more than 50% in the concentration of  $\text{Cl}^-$ ,  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$ ) and density. Microscale water parcels may also be formed *in situ* at the water table region by chem-

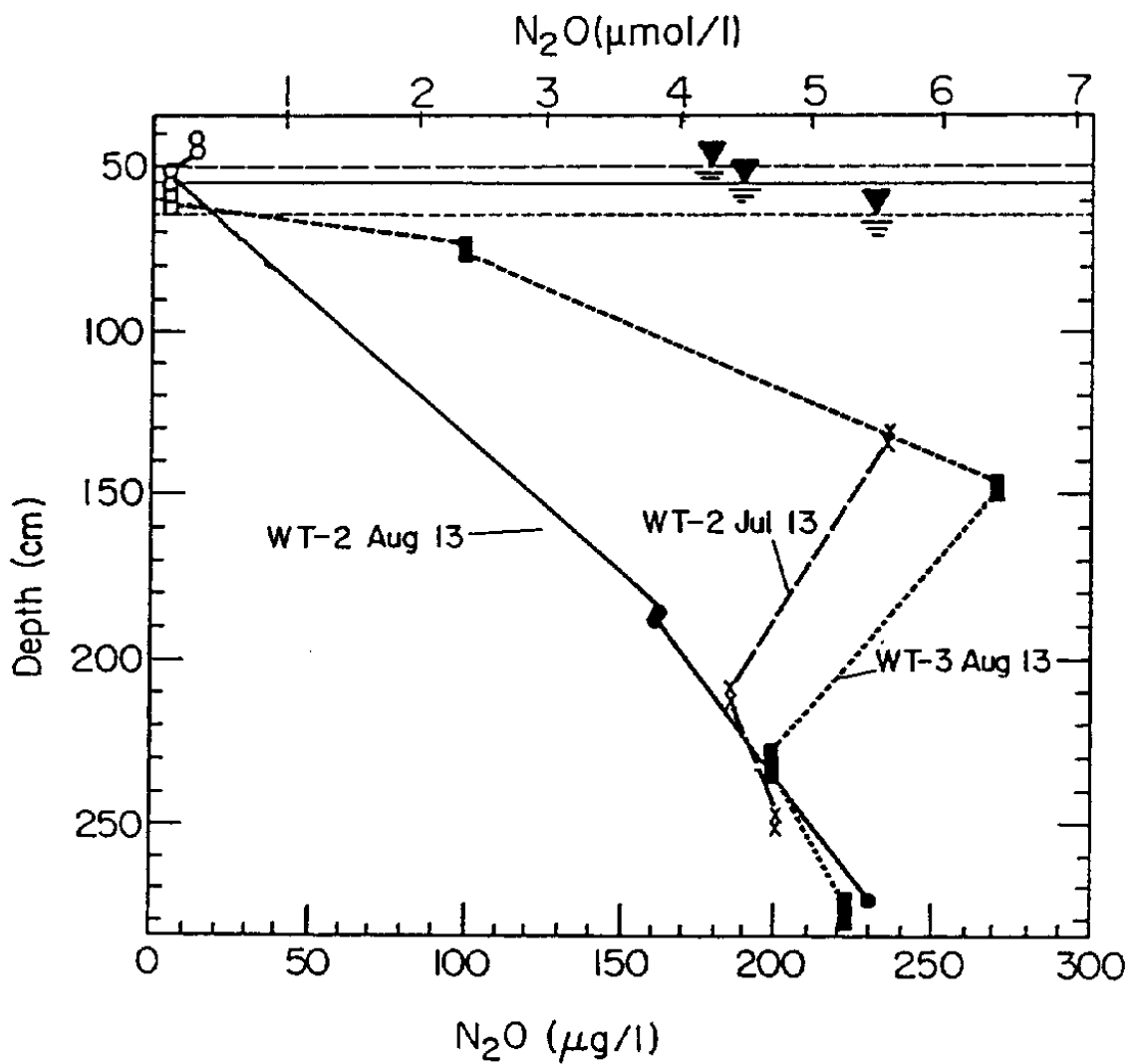


Fig. 7. Concentration profiles of nitrous oxide obtained in the water-table region of the Coastal Plain aquifer in Israel under land irrigated with sewage effluents (research well WT-2 and WT-3). Note the concentration of N<sub>2</sub>O found in the unsaturated zone just above the water table (empty squares and circles). The water tables corresponding to the different profiles are denoted by inverted triangles.

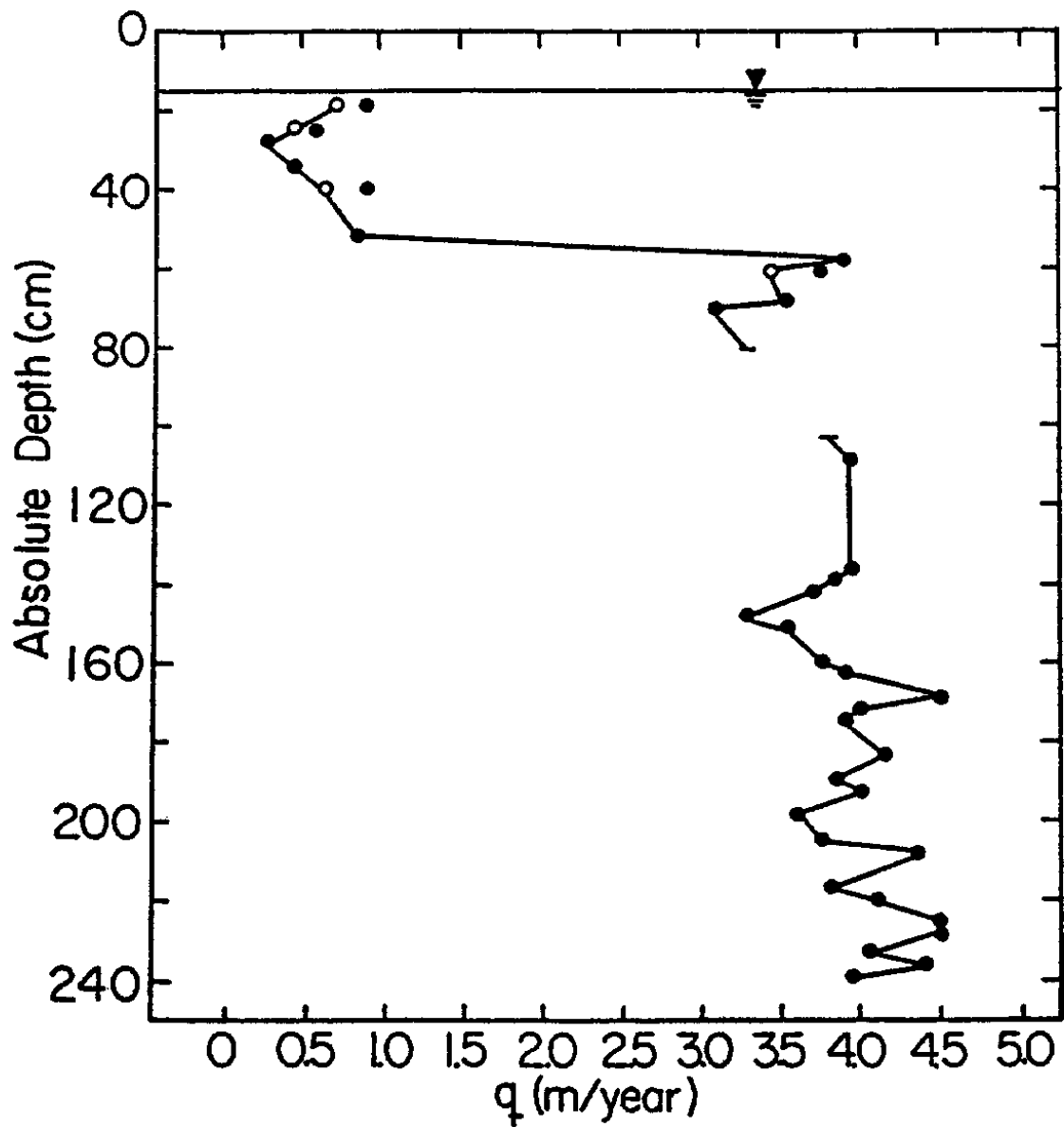


Fig. 8. Profile of the horizontal component of the specific discharge obtained with the multi-layer sampler in the water table region of a contaminated aquifer in Israel. The methodology employs a modified point dilution technique under natural flow conditions. The vertical axis shows the absolute depth from a predetermined reference level.

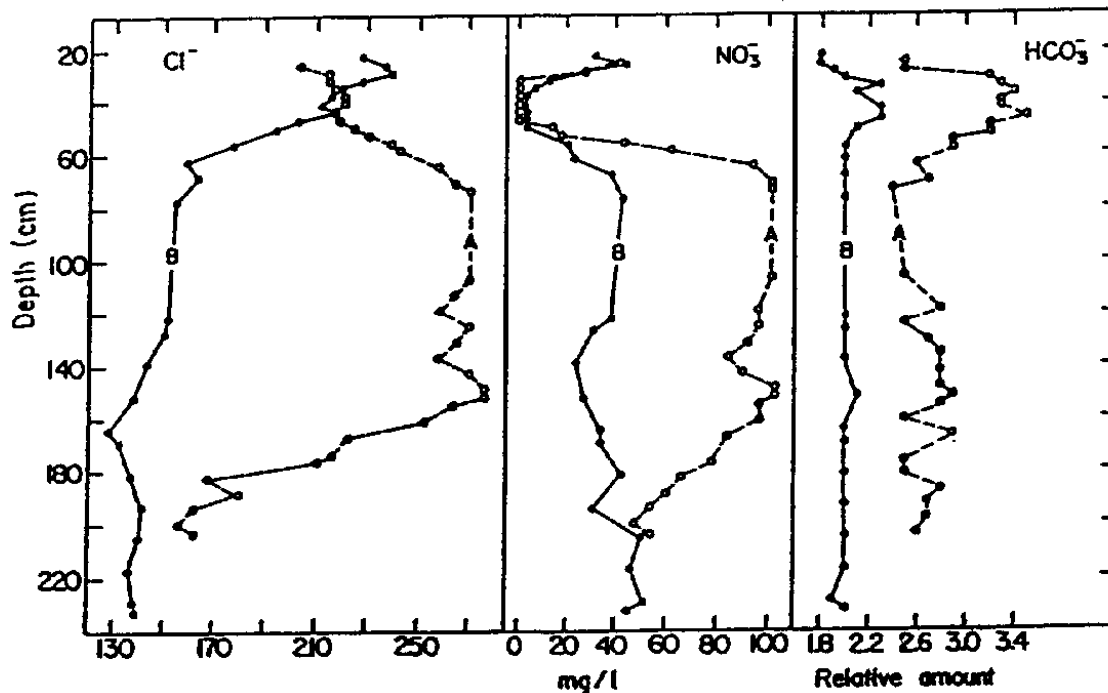


Fig. 9.  $\text{Cl}^-$  and  $\text{NO}_3^-$  profiles sampled with the multi-layer sampler in the water table region of a contaminated aquifer in Israel. Profile B was obtained 30 days after profile A. The concentration of  $\text{HCO}_3^-$  was measured in the laboratory and is given as the relative amount in relation to a standard.

ical or biochemical processes (e.g. nitrification, denitrification) which may change the chemical composition of small volumes of water. The sharp boundaries between overlying water parcels, which may have in some cases persisted over long periods of time (months), and the calculated range of the Peclet number ( $6.25 \times 10^{-2}$  to  $6.25 \times 10^{-3}$ ) for the flow field implies that mechanical dispersion by advection is not an important mixing mechanism at this zone. The observed rapid destruction of the boundaries between overlying water parcels, which may occur within one month, suggests haline convection. The isothermal overlying water parcels are at times gravitationally unstable due to destabilizing salinity - density - differences. The critical density difference which overcomes viscous drag forces is in the range of  $0.230$  to  $0.281 \text{ kg m}^{-3}$ . This value fits the estimated free convection parameter or modified Rayleigh number -  $4\pi^2$  - for porous media (Lapwood, 1948; Wooding, e.g. 1963, 1964; Bear, 1972). Haline convection should overcome stratification, which would develop under very slow laminar flow conditions, and therefore, greatly influence the influx of pollutants to bulk groundwater (Ronen et al., 1988b).

*b. The water table region under woodland in the Netherlands.*

A study was conducted at the Veluwe region in The Netherlands

(Krajenbrink et al., 1988). The aim of this study was to elucidate whether microscale chemical variability and oxygen consumption at the water table region is the result of the specific environmental situation described above (where the quality of the recharge water alternates between that of rain water and sewage effluents) or a generalized phenomena found in other granular aquifers under “natural” replenishment.

The investigation was conducted in a forest area subjected to the input of acid rain and ammonia volatilized from cultivated land and feed-lots. The aquifer is composed of gravels, coarse sand and clay-loam layers. The water table is at a depth of 7 m. Research wells were drilled by a spiral driller dry method (auger). PVC screens covered with nylon stocking were installed at the water table region of the research wells and the sediments were allowed to collapse onto the screens.

Microscale water parcels of different chemical composition and oxygen depletion were detected in this region of The Netherlands (Fig. 10) as well as in Israel. However, the decrease in the DO content is smaller than that observed at Glil Yam in Israel. This observation is consistent with the much smaller organic carbon load in the forest area as compared to that found in Israel under land irrigated with sewage effluents.

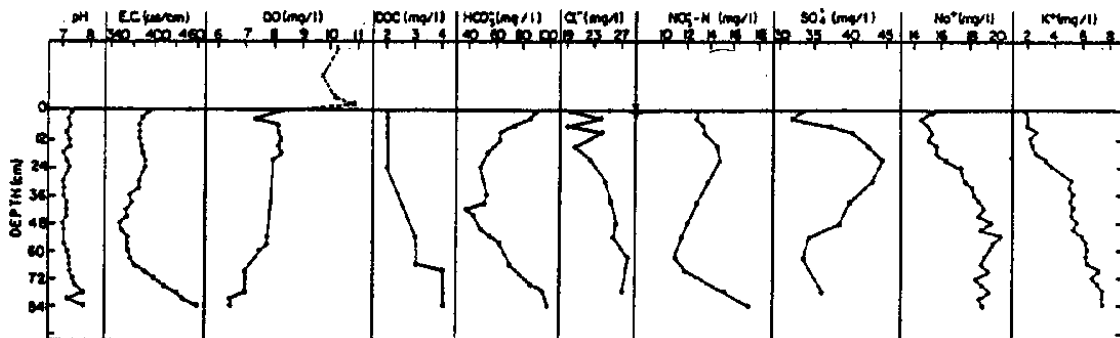


Fig. 10. Chemical profiles in the water table region under woodland in The Netherlands. Sampled by the multi-layer sampler.



## CONCLUSIONS

The potential of this methodology should be recognized for the development of "early warning" ground water monitoring systems. Sampling and measuring the actual contaminant fluxes reaching the water table from the unsaturated zone, before they are diluted in ground water, has several advantages: (1) it increases the detection sensitivity of the monitoring system, as pollutants arriving from the unsaturated zone will be found at maximum concentration in the water table region (Ronen and Magaritz, 1985); (2) it gives ample time (decades) for remedial actions to be undertaken before massive ground water contamination occurs, and (3) it enables establishment of a quantitative relationship between the amount of pollutant released in the soil and the amount that actually reaches ground water. The MLS is portable, inexpensive, easy to operate and thus not require any power source for its operation. The dialysis cells are in continuous dynamic equilibrium with the gas and liquid phases in the aquifer. Therefore, the MLS is a continuous sampling system. It may be lowered in any existing screened well and its sampling depth is not limited. Its dimensions are function of the well diameter. The sampling volume is mainly defined by the desired sampling intervals.

A patent application has been filed by the Israel Water Commission and YEDA Research and Development Co. Ltd. for the monitoring system described in this paper.

## ACKNOWLEDGMENTS

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