1 Processes

The unsaturated zone – a neglected component of nature

D. Ronen[1, 2], S. Sorek[2, 3]

[1] Water Quality Division, Israel Water Commission, POB 20365, Tel-Aviv 61203, Israel
[2] Ben-Gurion University of the Negev, J. Blaustein Institutes for Desert Research, Zuckerberg Institute for Water Research, Environmental Hydrology & Microbiology, Sde Boker Campus, 84990, Israel
[3] Ben-Gurion University of the Negev, Mechanical Engineering, Pearlstone Center for Aeronautical Engineering Studies, Beer Sheva 84105, Israel

Corresponding author: 14 Hamasger St., POB 20365 – Tel Aviv 61203 – Israel – Tel: +972.3.6369648 – Fax: +972.3.9604017 – E-mail: danronen@bgu.ac.il

Abstract

The unsaturated zone and the saturated/unsaturated interface region are important links between groundwater and the land surface. They provide storage capacity for both water and contaminants; a reactor medium for physical, chemical and biological processes; a delay time between the release of a contaminant into the unsaturated zone and its influx into the saturated zone and, a domain for the lateral and vertical transport of gases. We highlight some of the properties associated with these domains providing results of studies conducted in the phreatic Coastal Plain aquifer of Israel for the last 30 years.

Keywords

Unsaturated zone; saturated/unsaturated interface region; nitrates, chlorides.

Introduction

Understanding contaminant behavior in the unsaturated zone (UZ) and at the saturated/unsaturated interface region (SUIR) is a prerequisite for efficient management of groundwater resources. At the present level of knowledge the quantitative relationship between the amount of a contaminant released at the soil surface, e.g. by agricultural, or industrial and urban activity, and its resulting concentration in groundwater is uncertain. This is primarily due to lack of both knowledge and scarcity of data concerning the physical, chemical, biological and transport processes undergone by contaminants in the UZ and at the SUIR

The UZ and the SUIR are important links between groundwater and land surface. They provide: (1) storage capacity for both water and contaminants, (2) a delay time between the release of contaminants into the UZ and their influx into the saturated zone, (3) a reactor medium for physical, chemical and biological processes and, (4) a 3-D domain for the transport of gases and liquids.

In what follows we highlight some of the properties of the UZ and the SUIR on the basis of observations, conducted in the phreatic Coastal Plain aquifer of Israel for the last 30 years, as well as on modeling results. Namely, our idea is to draw attention to processes, fluxes and magnitudes of reservoirs, with the understanding that, even for the studied aquifer, some values presented are only preliminary estimates that disclose the complexity of the system.

The Coastal Plain aquifer of Israel

The Coastal Plain aquifer stretches for 120 km south of Mount Carmel; its width varies between 7 and 20 km and the surface area is 2,000 km^2. It has a wedge-like cross section with a maximum thickness of 180 m near the sea that tapers towards the east until it disappears near the foothills of the Samarian and Judean Mountains. The aquifer is composed of clastic sediments (sand, sandstone, calcareous sandstone, siltstone and red loamy soils; Issar 1968). The thickness of the unsaturated zone ranges from 4 to

98 m, averaging 34 m (Mercado 1975). The aquifer is naturally replenished by rain during the winter months, October to March (average rain of 500 mm yr^{-1}). Intensive agricultural development of the replenishment area of the aquifer took place at the beginning of the 20th century. Presently, major cities and industrial areas and more than 50% of Israel's total population reside on top of the Coastal Plain aquifer. The average concentration of chlorides (Cl^-) and nitrates (NO_3^-) in groundwater is increasing continuously as a result of agriculture, urban and industrial activities at an average rate, since the early 1970s, of 3 mg Cl^-/L yr (from 110 mg Cl^-/L in 1945 to 205 mg Cl^-/L in 2002) and 0.6 mg NO_3^-/L yr (from 45 mg NO_3^-/L in 1962 to 62 mg NO_3^-/L in 2002; Hydrological Service, 2003).

In 1980 it was estimated that the chloride influx to land surface (Fig.1) from rain, fallout, return flow and water import was of 106 Kt Cl^-/yr (kiloton chloride per year; Orenstein and Mercado 1980). In the early 1970's, it was calculated that 24 Kt N/yr is the net nitrogen input (Fig. 2) to the replenishment area of the aquifer (net denotes nitrogen amounts not utilized by vegetation; Ronen et al. 1983) from continuous contamination sources such as fertilizers and manure (58% of the net nitrogen input), sewage (16%), animal excreta (10%), irrigation water (7%), rain water (6%) and solid waste (3%). However, it was also postulated that most of the nitrates found in the aquifer reached the water table in the period 1930 to 1960, as a result of the oxidation of soil organic matter during reclamation of swamps and cultivation of virgin soils. It was estimated that this two exhaustive sources contributed about 1,100 Kt N during the period 1900 to 1930 (Ronen et al. 1983, 1984).

In some urban and industrial regions of the Coastal Plain, mainly in the Metropolitan Tel Aviv area, the aquifer is severely contaminated by Volatile Organic Compounds (Graber et al. 2002).

The UZ – a large storage reservoir

The amount of water stored in the unsaturated zone (Fig. 1) was estimated to be 11 x 10^9 m^3 (Mercado 1975, Orenstein and Mercado 1980). This is a considerable amount of water as compared to 21 x 10^9 m^3 water contained in the upper active region of the aquifer (about 66% of the saturated thickness of the aquifer) where most pumping wells are situated. Obviously, the interstitial water in the UZ has a chemical signature. For example, under areas irrigated with sewage effluents the maximum concentrations of chloride, nitrate and Dissolved Organic Carbon (DOC) detected were 500

mg/L, 600 mg/L (Gvirtzman et al. 1986) and 100 mg/L (Amiel et al. 1990), respectively.

What could be the magnitude of the chloride pool and the nitrogen and organic carbon mass stored in the UZ of the aquifer?

Using a simulation model (COMPFLOW, Unger et al. 1996) and based on the management pattern of the aquifer during the last hundred years, Mercado (2001) estimated (Fig. 1) that the amount of Cl^- stored in the UZ increased from 300 Kt Cl^- in the year 1900 to 2,070 Kt Cl^- in 1992. He also suggested that in the year 2015 this amount will increase to 3,105 Kt Cl^-. For the year 1980 Orenstein and Mercado (1980) estimated that the chloride flux into groundwater from the UZ was of 58.6 Kt Cl^-. At that time, the estimated amount of Cl^- in the unsaturated zone was of 1,590 Kt $Cl^-$and in the saturated zone 3,150 Kt Cl^-. The significant amount of chloride in the unsaturated zone was referred to as "the chloride time-bomb".

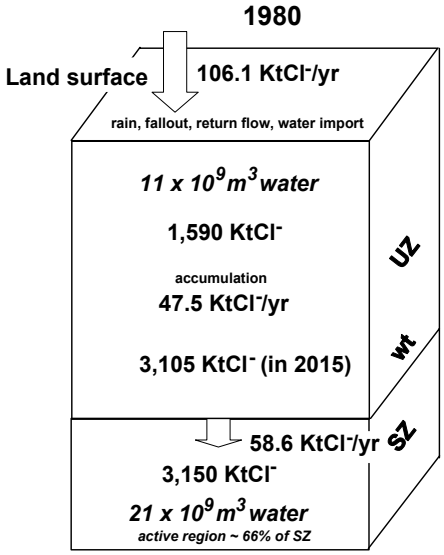

Fig. 1. Chloride pool and water pool in the unsaturated zone (UZ) of the Coastal Plain aquifer of Israel in the 1980's. The water pool in the saturated zone is calculated for the upper active region of the aquifer (66% of the saturated thickness of the aquifer) where most pumping wells are located. The upper arrow denotes chloride influx to land surface from rain, fallout, return flow and water import. The lower arrow denotes chloride flux from the UZ into the saturated zone (SZ). Also shown is the chloride pool in the SZ; wt - water table (after Mercado et al. 1975, Orenstein and Mercado 1988, Mercado 2001). According to the simulation model the amount of Cl^- stored in the UZ increased from 300 Kt Cl^- in 1900 to 2,070 Kt Cl^- in 1992. In 2015 this amount will increase to 3,105 Kt Cl^-.

Based on a series of 39 profiles from research wells representing most of the lithologic units of the aquifer and located in areas characterizing most current land uses (virgin soils, non-irrigated and irrigated crops, citrus groves, effluent irrigated areas, barn yards, sewage and solid waste disposal sites) Raveh (1972) estimated that the total amount of nitrogen stored in the UZ in the year 1970 was of 9,560 Kt N. Out of this amount 200 Kt N are present as NO_3^- ($N\text{-}NO_3^-$; Fig 1) and 160 Kt N as NH_4^+ ($N\text{-}NH_4^+$), the rest is organic nitrogen (N-NOrg). For the year 1970 Ronen et al. (1984) estimated that the input of nitrogen to the saturated zone was 1.3 Kt N and the amount of NO_3^- stored in groundwater 100 Kt N. Considering the calculated N/C ratios (Ronen et al. 1984) it was also estimated that the total amount of organic carbon (C-Org) in the UZ is of 105,000 Kt C-Org (Fig. 2).

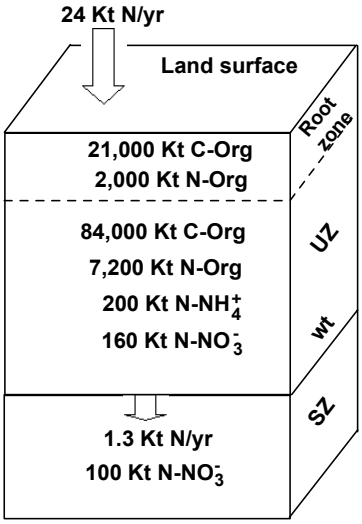

Fig. 2. Nitrogen and carbon pools in the unsaturated zone (UZ) of the Coastal Plain aquifer of Israel in the early 1970's. The upper arrow denotes net nitrogen influx to land surface from natural and anthropogenic sources. The lower arrow shows nitrogen flux from the UZ into the saturated zone (SZ). Also shown is the nitrogen pool in the SZ; wt – water table (after Ronen et al. 1984)

The nitrogen reservoir in the UZ is orders of magnitude higher than the nitrogen reservoir found in the saturated zone (most of it as NO_3^-) and the nitrogen fluxes to the soil surface and the saturated zone. Clearly, the organic matter in the UZ is also a potential source of both NH_4^+ and NO_3^-. On the other hand, the anaerobic decomposition of organic matter may lead to the reduction of nitrate.

The UZ and SUIR – a time-buffer zone

Calculations based on the aquifer replenishment and the water content of the UZ suggest that the average transit time of water to the water table is 27 years ranging from 1 to 50 years in most of the surface area of the Coastal Plain aquifer of Israel. For some restricted regions higher values to the extent of 800 years were calculated (Mercado 1975).

A detailed study where water in the UZ was traced according to its tritium content, utilizing the difference between the environmental tritium content of rain and irrigation water (Gvirtzman et al. 1986), demonstrated that in a clay loam layer the average vertical velocity is about 0.7 m/yr and in sandy sediments the mean rate of vertical water movement is 2.3 m/yr. The same study provided evidence of anion exclusion, where in the clay loam layer the vertical velocity of Cl^- and $SO_4^=$ was 1.35 m/yr.

An additional delay factor between land surface and the saturated zone is imposed by the SUIR. Ronen et al. (2000) calculated that for a SUIR having a thickness of 3 m, the residence time of recharge water may be greater than 5 years.

Based on these estimates, and considering retardation factors for chemical moieties, it can be suggested that, for the Coastal Plain aquifer of Israel, decades may elapse from the time that a contaminant is released at the replenishment area of the aquifer until the moment it reaches the saturated zone.

The SUIR – a singular biochemical reactor

The SUIR extends from an imaginary plane of 100% water saturation and positive water pressure ($p > 0$) to the surface of the capillary fringe (CF; Fig. 3a), the imaginary plane where $p < 0$ and water content (θ) is equal to the background residual water content of the UZ (Ronen et al. 2000). The SUIR is generally characterized by high pore water content as compared with residual pore water in the unsaturated zone, and by a relatively large gas-filled porosity as compared to that in the saturated zone (Fig. 3a; Ronen et al. 1997 and 2000). Moreover, tortuosity and the area available for liquid and vapor mass fluxes at the SUIR are both highly variable (as compared to the UZ proper) since moisture content is also spatially and temporally variable (Ronen et al. 2000). For example, in a study where 13 boreholes were located in relatively homogeneous sandy sediments within a radius of 5 m, the height of the CF (about 1.4 m) was found to vary by up to 50% (Ronen et al. 2000).

Field evidence indicates that high concentrations of DOC (DOC 20 to > 100 mg/L; Fig. 3b) are found throughout the 30 m thick UZ under land irrigated with sewage effluents since the early 1960's (Amiel et al. 1990). The study area, where bulk groundwater contains high Dissolved Oxygen concentrations (DO ~ 7.5 mg/L), is under a high organic carbon load. About 14 gr C-Org/m^2 were annually applied each summer, in contrast to the negligible amounts added to fields irrigated with fresh waters. DOC mobility is inferred from the lack of correlation between the content of DOC and Total Organic Carbon (TOC) in the sediments of the UZ (Amiel et al. 1990). The DOC is not completely biodegraded as it percolates from the soil surface to groundwater. A DOC mass balance indicates that the unsaturated zone still contains about 50% of the total DOC input. DOC persistence for more than 15 years under unsaturated conditions suggests that moisture content may be a significant controlling factor for biodegradation. Indeed, at the SUIR, where water content increases significantly, part of the DOC is biodegraded (Fig. 3b) and anoxic conditions develope (DO < 1 mg/L, Fig. 3c Ronen et al. 1987). In some cases the system becomes anaerobic and denitrification follows (Fig. 3d; Ronen et al. 1987).

Still to be answered is the question as to whether anoxification at the SUIR could be expected in other areas where fresh water is utilized for irrigation in the Coastal Plain aquifer of Israel. Few SUIR research wells are available in the aquifer, but the answer to this question may be inferred from the high oxygen content of groundwater as found in the deep pumping wells of the aquifer (Ronen et al. 1987). These pumping wells penetrate about two thirds of the saturated thickness of the aquifer. The residence time of water in this portion of the aquifer is about 25 years. As the average seepage time of water through the UZ is about 30 years, the present average oxygen content of groundwater in the pumping wells reflects the replenishment conditions in the 1940's. The intensive agricultural development of the Coastal Plain region started at the beguinning of the 20th century. If we consider retardation in the transport of DOC, it may be postulated that the organic matter, mobilized as the result of the onset of the agricultural activity (Ronen et al. 1984), has only lately reached the saturated zone. As explained before: (a) it was suggested that the massive contamination of groundwater by nitrates has resulted from the oxidation of soil organic matter due to the reclamation of swamps and the cultivation of virgin soils at the beguinning of the 20th cetury (Kanfi et al. 1983), and (b) the rate of percolation of anions through the unsaturated zone may be even faster than that of water (Gvirtzman et al. 1986). Therefore, nitrates may be expected to have reached groundwater earlier than the water soluble organic carbon released from the same source. Hence, the assumption that an anaerobic layer has been developed in large regions of the SUIR of the

Coastal Plain aquifer of Israel may not be dismissed on the basis of the present available data. The 95% decrease between nitrogen fluxes to land surface and to the saturated zone (Fig. 2) may be the result of denitrification at the water table region (Fig. 3d).

The biodegradation of DOC, under land irrigated with sewage effluents, leads to the production of gases in porous media. In air samples extracted from the SUIR, the concentration of CO_2 was up to 2% (Fig 3e; Affek et al. 1998) and the annual CO_2 flux from the SUIR towards the atmosphere (6.3 g C/m^2 yr) is balanced by a similar influx of DOC from the sewage effluents. At the SUIR, the $\delta^{13}C$ of CO_2 indicates that it is produced from the biodegradation of sedimentary organic carbon, probably as a result of competitive sorption (i.e., exchange between DOC and sedimentary organic carbon; Affek et al. 1998).

Nitrous oxide (N_2O) was also found to be produced at the SUIR and the concentrations detected in the liquid phase of the SUIR were up to 400 μg/L (Fig. 3f; Ronen et al. 1988) about three orders of magnitude higher than the concentration expected from equilibrium with the earth's atmosphere. In some cases the production of N_2O by nitrification may be inferred from the very high concentrations of N_2O found, and the concomitant decrease in pH and bicarbonate content which may be the result of nitrogen mineralization and cell synthesis of nitrifying organisms, respectively.

The biologically-produced gases may persist as gas bubbles in groundwater. Bubbles clog pores and therefore reduce the hydraulic conductivity without significantly reducing the volumetric water content (Ronen et al. 1989). This phenomenon is the result of the very high pressures required to force a bubble through a pore space and to overcome the resistance to flow offered by detached gas bubbles and liquid drops in capillary conduits. A second mechanism by which bubbles may be produced at the SUIR is during recharge. Entrapped air is one of the reasons for the hysteretic relationship between water content and pressure head during drainage and imbibition.

Calculations (Ronen et al. 1989) show that the critical depth below the water table ($p = 0$) at which bubbles are most likely to be found in the Coastal Plain aquifer of Israel, is of about 1 m. In the same aquifer, unsaturated conditions were detected below the water table till a depth of about 1.5 m (Fig. 3a) below the water table (Ronen et al. 2000). This estimate coincides with the depth of 0.60 m of an almost stagnant water layer found in an area where groundwater is driven by natural gradient flow conditions. The specific discharge was found to increase with depth from 0.5 m/yr (water velocity ~ 1 m/yr), near the water table, to 4.5 m/yr (water ve-

locity ~ 10 m/yr) at a depth of 2.4 m below the water table (Fig. 3g; Ronen et al. 1986) and up to 20 m/yr (water velocity ~ 44 m/yr) at a depth of 7 m.

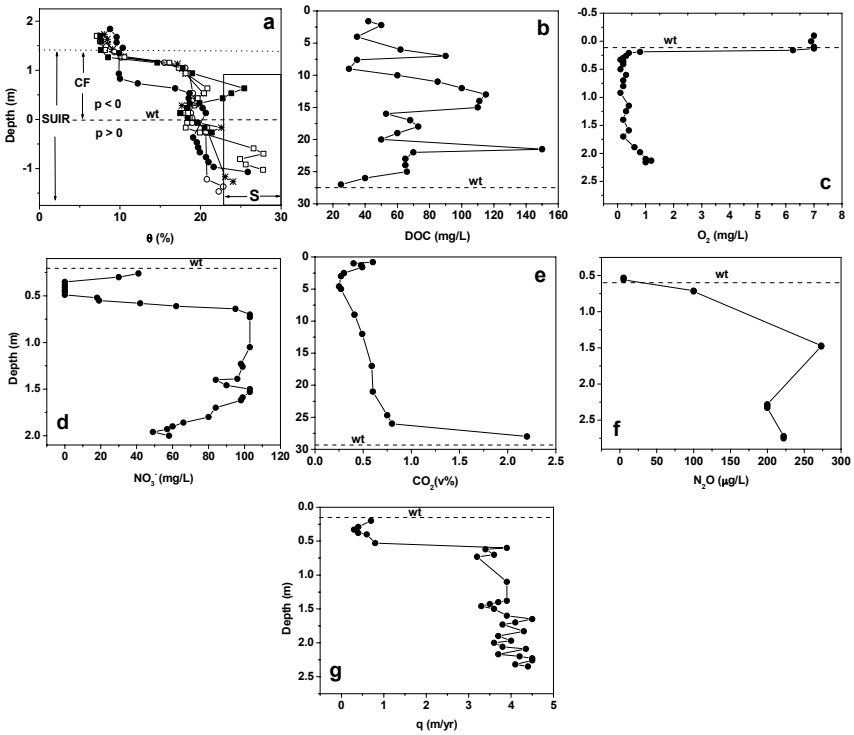

Fig. 3. Profiles obtained in the UZ and the SUIR of the Coastal Plain aquifer of Israel: (a) gravimetric water content (θ) in the SUIR. The inner frame denotes saturated conditions (S) at the SUIR, below and above the water table (wt); CF – capillary fringe (after Ronen et al. 2000; J of Contaminant Hydrology); (b) DOC in the UZ and CF (after Amiel et al. 1990; Research Journal WPCF); (c) anoxification in the SUIR (after Ronen et al. 1987, WRR); (d) profile showing denitrafication just below the water table (after Ronen et al. 1987, Journal of Hydrology); (e) CO_2 production at the CF (after Affek et al. 1998, WRR); (f) production of N_2O (Ronen et al. 1988, Nature); (g) stagnant conditions that develop due to bubble production and air entrapment (after Ronen et al. 1986, WRR).

UZ - a 3-D domain for transport of gases

Exceptionally high concentrations of volatile organic compounds (VOCs), e.g. Trichloroethylene (TCE) up to 124,000 μg/L-air in the unsaturated zone and up to 260,000 μg/L-water in the saturated zone, were measured at the SUIR in the metropolitan Tel Aviv area (at the Coastal Plain aquifer of Israel) where the land-atmosphere interface is characterized by large impermeable areas associated with urban infrastructure (Graber et al. 2002). Numerical simulations suggest that VOCs are being transported also in the gas phase of the unsaturated zone. Considering a single point source of TCE with a discharge rate of 0.2 mm/day, for 50 years, it was shown that TCE vapors may spread over an area of about 9 km^2 (Fig. 4). Vapor phase transport in the UZ is not related to the direction of water flow in the UZ or saturated zones. Thus, TCE vapors were found to become a secondary contamination source upstream of the single point source. Moreover, it was found that TCE vapors experience an upward flux at vertical impervious boundaries such that underground structures may be surrounded by VOC vapors. Indeed, VOCs were detected inside many buildings; the highest concentrations of TCE were 628 $\mu g/m^3$ air (Graber et al. 2002).

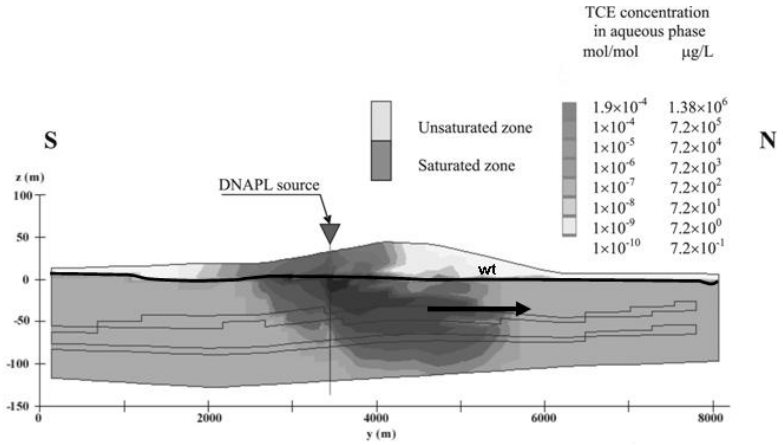

Fig. 4. Cross section of the Coastal Plain aquifer of Israel at the Tel Aviv area showing for the year 2000 the simulated distribution of TCE from one DNAPL source after a 50 years discharge rate of 0.2 mm/day. The TCE in the gaseous phase spreads in the UZ over an area of 9 km^2 also opposite to the direction of groundwater flow (arrow); wt – water table (after Graber et al. 2002).

Conclusions

The mass of a chemical component stored in the UZ of an aquifer may be considerable as compared to inputs from natural and anthropogenic sources. In the Coastal Plain of Israel, in the year 1970 for example, the total amount of nitrogen in the UZ was 398 times higher than the yearly net nitrogen input to land surface from all nitrogen contamination sources, and 7,353 times higher than the yearly $N\text{-}NO_3^-$ influx to groundwater. In this same aquifer if all chloride contamination sources in 1980 were removed, the Cl^- pool in the UZ would still continue to contaminate groundwater, with a similar chloride flux, during 27 years.

The SUIR is also an active interface that governs influx amounts reaching bulk groundwater and chemical speciation decades after contaminant penetration into the UZ. In some cases components of UZ sediments (e.g., sedimentary organic carbon) interact with interstitial water components playing an active roll in defining the chemical and isotopic composition of recharge.

The UZ operates also as a conduit for gases in urban and rural environments. The existence of industrial contamination sources in urban areas and the impervious boundary conditions that develop there create a unique problem that is not only related to groundwater quality but to the deterioration of the human habitat located within and above the UZ.

Obviously, the UZ chemical pools must be considered when developing managerial strategies for the prevention of aquifer contamination or for groundwater restoration. But do we know how to do it? For example, can we suggest reduction of fertilizer and manure inputs in the Coatal Plain aquifer of Israel, claimed to be responsible for an yearly input of 58% of all nitrogen contamination sources (14 Kt N), while the nitrogen pool in the UZ is almost 10,000Kt N? At this stage there is no clear answer to this dilemma.

In spite of all mentioned attributes the UZ of the Coastal Plain aquifer of Israel, and probably the UZ of many aquifers of the world, continue to be "no-man's land". This is largely the result of: (1) the inherent high cost of monitoring techniques in a highly heterogeneous system, (2) the difficulty in convincing water managers about the importance of a zone from which it is impossible to pump and supply water, and (3) the perception of decision makers that, in many cases, this zone will define the future of water resources and urban habitats only decades after their administrative cadence. Available evidence suggests that this may be a naive approach leading to irreversible degradation of aquifer and groundwater quality.

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