

Hydrogeochemical Processes in the Unsaturated Zone under Tropical Climate (State of São Paulo, Brazil)

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Abstract

To study the hydrogeochemical processes in the unsaturated zone under tropical climate experiments were carried out in situ and in the laboratory. The studies included hydrodynamics, variation of chemical composition of water and pollution in the unsaturated zone.

For the execution of these experiments tensiometers, extractors of water, rainwater collectors were installed, observation wells drilled and preliminary studies realized.

The results showed that the zero-flux plane, determined by tensiometric measurements, is situated at a depth of 0.50 - 1.50 m. The chemical composition of water in the unsaturated zone is controlled by the climate above the zero-flux plane and by the lithology below this plane.

With reference to the mobility of the studied polluting elements it was observed that the rate of rainfall had some influence on their leachings, however, the intensities of leachings depended on the initial concentrations present. This phenomenon was more pronounced at the beginning of the applications of the metals.

It was also observed that the retention of elements is due, principally to the presence of iron oxyhydroxides and that the concentrations are greater in the upper part of the soil. A latter mobilization might occur, depending on the quantity of infiltrating waters.

Introduction

During the infiltration of rainwater through the unsaturated zone, the chemical composition of water is constantly modified by interactions with the mineralogical constituents of rocks and soils.

The unsaturated zone, particularly in humid climatic regions is hydraulically dynamic and geochemically and biochemically very active. Recognizing that many potential groundwater pollutants originate in, are attenuated in, or are transmitted through the unsaturated zone and admitting that this zone is often cited as the preferred environment of waste disposal, a more active interest developed in studying the processes in this zone, which could ultimately result in detecting and determining geochemical barriers for the retention of pollutants.

The hydrogeochemical studies of the unsaturated zone processes have taken place mainly in countries with temperate climate in the Northern Hemisphere. The present investigations constitute the first attempts in tropical humid regions of Brazil.

Three principal lines of research were considered: hydrodynamics; variation of the chemical composition of water and pollution in the unsaturated zone.

The realization of the experiments and studies was possible by the support of several organizations: FAPESP, Mayorality of the University City, FINEP/PADCT, (CEPAS).

Materials and Methods

To carry out the proposed studies an Experimental Station was installed on the Campus of the University of São Paulo.

The sediments at the site are of the São Paulo Basin of fluvial origin, in some places lacustrine, consisting predominantly of sandstones and silty clays (HASUI & CARNEIRO, 1980). The thickness of the sediments

varies between 250-300m.

For the choice of the site, the following criteria were considered:

- the groundwater level should be neither too shallow, because in that case the unsaturated zone would be too thin for studies of variations in water composition; nor too deep which would difficult the installation of equipments (Groundwater level: ± 8.00 - ± 12.00 m).

Preliminary Determinations

Previous studies furnished the following data (mean at the site): rainfall (P): 1400 mm a⁻¹; infiltration time till the aquifer: 50 - 170 days; hydraulic conductivity (K): 10-4 cm s⁻¹, zero-flux plane: 0.50 - 1.50 m depth; grain-size: 0.002 - 0.2mm; lithology: alternating sandy, clayey, silty layers; geology: São Paulo sedimentary basin of Tertiary age. The mineralogy of the weathered sedimentary profile showed that it was composed of quartz, kaolinite, smectite, goethite and in lesser quantities muscovite and rarely microcline (SZIKSZAY & TOLEDOGROKE, 1989).

Installation of equipments and monitorings

The following equipments were installed at the site: 13 tensiometers at 50 cm intervals for the determinations of direction of water movement, till a depth of 6 m; porous cups for extracting water from the unsaturated zone (16 vertical and 7 horizontal) were also installed at 50 cm intervals till a depth of 7 m; 3 piezometers (P1, P2, PF) and 1 well (P) were drilled for sampling of water of the aquifer and a rainwater collector was placed at the site.

The physical, physico-chemical and chemical determinations were carried out weekly, during a period of 14 months both in situ and in the laboratory for the most part according to the Standard Methods for Examination of Water and Wastewater (1971).

With reference to the studies on pollution, the problem of polluting the groundwater was considered. Therefore, column samples were collected at the site for preliminary study in the laboratory. Representative samples were selected at ± 2.0 m depth with clayey and ferruginous contents. To obtain undeformed samples an apparatus was constructed, and the core samples were kept in the PVC tubes during the experiments (1 m length, 2" \varnothing). Chemical analyses were made of the core material by the Atomic Absorption Method, with results: (wt%) SiO₂ 85.56 - 92.61, Al₂O₃ 8.93 - 4.88; Fe₂O₃ 1.19 - 0.94; CaO 0.12 - 0.10; MgO 0.07 - 0.03; NaO 0.08 - 0.03; K₂O 0.19 - 0.12; P₂O₅ 0.05 - 0.03; TiO₂ 0.29 - 0.14; (in ppm): Mn 47 - 23; Pb 12 - 26; Cu <10; Ni 12 - <10; Cr 11.84 - 13.59; Zn 16.87 - 12.54; Co 1.33 - 1.2 (SZIKSZAY et al, 1992a).

Three types of solutions were prepared with concentrations of 100 ppm, 500 ppm and 1000 ppm of Zn, Co, Cu and Pb, and applied on the columns. During a period of one year 2 types of rains were applied monthly also. Type 1 - during 2 successive days 100 ml monthly; Type 2 - 100 ml for a week during 5 successive months and then during 7 months as Type 1. The percolating waters were collected for chemical analyses (SZIKSZAY et al, 1992b). Afterwards the column samples were opened and the core material analyzed also.

Results

The studies included determination of infiltration rate of rainwater and of the direction of water movement in the unsaturated zone.

The influence of the infiltrating rainwaters (determined by the artificial 3H injections) was observed 50 days after in P1 and P2 and 170 days in the well (P).

The tensiometric measurements showed that the zero-flux plane is situated at a depth of 0.50 - 1.50 m depending on the seasons. The data of these measurements were treated and represented tri-dimensionally (*Figure 1*). This showed that the hydraulic charge is smaller in all depths at spring and end of winter when there is principally evaporation, and increases in the months of January till April (rainy season) which would correspond to the recharge of the aquifer.

On *Figure 2* is shown the profile of the site with the corresponding variations (mean) with depth of chemical composition of water in the unsaturated zone. The high concentrations of the components in the upper part of the unsaturated zone is a consequence of successive processes of evaporation and infiltration. The

zero-fluxplane, indicated by the study of tensiometers, is situated at this depth. At greater depths cations exchange (Ca²⁺ for Na⁺) and adsorption takes place. The K⁺ is adsorbed and at still greater depths is furnished by the kaolinitization of detrital material (SZIKSZAY & TOLEDO-GROKE, 1989). NH₄⁺ is either adsorbed or oxidized first to NO₂, then to NO₃.

The groundwater at PF piezometer reflects the composition of water from the unsaturated zone and further downslope at (P) the chemical composition of water is characteristic of average phreatic aquifers.

On *table 1* are shown the total results obtained during a year, for the chemical analyses of percolated and collected waters of each column, referring to concentrations of Zn, Co, Cu and Pb. On the same *table 1* are also shown the elements found in the sediments before the application of the solutions and of the rains. As it can be seen not all applied elements were detected, indicating that there was retention on the solid material.

Afterwards, the core materials of the column samples were analyzed by the Atomic Absorption Method. On *table 2* are shown the Zn, Co, Cu, Pb (ppm) and Fe (wt%) content of the samples from the columns after the experiment. The results indicated that, in a general way, of the four elements the Zn was the most retained. In this experiment the following materials could be considered for retention: secondary ferruginous products, clay minerals and organic matter. As the kaolinite is a clay mineral with cation exchange capacity quite low (CEC= 3 - 15 meq/100g) and organic matter was practically absent, the ferruginous components have to be considered as the principal factors of retention (TOLEDO et al, in print). Being the cation exchange capacity of kaolinite 3-15 meq/100g and of oxyhydroxides 2-6 meq/100g, the retention was observed, in spite of this difference, on the iron hydroxide levels. In spite of the low cation exchange capacity of ferruginous products, as they are quite abundant in the region of the experiments, and not well crystallized, it can happen that these ferruginous products can also adsorb a certain quantity of metals.

Similar studies were realized by ALEXANDRE et al (in print) at a site of ±70 km distance from the city of São Paulo, on terrains of weathered schists. The results showed that the retention of Zn and Cu was due to adsorption on ferruginous hydroxides but Cu was also partially retained on organic matter. Pb mobility was influenced by infiltrating water circulation.

Conclusion

From all data obtained till now the following conclusions can be stated:

- that the rainwater infiltration is controlled, primarily by the permeability, consequently by the lithology and grain-size and secondary by the topography;
- the zero-flux plane is situated between depths of 0.50 - 1.50 m, depending on the season; the hydraulic charge is smaller at autumn, winter and spring seasons, when the evaporation occurs principally, and it is greater in the summer and beginning of autumn, when there is an infiltration corresponding to the groundwater recharge.
- the variation of the chemical composition of water in the unsaturated zone is controlled by the climate (and locally by the vegetation also) above the zero-flux plane and by the lithology below this plane, where the kaolinitization process takes place, releasing K⁺ to the waters. The variation of TDS (Total Dissolved Solids) is related not only to lithological variations but also to water dynamics.

With reference to the laboratory experiments the following observations were made with relation to the liquid phase (SZIKSZAY et al, 1992a):

- the presence of Zn and Co was detected on all percolated and collected waters with a little higher values when the 2nd rain type (more wet) was applied;
- after application of solutions there was an increase of elements in the collected waters in the first 3rd and 4th months;
- Cu was detected only when the applied concentration was highest (1000 ppm), even then, with insignificant values;
- the different rain types did not show significant changes in the mobility-;
- the Pb was not detected in any collected water in spite of being found in the sediment and

applied by the solutions.

With reference to the solid phase (TOLEDO et al, in print):

- in all columns the retention of elements was more important in the first 10 centimeters (top);
- the retention is due to the iron oxyhydroxides and not to the clays or organic matter.

Summarizing the results of experiments in regions of different lithologies and considering a climate with 1,400 mm annual rainfall and mean air temperature of 16° - 26°C, the final conclusions are, that:

- the precipitation rate of a climate is a considerable factor in water dynamics influencing the mobility of certain metals depending, however on their concentration:
- the leaching of metals is more pronounced at the beginning (first 3rd, 4th month) of the application, stabilizing afterwards;
- the retention is more important on the upper part of a soil profile depending however, on the presence or absence of retaining material (organic matter, iron hydroxides, clay minerals);
- the typical minerals in the weathered products, such as, ferruginous oxides, have greater retention power than the clay mineral kaolinite, typical of tropical climates.

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