

## Uranium and phosphate behavior in the vadose zone of a fertilized corn field

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Phosphate fertilizers contain approximately 200 mg·kg<sup>-1</sup> of uranium. The uranium and phosphate can move through the vadose zone and reach groundwater. Therefore, the knowledge of the ways in which these two elements are distributed, their partition relationships and their mobility behavior is of great interest. In order to study the latter, suction cup samplers, intended to collect soil water at different depths, were installed in an experimental site in a high plain of Mexico, where corn is cultivated and phosphate fertilizers are systematically applied. It was observed that the vadose zone contains high concentrations of uranium (1–50 mg·kg<sup>-1</sup>) and phosphates (22–33 mg·kg<sup>-1</sup>), which decrease at greater depths. Uranium concentration in the soil water varies between 10 and 3 mg·l<sup>-1</sup> and phosphates between 1 and 0.3 mg·l<sup>-1</sup>. Their evolution throughout the profile of the vadose zone is determined by the decrease in concentrations, due to the physico-chemical processes involved.

### Introduction

Phosphate fertilizers used worldwide are formed by soluble complex phosphates, which contain uranium and radium as impurities. The uranium concentration in the phosphate fertilizers used on Mexican lands ranges between 70 and 200 mg·kg<sup>-1</sup>.<sup>1</sup> These elements are capable of generating toxic effects in all the trophic levels if 2.1 mg·l<sup>-1</sup> are surpassed in soil<sup>2</sup> and 20 µg·l<sup>-1</sup> in the water supply.<sup>3</sup>

Uranium is incorporated into the soil during the phosphate fertilization process.<sup>4</sup> Phosphate fertilizers are dispersed in the soil, then dissolved by irrigation water, and finally they are carried out by the infiltration water until reaching the groundwater. These facts show that the transport mechanism in the vadose zone play an important role in the migration and redistribution of the uranium and phosphorus in soil and groundwater. Although phosphate mobility through the vadose zone has been widely studied for years,<sup>5–8</sup> that of uranium has not.<sup>9–11</sup>

To better understand the phosphate and uranium mobility through the vadose zone, it is necessary to study the chemical composition of the soil water. In this way, it should be possible to assess the risk of potential contamination of soil and groundwater in agricultural areas. In order to carry out this study, it is necessary to take soil water samples through the vadose zone profiles. For this reason, various sampling techniques, such as suction cups, lysimeters and soil assays are often used in the field.<sup>12</sup> Nowadays the most popular technique for soil water sampling is the use of porous cup suction samplers, although it is the first time that uranium sampling has been assessed. The popularity of this technique is due to the easy assembling and handling of samplers as well as its installation on the field. Furthermore, it is more dependable when getting

samples from the same point without any problems of data reproduction.<sup>13</sup>

The aim of the present work is to determine the uranium and phosphate concentration in the soil water and identify their mobility in function of the associate processes that affect them throughout the vadose zone.

### Experimental

#### Site description

The 120 m<sup>2</sup> experimental land chosen for our purpose is located in the Toluca Valley, in Central Mexico (Fig. 1). The average annual rainfall is approximately 920 mm·year<sup>-1</sup>, with a peak in July and a distinct dry season from October to April. The mean annual temperature is 15–18 °C. The surface elevation at the valley ranges from 2,500 to 2,600 m. Corn (*Zea mays sp.*) is the principal crop, grown on 90% of arable land.

In order to study the physical-chemical processes that take place during the infiltration of water through the vadose zone, the experimental site was equipped with porous ceramic suction cup samplers installed in the vadose zone, at depths of 30, 60, 90, 120, 150 and 180 cm (two samplers at each depth).

#### Activities carried out on the experimental site

Agriculture is seasonal in the Toluca Valley, so that the crops depend heavily on the rainy season. At times, however, groundwater is used for support or extra irrigation. Usually, fertilizers are applied four times a year. A mixture of fertilizer containing urea, granular triple superphosphate and potassium chloride is applied at the end of March while nitrogen fertilizer is applied in April, May and June.

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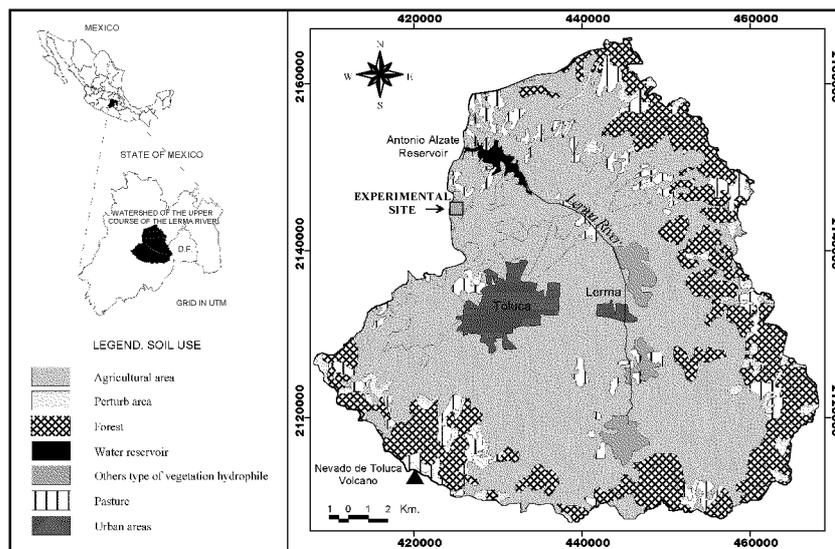


Fig. 1. Localization of the Valley of Toluca (Mexico), showing position of the experimental site

#### Sampling cups testing (phosphates and uranium)

The sampler chosen to collect the solutions is endowed with a PVC tube attached to the ceramic porous cup at one end. Thus a narrow Teflon<sup>®</sup> pipe was inserted at the other end to create vacuum and to recover the suctioned water. The main mineral components of the ceramic porous cups are gismondine (a calcium silica aluminate mineral  $\text{CaAl}_2\text{Si}_2\text{O}_8 \cdot 4\text{H}_2\text{O}$ , JCPDS card No. 20-0452),<sup>20</sup> and aluminum oxide (corundum,  $\text{Al}_2\text{O}_3$ , JCPDS card No. 43-1484),<sup>20</sup> used to increase the hardness of the cup.

The experiments to determine the uranium and phosphate recovery yield, collected in ceramic porous cups samplers, were carried out as follows:

Without previous cup treatment, the samplers were introduced in a baker with a  $100 \text{ mg} \cdot \text{l}^{-1}$  uranium solution, applying 60 cb pressure to collect the solution into the cups. After that, the sampler was again introduced into a baker with a  $100 \text{ mg} \cdot \text{l}^{-1}$  of phosphate.

Then the cups were washed with deionized water. After this, the sampler was introduced into a  $100 \text{ mg} \cdot \text{l}^{-1}$  uranium solution to collect and analyze the seep in liquid. The same process was repeated using a phosphate solution.

The cups were washed using 1M hydrochloric acid solution, then with deionized water several times, up to a 1000 ml total water volume. After finishing this operation, the sampler was submerged into a  $100 \text{ mg} \cdot \text{l}^{-1}$  uranium solution. This process was reproduced by a phosphate solution, too.

#### Sampling period

The sampling period for soil water was performed for 9 months from June 1997 to March 1998, in 6 sampling periods. Five of them were carried out after intensive rainfalls and the last one after irrigation with groundwater. A rainwater sample was taken each time when pluvial precipitation occurred. Groundwater was sampled in March 1998.

#### Soil and water sampling

Soil samples were collected at 30, 60, 90, 120, 150 and 180 cm deep levels, using a spiral auger. The collection of soil water was made after each pluvial precipitation and after irrigation by applying vacuum to the cup samplers. The rainwater samples were collected in a meteorological station, about 300 m from the experimental site. The point of sampling for the irrigation water was a deep well located in the environment of the site. The groundwater samples were taken from a well located within a 5 km radius around the site. The well sampling was carried out after a one hour pumping session.

#### Analysis of soil samples

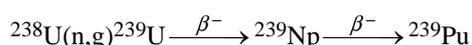
Texture, pH, electrical conductivity and organic matter content of soil samples were determined.<sup>14</sup> A mineralogical analysis by X-ray diffraction was also effected while the surface area was estimated by the BET method. Phosphate determination was achieved

according to PULIDO et al.,<sup>14</sup> using the tin chloride method. The uranium determination by neutron activation analysis (NAA) followed the methodology proposal by ROMERO et al.<sup>1</sup>

#### *Analysis of water samples*

All water samples for chemical analysis were refrigerated at 4 °C, approximately, after collection. Chemical analysis of the anions, bicarbonates, chlorides, sulfates and nitrates, as well as cations like magnesium, calcium, sodium and potassium, along with phosphate and uranium were made. The electrical conductivity, temperature and pH of water samples were measured in situ by a Checkmate<sup>®</sup> portable equipment.

The description of the analytical methods applied can be found in APHA, AWWA and WPCF (1995)<sup>15</sup> and in the Mexican norms. The alkalinity and chloride ions were determined by the titration method, sulfate by the turbidimetric method, nitrate and phosphate by UV/Vis spectrophotometry and cations by atomic absorption. The uranium content in water samples and soils was determined by NAA. Uranium purification was performed by the partition chromatographic method using di-2-ethylhexyl phosphoric acid (D2EHPA) as stationary phase, supported over polytetra fluoro ethylene beads (PTFE), where the mobile phase was a 0.6M hydrochloric acid solution. In these conditions, the uranium was retained in both IV and VI oxidations states. The solutions containing uranium and standards were introduced into polyethylene vials, then irradiated in a nuclear reactor Triga Mark III at ININ for 1 minute in a neutron flux  $10^{13} \text{ n}\cdot\text{cm}^{-2}\cdot\text{s}^{-1}$ . After irradiation the samples were left for 2–3 days to allow the formation of <sup>239</sup>Np. For this quantification the following reaction was used:



Although it emits eight characteristic energies, only those of 277, 228 and 210 keV were used for the determination of uranium, without interferences.<sup>1,16</sup> Additionally, phosphate determination was performed according to PULIDO et al.,<sup>14</sup> using the tin chloride method.

#### *Analysis of data*

The application of hydrogeochemical models, such as the NETPATH model,<sup>17</sup> is of great utility to determine and quantify each one of the physicochemical processes involved during the movement of the water through the vadose zone. This NETPATH software includes several programs: DB, WATEQF and NETPATH. The interactive DB program allows for the

storage of chemical analysis data to be used later in the WATEQF program. The WATEQF program is capable to calculate the distribution of different species in solution and to define, molalities and activities of each of the ions and the ion pairs that may be formed. It also calculates the saturation indices of all the phases defined on the input of analytical data. The results obtained are used later on by NETPATH. The NETPATH model is a program designed to define and quantify chemical reactions consistent with the initial chemical data along a flow line. To be used, it requires the chemical composition of two points situated on the same flow line and the chemical composition of the set of minerals, gases or organic compounds that represent the reactants or products of the reaction. The program calculates the mass transfer needed to justify the chemical changes observed between the two points.

In order to establish the complexes formed with uranium and phosphate in water the MEDUSA program<sup>18</sup> was used. It allows to determine the existence and prevalence of the main chemical species formed in the water system and to calculate their distribution diagram. The software has three main components. (1) HYDRA is used to create data files from equilibrium constants available in an electronic database, (2) MEDUSA (Make Equilibrium Diagrams Using Sophisticated Algorithms) is a Windows interface to the programs that calculate equilibrium diagrams from equilibrium constants in an electronic database, (3) INPUT-SED-PREDOM software package, which has three programs: INPUT: handles data-files: creation, editing, merging, etc; SED: creates fraction, logarithmic and solubility diagrams and PREDOM: creates predominance area diagrams.

## **Results and discussion**

#### *Sampling cups testing*

The results of the test are summarized in Table 1. The recovery of uranium and phosphate with cups without treatment was high: 98% for uranium and 95% for phosphate. When the cups were washed with deionized water, the uranium and phosphate recovery was, also, satisfactory.

Some authors, like TINDALL and VENCILL,<sup>19</sup> have reported that it is advisable to make a previous treatment of the cups with 1M hydrochloric acid in order to eliminate certain impurities and liberate some ions present in the cup walls in order to increase the ion recovery. In the present case, the recuperation percentage was of 91% for uranium and 94% for phosphates.

Table 1. Results of the different treatments applied to the cup samplers

Experiment	Test solution	Uranium, mg·l <sup>-1</sup>		Test solution	Phosphorus, mg·l <sup>-1</sup>	
		Collected solution	Recovery, %		Collected solution	Recovery, %
Not tried	101.3 ± 1.2	98.6 ± 2.1	98	106.2 ± 1.4	102.5 ± 2.5	95
Deionized water	100 ± 1.3	91.4 ± 1.5	91	107.1 ± 1.0	101.5 ± 1.1	94
Hydrochloric acid	100.3 ± 1.3	91.4 ± 1.5	91	107.1 ± 1.1	101.5 ± 1.1	94

Table 2. Physicochemical characteristics of vadose zone at different depths

Parameter	Unit	Depth, cm					
		0–30	30–60	60–90	90–120	120–150	150–180
Clay	%	42 ± 4	52 ± 2	62 ± 5	48 ± 3	45 ± 7	48 ± 4
Silt	%	51 ± 5	43 ± 6	36 ± 3	30 ± 8	35 ± 4	47 ± 6
Sand	%	7 ± 4	5 ± 2	2 ± 6	22 ± 3	20 ± 6	5 ± 2
Surface area	cm <sup>2</sup> ·g <sup>-1</sup>	19.3 ± 3.7	20.3 ± 2.3	53.3 ± 1.6	44.7 ± 2.1	30.6 ± 2.4	45.0 ± 1.7
pH		6.2 ± 0.1	6.4 ± 0.4	6.5 ± 0.6	7.3 ± 0.1	6.9 ± 0.1	6.7 ± 0.3
E.C.	μS·cm <sup>-1</sup>	62 ± 14	68 ± 17	97 ± 11	155 ± 20	111 ± 25	95 ± 30
Organic matter	%	0.9 ± 0.4	1.7 ± 0.7	0.5 ± 0.1	0.3 ± 0.2	0.2 ± 0.3	0.3 ± 0.2
PO <sub>4</sub> <sup>3-</sup>	mg·kg <sup>-1</sup>	30.2 ± 4.5	22.5 ± 3.8	37.4 ± 5.3	28.0 ± 4.5	22.7 ± 2.9	24.0 ± 5.1
UO <sub>2</sub> <sup>2+</sup>	mg·kg <sup>-1</sup>	31.2 ± 5.9	50.6 ± 4.7	37.0 ± 3.3	28.1 ± 4.0	15.6 ± 3.6	19.5 ± 2.4

E.C.: Electrical conductivity.

Table 3. Physicochemical characteristics of rain and irrigation waters

Sampling	Water	Date	T, °C	pH	E.C., μS·cm <sup>-1</sup>	PO <sub>4</sub> <sup>3-</sup> , mg·l <sup>-1</sup>	N-NO <sub>3</sub> , mg·l <sup>-1</sup>	SO <sub>4</sub> <sup>2-</sup> , mg·l <sup>-1</sup>	HCO <sub>3</sub> <sup>-</sup> , mg·l <sup>-1</sup>	Cl <sup>-</sup> , mg·l <sup>-1</sup>	Ca <sup>2+</sup> , mg·l <sup>-1</sup>	Mg <sup>2+</sup> , mg·l <sup>-1</sup>	Na <sup>+</sup> , mg·l <sup>-1</sup>	K <sup>+</sup> , mg·l <sup>-1</sup>	UO <sub>2</sub> <sup>2+</sup> , mg·l <sup>-1</sup>
1S	Rain	Jul/23/97	18.4	4.94	23	0.08	3.1	19	3.6	1	0.4	0.1	0.001	0.2	ND
2S	Rain	Aug/27/97	23.5	5.43	16	0.07	3.9	1	2.5	1	0.4	0.04	0.001	0.1	ND
3S	Rain	Sep/12/97	17.8	8.58	18	0.05	4.4	1	11.9	2.7	0.2	0.001	0.001	0.3	ND
4S	Rain	Sep/29/97	19.6	4.46	76	0.14	6.2	26	6.6	1	1.3	0.2	0.001	0.3	ND
5S	Rain	Oct/20/97	13.9	6.21	31	0.07	3.3	0.6	5.3	1.8	0.1	0.1	0.001	0.2	ND
6S	Groundwater	Mar/9/98	14.5	7.30	453	0.05	5.3	10	136.5	6	32.3	18.5	33.9	18.4	0.6

ND: Not detectable.

E.C.: Electrical conductivity.

### Characteristics of the vadose zone

The physicochemical characteristics of the vadose zone at different depths are shown in Table 2. The organic matter percentage ranged between 0.2 to 1.7% and the pH varied from 6.2 to 7.3. The phosphate concentration throughout the vadose zone was found to decrease with depth; the same was observed as for uranium. It is noteworthy that the uranium concentrations were relatively high, with values above 15 mg·kg<sup>-1</sup>, ten times higher than the maximum level (2.1 mg·kg<sup>-1</sup>) permissible for soils.<sup>2</sup> The values for the surface area, which are the highest in those samples with the greatest content of clay (60–90 cm deep), should also be noted. As for the mineralogy of the vadose zone, albite NaAlSi<sub>3</sub>O<sub>8</sub> (JCPDS card No. 10–0393)<sup>20</sup> and

anorthite CaAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub> (JCPDS card 20–0528)<sup>20</sup> were among the more prevalent minerals identified. The organic matter percentage ranged between 0.2 to 1.7% and the pH varied from 6.2 to 7.3.

According to the uranyl properties,<sup>24</sup> uranium is able to form organic complexes with organic matter and the uranyl species formed are strongly bound to the soil components. The uranyl concentration is directly related to the organic matter. When organic matter increases in soil, uranyl concentrations increase too and vice versa (Table 2). It is interesting to mention, that the sorption by clay minerals and the reactions with the organic compounds are most important for the migration behavior of uranyl ion. It is usually coordinated by inorganic ligands, e.g., phosphates and carbonates, when they are in a high concentration.

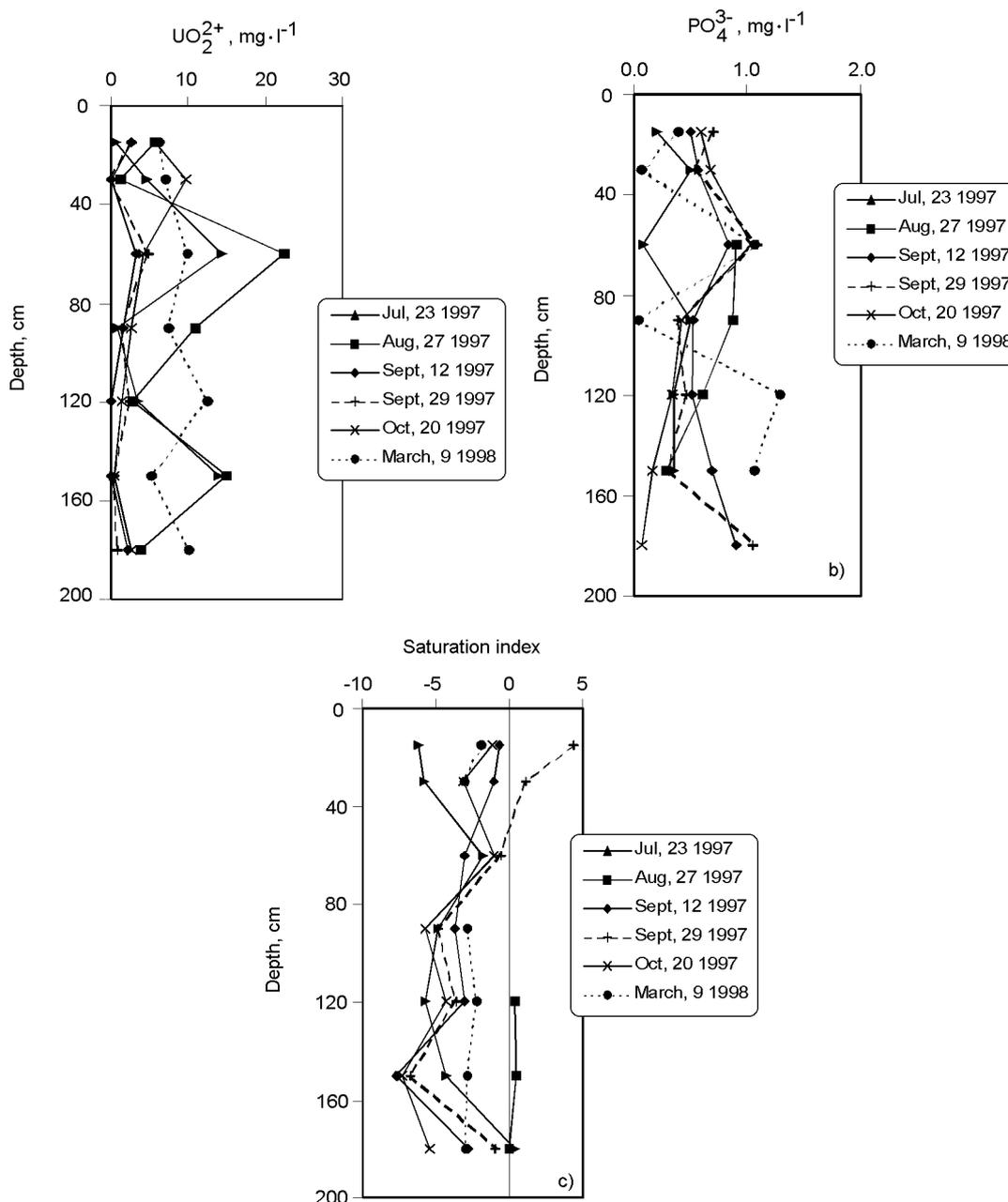


Fig. 2. Temporal evolution of the uranium concentrations in the vadose zone (a); temporal evolution of the phosphate concentrations in the vadose zone (b), and saturation index of soil water (c). Hydroxyapatite,  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$

*Physicochemical characteristics of rain and irrigation waters*

The results of the physical-chemical analyses obtained from the five rainwater samples (samplings from 1S to 5S, S=Sampling) and one sample of groundwater used for irrigation (6S) are shown in Table 3. Low salinity was detected in the rainwater; bicarbonate and calcium are the most abundant ions. On the other hand, groundwater presented a higher salinity

with high concentrations of bicarbonate, calcium and sodium. Both rainwater and groundwater are suitable for agricultural irrigation according to the Mexican water quality standards.<sup>21</sup>

*Behavior of uranium and phosphates in the vadose zone*

The contribution of uranium ions from rain and irrigation water to the subsoil turns out to be negligible (Table 3), so that the presence of uranium into the

vadose zone was owed almost exclusively to the application of the phosphate fertilizers. On this site, 198 kg·Ha<sup>-1</sup> of granular triple superphosphate was applied, which contained 198 mg of uranium and 195 g of phosphate per kg of fertilizer.<sup>1</sup>

Uranium mobility in different sampling periods is shown in Fig. 2a. During the first two periods (July and August, 1997), it can be seen that the highest content of uranium was found at two depths, 60 and 150 cm, where the values were greater than 12 mg·l<sup>-1</sup>. In subsequent samplings (except the last, of March 1998), the uranium concentration was lower throughout the whole profile of the vadose zone, reaching concentrations lower than 2 mg·l<sup>-1</sup>, below a 60 cm depth.

In the last sampling period (March, 1998), which was achieved after irrigation with groundwater, an increase in the uranium concentration was observed in the whole profile of the vadose zone. Such increase might be related to the ion dissolution, caused by the permeation of water with physicochemical characteristics widely different from those of rainwater (Table 2).

Uranium solution, mineral equilibrium, sorption process, ionic exchange, precipitation and formation of complexes and colloids control the migration of uranium.<sup>9,24</sup> The existence of uranyl complexes with organic and inorganic compounds (hydroxide, carbonate, fluoride, sulfate, nitrate and phosphate) depends on the water and vadose zone properties.

The uranium content in the soil water can be considered high, as similar contents of uranium are found only in infiltration water of uranium mines and deposits (2.6 mg·l<sup>-1</sup>)<sup>22</sup> and in the drainage of agricultural areas (2.3 mg·l<sup>-1</sup>).<sup>11</sup>

The phosphate contribution to the soil due to rain and irrigation water was minimal (Table 3). Thus, their presence can be attributed only to application of phosphate fertilizers. The mobility of phosphate throughout the profile of the vadose zone is shown in Fig. 2b. Phosphate mobility shows a similar pattern for the entire period, with a maximum depth of 60 cm, with concentrations greater than 0.7 mg·l<sup>-1</sup> and, below this depth, a progressive decrease until it reached 0.2 mg·l<sup>-1</sup>.

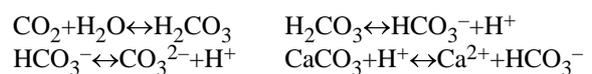
In the sampling corresponding to irrigation with groundwater, the mobility of phosphate is similar to that of the previous samples although, below a 90 cm depth, an increase in concentration was observed. The data show that approximately 90% of the phosphate remain in the soil and only a small proportion of it migrated through the vadose zone. These data match with those found by TEUSCHER and ADLER,<sup>23</sup> who reported that only 15% of the phosphorous was found in a mobile

state while the remaining 85% makes up the phosphorous reserve in the soil.

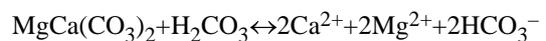
This decrease in phosphate concentration, might be basically due to the precipitation of calcium phosphates, such as apatite forms,<sup>7</sup> given that the pH is basic and calcium is present in the medium. The calculation of the hydroxyapatite saturation index of soil water (Fig. 2c) points to this precipitation process. In the first sampling (June 1997) the soil water was under-saturated with respect to hydroxyapatite and yet the soil water shows important over-saturation in the August and September sampling. This variation in saturation index is the result of the phosphate fertilizer not dissolved immediately after its application. Phosphate dissolution is very slow and begins at the moment when the pluvial precipitation begins (June and July, 1997); in this way, the precipitation process can not be taken place until the dissolution process is completed.

#### *Behavior of the principal ions*

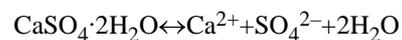
In general, the mobility of the most abundant ions throughout the vadose zone shows an increase in concentrations at a 60 cm deep level, and a decrease at lower depths (Fig. 3). The highest values at the 60 cm level could be due to a high concentration of clay material giving rise to a large superficial area, where water and solid particles come into contact, which facilitates the dissolution of minerals present. The rest of the variations detected may be the result of physico-chemical processes identified in the vadose zone, such as the precipitation-dissolution of calcite, dolomite and gypsum, ionic exchange, acid-base reactions of the carbonate equilibrium and the enrichment and loss of CO<sub>2</sub>. These physico-chemical processes are represented by:



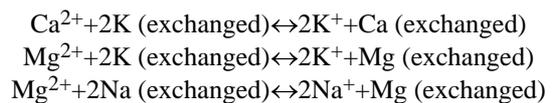
Dissolution-precipitation of calcite:



Dissolution-precipitation of dolomite:



Dissolution-precipitation of gypsum:



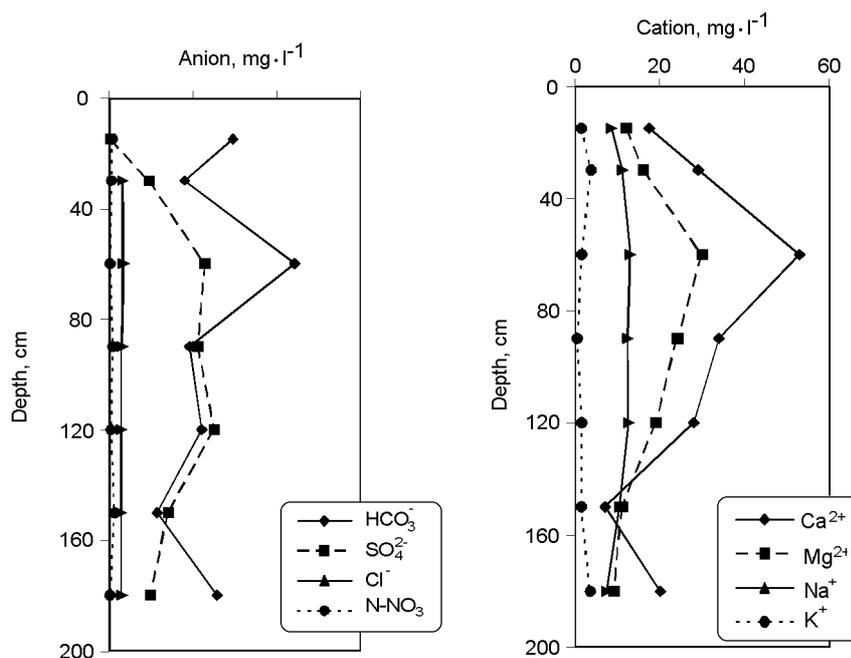


Fig. 3. Evolution of chemical characteristics in the vadose zone. September, 12, 1997

Table 4. NETPATH modeling results for sampling of July, 1997

Reaction	Depth, cm					
	0–30	30–60	60–90	90–120	120–150	150–180
Precipitation-dissolution calcite	-0.455	-0.741	-0.521	0.053	0.523	0.633
Precipitation-dissolution dolomite	0.922	0.510	-0.126	-0.005	-0.358	0.072
Precipitation-dissolution gypsum	0.481	0.342	0.229	0.014	-0.318	-0.747
Exchange Mg–Na	0.303	-0.016	0.093	0.019	-0.155	0.030
CO <sub>2</sub> gas	1.349	1.555	-0.487	0.379	-1.057	-3.492

+ dissolution, Mg fixing, CO<sub>2</sub> enrichment.

Table 5. Uranium-phosphate and uranium-carbonate species in the soil water samples

Reaction	Species
$3\text{UO}_2^{2+} + 2\text{PO}_4^{3-} \leftrightarrow (\text{UO}_2)_3(\text{PO}_4)_2(\text{C})$	Triuranyl diphosphate
$2\text{H}^+ + \text{UO}_2^{2+} + 2\text{PO}_4^{3-} \leftrightarrow \text{UO}_2(\text{HPO}_4)_2^{2-}$	Uranyl monoacid biphosphate
$\text{UO}_2^{2+} + 2\text{CO}_3^{2-} \leftrightarrow \text{UO}_2(\text{CO}_3)_2^{2-}$	Uranyl bicarbonate
$2\text{UO}_2^{2+} + \text{CO}_3^{2-} \leftrightarrow 3\text{H}^+ + (\text{UO}_2)_2(\text{OH})_3\text{CO}_3^-$	Biuranyl trihydroxylcarbonate
$\text{UO}_2^{2+} + \text{Ca}^{2+} \leftrightarrow 4\text{H}^+ + \text{CaUO}_4$	Calcium uranate

The results obtained by using the NETPATH model<sup>17</sup> (Table 4) showed that between the soil surface and a 90 cm deep stratum, the reactions that might take place are precipitation of calcite and dissolution of dolomite. The values of mass transfer show that the most important process at the topmost level of the vadose zone is the enrichment of CO<sub>2</sub>, with a maximum value of 1.5 mol·l<sup>-1</sup>, and the dolomite dissolution which amounts between 0.9 and 0.5 mol·l<sup>-1</sup>. The calcite precipitation shows values around -0.6 mol·l<sup>-1</sup>.

Below this depth, there seems to be a trend for calcite dissolution and dolomite precipitation. Calcium also

participates, together with sulfate, in the gypsum dissolution-precipitation process. There seems to be gypsum dissolution above 90 cm, which later precipitates between this depth and 180 cm. Another process found was the ionic exchange of magnesium and sodium, resulting in a fixation of magnesium. The quantification of these reactions shows that the most intensive reactions are the CO<sub>2</sub> loss (-3.5 mol·l<sup>-1</sup>), the calcite dissolution (0.6 mol·l<sup>-1</sup>) and the gypsum precipitation, with a maximum value of -0.7 mol·l<sup>-1</sup>.

The Mg-Na ionic exchange process through the vadose zone is a less important reaction, with amounts between  $-0.02$  and  $0.3 \text{ mol}\cdot\text{l}^{-1}$ . It was also noticed that potassium concentration decreased with depth, since the clay minerals allow the exchange calcium–potassium and magnesium–potassium, with a potassium fixing.

The models developed for another samplings are similar, although the amount of reactants and reaction products vary. This fact can be verified if the values obtained for each of the reactions in the sampling carried out after pluvial precipitation are compared to the values obtained after groundwater irrigation. It was observed that ions participate in greater concentrations in the reactions after irrigation with groundwater. The calcite precipitation presents values for mass transfer between  $-1.07$  and  $-0.5 \text{ mol}\cdot\text{l}^{-1}$  and the dolomite precipitation around  $-0.6 \text{ mol}\cdot\text{l}^{-1}$ . At a point 180 cm deep, the more important reactions are the gypsum precipitation ( $-1.38 \text{ mol}\cdot\text{l}^{-1}$ ) and the calcite dissolution ( $1.45 \text{ mol}\cdot\text{l}^{-1}$ ). It was also noticed that potassium concentration decreased at greater depths, since the clay minerals allow the exchange with calcium, and magnesium absorbs potassium.

Similar physico-chemical processes were identified after irrigation with groundwater. It was also observed that ions participate in greater concentrations in the reactions, in comparison with the values obtained from the samplings of soil water collected after the pluvial precipitation. These results are clearly due to the fact that the groundwater used for irrigation presents a greater mineralization.

Comparing the results under these conditions, uranyl seems to dissolve and, reacting with the inorganic ligands present in a high concentration, it appears to move depending on the species formed. For these reasons, the retention of uranium in the vadose zone in the 30–60 cm layer may be due to the organic matter content. Uranyl is able to be sorbed by or desorbed from organic matter as a function of the pH and its remobilization depends on the soil water characteristics.

#### *Modeling of uranium and phosphate behavior*

An additional process in which phosphate participates, is the formation of uranyl complexes, which were identified by the MEDUSA software<sup>18</sup> (Table 5). The results allowed to detect the formation of uranyl monoacid biphosphate  $\text{UO}_2(\text{HPO}_4)_2^{2-}$  and triuranyl diphosphate  $(\text{UO}_2)_3(\text{PO}_4)_2\cdot 4\text{H}_2\text{O}_{(c)}$ . The second compound could be found in a crystalline form, which may indicate a precipitation process. This reaction could consider another process in the retention of phosphates and uranium in the vadose zone. In addition,

the rest of the uranyl ions could participate in the formation of other complexes such as uranyl bicarbonate  $\text{UO}_2(\text{CO}_3)_2^{2-}$ , biuranyl trihydroxylcarbonate  $(\text{UO}_2)_2(\text{OH})_3\text{CO}_3^-$  and calcium uranate  $\text{CaUO}_4(c)$  (Table 5), the last one being a solid compound. Therefore, the compounds in solution may be  $\text{UO}_2(\text{CO}_3)_2^{2-}$ ,  $(\text{UO}_2)_2(\text{OH})_3\text{CO}_3^-$  and  $\text{UO}_2(\text{HPO}_4)_2^{2-}$  which might migrate through the vadose zone. Such species, as free uranyl, which did not precipitate, could be subjected to other processes. For example, the presence of clay minerals, which are cationic exchangers, must be kept in mind, as these may give rise to a sodium-uranyl exchange process.<sup>24</sup> The same minerals, in addition to the organic matter, may also produce a physical sorption process of the anionic complexes of uranyl ions.<sup>25</sup> The biological processes must be considered as well, since plants may assimilate both the uranium and the phosphorous.<sup>26</sup>

The processes that influence the mobility of these ions can not be studied in an isolated way, but they must be correlated with other physical-chemical processes that occur in the vadose zone. A particular ion in point that reacts with phosphate is calcium, which is involved in the precipitation-dissolution reactions of calcite and dolomite.

It has been shown that both the uranium and the phosphate could participate in various physical-chemical processes, involving their immobilization in the solid phase; thus, these ions are found in much higher concentrations within the vadose zone than in soil water (Table 2). Such differences indicate a high intensity in the fixation-immobilization processes. The retention of uranium in the vadose zone may be temporary, and the zone could act as a barrier only until the retention capacity is exceeded. Then the zone could act as a diffuse source due to remobilization. So, in our case, the uranyl is first retained in the 30–60 cm layer, enriched with organic matter and later the uranyl is remobilized with interstitial water, taking it to the 60–90 cm layer. The uranyl has the capacity to form many aqueous species as a result of hydrolysis and complexation reactions. The distribution of these species is highly dependent on chemical conditions, especially the pH and concentrations of complexing ligands, in this case phosphates and carbonates. Then, the sorption may be influenced by the presence of phosphates and carbonates in solution; such ligands may compete with sorption sites for the coordination of uranyl and decrease uranyl sorption by the formation of nonsorbing aqueous complexes. The latter have the capacity to move through the vadose zone reaching groundwater when the retention capacity of soil is exceeded.

The minimal presence of uranium in groundwater ( $0.6 \mu\text{g}\cdot\text{l}^{-1}$ ) shows that the process of uranium retention in the vadose zone is very efficient. It must be understood, also, that there is a multi-layered aquifer in the area under study, where there are materials of low permeability, which might act as a barrier to the infiltration of pollutants coming from agricultural activities.

### Conclusions

The sampling of soil water intended to analyze phosphate and uranium ions was performed with ceramic porous cups. The use of USA suction samplers with ceramic porous cups proved to be very suitable. A previous treatment with 1M hydrochloric acid and deionized water was required to eliminate interfering ions.

The behavior of uranium and phosphates throughout the vadose zone is a function of the properties of the soil and interstitial water. The presence of uranium in the soil water decreases with depth, and its concentration is higher in the samples taken during the months immediately after fertilization. On the other hand, the mobility speed of the phosphates in the vadose zone is determined by the decline of the ionic concentration with depth.

The processes that most affect phosphate migration in the vadose volume are physical sorption on solid particles, precipitation-dissolution of apatite, assimilation by plants and the formation of uranyl-phosphate complexes. In the case of uranium, these processes appear to be physical sorption in solid particles, the formation of complexes with calcium, phosphates and bicarbonates, the precipitation of  $\text{UO}_2(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}_{(c)}$  and  $\text{CaUO}_4_{(c)}$  and the ionic exchange.

The identified physico-chemical processes do not act in an isolated way, but rather there is an interaction among them and the participating chemical elements. These processes contribute to the fixation of ions in the soil, that is why the concentrations of phosphates and uranium are low in the groundwater.

The migration processes of phosphates and uranium are controlled by the physico-chemical characteristics of the vadose zone, by the reactions that are produced in the interstitial water and between the water and the soil, as well as by the entrance of uranium and phosphorous present in the phosphate fertilizer.

The vadose zone has high concentrations of organic matter, therefore, reactions between uranium and organic compounds can be taken place.

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