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THE POTENTIAL RISK OF GROUNDWATER CONTAMINATION BY HEAVY METALS UNDER DIFFERENT AGRICULTURAL PRACTICES

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ABSTRACT

The risk of groundwater contamination from applied heavy metals into agricultural soils was determined in monolith lysimeters containing three different soil profiles. Two different irrigation intensities and two application rates and methods (with water or directly into soil) of heavy metals (Cd, Cu, Pb, and Zn) were applied in order to investigate the leaching potential of heavy metals under different irrigation practices. During the initial stage of leaching, the applied water moved through heavy soil faster than the lighter soils when high intensity was applied. The early breakthrough of heavy metals suggested that preferential flow (influenced by soil type and irrigation intensity) was an important flow process affecting water and solute leaching. The different leachable fractions of heavy metals in the soils were highly dependant upon irrigation intensity and to a less extent upon application rate and soil type. Based on total recovery, which ranged from 0.2 to 2.2 %, the mobility order of heavy metals in this study was $Cd > Pb > Zn > Cu$ under all treatments. Organic matter and clay were suggested as the main factors for metal retention. The use of different application methods significantly contributed at different levels in the *leaching potential and the application of $CaCl_2$ increased the leaching potential of the used heavy metals especially Zinc. Thus the potential for metal contamination at a specific point in time may be represented by the amount of a metal in soil solution.*

***Keywords**: Heavy metals (Cd, Cu, Pb and Zn), leaching potential, agricultural practices, $CaCl_2$, irrigation intensity, application rate, lysimeters, organic matter, clay, soil type, leachable fractions, metal retention.*

RÉSUMÉ

Le risque de contamination des nappes phréatiques par les métaux lourds, appliqués sur différents sols a été déterminé dans des lysimètres monolithes et perturbés. Deux intensités d'irrigation et deux concentrations différentes de métaux lourds (Cd, Cu, Pb et Zn) ont été appliquées pour évaluer le potentiel de lessivage de ces métaux sous différentes pratiques culturales. Sous l'irrigation de haute intensité et durant la phase initiale du lessivage, le mouvement de l'eau a été plus rapide dans les sols lourds que dans les sols légers à cause des voies préférentielles caractérisant les sols lourds. L'apparition des métaux lourds dans l'eau drainée, au début du drainage, suggère que ces derniers ont été transportés par le flux préférentiel qui a une grande influence sur le mouvement de l'eau et des solutés dans les lysimètres monolithes. Les différentes fractions des métaux qui ont été présentes dans la solution du sol étaient fortement dépendantes de l'intensité de l'irrigation et dans une moindre importance, du taux d'application et du type du sol. La récupération totale des métaux lourds, qui a variée entre 0,2 et 2,2 %, nous donne l'ordre suivant de mobilité Cd>Pb>Zn>Cu dans tous les traitements. La matière organique humifiée et l'argile ont été considérés comme les facteurs principaux de rétention des métaux. L'utilisation de différentes méthodes d'application, comme différentes sources de contamination, a contribué significativement et à plusieurs niveaux au potentiel de lessivage des métaux lourds. L'application du $CaCl_2$ a augmenté le potentiel de lessivage des métaux utilisés surtout le zinc. Ainsi, le potentiel de contamination par les métaux à un moment donné peut-être représenté par la quantité de métaux lourds présente dans la solution du sol.

***Mots clés :** Métaux lourds (Cd, Cu, Pb and Zn), potentiel de lessivage, pratiques culturales, $CaCl_2$, intensité d'irrigation, le taux d'application, lysimètres, matière organique humifiée, argile, type du sol, solution du sol, rétention des métaux.*

INTRODUCTION

Contamination of soils by heavy metals constitutes the major environmental problem that has received much attention in recent years. The contamination by these chemicals becomes a major concern due to their potential toxic impacts on humans, animals, and plants (Purves, 1985). The main sources of heavy metals contamination of soils are impurities in fertilizers, animal manures, pesticides, sewages, atmospheric depositions, and polluted irrigation water (Cala *et al.*, 1985; Soon and Abboud, 1991; Paz-Gonzales *et al.*, 2000). Lead, cadmium, copper, and zinc, for instance, are among the most frequently observed metal contaminants (Hong *et al.,* 2001). The continuous application of heavy metals into soil may increase the concentration of these elements up to levels toxic for plant growth (Chang *et al.*, 1987) and potentially affect the health of humans and animals by using them as food sources (Berti and Jacobs, 1996).

Once heavy metals are released into soil matrix, they are likely retained in the soil matrix or leached into groundwater depending upon soil properties (Zabowski and Zasoski, 1987; Fontes *et al.*, 2000; Samaras and Kallianou, 2000), and heavy metal type (Pardo, 2000). Some studies showed evidence of the movement of heavy metals through soil profile (Dowdy *et al.,* 1991; El-Hassanin *et al.,* 1993) and the possibility of reaching the groundwater. Thus, the contamination of groundwater by heavy metals has received much attention in recent years (Pierzynski *et al.*, 1994). The maximum admissible contaminants level in potable water set by USEPA for heavy metals is between 0.002 and 5 mg/l (ATSDR, 2000).

Bekaa groundwater is exposed to contamination due to agricultural and industrial practices. Thus, the protection of these water resources from heavy metals and other chemical contamination is a high priority and there is a need to assess the environmental fate of these contaminants. The primary concern in this study is to evaluate the leaching potential of applied heavy metals, directly to soil or with irrigation water, through different soil profiles under different irrigation practices which are applied in Lebanese farming systems.

MATERIALS AND METHODS

Repacked Lysimeters

Sieved soil (≤2mm) taken from Tel Amara (clay loamy soil) was gradually filled in eight small PVC repacked lysimeters of 29.7 x 5.5 cm. Volumetric flasks were used to irrigate the lysimeters. The lysimeters were divided into two groups (1s – 4s) and (5s – 8s). Heavy metals and bromide were applied with irrigation water (1s - 4s), or directly into soil (5s – 8s) before irrigation. The same amount of all solutes was applied into all lysimeters and each lysimeter was given 1 g of bromide, 2.5 mg of Cd, 50 mg of Cu, 50 mg of Pb and 100 mg of Zn.

Four irrigation events were conducted, first one with 2 l of contaminated or uncontaminated water, the second and third irrigation with 250 ml of clean water and the last one with a 250 ml of 0.01 M $CaCl_2$. Drainage water was collected and samples were taken for bromide and heavy metals analysis.

Monolith lysimeters

Three soils - Tel Amara (TEL) (clay loamy), Torbol (TOR) (clay loamy) and Darzanoun (DAR) (clay) – were distributed in 48 monolith lysimeters, 16 for each soil and drip irrigation system was used to irrigate the lysimeters at two rates r1= 1 l/hr (low irrigation) and r2 = 2 l/hr (high irrigation).

Potassium bromide was used as tracer at two application rates of 700 and 1000 mg. The lysimeters were contaminated with two application rates of heavy metals (Tab. 1).

Table 1: Concentration of heavy metals applied to the lysimeters.

Metals	Low Application (LA)	High Application (HA)
Cadmium	0.1700 g/lysimeter	0.2500 g/lysimeter
Copper	3.500 g/lysimeter	7 g/lysimeter
Lead	1 g/lysimeter	2 g/lysimeter
Zinc	6 g/lysimeter	12 g/lysimeter

The lysimeters were irrigated before contamination and samples of drainage water were taken to detect the background level of heavy metals in soil. After contamination, 5 irrigation events with the same amount of irrigation water were applied at two different rates, indicating that the lysimeters were exposed to two different periods of irrigation events. Leachate samples were collected and recorded during and after each irrigation event. Finally, samples of drainage water were then analyzed for bromide and heavy metals content. Bromide in drainage water was analyzed using an ion meter, Delta 350, with a Jenway Bromide combination ion selective-electrode. The heavy metals analysis was done with a flame atomic absorption spectrophotometer (AAS) machine type Shimazu, AA-6800/6605 (ASC 6100 autosampler) connected to a data management system.

RESULTS AND DISCUSSION

Soil properties

The soil properties shown in table 2 revealed that there was no significant variation (*P*>0.05) in the properties for each soil between depths. DAR soil had the lowest content of sand whereas the soils taken from TOR and TEL had much less content of silt and organic matter than DAR soil.

Table 2: Physical and chemical characteristics of the used three soils.

Soil	Depth (cm)	Sand (%)	Silt (%)	Clay (%)	OM (%)	pH	CEC	CaCO3 Total ppm	CaCO3 Active ppm	Na ppm	Ca ppm	Fe ppm
DAR	0-10	8	36	52	2.8	8.4	34	45	16	100	5840	2
	10-20	8	44	48	2.8	8.4	35	45	16	80	6240	2
	20-35	8	40	50	2.7	8.4	35	45	15	110	6240	2
	35-55	8	38	50	2.6	8.4	34	43	15	100	5920	2.5
TEL	0-10	29	24	44	1	8.4	31	1	0	60	5520	1
	10-20	28	22	46	1.1	8.3	31	2	1	60	5600	1
	20-35	27	22	46	1.1	8.4	31	3	1	80	5600	1
	35-55	28	22	46	1.1	8.3	31	3	1	70	5760	1
TOR	0-10	23	22	54	1.4	8	38	2	1	100	6480	2
	10-20	23	20	54	1.5	8	37	1	1	100	6080	1
	20-35	25	20	54	1.5	8	62	3	0	90	11120	3
	35-55	24	20	54	1.3	7.9	64	3	1	110	11600	2

Leaching of heavy metals through repacked lysimeters

Table 3 showed that the total recovery of heavy metals (%) from the repacked lysimeters exposed to contaminated irrigation water was significantly, as represented by the standard errors, higher than that from lysimeters containing surface-contaminated soils. These results also showed that the relative leaching amount of Zn and Cd was much higher than that of Pb and Cu.

Table 3: Total recovery of heavy metals (%) and standard error.

		Pb	Zn	Cu	Cd
Applied with water	% Leached	0.55	2.67	0.73	2.78
Applied into soil	% Leached	0.35	1.29	0.48	1.61
	± Standard Error	0.10	0.69	0.12	0.58

The results shown in figure 1 indicated that Zn was more mobile under the applied conditions than the other metals. These results also showed that the application of exchange solution ($CaCl_2$) in the last irrigation event increased significantly ($P<0.01$) the leaching potential of Zn comparing to other metals as shown by the pattern of leaching breakthrough curves. It could be suggested that the application of $CaCl_2$ solution might have displaced the metal Zn from adsorption sites on the soil particles as stated by Barak and Helmke (1993).

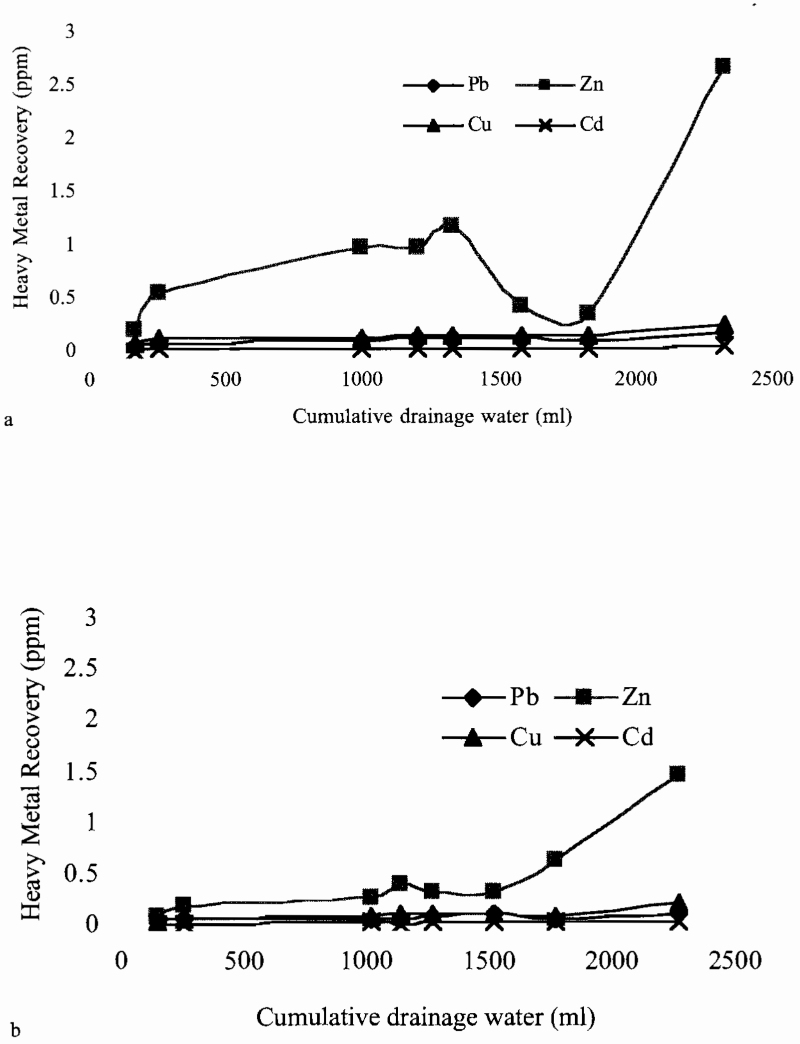

Figure 1. Breakthrough curves of the heavy metals recovery from repacked lysimeters

a: Contaminated water

b: Contaminated top soil

Drainage water

The statistical analysis showed no differences in the amount of drainage water between the lysimeters of each soil exposed to the same irrigation practice. During the first irrigation event, there was no significant variation in the amount of drainage water collected under r1 ($P>0.05$) between different soils. But there was under r2 ($P<0.05$). The variation between soils at the end of the experiment was not significant ($P>0.05$) under both irrigation practices (Fig. 2).

It was noted that more water was retained under r1 than under r2, the cumulative amount of drainage water from r2 was significantly higher ($P<0.01$) than those collected from r1. This indicated that water had moved downward through short-vertical pathways (Quisenberry and Philips, 1976; Issa *et al.*, 1996) under high irrigation intensity.

Overall, the influence of water intensity upon water movement within soils was itself influenced by soil type (water pathways and soil conditions).

Leaching of bromide

The cumulative recovered amount of bromide under different treatments is shown in table 4. These results showed that the total recovery of bromide under HA and r2 was higher than under LA and r1, respectively. The application of high irrigation intensity (r2) resulted in higher recovery of bromide from all lysimeters as total or relative amount even when low application of bromide was applied ($P<0.01$). The statistical analysis also showed that the difference between soils was stronger under treatment r1 than r2. These results suggested that irrigation intensity was more important than application rate of solutes in determining leaching potential. As bromide was detected in all leachates before saturation, the contribution of preferential flow was suggested.

Table 4: The cumulative (mg) and relative (%) amounts of recovered Br under different treatments.

Soils	LAr1	HAr1	LAr2	HAr2
DAR	320.3 (45.7 %)	462.5 (46.2%)	421.7 (60.2%)	579.7 (57.9%)
TEL	199.9 (28.5 %)	314.4 (31.4%)	560.5 (80%)	725.3 (72.5%)
TOR	365.1 (52.1%)	607.9 (60.7%)	578.2 (82.6%)	793.5 (79.5%)
Mean	*295.1*	*461.6*	*520.1*	*699*
± SE	*49.03*	*84.7*	*49.5*	*63.1*

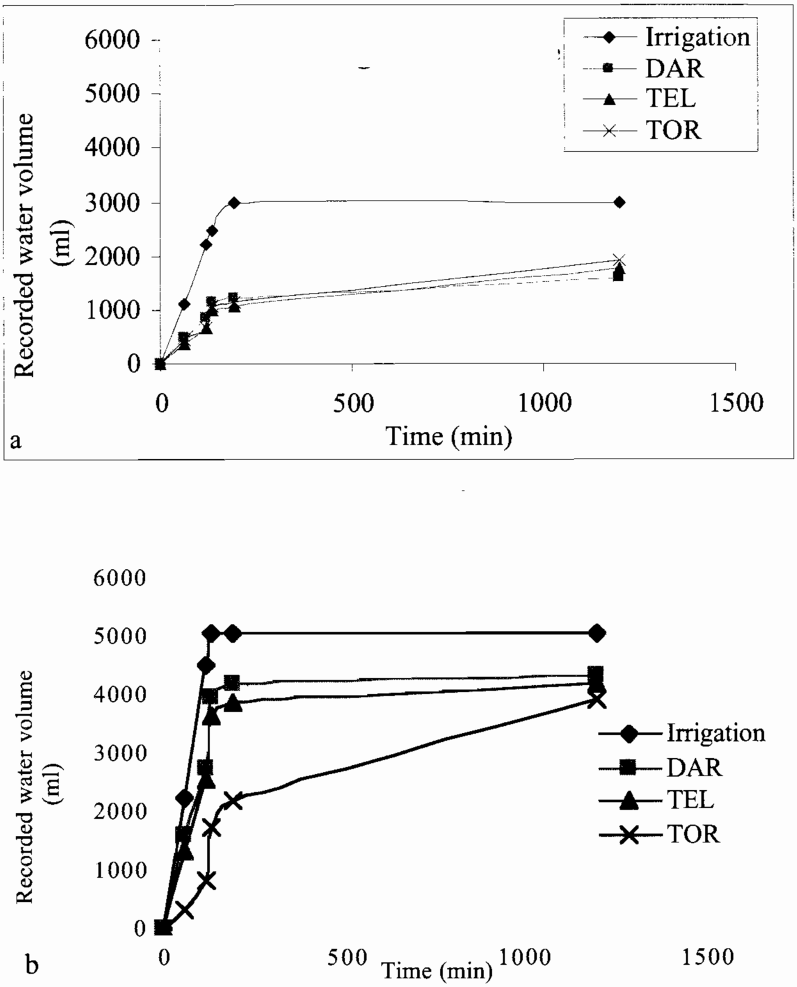

Figure 2. The cumulative drainage water collected during first irrigation event

a: Low irrigation practice

b: High irrigation practice.

Leaching of heavy metals under monolith lysimeters

Heavy metals were detected in all leachates (Fig. 3 as an example) and even before the soil got saturated which indicates the contribution of preferential flow even for solutes exposed to different degrees of adsorption. Though the pattern of leaching was similar for all soils, the relative amount of recovered heavy metal (%) might suggest that the retention rate of soils for the used heavy metal against drainage water was greatly influenced by their properties, metal type, and irrigation practices. The increase in irrigation intensity increased the flow of water through lysimeters and thereby the leaching potential of heavy metals and it was clear that soil did not need to be saturated for irrigation water to move rapidly through macropore as reported by Radulovich *et al.* (1992), and Issa *et al.* (1996). The recovery from HA lysimeters under r1 and r2 were much higher than LA in agreement with Taylor and Griffin, (1981). However, the relative leaching rate revealed that LAr2>HAr1, indicating the importance of irrigation practice. Thus, preferential flow appeared to be the main mechanism contributing to rapid solute leaching (Camobreco *et al.,* 1996).

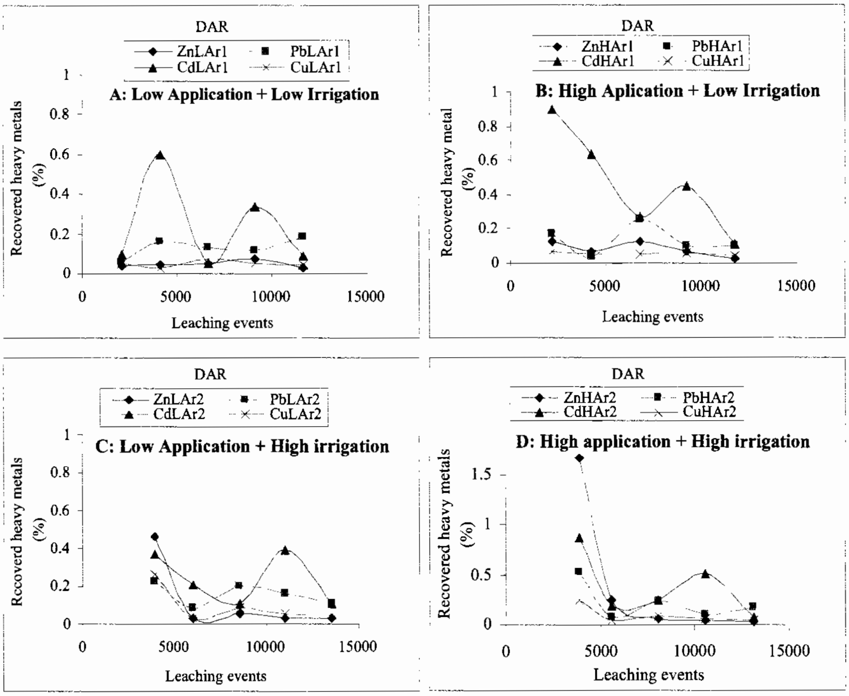

Figure 3. The relative amount (%) of leached heavy metals from DAR soils exposed to different agricultural practices.

The order of heavy metals based upon their recovery was similar for all treatments Zn>Pb>Cd>Cu (Table 5) in agreement for Zn but not for Pb with the works of Li and Shuman (1996) and Han *et al.* (2001). The used heavy metals varied significantly ($0.001<P<0.05$) in their leaching rate as percentage of the initial applied amount from each treatment. It can be seen that the soils differed in their leaching potential for each metal under each treatment (Tab. 5). The variation between metals under each treatment was also clearly observed in this study.

The leaching order of heavy metals under all treatments Cd>Pb>Zn>Cu was more likely related to the adsorption capacity of the used metals than to solubility order Zn>Cu>Pb>Cd (Shen and Stevenson, 1986; Han *et al.*, 2001). The variation between heavy metals in their correlation with drainage water might suggest that the soil solution of the used soil had different amounts of free metals despite the same initial amount applied and the same amount of water (Tab. 6). Thus, the leaching potential of a metal at a specific point in time is represented by the amount in soil solution, supporting the former suggestion about the role of adsorption capacity upon the leaching potential.

Table 5: The total relative amounts (%) of heavy metals recovered in drainage water.

	Zn	**Pb**	**Cd**	**Cu**	**Mean**	**± SE**	**Leaching order**
DAR-LAr1	0.231	0.652	1.165	0.249	0.574	0.219	Cd>Pb>Cu≥Zn
TEL-LAr1	0.218	0.609	1.312	0.249	0.597	0.254	Cd>Pb>Cu>Zn
TOR-LAr1	0.297	0.524	1.312	0.265	0.599	0.244	Cd>Pb>Zn>Cu
Mean	0.249	0.595	1.263	0.255			
± SE	0.024	0.037	0.049	0.005			
	Zn	**Pb**	**Cd**	**Cu**	**Mean**	**± SE**	
DAR-HAr1	0.211	0.330	1.184	0.137	0.466	0.242	Cd>Pb>Zn>Cu
TEL-HAr1	0.622	0.455	0.878	0.145	0.385	0.167	Cd>Zn>Pb>Cu
TOR-HAr1	0.213	0.310	0.878	0.139	0.385	0.167	Cd>Pb>Zn>Cu
Mean	0.349	0.365	0.980	0.140			
± SE	0.136	0.045	0.102	0.002			
	Zn	**Pb**	**Cd**	**Cu**	**Mean**	**± SE**	
DAR-LAr2	0.604	0.784	1.175	0.478	0.760	0.151	Cd>Pb>Zn>Cu
TEL-LAr2	0.668	0.855	2.198	0.478	1.050	0.390	Cd>Pb>Zn>Cu
TOR-LAr2	1.609	0.836	1.432	0.398	1.069	0.278	Zn>Cd>Pb>Cu
Mean	0.960	0.825	1.602	0.452			
± SE	0.324	0.021	0.307	0.026			
	Zn	**Pb**	**Cd**	**Cu**	**Mean**	**± SE**	
DAR-HAr2	1.027	0.551	0.945	0.241	0.691	0.182	Zn>Cd>Pb>Cu
TEL-HAr2	0.52	0.553	0.879	0.241	0.551	0.130	Cd>Pb>Zn>Cu
TOR-HAr2	0.574	0.466	0.908	0.204	0.538	0.145	Cd>Zn>Pb>Cu
Mean	0.710	0.523	0.911	0.229			
± SE	0.159	0.028	0.019	0.012			

Table 6: Correlation between drainage water and heavy metal recovery (%).

DAR soils	*Correlation*	TEL soils	*Correlation*	TOR soils	*Correlation*
ZnLAr1	0.887	ZnLAr1	0.803	ZnLAr1	0.748
PbLAr1	0.946	PbLAr1	0.725	PbLAr1	0.947
CdLAr1	0.406	CdLAr1	0.459	CdLAr1	0.420
CuLAr1	0.915	CuLAr1	0.921	CuLAr1	0.870
ZnHAr1	0.703	ZnHAr1	0.283	ZnLAr2	-0.161
PbHAr1	0.805	PbHAr1	0.694	PbLAr2	0.877
CdHAr1	0.320	CdHAr1	0.507	CdLAr2	0.531
CuHAr1	0.811	CuHAr1	0.738	CuLAr2	0.765
ZnLAr2	-0.039	ZnLAr2	-0.183	ZnHAr1	0.382
PbLAr2	-0.054	PbLAr2	0.950	PbHAr1	0.687
CdLAr2	-0.333	CdLAr2	0.195	CdHAr1	0.538
CuLAr2	0.020	CuLAr2	0.580	CuHAr1	0.854
ZnHAr2	-0.114	ZnHAr2	0.165	ZnHAr2	-0.233
PbHAr2	-0.443	PbHAr2	0.668	PbHAr2	0.807
CdHAr2	-0.312	CdHAr2	0.703	CdHAr2	0.618
CuHAr2	-0.054	CuHAr2	0.605	CuHAr2	0.795

CONCLUSION

The applied water moved through the monolith lysimeters of different soils below the root zone before the soil surfaces became saturated. The velocity of percolating water was related to soil type and irrigation intensity.

The applied solutes (Br and 4 heavy metals) to the soil surface of each lysimeter were recovered in the first leachate shortly after the application of irrigation water, and in all leachates collected throughout the study.

This rapid movement was suggested as a result of preferential flow through macropores. The contribution of preferential flow varied with the applied treatments and the conditions of this study. The contribution of matrix flow was much smaller than that of preferential flow especially at initial stage.

The breakthrough curves of each treatment showed peaks and valleys especially during the initial stage of leaching, indicating that different fractions of the applied heavy metals at the time of irrigation event had the potential for leaching. Each fraction was a function of each applied treatment.

Soil types significantly affected the mobility of applied metals during initial stages of irrigation. The high content of organic matter and fine particles of clay can be suggested as the main factors for metal retention and, as a consequence, the available fraction of metals for leaching.

Although 0.2 to 2.2 % of the total applied amount was recovered in drainage water, the leaching potential of these metals may represent a significant risk for groundwater quality.

Based on total recovery, Cd was the most available metal for leaching, followed by Pb and Zn, while Cu was the least mobile metal under all treatments.

The order of total relative recovery did not significantly vary between treatments, suggesting that the application practices and soil properties were not likely being sufficient to assess the ranking order of heavy metals. Thus, the hydraulic parameters, especially water flow velocity were more likely important in determining the leaching potential and explaining the variability in the leaching curves.

Heavy metals were likely to impose more risk for groundwater contamination when applied with irrigation water as wastewater than when applied with solid materials.

Overall, the release of heavy metals into the environment might be followed by very complex series of events, which could transport the heavy metals through soil profiles into unsaturated and saturated zones (groundwater). Despite this complexity and the presence of significant gaps in the knowledge of heavy metals movement and fate in the environment, it was possible to identify situations that could pose concern and thereby minimize unnecessary release of heavy metals into the environment for more safety and less risk.

It is necessary to enforce regulations and implement practices in order to reduce the risk of groundwater contamination.

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