

EXPERIMENTAL MODELLING OF THE TRACE ELEMENTS DISTRIBUTION BETWEEN THE PARTICULATE AND LIQUID PHASES OF THE RUN-OFF*

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Changes in distribution of As, Cd, Cu, Pb, and Zn between the solution and particulate matter of the run-off with time were studied in dependence on pH of the model system. Fine fraction of three types of the run-off was employed in the laboratory experiments. The type A was prepared in a laboratory from soil extremely contaminated by trace metals. The other two types were collected in the field, both from uncontaminated regions: the type B from acidic soil, and C from soil with higher buffering capacity. Laboratory experiments were arranged to cover the time span of equilibration of 1 and 2 weeks, respectively. Experiments with heavily contaminated particulate matter were characterized with fast initial step of equilibration resulting in high concentration of elements in solution, which was followed by further gradual and slow increase of their dissolved forms with time. Higher content of dissolved forms of elements was found in suspensions with higher pH value. On the other hand, experiments with the uncontaminated run-off types confirmed the significance of fine soil fraction for the fixation of reactive dissolved forms of contaminants in surface waters. Experiments also proved the significance of Fe- and Mn-hydrated oxides for the fixation of trace elements in surface waters.

soil; contamination; run-off; particulate- and liquid phases; trace elements; distribution

INTRODUCTION

The erosion run-off is often the most important process of the trace element transport between the soil cover and the surface water. If the study is focused on the toxic trace elements, then the knowledge of their speciation

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I. Essential chemical and physical characteristics of the applied experimental run-off

Content oxide	Run-off A	Run-off B	Run-off C
	%	%	%
SiO ₂	66.91	64.36	66.00
TiO ₂	0.78	0.80	0.61
Al ₂ O ₃	10.75	13.68	10.50
Fe ₂ O ₃	2.65	3.23	3.70
FeO	0.58	1.32	–
MgO	0.68	2.09	1.18
CaO	0.53	1.84	2.90
Na ₂ O	1.91	2.69	0.94
K ₂ O	1.59	1.49	2.18
P ₂ O ₅	0.33	0.23	0.28
C _{org}	12.74	7.94	–
Ignition loss	–	–	10.57
Element	ppm	ppm	ppm
As	128	5.54	15.1
Cd	9.47	0.142	0.34
Cu	56	8.53	26.8
Fe	2.30%	3.29%	–
Mn	1330	518.8	794.0
Pb	1455	16.1	21.3
Zn	632	59.7	70.4
Se	205	–	–
Sb	89.3	–	–
T _{mchl} , mmol/100 g	17.8	14.7	15.2
S (base)	15.3	5.7	15.2
V (sat.) %	86.0	38.8	100.0
H ⁺ exch.	2.5	9.0	–2.5
Grain size			
Phys. clay %	8.6	10.2	
< 0.01	35.0	46.0	
0.01–0.05 %	28.0	45.9	
0.05–0.25 %	26.0	8.0	
> 0.25 %	11.0	0.1	

wet precipitation in Central Bohemia. Bulk chemical composition, pH and initial content of studied trace elements (in the case of experiments with the uncontaminated run-off, see later) are given in the Table II. (Contents of SO₄²⁻ and NO₃⁻ were proportionally higher, when the solution was acidified by a mixture of sulfuric and nitric acids.) Density of all sets of suspensions expressed as V/m (ratio of their volume in cm³ to the mass of the d.w. solid matter in g) was 1000, time span of the individual sets of experiments was 10 min to 7 days, in the case of the contaminated run-off A to 14 days. Separation of phases of the individual batch after the selected equilibration time was carried out by centrifugation (Janetzki, type T 24, former GDR) and by membrane filtration using the Sartorius Filter Holder (type SM16510, FRG) through the nitrocellulose membrane filters with pore size 0.45 μm. Resulting pH of the batch was then measured in part of the filtrate with portable pH-meter WTW (type pH-91, FRG), whereas the remaining liquid sample was stabilized by

II. Bulk chemical composition, trace element content and pH of the experimental "contaminated" rainwater (R₀). Equilibrium concentrations of the studied trace elements and pH in both types of the experimental run-off (B₀, C₀)

Element / ion	Concentration (ppb)		
	R ₀	B ₀	C ₀
Na	370		
K	300		
Ca	400		
Mg	80		
NH ₄	700		
SO ₄	3400		
NO ₃	2600		
Cl	770		
As	100		
Cd	9.5	< 0.05	< 0.04
Cu	20.9	< 0.5	< 0.5
Fe	< 30	340	< 30
Mn	< 0.2	100	3.6
Pb	130	< 0.5	< 0.5
Zn	260	8	< 8
pH	4.44	5.79	7.35

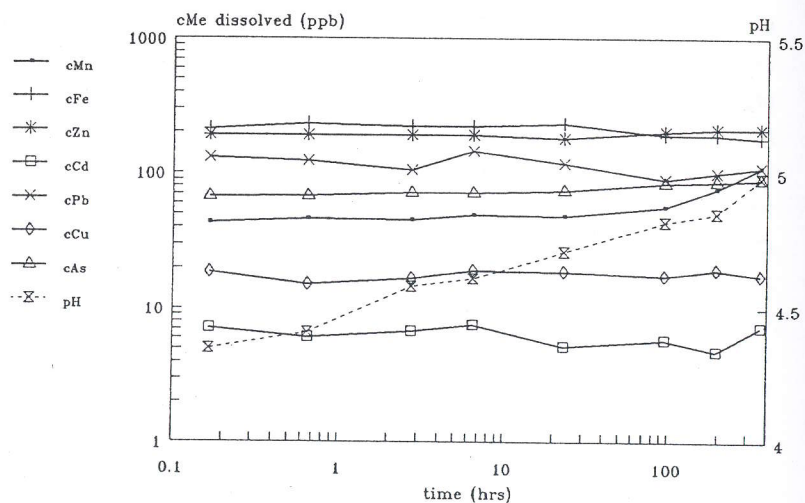
diluted (22% v/v) HNO₃ (Merck, Suprapur, FRG), 1 ml of acid per 100ml of sample, and stored in a cooler at +4 °C until its analysis by the AA Spectrometry (Varian SpectrAA 300 Spectrometer, USA). Mn, Fe, and Zn were determined by flame-, Cd, Cu, and Pb by graphite furnace-, and As by hydride generation procedures.

RESULTS AND DISCUSSION

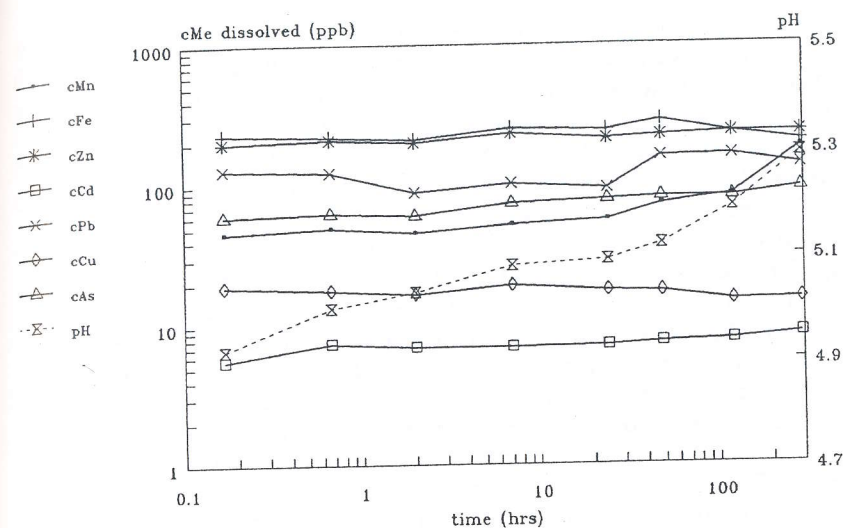
Experiments with strongly contaminated run-off

The first series of experiments with heavily contaminated experimental run-off (type A) should provide information on temporal changes in the distribution of its contaminants when it is in contact with surface water of various initial pH. The course of gradual changes in concentrations of the dissolved forms of studied elements is shown in Figs. 1 to 3. Each Fig. displays results of one set of equilibration experiments with equal initial pH of the system. The initial values were chosen to cover the acidic pH range which may occur in real environmental conditions.

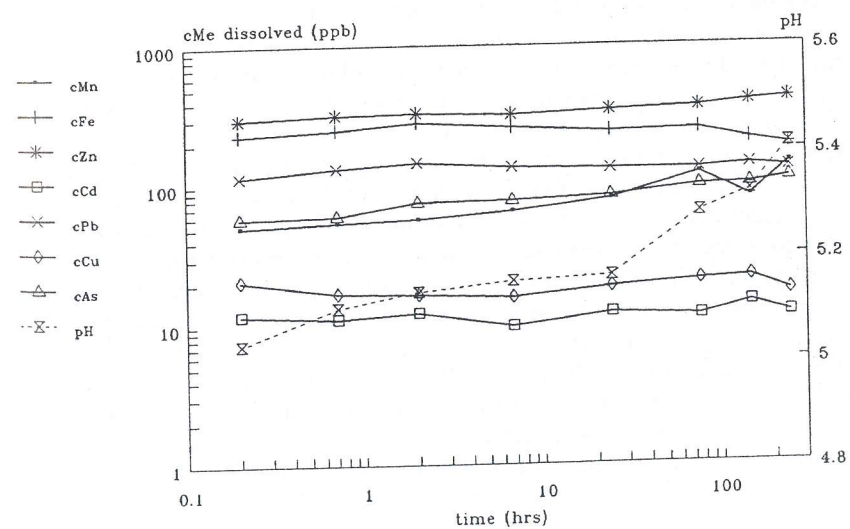
The course of pH of the system and its final value indicate low buffering capacity of the particulate matter, which is in agreement with its bulk chemical composition (see the Table I). The gradual increase in pH of the system



1. Contaminated run-off A desorption of Mn, Fe, Zn, Cd, Pb, Cu, As (pH R₀ = 3.71)



2. Contaminated run-off A desorption of Mn, Fe, Zn, Cd, Pb, Cu, As (pH R₀ = 4.28)



3. Contaminated run-off A desorption of Mn, Fe, Zn, Cd, Pb, Cu, As (pH R₀ = 4.85)

proceeds throughout the whole time span of the individual experiments. This documents the slow rate of reactions establishing the equilibrium pH, which is here probably affected also by the biological activity of microorganisms which are always present in a system containing the natural matter. On the other hand, the rate of distribution of all studied elements between the solid and liquid phases is high, as the equilibrium is principally established during the first ten minutes of the experiment.

Course of the distribution of studied trace elements between the solid and liquid phases is significantly affected by forms of Fe and Mn in the solid matter; their hydrated oxides act as phases fixing the trace elements from solution. The course for both Fe and Mn at various initial pH's of the system is shown together with the trace elements in Figs. 1, 2, and 3. Concentration of dissolved Fe initially increases and later sinks, whereas in the case of Mn it is persistently growing. The described distribution course of these two elements is primarily affected by two simultaneously changing factors: the pH and Eh of the system. Concentration of the positively charged hydroxylated species of Fe (and Mn) in solution decreases with increasing pH of the system, which should be accompanied by the overall decreasing solubility of these elements. On the other hand, the solubility of Fe and Mn is strongly affected by the Eh value of the system.

Towards the end of each experiment, in the course of supposed gradual and moderate decrease of Eh, Mn coatings from the surface of the solid phase were reduced and dissolved, while Fe(III) species were not reduced yet. Initial moderate growth of Fe content in solution can be explained by the significantly differing reaction rates of processes determining the distribution of Fe between the liquid and solid phases: Dissolution of the amorphous surface coatings which is caused by the decrease in pH of the system, creation of new sorption centers after the hydration of the crystalline phases etc. The subsequent decrease of dissolved Fe in the course of growing pH can be explained by the gradual decrease in solubility of its forms in higher oxidation state.

Distribution of examined trace elements throughout the time span of laboratory experiments has to be studied in context with the gradual growth of pH and with respect to the above described behavior of Fe and Mn. Among the other studied trace elements, only the concentration of dissolved arsenic is significantly and steadily growing throughout all the three presented experiments. Behavior of As is determined by the anionic character of its As(III) and As(V) oxidation states, which is reflected in their affinity to the positively charged surfaces, such as ferric oxyhydroxides (Pierce, Moore, 1982; Skřivan, Hladíková, 1987; Howell 1994), and by the commonly occurring transformation of these oxidation states, which significantly differ in their physical-chemical properties. The following common features, nevertheless,

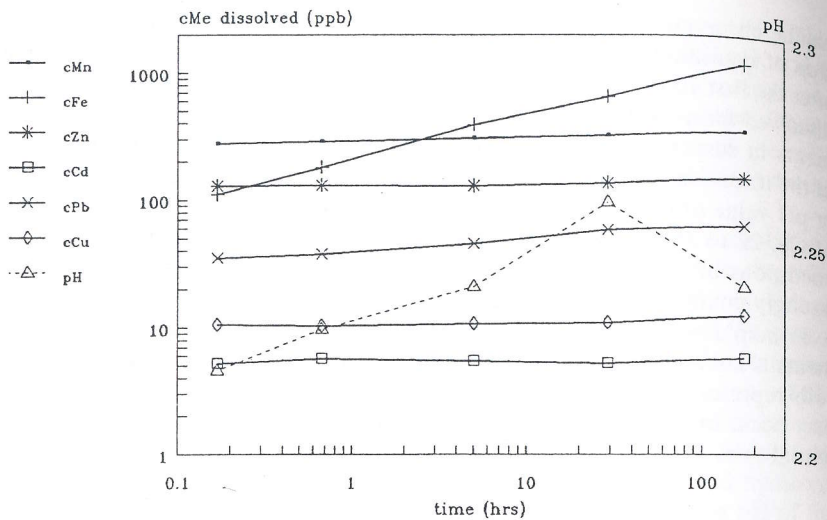
can be observed in the behavior of studied trace elements: 1. Very fast initial step of equilibration resulting in high concentration of elements in solution after the first 10 minutes, 2. Prevailing gradual increase in concentration of their dissolved forms with time, 3. Rather higher content of dissolved forms of elements in suspensions with higher pH value, and 4. Commonly high content of the trace contaminants in solution, without regard to the age of suspensions or pH value of the system: approximately 25 to 60% of As, 40% of Cd, 35% of Cu, 22 to 38% of Zn, and 6 to 9% of Pb are in solution under the chosen conditions of experiments, which means that the sorption capacity of such a strongly contaminated run-off is to a large extent limited.

Principal piece of information following from the presented sets of experiments is not encouraging: run-off originating in areas with such contaminated soils represents serious hazard for the corresponding surface streams, as there may occur high concentrations of toxic trace elements in solution after a torrential rain.

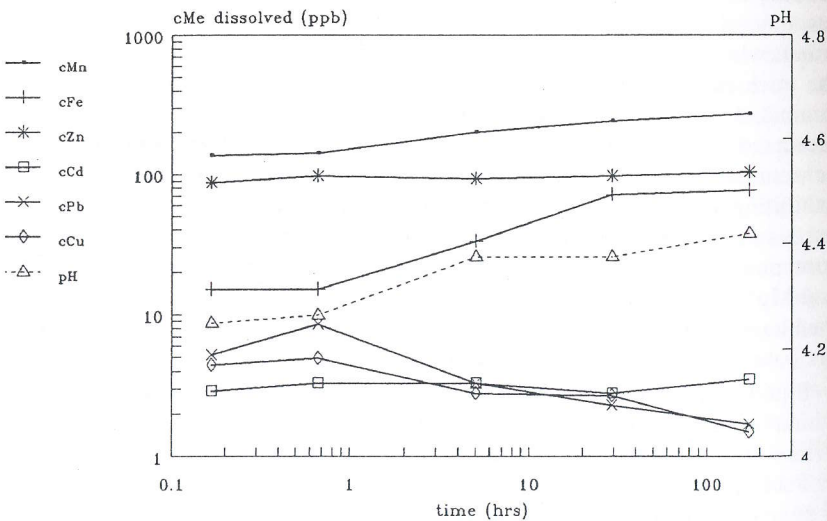
Experiments with uncontaminated run-off

Experiments with both the types of this experimental material should simulate the interaction of relatively pure particulate matter of the run-off (with low natural content of studied trace elements mainly of lithogenic origin) with water, whose bulk chemical composition was donated by a certain amount of the trace elements. Liquid phase represents, in this case, a moderately contaminated surface stream or rainwater (solution R_0 whose composition is presented in Table II). Trace elements Cd, Cu, Pb, and Zn were chosen as contaminants for laboratory experiments with two types of solid phase exhibiting different buffering capacity. This characteristics reflects differences in the chemical composition of both the types of material. Surprisingly, content of base metals in the run-off B and C (first of all the content of Ca and Mg) is almost the same. Variations in the buffering capacity (see below) then have to be attributed to various degree of reactivity of the forms in which the base metals are present in the solid phase.

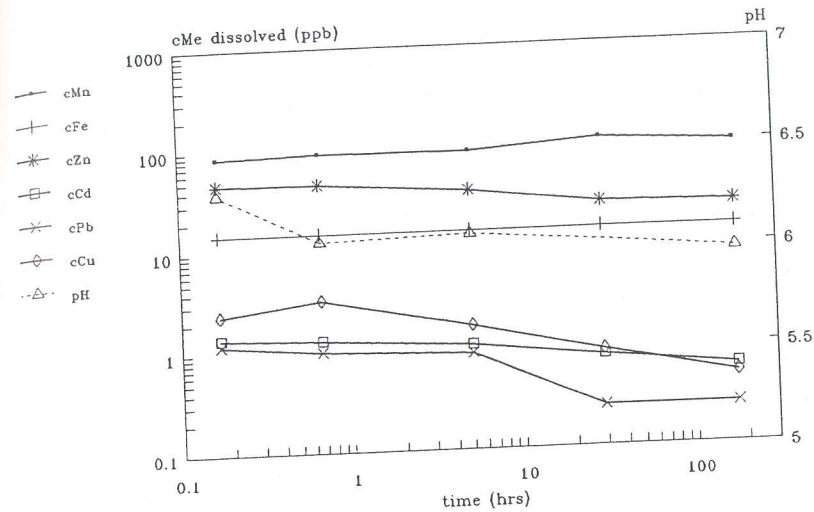
Equilibrium concentrations of trace elements dissolved from the solid phases which were immersed into the bidistilled water (24 hrs. of equilibration, $V/m = 500$), together with the resulting pH of the suspensions, are also shown in Table II (values for B_0 and C_0). Results of the experiments – course of the change of concentration of all the studied elements with time at varying initial pH of the experimental suspensions – are presented in the diagrams (Figs. 4 to 6 show results of experiments with the run-off B and Figs. 7 to 9 with the run-off C). Thin lines depict the concentrations of dissolved elements which



4. Uncontaminated run-off B desorption of Mn, Fe, Zn, Cd, Pb, Cu, As (pH R₀ = 1.98)



5. Uncontaminated run-off B desorption of Mn, Fe, Zn, Cd, Pb, Cu, As (pH R₀ = 3.76)

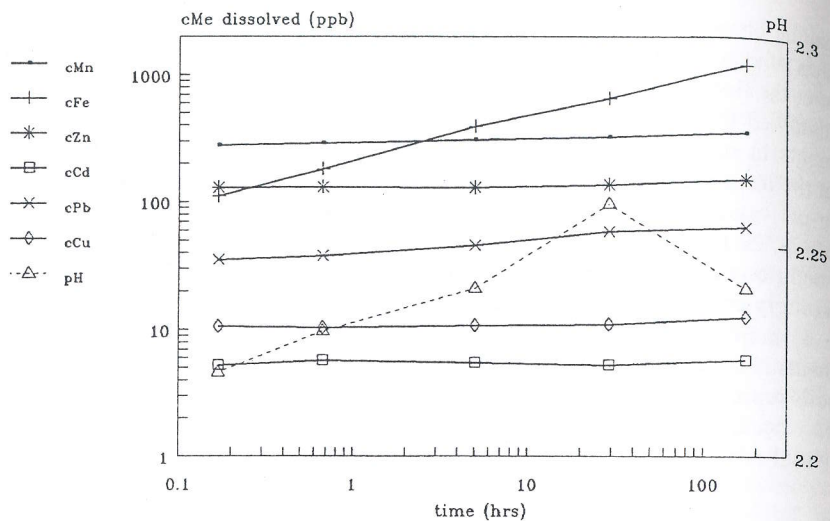


6. Uncontaminated run-off B desorption of Mn, Fe, Zn, Cd, Pb, Cu, As (pH R₀ = 6.80)

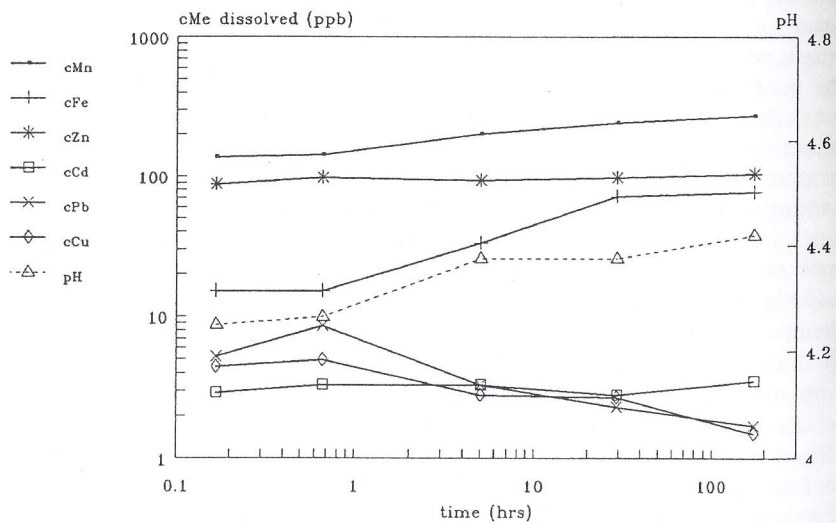
were below the detection limit of the analysis throughout the whole time span of the experiment.

Considerable differences between these two types of experimental run-off follow first of all from the course of pH values of the individual sets of experiments: The B type has very low, and the C type, on the opposite, high buffering capacity. The pH values of suspensions containing the B type run-off follow the chosen initial values for R₀ and they are only moderately increasing (for R₀ = 6.80 they are even decreasing). On the other hand, the pH values of suspensions containing the C type run-off are immediately and significantly increasing for all presented initial pH values, with except of the initial value of R₀ = 2.02, where the buffering capacity of the solid matter (at given value of V/m) is already exhausted. This principal characteristics of both the types of suspensions significantly affects the course of interactions taking place on the interface of the particulate- and liquid phases.

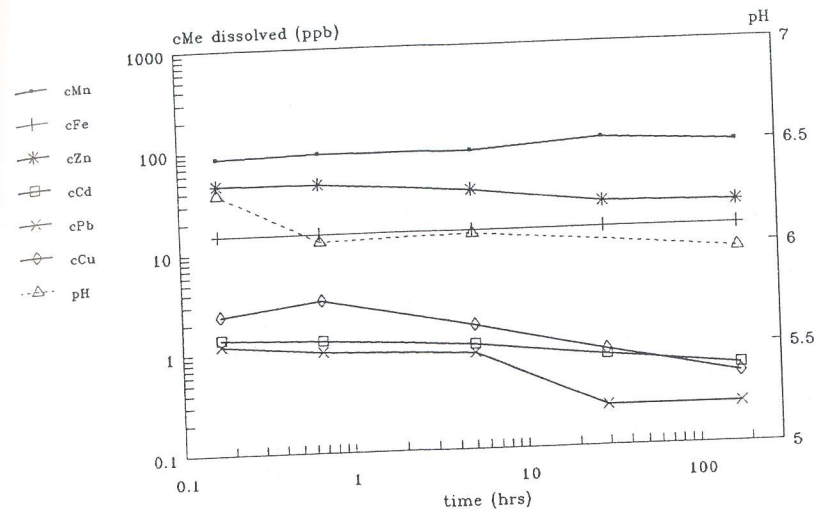
Course of the distribution of Fe and Mn between the solid and liquid phases is again of considerable importance in the studied systems, as these two elements in form of their oxyhydroxides represent important solid phases in the adsorption/fixation process of a number of trace elements from the corresponding solutions. Concentration of dissolved Fe was always below the detection limit (30 µg.L⁻¹) in suspensions with actual pH value higher than 5.0. Desorption/dissolution of Fe from suspensions containing the experimen-



4. Uncontaminated run-off B desorption of Mn, Fe, Zn, Cd, Pb, Cu, As (pH $R_0 = 1.98$)



5. Uncontaminated run-off B desorption of Mn, Fe, Zn, Cd, Pb, Cu, As (pH $R_0 = 3.76$)

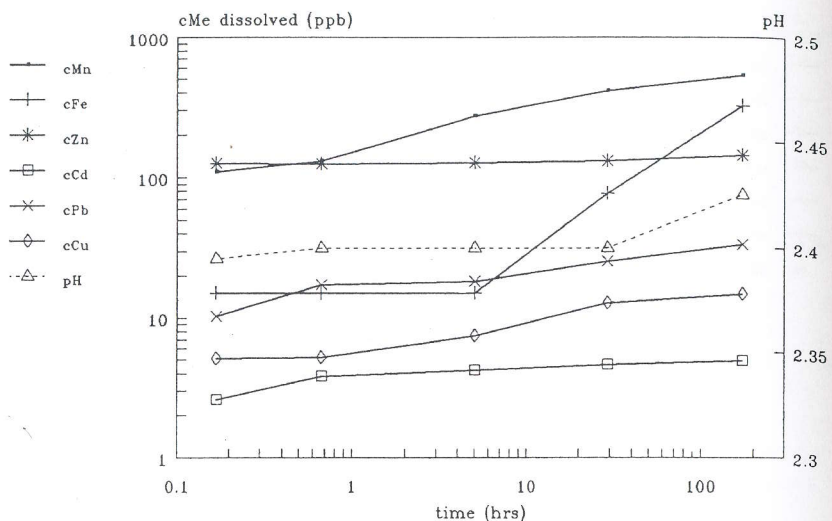


6. Uncontaminated run-off B desorption of Mn, Fe, Zn, Cd, Pb, Cu, As (pH $R_0 = 6.80$)

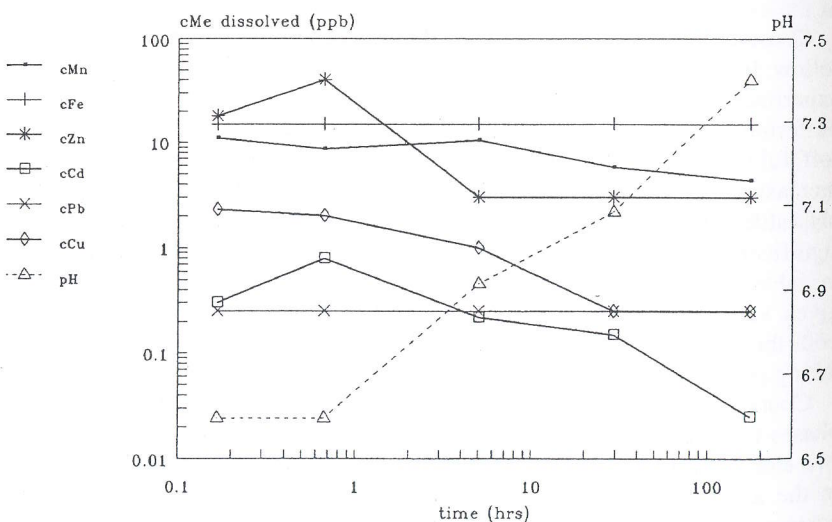
were below the detection limit of the analysis throughout the whole time span of the experiment.

Considerable differences between these two types of experimental run-off follow first of all from the course of pH values of the individual sets of experiments: The B type has very low, and the C type, on the opposite, high buffering capacity. The pH values of suspensions containing the B type run-off follow the chosen initial values for R_0 and they are only moderately increasing (for $R_0 = 6.80$ they are even decreasing). On the other hand, the pH values of suspensions containing the C type run-off are immediately and significantly increasing for all presented initial pH values, with except of the initial value of $R_0 = 2.02$, where the buffering capacity of the solid matter (at given value of V/m) is already exhausted. This principal characteristics of both the types of suspensions significantly affects the course of interactions taking place on the interface of the particulate- and liquid phases.

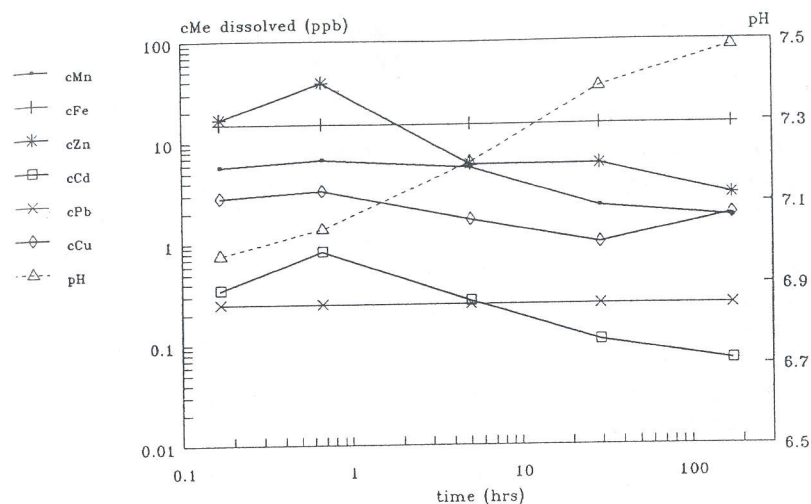
Course of the distribution of Fe and Mn between the solid and liquid phases is again of considerable importance in the studied systems, as these two elements in form of their oxyhydroxides represent important solid phases in the adsorption/fixation process of a number of trace elements from the corresponding solutions. Concentration of dissolved Fe was always below the detection limit ($30 \mu\text{g}\cdot\text{L}^{-1}$) in suspensions with actual pH value higher than 5.0. Desorption/dissolution of Fe from suspensions containing the experimen-



7. Uncontaminated run-off C desorption of Mn, Fe, Zn, Cd, Pb, Cu, As (pH $R_0 = 2.02$)



8. Uncontaminated run-off C desorption of Mn, Fe, Zn, Cd, Pb, Cu, As (pH $R_0 = 3.72$)



9. Uncontaminated run-off C desorption of Mn, Fe, Zn, Cd, Pb, Cu, As (pH $R_0 = 4.52$)

tal run-off type C occurred only at pH < 2.5, and after more than 24 hrs. of equilibration. On the other hand, content of Mn in solution is affected – besides the concentration of H^+ ions – by even moderate decrease of Eh of the suspension which could be induced by microbial activity. This factor complicates indeed the course of curves for Mn. Nevertheless, the concentration of manganese, together with concentrations of studied “contaminants” (Cd, Cu, Pb, Zn) decreases in principal with increasing pH of the suspensions (Mn only at pH > 7, the other elements already at pH > 4–5), throughout the examined time span of equilibration. Suspensions prepared from both types of the run-off (B and C) with pH < 3 are characterized by gradual increase of the dissolved forms of all the studied “contaminant” elements.

Results of the presented laboratory experiments with uncontaminated particulate matter of the run-off proved again, that substantial changes in the distribution of elements between the solid and liquid phases take place during the short initial stage of the experiment. The time interval between the preparation of suspension with selected parameters (at $t = 0$) and the first separation step (after the first 10 min. of equilibration), even in such diluted suspensions (with $V/m = 1000$), is the most important. This is documented not only by the initial significant changes in pH, but also by differences of the evaluated concentration of elements in solution at $t = 0$ and the determined concentrations at $t = 10$ min and after one week, at the end of the individual experiment.

Suspensions with low pH value show initial decrease in concentration of dissolved trace elements, which is followed by the gradual concentration increase, caused by the repeated desorption of elements from the solid phase. This phenomenon can be explained by gradual degradation of the solid surface through partial dissolution of its components, which results in the lowering amount of the active sorption centers. The explanation is in agreement with the observations of Takamura et al. (1989), Borovec (1997) and others. Gradual increase in concentration of dissolved Mn could serve as a proof of the active role of Mn- oxyhydroxides in the sorption processes, as the negative charge developing in aqueous environment on their surface creates favorable conditions for the fixation of cations and their complexes from the liquid phase.

Results of experiments with the run-off obtained from uncontaminated soils with good buffering capacity confirm the significance of the fine soil fraction for the fixation of mobile forms of toxic elements (contaminants) which could occur in surface waters.

CONCLUSIONS

Distribution of selected toxic trace elements between the heavily contaminated particulate matter of the experimental run-off and aqueous phase under various pH's is characterized by a fast initial step resulting in considerably increased concentrations of elements in solution after the first 10 minutes of the experiment. This is followed by further gradual and slow increase in concentration of their dissolved forms with time. Higher content of dissolved forms of elements was found in suspensions with higher pH value. On the other hand, experiments with both types of the uncontaminated run-off (exhibiting low or high buffering capacity) and water containing enhanced concentrations of the studied elements were also characterized by a rapid step of equilibration, resulting in considerably decreased concentrations of elements in solution and in extensive pH changes of the system. This step is again followed by a slow gradual increase of the dissolved forms of all the studied elements in solution. Partition of Fe and Mn, which is affected (except for the suspension pH value) also by its Eh, considerably affects the distribution of the trace elements. This fact is explained by the significance of Fe- and Mn- hydrated oxides for the fixation of trace elements in surface waters.

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Experimentální modelování distribuce stopových prvků mezi tuhou a kapalnou fází smyvu.

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Byly studovány časové změny v distribuci As, Cd, Cu, Pb a Zn mezi kapalnou a tuhou fází smyvu v závislosti na pH modelového systému. K laboratorním experimentům byly použity jemné frakce tří rozdílných typů smyvu. Typ A byl připraven v laboratoři z půdy extrémně kontaminované stopovými kovy. Druhé dva typy byly odebrány v terénu, oba z nekontaminovaných oblastí: typ B z kyselých půd, typ C z půd s vyšší pufrací kapacitou. Laboratorní experimenty byly uspořádány tak, aby pokryly ustavení rovnováhy v časovém rozpětí jednoho, event. dvou týdnů. Experimenty se silně kontaminovanými částicemi smyvu byly charakterizovány rychlým uvolněním prvků z tuhé do kapalně fáze, po němž následovalo další postupné a pomalé zvyšování koncentrace prvků v roztoku. Vyšší obsah rozpustných forem prvků byl nalezen v suspenzích o vyšším pH. Experimenty s nekontaminovanými smyvami naopak potvrdily význam jemné půdní frakce pro fixaci reaktivních rozpuštěných forem kontaminantů v povrchových vodách. Experimenty zároveň prokázaly významnou roli hydratovaných oxidů Fe a Mn pro fixaci sledovaných stopových elementů tuhou fází.

půda; kontaminace; smyv; kapalná a tuhá fáze; stopové prvky; smyv

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