

Determination of in situ Metal Partitioning Between Particulate Matter and Groundwater

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Mobile particulate matter in groundwater is the main carrier of transition metals in aquifers [1–4]. Here we report on the in situ partitioning of Ag, Al, Cu, Cd, Fe, Mn, Pb and Zn between carbonate, oxide and organic fractions of particulate matter and groundwater in an aquifer contaminated by industrial effluents. Samples were collected from an observation well which is cased with polyvinyl chloride screens and drilled through a thin loess veneer into the Eocene chalk aquifer of southern Israel. The water table is 15 m beneath the surface.

A multi-layer sampler [5] (Fig. 1) was used to collect groundwater and particulate matter. The particulate matter composed of loess ranging in grain size from 0.1 to 5 μm mainly, was deposited on the sampler during the 30 days it was left in the well. These particulates were subsequently rinsed off of four separate segments of the 2-m sampler with ultra-high purity water. Appropriate care was taken to avoid contamination [6, 7].

Particulates were treated sequentially with three chemical extractants [8, 9];

the extracts operationally represent metals in the carbonate, oxide and organic fractions. Groundwater and extracts were analyzed for metals by both flame and furnace atomic absorption spectroscopy. Spike recoveries for all analyses ranged between 90–110%. Percent carbonate and organic matter in each sample was determined by thermal gravimetric analysis, and percent oxide was calculated from Al, Fe and Mn concentrations [9]. The chemical characteristics of the water profile are shown in Fig. 2.

Figure 3 shows that particulate matter from the uppermost sampling interval is distinctly enriched in many metals: the trend is demonstrated by Cu, Pb and Zn in all fractions, Cd and Mn in oxide and organic fractions, and Ag in the oxide fraction. Aluminium noticeably increases with depth for the oxide fraction. The profiles of dissolved metals in groundwater (Fig. 4) show that metals are distributed homogeneously downwell for Ag, Cu and Fe, but surface-enriched for Al, Cd, Zn. Dissolved-metal concentrations were averaged for four depth intervals corresponding to the four separate

sampling intervals for particulate matter. The partition coefficient (K), for each depth interval, is here defined as

$$K = \frac{M_{\text{solid}}}{M_{\text{solution}}}$$

where M_{solid} is the metal content for a specific fraction (carbonate, oxide, organic) expressed in $\text{mg M} \times (\text{kg dry sample})^{-1} \times (\text{percent weight of the fraction})^{-1}$. The percent weight of the fractions is given in the legend to Fig. 5. The average partition coefficients, depicted in Fig. 5, are essentially homogeneous across the bottom three depth intervals (46–180 cm depth range). The largest variation used in averaging was a factor of 5, but most were within a factor of 2 or less. Carbonate partition coefficients are the smallest of the three fractions and range between 10^3 and 10^4 , while oxide and organic partition coefficients together form two groups, one in the 10^4 – 10^5 range and one in the 10^6 – 10^7 range. The partitioning of metals into carbonate is greatest for Cd and Pb, both of which are most stable in water in the carbonate form [10, 11], however, there is still an order of magnitude less partitioning of Cd and Pb to carbonate

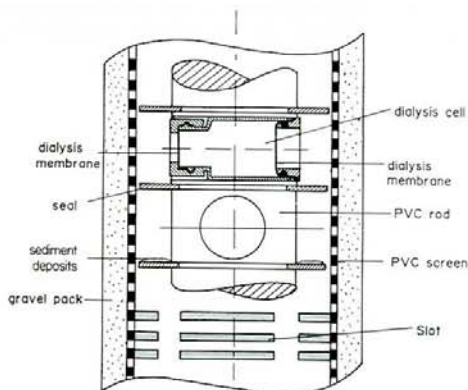


Fig. 1. Schematic diagram showing the multi-layer water sampler positioned in the research well and the area on which groundwater particulates are deposited. For simplicity, slots are shown only on the lower part of the PVC screen

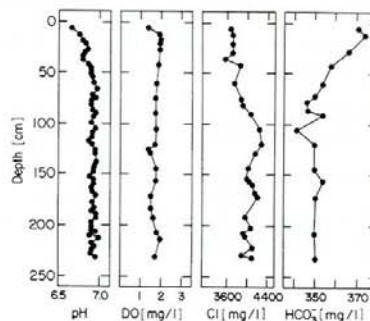


Fig. 2. Chemical characteristics of the water profile. Cl^- was analyzed by ion chromatography, dissolved inorganic carbon (HCO_3^-) by titration, dissolved oxygen with a DO probe and pH with a stick pH meter. HCO_3^- , DO and pH were determined in the field. Note that the HCO_3^- decrease from 370 to 350 mg l^{-1} at a depth of 70 cm is correlated to the concomitant increase of pH from 6.7 to 6.9. The DO content indicates undersaturation relative to the expected equilibria concentrations at 22 °C (8.7 mg l^{-1})

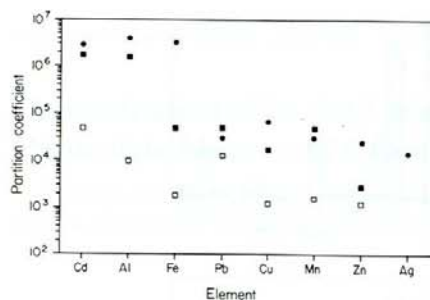


Fig. 5. Partition coefficients (K) for metals in three particulate matter fractions relative to water. Sediment concentrations used in this calculation are metal per gram carbonate (□), oxide (●) or organic matter (■), where the percent weight of each is given for the sampling intervals 1–45, 46–90, 91–135 and 136–180 cm, respectively. Thus, carbonate 22, 15, 13, 12; oxide 1.3, 0.97, 1.1, 1.5; organic 1.0, 0.89, 0.89, 1.1

than to oxides or organics. Oxides and organics show an almost identical degree of partitioning except for Fe and Zn. As weathering products of clays and principle colloid components [12, 13], Fe and Al are not surprisingly enriched up to several million times in oxides.

Partition coefficients for the 0–45 cm depth interval were lower for Al in all three fractions, and for Cd in the carbonate fraction and higher for Cu and Pb in oxide and organic fractions. One obvious reason for this is the proximity to the water table, which is a dynamic interface where solution and particles arriving from the unsaturated zone interact with those of the saturated zone. Redox potential and organic matter content may change greatly across this interface [14]. Moreover, pH and the concentrations of Cl^- and HCO_3^- at the water table region differ greatly from those found in deeper horizons (Fig. 2). Changes in the above conditions effect reactions such as dissolution/precipitation and adsorption/desorption [4, 14]. If these reactions occur rapidly, we do not expect the partition coefficients at the 0–45 cm depth interval to be different than those observed in the deeper parts (46–180 cm depth) of the aquifer.

Thus for Al and Cd in the fractions mentioned, there is removal downwell to the solid phase from the noted surface enrichment in water (Fig. 4), while Cu and Pb are concomitantly released from the solid phase to groundwater. Removal of Al and Cd can be explained by an increase in pH across the interface. Aluminium is very sensitive to pH [15] and change to ligand concentrations, and hence it is removed from solution in all fractions, whereas Cd is suggested to be removed primarily in the carbonate fraction [10, 11]. It is also suggested that Cu and Pb are desorbed from oxides and organic matter as a result of an increase in ionic strength and/or ligands in solution [16]. These results imply that Cu and Pb are transported through the unsaturated zone adsorbed on particulate matter and upon arrival at the water table are subsequently released into groundwater. In the studied samples carbonate averages 15% of the bulk solid, oxides and organics both amount to no more than 1.5%; most of the remainder is fine crystalline quartz. This is a dramatic indication that large amounts of potentially labile and toxic metals [4] in the environment are partitioned into a very small part of the particulate phase.

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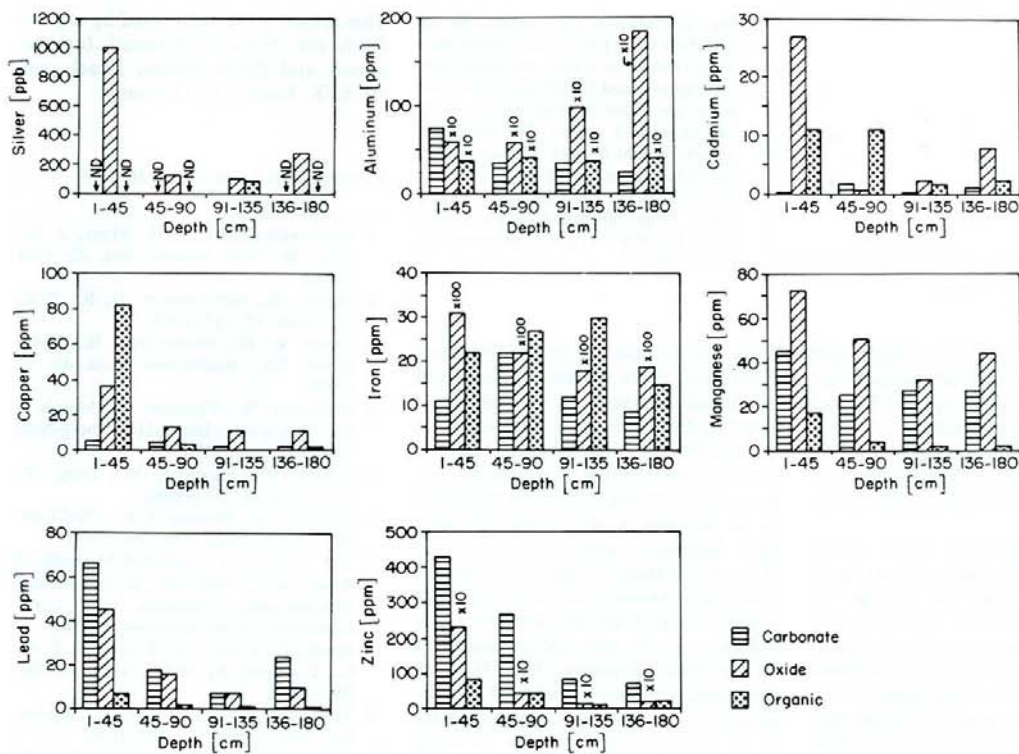


Fig. 3. Metal concentrations in carbonate, oxide and organic particulate matter fractions of four samples from different depth intervals. Chemical extractants for each fraction are listed in the sequence used: a) sodium acetate buffered to pH 5 with acetic acid (carbonate extraction), b) sodium thiosulfate, sodium citrate and citric acid at 96°C (oxide extraction) and c) 30% hydrogen peroxide (organic extraction) [8]. Concentrations are reported per gram bulk sample and hence reflect relative partitioning of metals between each fraction

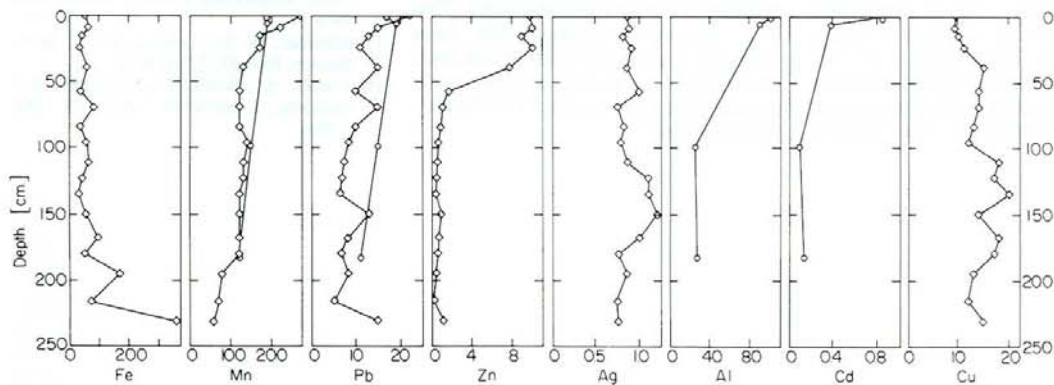


Fig. 4. Profiles of dissolved metals from two sampling dates 1 month apart, denoted separately by diamonds and circles. Groundwater samples were collected by using the dialysis cell sampling methodology [5] (Fig. 1) with 0.2 μm pore size nylon membranes and acidified to pH < 2 before analysis. Metal concentration is given in ppb except Zn in ppm. Note that those metals which have determinations for both dates, show no change in distribution