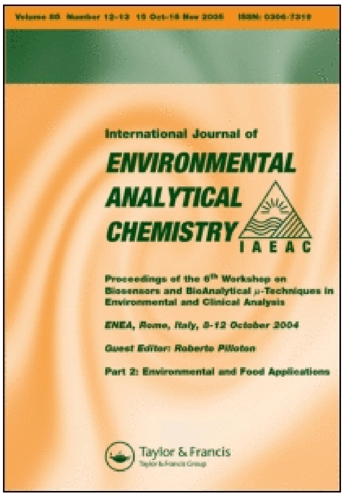

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BEHAVIOUR AND FATE OF POLLUTANTS IN RAINWATER SEEPAGE

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Within the framework of an integrated project of the Federal Ministry of Research and Technology, the behaviour and fate of inorganic and organic rainwater components were examined at two seepage sites in Berlin. The findings are given for Pücklerpfuhl in Berlin-Dahlem, the catchment area of which is characterised by a relatively high volume of traffic.

It was found, that the low salt infiltration water dilutes the more salty groundwater flow. Furthermore, the sludge sediment layer of the seepage pond proved to be a trap which prevents both heavy metals and organic pollutants from reaching the groundwater. Radionuclide measurements undertaken in parallel with the pollutant investigations made it possible to chronologically classify the pollutant discharges over the last four decades. This revealed that statutory measures to limit and reduce pollutants clearly had an effect and did reduce environmental pollution.

KEY WORDS: Rainwater, sewage sludge, groundwater, infiltration, heavy metal, PCB, PAH.

INTRODUCTION

Between 1989 and 1992 the Federal Ministry of Research supported an integrated project which focused on the various aspects of rainfall seepage and its effect on subsoil and groundwater[1]. The Institute for Water, Soil and Air Hygiene was assigned the task of investigating the behaviour and fate of selected rainwater components at two central seepage sites[2]. In co-operation with the Berlin Water Authorities, the Pücklerpfuhl seepage pond in Berlin-Dahlem and the Spekte seepage basin in Berlin-Spandau were selected. In contrast to the Spekte basin, a catchment area which is characterised by a residential area with open buildings and allotments with a normal volume of traffic, the Pücklerpfuhl catchment, (115 hectares in size) has several mainroads with a relatively high volume of traffic, e. g. the main traffic route, Clayallee, alone with up to 4.500 vehicles per day (Figure 1). Once the differences in the preliminary investigations had been confirmed with respect to pollutant contamination, the Pücklerpfuhl location was given priority in the further investigations; the findings obtained are listed below.

In order to observe the path of the substances concerned, samples were examined from rainfall or street gulleys, surface water in Pücklerpfuhl, upstream and downstream flows

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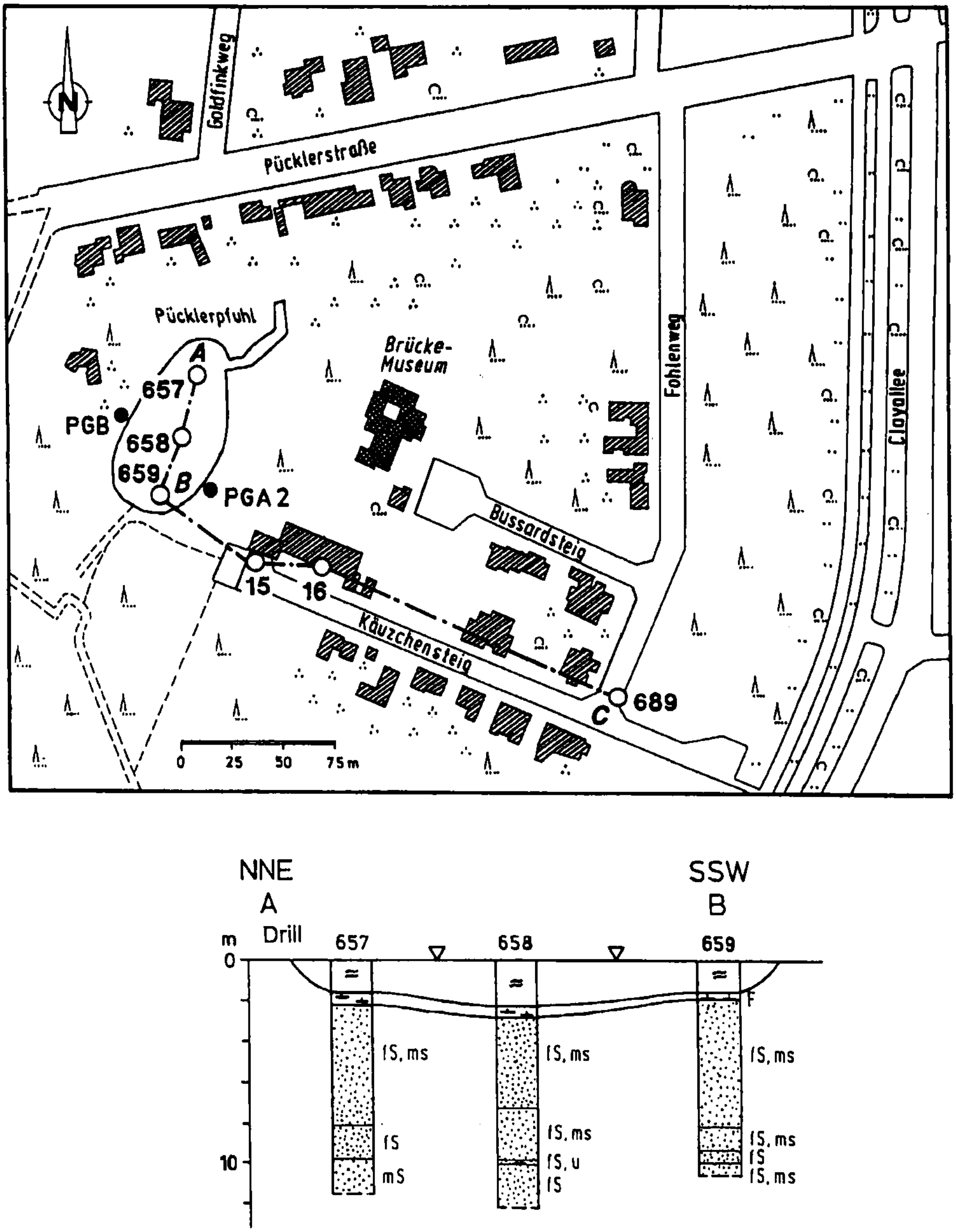

Figure 1 Location and geological profile of the rainwater seepage basin, Pücklerpfuhl in Berlin-Dahlem.

of groundwater, the sludge sediment layer of the Pfuhl, and the deeper fine sandy to medium sandy sediment layers.

Earlier examinations of road runoff in the city of Giessen/Hesse (Gäth, Sternheim and Frede)[3] and from a municipal catchment area in the city of Bayreuth/Bavaria (Kari, and Herrmann)[4] had shown relatively high concentrations of lead, copper, benzo(a)pyrene and PCB in rainwater runoff.

Therefore, at least these substances with a remarkable toxic potential had to be taken into our analytical programme which was expanded by determining further elements and organic compounds of environmental significance for rainwater infiltration.

EXPERIMENTAL

Analytical procedues

Water and sediment samples were characterised according to their physical properties (pH-value, conductivity, oxygen content, temperature), the sum parameters dissolved organic carbon (DOC) and adsorbable organohalogen compounds (AOX), the heavy metals of environmental relevance – lead, cadmium, copper, nickel, zinc-and organic substances such as highly volatile halogenated hydrocarbons, aromatic and aliphatic compounds originating from fuels, polychlorinated biphenyls (PCB) and organochloropesticides as well as polycyclic aromatic hydrocarbons (PAH).

The physico-chemical characterization of the water and sediment samples followed the German standard methods (DIN methods).

The anions were determined by ion chromatography (Dionex D 12/column HPLC AS 3), the cations by atomic emission spectrometry with inductively coupled plasma (ICP-AES Philips PV 8490) or ICP mass spectrometry (Fisons Plasmaquad 2 plus).

PCB, organochloropesticides and PAH were analyzed by means of a specially developed preparation method, simultaneous steam distillation extraction (SDE), and clean-up by adsorption column chromatography. The PCB and chloropesticides were identified and quantifed by splitless injection onto two different polar capillary columns using high resolution gas chromatography and two electron capture detectors (ECD).

Hereby the following preparation and conditions were used: 20 g sediment/sludge or 1 l H_2O were extracted with 100 ml hexane(4 h SDE) and the extract concentrated to 2 ml. The concentrated extract (1 ml) was purified on a silica gel/$AgNO_3$ column and was eluted with 60 ml of hexane to separate the PCB and with 80 ml hexane/ether (95:5 v/v) to separate the organochloropesticides. Another 1 ml of the extract was purified on alumina (Super I B) column and was eluted with 60 ml hexane/dichloromethane (80:20 v/v) for subsequent determination of the PAH.

The analytical conditions for the first fraction were the following:

Apparatus	: Hewlett-Packard GC/HP-5890 ll
Column	: Fused silica, 30 m, 0.25 mm i.d., 0,2 μm film thickness, HT-5 and HP-17
Carrier gas	: He, pressure 150 kPa
Temperature programme	: 1 min 60° C, 20°/min to 150° C, 3°/min to 270° C
Detection	: ECD/ECD 320° C
Injection	: 2 μl splitless KAS 3

The total amount of PCB was calculated by adding the six single PCB congeners IUPAC Nos. 28, 52, 101, 138,153,180, according to DIN 51 527 Part 1, and then multiplying by a factor of 5 in accordance with the German Waste Oil Regulation (AltölV).

The PAH were separated by means of high pressure liquid chromatography (Waters 600) using a Supelcosil column (LC-PAH 25 cm × 4,6 mm i.d., 5 μm diameter particles) and gradient elution with water/acetonitrile. A UV diode array detector (Waters 990) was used to identify and a fluorescence detector to quantify them[5]. The diode array detector is useful for qualitative and quantitative analysis of PAH in soil samples in the nanogram range, whereas the fluorescence detector is recommended for the analysis of PAH from water samples in the picogram range. The highest sensitivity can be obtained only when the excitation and emission wavelengths have been optimizid for the individual PAH.

In the evaluation, the total amount of PAH was calculated according to in the German Drinking Water Regulation (TrinkwV).

Water sampling

Water samples from the stormwater runoff were taken manually from an open outlet pipe ND 80 at the stormwater collecting and infiltration pool (Pücklerpfuhl) using corresponding glass and plastic vessels. Investigation wells (5,08 cm internal diameter) with a final depth of 18 m were brought down direct upstream and downstream in the groundwater flow of the infiltration pond to examine groundwater quality. In order to observe the background contamination of the saturated soil zone in the area under study, groundwater observation wells of the Senat of Berlin (PGA 1 in Figure 3), positioned upstream of the seepage site, were included in the sampling strategy.

In order to obtain infiltration water samples from the unsaturated soil layer below Pücklerpfuhl[2] bottom ceramic suction candles were installed at soil depths of 1, 1.5 and 2 m.

A RUTTNER dipper was used to collect samples from the surface water of the pool site.

Samples were taken once a month from the groundwater measurement points using a fully encapsulated COMBI-COMET submerged pump. Prior to sampling, water was pumped from the wells for ca. 15 minutes while in a special vessel, electrical conductivity and pH-value were continually monitored. This led to information on a sufficient pumping time, necessary for constant groundwater conditions. When electrical conductivity and pH value were constant, it was assumed that taking of a representative sample was possible. When taking samples the pH-value, water temperature, electrical conductivity and dissolved oxygen were measured.

Samples from the ceramic candles were taken at irregular intervals for investigation of the soil water pollution in three different depths in the natural sediment of the infiltration pond.

Sludge and soil sampling

In order to determine the migration and distribution behaviour of inorganic and organic parameters, sediment samples were taken by means of piston drill down to a depth of 2 m Pücklerpfuhl.

For the evaluation of the distribution of contaminants in the anaerobic sludge layer, a sampling grid with 16 sampling points was selected. A Beckmann-Birge gripper was used to take sludge samples from the upper sludge layer.

A new cryotransfer sampling technique was applied specifically in order to differentiate between the pollution load in the muddy, more liquid sludge layer and the solid soil layer underneath. This made possible to take samples from 150 cm of an undisrupted sediment sequence and to come to a more detailed statement on the depth distribution of the pollutants.

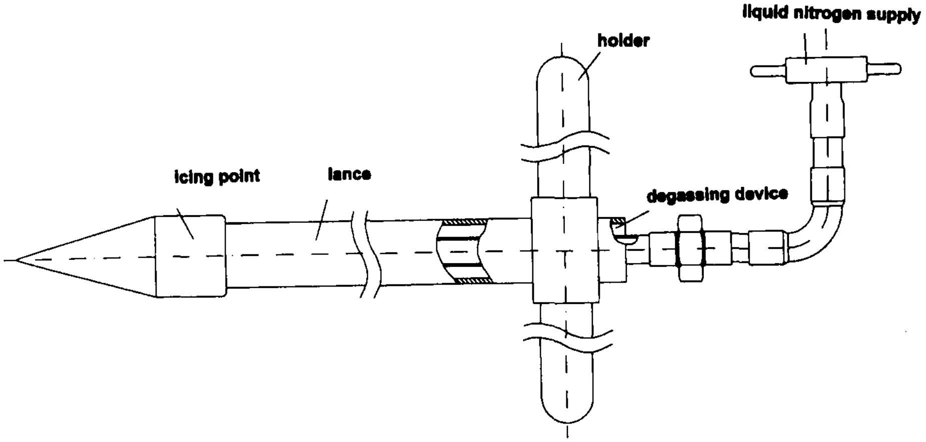

Figure 2 Sampling device for depth distribution of the pollutants.

A lance-shaped, special steel pipe (Figure 2) was driven through the sludge layer down in to the unsaturated soil layer. Then, liquid nitrogen was pumped through the pipe. Within 20 minutes a sufficient amount of water, sludge and soil material necessary for the examinations froze outside around the pipe. The frozen core with a diameter of about 10 cm over the entire sampling depth was drawn out and divided into 10 cm segments which were analysed.

RESULTS AND DISCUSSION

Inorganic substances in groundwater flow

What were noticeable were the relatively high anionic and cationic concentrations in the groundwater in the observation wells downstream of Pücklerpfuhl of up to 60 mg/l chloride, 180 mg/l sulphate and 185 mg/l calcium. In comparison, on average only 20 mg/l chloride, 40 mg/l sulphate and 35 mg/l calcium were found in the rainwater inlet at Pücklerpfuhl. By contrast, downstream of the groundwater only up to 6 mg/l chloride, 20 mg/l sulphate and 55 mg/l calcium were measured. This, together with the data on electrical conductivity not presented here, indicates that rainwater seepage obviously leads to a dilution of the high anionic or cationic concentrations upstream of groundwater, concentrations which stem from the application of de-icing salt over a period of many years in winter (Figure 3).

Heavy metals

In street gulleys, average concentrations of 900 μg/l zinc, 120 μg/l copper, 30 μg/l lead and 10 μg/l nickel were found.

By contrast, the upper 10 cm of the sediment layers which had settled in the fringe areas of the seepage site had a heavy metal contamination of 190 mg/kg zinc, 50 mg/kg lead, 18 mg/kg copper and 12 mg/kg nickel. However, at a depth of 60 cm of the sediment layer, only 75 mg/kg zinc, 8 mg/kg lead and 3–5 mg/kg copper and nickel could be determined.

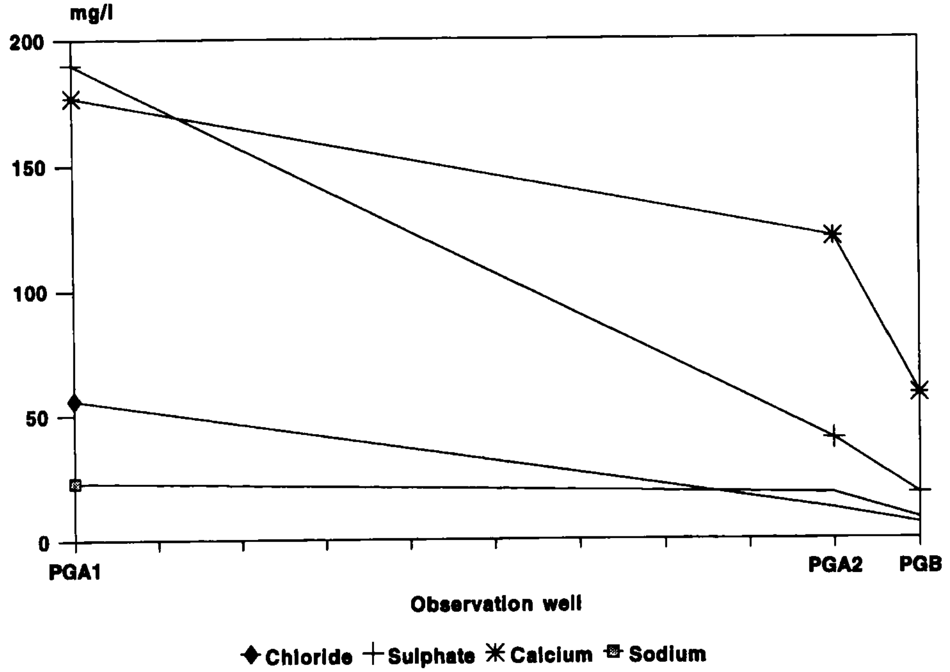

Figure 3 Course of groundwater contamination by chloride, sulphate, calcium and sodium along the groundwater flow direction at Pücklerpfuhl.

The seepage water collected by means of suction candles from the seepage area contains, with the exception of zinc, minor concentrations of lead, copper and nickel. In the case of lead and copper no correlation with depth could be established; by contrast in the case of nickel a low increase and in the case of zinc a clear increase in concentration could be identified at a depth of 1.5 m.

The sludge samples taken from different layers of the seepage site had a considerably higher heavy metal contamination than the sediments on the fringes of the seepage site. Up to 4000 mg/kg zinc, 800 mg/kg lead, 660 mg/kg copper and 100 mg/kg nickel were detected in the upper 10 cm of the sludge. Figure 3 clearly shows the depth distribution of the heavy metals in the digested sludge at the seepage site. Zinc and copper accumulated most in the top sludge layer. Lead content decreases in the later sludge deposits and this can be attributed to the increasing use of unleaded petrol in motor vehicles. This is convincing proof of the efficacy of the Federal German Petrol Lead Act.

Polychlorinated biphenyls and polycyclic aromatic hydrocarbons

In rainwater and in seepage water from the unsaturated zone at the seepage site, organic micropollutants could not be detected at an accumulation of 1:1000 in a concentration of > 1 µg/l.

By contrast, PCB and PAH could be detected in the sludge at all 16 sampling points at the seepage site. Compared with data from Drescher-Kaden *et al*[6], who compiled data

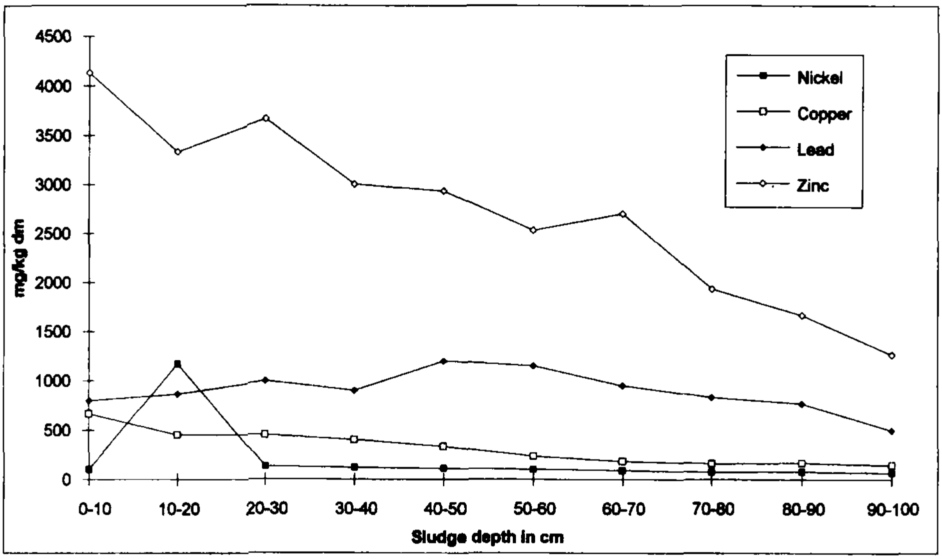

Figure 4 Distribution of heavy metals in the sludge layer at Pücklerpfuhl.

on the PCB contamination of sewage sludge in the Federal Republic of Germany, gave a concentration range of 0.05–15 mg/kg. The sludge samples taken from the surface of the seepage site, at Pücklerpfuhl, had on average a PCB contamination of only 0.4 mg/kg. There was a similar situation with the PAH which were determined in sewage sludge in concentrations of 1–110 mg/kg, whereas at the seepage site, present in low concentrations on average 1.85 mg/kg.

However, at deeper levels in the digested sludge far higher concentrations of both groups of substances were observed. This becomes clear when examining the results of the investigations of the frozen core undertaken according to the cryotransfer process, as mentioned above. These samples were taken from the most highly contaminated area at Pücklerpfuhl (Figure 5). In earlier years and at greater sludge depths, the discharge of PAH from combustion process and PCB from various diffuse sources were considerably higher.

In order to date the differential high discharges of these substances, the Laboratory for Radioactivity Studies of our Institute (Dr. H.-U. Fusban) carried out analysis on the same sample material for caesium 134, which was used as an indicator for the nuclear accident in Tschernobyl in 1986 and for caesium 137, which was used as a time marker for the various atomic bomb trials in the atmosphere in 1961/62 (Figure 6). From this data it is possible to establish an approximate sludge deposition rate of ca. 6 cm/a in the unstable upper layers and of 2 cm/a in the compact lower sediment. In this way it was possible to pin down chronologically the high PAH and PCB discharges into the sediment at Pücklerpfuhl in the 1960s up to the beginning of the 1970s.

Since 1978 the use of PCB has been permissible in closed systems only and the disposal of these substances is subject to stringent regulations. This means that today only comparatively low amounts of PCB reach the environment from diffuse sources. This has already been documented in 1989 by Marcomini *et al.*[7] on the basis of investigations on sewage sludge monolandfills into the development of sewage sludge contamination by PCB. Now, it was also possible to clearly document this for the PCB contamination of sediment from rainwater and street gulleys.

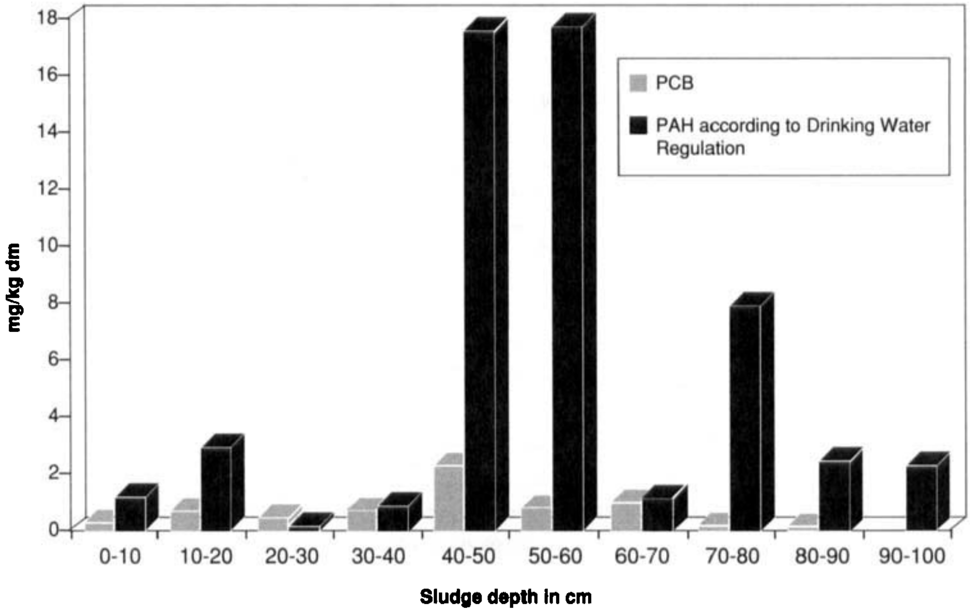

Figure 5 PCB and PAH depth distribution in the sludge layer at Pücklerpfuhl.

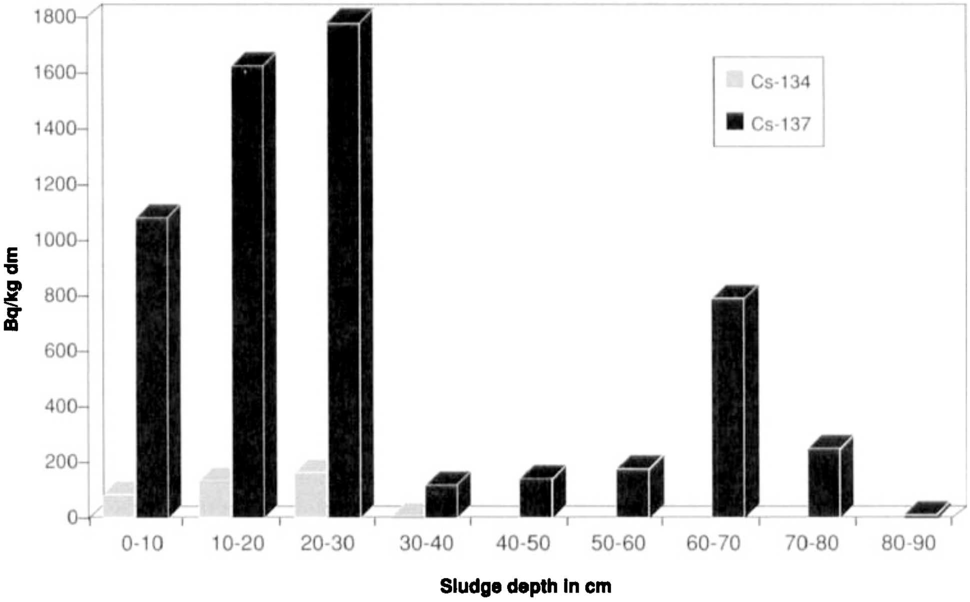

Figure 6 Distribution of radionuclides Cs-134 and Cs-137 in the sludge layer at Pücklerpfuhl.

CONCLUSION

It was not possible to prove that the discharge of anthropogenic pollutants influenced groundwater by way of rainwater seepage in a seepage pond with a sufficiently thick anaerobic sludge layer. The inorganic and organic components which were analysed in the rainwater gulley and in the water at the seepage site were obviously fixed or bound in the sediment and in the sludge of the seepage site.

In the case of heavy metals, clear effects could only be established for the more mobile elements zinc and nickel in the seepage area.

The inorganic and organic micropollutants are adsorptively bound in the sludge and/or sediment at the seepage site. The anaerobic sludge layer with its high proportion of organic components has a greater adsorption capacity than sandy sediment. A depthoriented deposition of these substances was clearly visible in the sludge and allowed for their chronological classification. This provided sound evidence of the efficacy of statutory measures to protect the environment particularly in the case of lead and PCB.

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