Sorption of Pb(II), Cr(III), Cu(II), As(III) to peat, and utilization of the sorption properties in industrial waste landfill hydraulic barrier layers

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ABSTRACT

The low conductivity landfill barrier layers protect the groundwater and soil by limiting the water flow through the bottom layers of the landfill material. Many materials used in hydraulic barrier layers also have sorption properties which could be used to reduce environmental risks. The adsorption of lead, chromium, copper, and arsenic to peat was studied with a batch-type test and a column test for compacted peat, both without pH adjustment in acidic conditions. Peat adsorbed all the metals well, 40 000 mg/kg of lead, 13 000 mg/kg of chromium, and 8400 mg/kg of copper in the column test. Arsenic was only tested in a batch-type test, and in that peat adsorbed 60 mg/kg of arsenic. The column test showed heavy metals to be adsorbed on the surface layers of the compacted peat sample, on the first centimeter of the sample. The adsorption was much greater in the column test than in the batch-type test, partly due to the different pH conditions and the buffer capacity of the peat in the column test. The liquid/solid ratio of the column experiment represented a time period of approximately 40 years in a landfill, under Finnish climate conditions. The hydraulic conductivity of the peat decreased as it was compressed, but it already met the hydraulic conductivity limits set by European Union legislation for the hydraulic barrier layer (1×10^{-9} m/s at a pressure of 150 kPa for a 5-m layer), with a pressure of 50 kPa. The results show that peat would be an excellent material to construct compacted, low hydraulic conductivity layers with adsorption properties in, e.g. industrial waste landfills.

1. Introduction

The purpose of the bottom layers of a landfill is to first and foremost prevent contamination of the soil, groundwater and surface water. In current structures, this has been accomplished by preventing or slowing down the water flow through the structures. This is achieved mainly in two different ways: with the drainage layer, which is used to collect as much leachate as possible and with the hydraulic barrier layer, which prevents the leachate from flowing out of the landfill. However, it is almost impossible to construct a barrier layer that would not let some water through [1]. This is one reason why the contamination and migration should also be restrained by using adsorptive construction materials. These kinds of structures are especially useful in situations, where there is a great amount of leachate (e.g. in disposal areas for tailings from mineral separation activities), or if the leachate collection and treatment is hard to organize, as well as in destinations where the leachate only contains a few harmful substances, like the final placement areas of polluted soil. By using adsorptive materials, it is possible to design even safer bottom structures while also saving on construction materials.

In the mining industry, for example, tailings are produced from mineral separation. It has been estimated that 400 million tons of mining waste is produced within the European Union, which is approximately 29% of the entire waste amount produced in the EU. The new European Union directive concerning mining waste, which stipulates stricter rules concerning mining waste disposal, became valid on 15 March 2006 (The directive of European parliament and council 2006/21/EY).

Tailings are stored in disposal ponds. The environmental impacts of tailings vary greatly—some can be almost as pure as natural sands while some are classified as hazardous waste. The most problematic are the sulfidic tailings, which produce acids when they are oxidized. The acids can then dilute metals from the tailing. A vast amount of waste rock is produced also in mining. When sulfidic, waste rock incurs the same problems as tailings. Heavy metal-containing waste is produced also in other industries as well, such as for example ashes. The polluted soils that are placed in hazardous waste landfills also often contain heavy metals. According to

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Nomenclature

b	maximum adsorption capacity in soil (mg/kg) or (mmol/g)
b_F	Freundlich isotherm exponent
C_e	equilibrium concentration of the contaminant in the liquid (mg/l) or (mmol/l)
K_d	linear isotherm constant (l/kg)
K_F	Freundlich isotherm constant (l/kg)
K_L	equilibrium adsorption constant (l/kg) or (l/g)
L	volume of water (l)
m	wet mass of peat sample (g)
m_{dry}	dry mass of peat sample (kg)
m_w	mass of water in peat (g)
P	pressure (kPa)
q_e	the concentration of the adsorbed contaminant in the soil (mg/kg) or (mmol/g)
Q	current (l/day)
r^2	regression coefficient
T	temperature (°C)
w	average water content (%)
x/m	adsorbed amount of metal in dry soil (mg/kg)

Greek letter
γ_d	dry unit weight (kN/m^3)

Subscripts
calc	calculated
CCA	wood impregnate including chromium, copper and arsenic salts
meas	measured
L/S-ratio	the liquid/solid ratio (l/kg)

2. Materials and methods

2.1. Materials

2.1.1. Peat

Peat was chosen as study material, because it is cheap material that is readily available almost everywhere in Finland, it has physical properties that make it suitable for hydraulic barrier layers and there are lots of promising results about heavy metal adsorption in peat, as mentioned above. In other studies as well [4] peat has been used as an adsorptive material, because it is locally readily available.

The peat studied, supplied by the Finnish peat producer Vapo Corp., was dark, medium rough and highly mineralized. Its degree of decomposition was H7 on the von Post scale and its moisture content was 74.8% of the mass of the wet sample. The plant species determination showed 30% of the peat to consist of an unidentified mass together with secondary particles, 25% was root tissue of *Carex* plants (*Carex chorrdorrhiza*) and approximately 25% were leaf parts of *Sphagnum* and *Bryales* mosses. The peat also included some rudiments of cotton grass (*Eriophorum* sp.), wood, and slightly massed twigs. The peat layer was probably laid down under highly or moderately nutritious conditions and the place had an abundance of springs.

The pH of the peat, determined according to the ISO 10390 standard, was 4.1 on average. The cation exchange capacity, determined with 1 M ammonium acetate diffusion at pH 7 for a sample that was air dried according to the ASTM D2974-00 standard method B, was 112.3 mequiv./100 g. The chemical elements and the ash content in peat are presented in Table 1. The ash content was determined by burning the peat sample at a temperature of 550 °C, according to the CEN/TS 14775: fi-standard.

current legislation, all these waste disposal areas require thick and compacted hydraulic barrier layers. The municipal waste landfills are not included in this study, because the leachates from municipal waste contain so many other harmful substances – such as sulfates and chlorides – that studying only the heavy metal adsorption capacity in these structures is not sufficient.

In Finland, peat is used in landfill barriers because it has physical properties that make it suitable for hydraulic barrier layers. However, its adsorptive properties have not been considered in the design. There are promising studies regarding adsorption in peat and other organic materials. Peat and humic acids have been shown to adsorb large amounts of chromium and copper in batch-type tests, for example [2,3], and cobalt in column tests [4]. Good results have also been obtained with the adsorption of lead [5–7] and zinc [6,8,9] in peat and other organic material. Several studies have also confirmed the natural ability of peat bogs to retain heavy metals [10,11].

Most of the adsorption studies so far have been carried out using batch-type tests, but little comparison has been made with column tests. Adsorption has scarcely been studied at all in compacted, low hydraulic conductivity samples, and not many practical applications for peat or other compactable and adsorptive materials have been presented. In this paper, the main objective was to evaluate the adsorptive capacity of peat and the possibilities for using peat as a barrier layer in the bottom structures of industrial waste landfills and final placement areas for contaminated soils. We also compare two methods for adsorption tests and aim to produce migration parameters that can be used in larger design.

Table 1
The chemical composition and the ash content of the peat

Chemical element	Concentration in dry matter (mg/kg)
Al	3480.0
As	6.0
B	<4.0
Ba	42.0
Be	<0.5
Ca	4550.0
Cd	<0.3
Co	2.0
Cr	6.0
Cu	<10.0
Fe	6460.0
K	350.0
Mg	1140.0
Mn	180.0
Mo	1.0
Na	<30.0
Ni	4.0
P	1000.0
Pb	6.0
S	1950.0
Sb	<4.0
Se	<4.0
Sn	<2.0
Ti	140.0
V	12.0
Zn	11.0
Total N (% of dry matter)	2.4
Total C (% of dry matter)	52.9
Ash content (%)	8.1

2.1.2. Chemicals

The research was carried out with four heavy metals: chromium (Cr^{3+}), copper (Cu^{2+}), arsenic (As^{3+}) and lead (Pb^{2+}). These particular waste residue elements were chosen because chromium, copper and arsenic appear together especially in impregnated wood, which can be found in contaminated wastelands. They started using CCA wood protection in Finland already in the 1950s. Most commonly used were mobile wood pressure treatment equipment in which the lumber was inserted in a steel cylinder and treated with CCA by applying either positive pressure or low pressure. The highest amounts of impregnant at lumber treatment plants are usually found in front of the impregnating cylinders, from which impregnant often dripped off treated lumber. The liquid had been allowed to flow out of the tank at its own pressure through hoses right onto and seep through the lumber, which was the reason why the contamination was especially extensive [12].

The arsenic, chromium and copper concentration in the soils of CCA plants can be very high ranging from several hundreds of mg/kg to thousands of mg/kg. Usually, chromium and copper are concentrated in a smaller cubic capacity than arsenic, which is more mobile in soil.

Lead, on the other hand, can be found in the soils of old shooting ranges. Soils contaminated by such substances are commonly relocated to the same end disposal sites. All these pollutants can also be found in tailings and industrial waste and all are very harmful and toxic to human health. The concentrations were such as could be found in toxic waste landfills, 1–20 mg/l in the batch-type tests. (For the actual concentrations in each solution, see Section 3.) The solubilities were assessed based on Finnish legislation concerning hazardous waste landfill sites. In Finland, the solubility limit rates of hazardous waste for the above-mentioned metals are 25–100 mg/kg at an L/S ratio of 10, in which case the average concentration in the solution would be ca. 2.5–10 mg/l. Higher concentrations (40–250 mg/l) were used in the column tests, to shorten the time of each experiment.

The lead solution was made from the lead nitrate $Pb(NO_3)_2$ and the chromium, copper and arsenic solutions were made from the respective oxides: CrO_3, CuO, and As_2O_3. The oxides were used, because in salt impregnates metals appear in an oxide form. On the other hand, Cr^{6+} was used because chromium appears in salt impregnates as a hexavalent. However, hexavalent chromium reduces almost completely in wood and water and becomes trivalent. The chromium and copper oxides were dissolved directly into water. The relationship of the chromium, copper, and arsenic with each other was the same that has been used in salt impregnates. The arsenic trioxide was dissolved in NaOH and neutralized with nitric acid before dilution. The pH of the other solutions was not adjusted, and only the concentrations affected the pH of the metal mixture. The exact pH-values of the solutions have been presented in "Section 3".

2.2. Analytical methods

The analyses were carried out at the laboratory of the Finnish Institute of Occupational Health in Oulu and at the Geochemical Laboratory at the University of Oulu.

Before the metal analyses, 1 g of peat was weighed out into a decanter. Subsequently, 5 ml of concentrated HNO_3 and 5 ml of concentrated HCl was added. The sample was allowed to bubble under a glass cover and was carefully warmed until the foaming stopped. The liquid was then heated in a hot sand bath (120 °C) until the sample was nearly dry, after which 2.5 ml of concentrated HNO_3 was added, and the sample was washed into a 25-ml measuring flask. The analyses were performed using a PerkinElmer AAnalyst 800 AAS, both by the flame technique (Pb, Cu, tot. Cr) and by the

graphite oven technique (tot. As). The metal analyses conformed to the standards OSHA ID-121, NIOSH 7300 and NIOSH 7301.

2.3. Experimental procedures

2.3.1. Hydraulic conductivity test

The hydraulic conductivity of the peat was measured in flexible-wall permeameters according to the ASTM D 5084–90 standard. In a flexible wall permeability test the sample is wrapped with a rubber compound, which condenses onto the sample due to the aquatic pressure in the cell. The test was performed on two similar samples in each case. The peat samples were compressed under a pressure of 50 kPa before the test. The samples were compressed even further during the test, after which the compression was measured. The test was performed at efficient vertical pressures of 50, 100, 200 and 300 kPa, the gradient being lifted from 5 to 30 during each pressure step. The samples were 100 mm high and wide, and the test was carried out with deionised water.

2.3.2. Batch-type adsorption test

The batch-type test was carried out according to the directions published by EPA [13], which are based on the ASTM D 4646–87 standard. The results represent adsorption in non-compact soil, but do not directly represent the adsorption properties of undisturbed soil.

The test was performed with a rotary extractor that circulated at a speed of 29 rpm, and the peat was at its natural humidity. The rotary extractor was used, because it was found to be the best device for shaking the samples (giving low variation between laboratories and samples) in the EPA Technical report [13]. The samples, of volume 200 ml, were in 250 ml Teflon bottles.

The test was performed using water solutions of all four heavy metals, arsenic, chromium, copper and lead, combined. A soil-solution ratio of 1:60 was used. The mixing time for all samples was 24 h, which was enough to reach equilibrium. The test was performed at room temperature, so that all the samples were shaken at the same time, and the temperatures were observed by measuring it before the test as well as after the test using the same gauge as was used to measure the pH. The temperatures of the samples were very steady, remaining between 21.2 and 21.4 °C allthroughout the experiment.

The concentrations in the test were chosen so as to represent ones that could be expected to dissolve from waste. Concentrations were in the range of 1.3–12.6 mg/l for lead and copper, 1.7–18.4 mg/l for chromium, and 0.6–6.1 mg/l for arsenic. (For the exact concentrations in each sample, see Table 4 in Section 3.) The adsorption terms were produced with the help of the constant soil/solution ratio isotherm (CSI) method, in which the concentration of the initial state of the solution changed, but the soil–solution-ratio was kept constant.

The metal concentrations were analysed with the PerkinElmer atom adsorption spectrophotometer (AAS) by using the flame technique for Pb, Cr and Cu, and the graphite oven technique for As. The analyses were done according to the standards SFS 3044 and SFS 3018 from filtered samples at the Geochemical Laboratory of The University of Oulu.

2.3.3. Column adsorption test

The column adsorption test was used to study adsorption in a condensed soil sample. The adsorption test performed on a column represents real adsorption conditions in a landfill situation better than does the batch-type test, because the water flow and the liquid/solid ratio (L/S ratio (l/kg)) are much more realistic. Contaminated water was pumped into the soil sample at a speed that matched its hydraulic conductivity and this was continued until
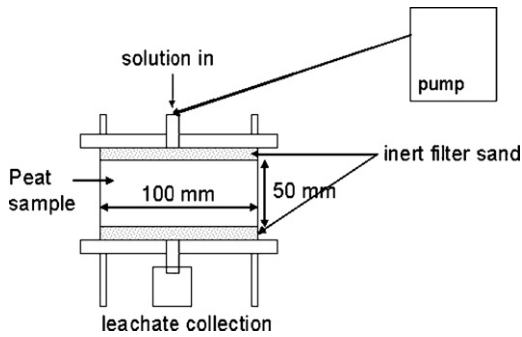
Fig. 1. Principle of the adsorption column.

the desired L/S ratio was achieved. The contaminant concentration in the feed solution was known. The soil samples in this test were cylindrical, 50 mm thick and the diameter of the samples was 100 mm. All samples were compressed under a pressure of 50 kPa in a similar manner and at the same time as the samples used in the hydraulic conductivity test. The sample height in the column test was smaller than usual, because of the low hydraulic conductivity and high adsorption capacity, but this did not detract from the results.

The porosity of the samples was 80% and the dry unit weight was 3 kN/m^3. A pumping speed of 0.01 ml/min was used. The hydraulic conductivity of the samples was approximately 5×10^{-9} m/s under the test conditions (Fig. 1).

The columns were made of acid-proof steel to prevent any adsorption on column walls. A filter paper and 5 mm thick layer of inert 1–2 mm quartz sand was placed under and on top of the sample. This ensured an even flow of water all over the column. The contaminant solutions were pumped into the samples with a Gilson Minipuls3 pump which had acid and chemical-proof Isoversinic^{TM} tubes. All the samples were saturated with distilled water before the test by pumping water in the samples until the flow was even and no air bubbles came out. This was done, because the desire was to represent retention at a saturated state.

Two solutions were used, the first containing lead only, the second chromium and copper. Samples of the leachate were taken once every 2 weeks. Solutions containing detrimental elements were simplified as compared with the shake test, because the aim was to get more universally applicable results that can be compared with other studies. Therefore, a one-metal solution as well as a two-metal solution was made. The solution containing lead represents the detrimental elements draining from the soils of shooting ranges, whereas chromium and copper represent salt impregnates.

The experiment was stopped after 12 months (362 days). As the concentrations in the leachate were not even close to the feed concentrations, discharge curves could not be used, but instead the adsorption was estimated by cutting the samples into 10 mm slices and analysing the concentrations of Pb, Cr and Cu directly from the peat as explained previously (see Section 2.2). This revealed the amounts and vertical distributions of the contaminants in the peat.

The concentrations of the contaminants in the feed solutions are presented in Table 2a. The concentrations used changed slightly

Table 2a
The concentrations of the heavy metals in the feeding solutions of the column test (mg/l)

Sample	Days 0–76	Days 76–139	Days 139–362
Chromium (mg/l)	75.00	72.50	64.69
Copper (mg/l)	50.76	52.83	39.97
Lead (mg/l)	105.50	118.10	239.30

Table 2b
The dry masses of the peat samples (m_{dry}), the flow speed (Q), the amount of collected leachate (L) and the L/S-ratio at the end of the column test

Sample	m_{dry} (kg)	Q (l/day)	L (l)	L/S (l/kg)
Chromium	0.1280	0.0135	4.875	38
Copper	0.1280	0.0135	4.875	38
Lead	0.1190	0.0155	5.600	47

when a new solution was made for the test as can be seen from Table 2a This did not have effect on the results, and the concentrations of the initial solutions did not vary in the experiment. They only varied when a new solution was added when the old one had run out. The concentration of lead was raised towards the end of the test in order to see if this would speed up the test. The presumption was that the test would thus be sped up, because the available sorption sites would fill faster. However, raising the concentration level did not speed up the experiment significantly and did not have an effect on the final results. The amount of water that had flowed through each sample was 4–5 l (Table 2b), and the L/S-ratio, i.e. the ratio of the volume of the liquid that has flowed through the sample to the dry mass of the sample (l/kg), was between 38 and 47 (Table 2b) The pH of the leachate from both the columns was between 4 and 4.3 during the whole test.

2.4. The adsorption isotherms and their fitting

The linear adsorption isotherm (1) describes ideal sorption that is constant with all contaminant concentrations. This is rarely the case in real situations, but the linear isotherm can also be used to evaluate the adsorption for the linear sections of the non-linear adsorption curves.

$$q_e = K_d C_e \tag{1}$$

where q_e is the concentration of the adsorbed contaminant in the soil (mg/kg) or (mmol/g), K_d is the linear isotherm constant (l/kg) and C_e is the equilibrium concentration of the contaminant in the liquid (mg/l) or (mmol/l) [14].

The Freundlich adsorption isotherm (2) is suitable for non-ideal sorption on heterogeneous surfaces and for multilayer sorption. Mathematically it is of the form:

$$q_e = K_F C_e^{b_F} \tag{2}$$

where K_F is the Freundlich isotherm constant (l/kg) and b_F is the Freundlich isotherm exponent [14].

The Langmuir isotherm (3) is perhaps the best known and most widely used, because it can be fitted to many kinds of experimental results. It is based on the idea that there are a limited number of sorption sites on a solid surface. The Langmuir isotherm is

$$q_e = \frac{K_L b C_e}{1 + K_L C_e} \tag{3}$$

where K_L is the equilibrium adsorption constant (l/kg) or (l/g) and b is the maximum adsorption capacity in soil (mg/kg) or (mmol/g) [14].

The isotherms were fitted by minimising the error using the smallest sum of squares method:

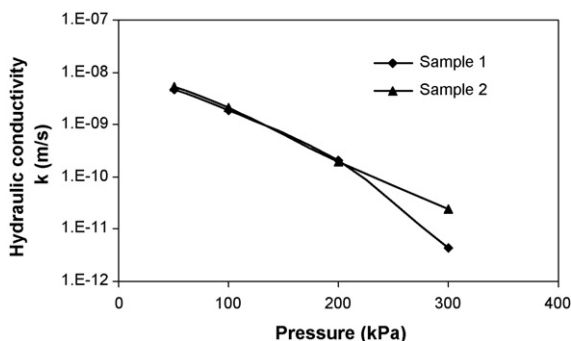$$r^2 = \sum_{i=1}^{p} (q_{e,meas} - q_{e,calc})_i^2. \tag{4}$$

Fig. 2. Hydraulic conductivity of the peat as a function of pressure for two parallel samples.

Table 3
Dry unit weight (γ_d) and water content (w) of the samples used in the water conductivity test at different pressures (P). m_w is the mass of water in peat (g), and m is the wet mass of the peat sample (g)

P (kPa)	γ_d (kN/m^3)	w (%) $= (m_w/m) \times 100$
50	2.98	70.3
100	3.15	68.5
200	3.57	61.7
300	4.00	58.7

3. Results

3.1. Hydraulic conductivity of peat

The hydraulic conductivity (k) of the peat was very low, starting from 4.5×10^{-9} m/s at a pressure of 50 kPa and ending at approximately 1.5×10^{-11} m/s at 300 kPa (Fig. 2). The results for the parallel samples were convergent, up to values of 10^{-10} m/s, at which point the measuring technique started to cause inaccuracy in the results. As the pressure rose, the dry unit weight of the peat increased and the water content decreased (Table 3). The water conductivity was strongly dependent on the dry unit weight and decreased almost linearly as the dry unit weight increased. The same will happen in the landfill, as the amount of the waste, and along that the pressure, increases.

3.2. Adsorption of heavy metals on peat in the batch-type test

The adsorbed amount of the metals in the batch-type test varied depending on the concentrations (Fig. 3a–d). The presence of multiple metals in a solution creates competition for available adsorption sites on the adsorbent surface [15]. The results indicate that lead and copper have a higher affinity for sorption than chromium and arsenic. This is affected by the different binding affinities and complexation values of the metals. However, it was not the aim to further clarify the adsorption mechanisms in this study. The amounts of lead and copper adsorbed increased steadily as the concentrations increased, up to 489 mg/kg for lead and 308 mg/kg for copper, whereas the adsorption of arsenic was almost constant at all concentrations (up to 60 mg/kg) and that of chromium increased at first, reaching 210 mg/kg, but then started to decrease as the concentrations of other metals increased. The same was partly also observed for arsenic. The pH of the samples remained very low althrougout the experiment (Table 4). This is because Cr^{6+} is a strong acid. The equilibrium pH of the samples also decreased as the initial concentration of the metals increased (Table 4) and was consistently lower than in the column test. This has also been noted by Ho et al. [16] and is consistent with the principle of ion exchange since as more metals are adsorbed on the peat, more hydrogen ions are released, thereby decreasing the pH. The temperature during the test was stable and the electrical conductivity varied in the range 222–300 mS/m depending on the pH (Table 4).

Adsorption isotherm fitting was done to the individual metals. As any isotherm did not fit the adsorption curves of arsenic and chromium as a whole, therefore no isotherm fitting was done for them. For copper the most suitable isotherm was the Langmuir isotherm with the constants $K_L = 3896$ l/kg and $b = 320$ mg/kg ($r^2 = 0.961$). For lead the most suitable isotherm was the Freundlich isotherm with the constants $K_F = 349.34$ l/kg and $b_F = 0.235$ ($r^2 = 0.979$).

3.3. Adsorption of contaminants to compacted peat

Lead, chromium and copper were adsorbed very strongly on the upper layers (first 2 cm) of the peat (Fig. 4), and the amounts of metals adsorbed were in general higher than in the batch-type test: 40 000 mg/kg for lead, approximately 13 000 mg/kg for chromium and 8400 mg/kg for copper. The amount of chromium adsorbed,
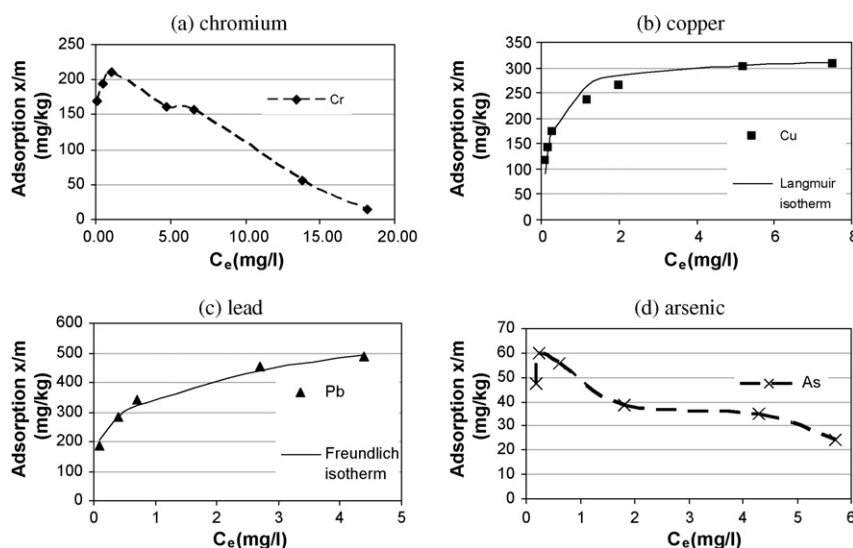

Fig. 3. (a–d) Amounts of chromium, copper, arsenic and lead adsorbed on peat in the batch-type test (mg/kg) as a function of the equilibrium concentration and the fitted isotherms. All the metals were in the same solution.

Table 4
The initial heavy metal concentrations and the pH, temperature (T) and electrical conductivity in the samples during the batch-type test

Sample	Pb (mg/l)	As (mg/l)	Cr (mg/l)	Cu (mg/l)	pH	T (°C)	Electrical conductivity (mS/m)
1	1.275	0.976	2.948	1.275	3.16	21.4	222
2	2.040	1.220	3.685	2.040	2.94	21.4	235
3	3.188	1.525	4.606	3.188	2.74	21.2	246
4	5.100	2.440	7.370	5.100	2.38	21.2	267
5	6.375	3.050	9.213	6.375	2.23	21.3	276
6	10.200	4.880	14.740	10.200	1.94	21.3	293
7	12.500	6.100	18.430	12.600	1.82	21.3	300

for example, was 30 times greater than the total amount of metals adsorbed in the batch-type test, although the amounts of copper and chromium were very similar to those recorded in batch-type tests carried out at pH 4 elsewhere [2]. Therefore, it should be noted that the results of the batch-type test and column test performed in this study cannot be compared directly with one another, because the pH in the tests and the composition of the solutions were both very different in each test. Moreover, the adsorbed amounts of copper and lead were very similar to those measured in column tests by Aho [6]. The differences can be explained with differences in the peat used. The adsorbed amount in the top layer was close to maximum, because some of the contaminants had already started to leach to the lower layers, hence the comparison can be made.

The metal concentrations in the leachate were small (Fig. 5a–c). The concentrations of chromium and copper were on an average smaller than the legal limits set for drinking water in Finland (0.05 mg/l for chromium and 0.5 mg/l for copper) and the lead concentration was on an average smaller than the limit set for wastewater (0.5 mg/l). The spikes in the concentrations are most likely due to byflows in the column at the start of the test. According to the leachate concentrations, over 99% of all the metals were adsorbed to the peat.

The background concentrations of the metals in the peat were relatively small (6 mg/kg for Pb, 6 mg/kg for Cr, <10 mg/kg for Cu and 6 mg/kg for As) and did not affect the evaluation of adsorption to any appreciable extent, although in the bottom layers where the concentrations are small, some of the metal very probably already existed in the peat.

## 4. Discussion

4.1. Comparison of the test methods

Originally, the shake test and the column test were not designed to be mutually comparable. When comparing the tests, one must recognise that the conditions were not identical in all cases, although they were not altered artificially, and the metal combi-

nations were not identical, either. Especially the different pH in the tests has considerable effect on the differences observed in this study. Variations in peat type, peat preparation, methodology, and metals studied make the comparison with other studies difficult [15]. For example, in this study the metal concentrations used in the batch test were lower than in most studies.

Adsorption was as much as 30 times higher in the column test than it was in the batch-type test, although adsorption results in batch tests carried out at pH 4 have been of the same order as those
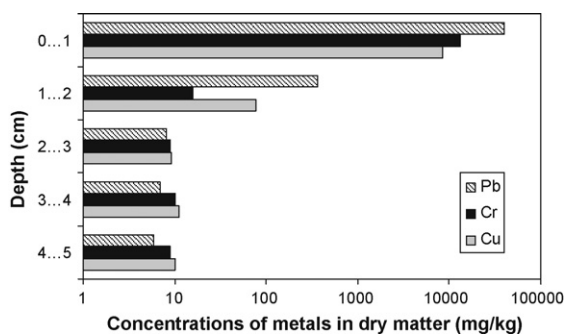
Fig. 4. Concentrations of lead, chromium and copper (mg/kg) at different depths in sliced peat samples. Lead was examined separately from chromium and copper and its depth was measured from the top of the sample.
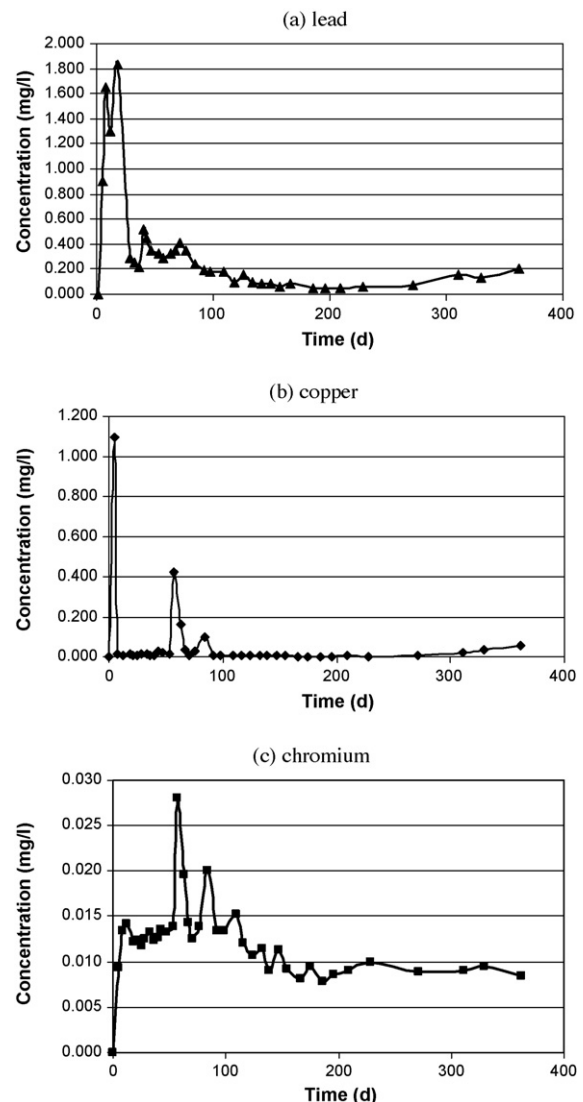
Fig. 5. (a–c) The concentration of lead, copper and chromium in collected leachate in column test. Chromium and copper were in the same sample while lead was at its own.

in the column test [2]. Substantial differences between column and batch-type tests have been reported elsewhere as well, the adsorption of zinc, for example, being twice as high in a column test as in a batch test [9]. Also Aho [6] has reported similar differences between the column and batch-type tests, as have von Wandruzka and Newell [9].

The effect of the pH of the liquid is great in a batch test—larger than it would be in a real environment, as can be seen from the column test. On average, metals and other inorganic ions tend to adsorb more readily at higher pH, although it has been reported that pH does not have any significant effect on the adsorption behaviour of arsenic (As^{3+}) in a batch-type test [13]. For the other metals the optimum pH range for adsorption is generally 3.5–6.5 [7,8,14]. In the batch test, the pH was lower than 3.5 in all samples. In the column test, as in a real structure, the peat buffered the pH much better, because the ratio of water to soil was more realistic. Thus the pH was in the optimum range.

If the real situation is evaluated only with a batch test, the pH of the solution should be varied, but in that case the real, undisturbed leachates for example cannot be used. If the pH in the solution is too high, the maximum adsorption can also be too high, because the pH in peat is acidic all the time, for example. The high pH can also affect the solubility of the contaminants.

The results of the batch test were influenced to a great deal by the fact that all four metals were in the same solution. In the other tests mentioned before, there has only been one metal in one sample. The metals compete very strongly with each other of the adsorption places in the sample. If the batch test had been made as a single metal test, the adsorption would have been higher. This indicates that when utilising the results in practice, one must consider all the metals included in larger amounts in the leachate. Also the results of this research are only suitable for situations, where the leachate contains only one or two metals in larger amounts. This, however, is often the case with mining waste.

Other factors that contribute to the big difference between the tests are the different concentrations in the solutions used (much bigger in the column test), and the very large L/S-ratio in the batch test. In the column experiment the adsorption is more efficient than in the batch test [6]. Akranatakul et al. [17] have also reported that the pore water velocity affects the adsorption in soils especially when comparing static situation and dynamic flow. This is due to the intensified ion exchange when there is a continuous source of ions and continuous sink for the desorbed ions. The batch-type test is similar to the static situation, because it also happens in a closed environment.

The metals were adsorbed strongly to the surface of the sample in the column test, and started to migrate deeper only when almost all the sorption sites on the surface were full. This phenomenon cannot be studied with the batch test.

The results of the column tests show that the batch-type test alone is insufficient for evaluating adsorption in compacted soil layers, as adsorption does not seem to occur in the same way or as fully as in the column test, where the liquid/soil ratio and the water flow and sorption time are more realistic. The liquid/solid ratio can be as high as 500:1 in the batch test, which is totally unrealistic. Consequently, the buffering capacity of the peat does not become visible and the qualities of the liquid affect the sorption much more than they would in a real situation. Also, the vertical distribution of concentrations cannot be examined with the batch test.

As for the sorption mechanisms, peat as well as plants contains significant quantities of organic ligands such as proteins, carbohydrates and carboxylic acids, as well as nucleic acids, lipids and steroids. Whenever metal ions and ligands are present, equilibria between them will be established. Metals can form complexes with these ligands through a peptide –CO–NH– backbone, phosphonate groups, aromatic rings, and other donor atoms/groups. In a multi-component system different metals and protons compete over different complex formation sites [18]. These equilibrium reactions have an effect on the adsorption of metals to peat. Other possible mechanisms are ion exchange reactions at a sufficiently high pH [19]. Usually, metal sorption in peat is not the result of one mechanism, but several [15]. The precipitation of metals did not take place in this research because of the low pH of the peat and the solutions used [20]. The aim of the study was not to find out the sorption mechanisms, hence they are not considered here more profoundly.

4.2. The use of peat in industrial waste landfill structures

In the conditions of the test (one or two metals in acidic solution) the column test results suggest that a 1-m thick layer of peat compacted to a dry weight by a volume of 3 kN/m³ can adsorb the following amounts of heavy metals: lead approximately 12.2 kg/m², chromium 4 kg/m² and copper 2.6 kg/m². It is not reasonable to estimate the arsenic adsorption from the batch test only, arsenic will therefore be left out from this consideration.

With this layer thickness (1 m) and under the climatic conditions prevailing in Finland (average precipitation 550 mm/year and average evaporation 300 mm/year), the column test would represent a period of 40 years in an uncovered waste disposal area where all the water can flow through the layer. Even at this point, and with the quite large concentrations used in the test (approximately 10 times as much as they really would be), only a fifth of the adsorption capacity of the peat for these metals would be used. A 1-m layer of peat could thus adsorb very high concentrations of metals for 200 years. For a shorter period of time and for lower concentrations that could really exist, a much thinner layer would be sufficient. As can be seen from this example, the adsorption capacity of the material has a significant effect on the migration of contaminants in landfill structures and this should be taken into account when designing such structures. Many studies [21,22] have done research on the possibility of using peat for purifying seepage water, but by placing the peat directly in the actual structure itself, the water purification would occur at least partly as the water percolates through the structure.

5. Conclusions

Based on the tests done, the following conclusions can be made:

(1) The peat that was researched was able to adsorb high amounts of all studied metals in the conditions that prevailed; 40 000 mg of lead onto kg of dry peat, 13 000 mg of chromium onto kg of dry peat and 8400 mg of copper onto kg of dry peat.
(2) The hydraulic conductivity of the compacted peat was such that it is suitable for a hydraulic barrier layer.
(3) The batch-type test did not describe the adsorption on compacted peat very well, because it underestimated the adsorption, due mostly to the effect of pH and an unrealistic L/S-ratio. Column tests should be used in its place, because this will better represent real conditions.
(4) The adsorption capacity of the material has significant effect on the migration of contaminants in a landfill structure. For a 1-m thick layer in Finnish weather conditions, the column test represented a period of 40 years, while only 1/5 of the adsorption capacity was used. This should be taken into account when designing such structures, so that the structure can be optimised.

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