PN-ABT-981

Technion
Israel Institute of Technology

Faculty of Agricultural Engineering
The Laboratory for Management of Environmental Systems
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PEAT AND COMPOST FILTERS FOR THE SEPARATION OF HAZARDOUS WASTES FROM WATER.

CDR Grant no. TA-MOU- C12- 050

(Our no. 150-708)

SEMI ANNUAL REPORT

Principal Investigators:

Yoram Avnimelech
Irena Twardowska

Participating Scientists:

Malka Kochva
Irena Kitchin

List of activities.

1. Yoram Avnimelech visited the Inst. of Environmental Engineering of the Polish Academy of Sciences on Oct. 1-4/93. Discussions of scientific plans and administrative problems were discussed. (See appendix 1).

2. Samples of peat and composts were collected.

3. Methods for the conductance of adsorption isotherms were developed. The main problem was to run the adsorption trials at a pH close to neutrality, yet at a pH in which precipitation will not occur. It was decided to run the trials at a pH of 5.5. The control of the pH in a system that contain peats of different pH values was a problem that demanded a number of trial and error repititions.

4. A reproducible method was established. (Appendix 2)

5. Adsorption isotherms of Cu and Zn were established according to the plans. (Examples given in appendix 3).
   The laboratory in Israel is now starting with the characterization of the substrates and the study of the correlation between the substrate's properties and adsorption parameters.

6. The work in poland was delayed due to both administrative problems and difficulties to sample in the winter. The work is planed to start presently. (Appendix 4).

APPENDIX 1

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The first phase will be devoted also to laboratories quality control.
2-3 samples, 2 Kg each will be exchanged among the two laboratories following sampling (Air mail shipment).

TIME TABLE FOR FIRST PHASE.

SUB PROJECT	RESPONSIBILITY
1. 10+ Peat sampling, Poland	I.T.
2. 10+ peat, compost, sludge sampling	YA
3. Test adsorption isotherm techniques and send to Poland (IT sends the technique she uses).	YA
4. send polar & non-polar adsorption methods to Israel	IT

Running adsorption isotherms (according to methods of 3) with Zn & Cu	IT, YA
Test adsorption of organics	YA

Send results to each other	IT, YA
Planning of Phase II	IT, YA
Probable visit of Dr. Malik Kochba to Poland	

APPENDIX 2

TECHNION
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5.3.94

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POLAND
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FAX # 0048 32 717470

Dear Irena:

Thank you very much for your recent letter. I am happy that the administrative arrangements are finally being settled and that we can start the work.
Since we met we have collected a few samples of peat in the Hula Valley, 3 imported samples and a few samples of compost.
Running the isotherms at a neutral pH was a problem, since at the very high adsorption capacity of the substrates, we ran into a problem of the heavy metals precipitation. Thus we suggest to compromise and run the isotherms at a pH of 5.5. The adsorption of the metals decrease at acidic pH, yet it seems that the practical pH values that we will be involved with in industry are acidic.

Enclosed, please find a few examples of adsorption isotherms that we have obtained. The adsorption capacities found were in the range of about 4 - 8 mg/g. With compost we got (has to be rechecked) a lineare adsorption with no hint for a saturation. We are now going to run more isotherms and to be able to take samples that will represent high and low adsorption capacities.

A STANDARD METHOD TO OBTAIN AN ADSORPTION ISOTHERMON PEAT.

Introduction.

The goal of this proposed standard method is to measure heavy metals adsorption on a variety of oragnic substrates (Different peats, composts, sludges).
The major external chemical variables that are known to affect this process are firstly the pH as well as the electrolyte concentration, ionic composition and the solid/solution ratios. These variables have to be kept constant.

Materials and equipement.

Acetate buffer:
87.5 ml Na-Acetate, 2N
12.5 ml Acetic acid
complete to 1000 ml.

Stock solutions of $CuSO_4$ and $ZnSO_4$, having a metal concentration of 1000 mg/l. (2.744 g $ZnSO_4.H_2O$, 3.929 g $CuSO_4.5H_2O$ per 1000 ml).
Ph Meter
Conductivity Meter
Centrifuge
Atomic adsorption spectrophotometer
Funnels
Filter paper (Whatmen # 1 or 42)
Plastic bottles (200 ml)

Preparation of the sample.

Sample of the material (1-3 l) is placed in a wide diameter Buchner funnel over a Whatman # 1 or 42 filter paper. The substrate is leached slowly with distilled water, by a water:solid ratio (W:W) of 5:1.
The washed sample is than vacuum dried and kept refrigirated (ca 5°C).

Since peats have a high buffer capacity and a variable pH range, the pH of the peat suspension has to be adjusted before the start of the experiment. It was found that the suspension of the sample in a buffer solution does not satisfy the need for the maintanance of a constant pH. A pretreatment addition of acid (or base) is needed for each kind of peat. The pretreatment addition has to be determined for each type of material.
Different amounts (0-50 ml) of HCl 0.5N are added to ten g samples of the substrate. Volume is made to 50 ml. with the acetate buffer. pH is measure following an overnight (16 h) shaking period. An acid addition that yield a pH of 5.5 is used later for the given peat substrate.

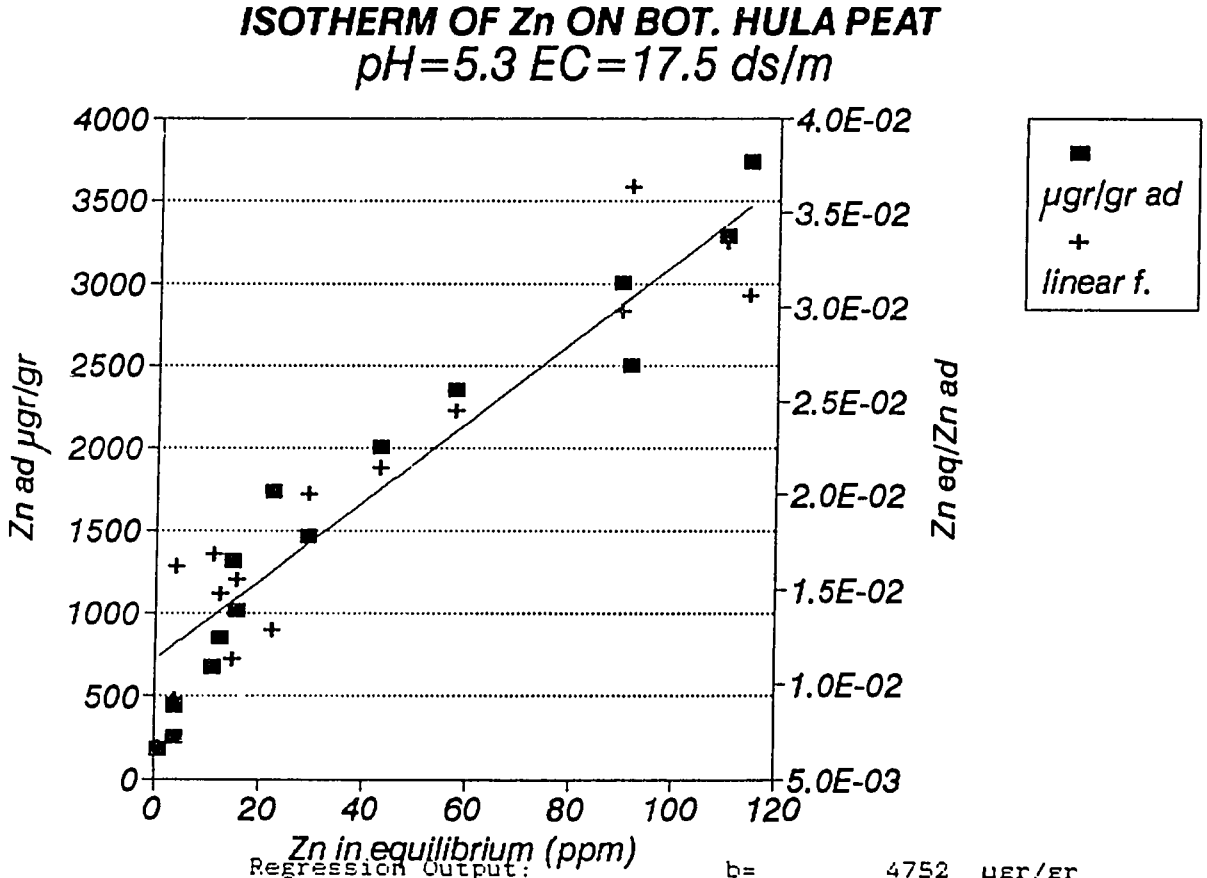
Measurement of the adsorption isotherm.

Buffer and HCl mixture (50 ml) are added to 10 g samples of substrate. The suspension is pre-equilibrated over night (16 h). Fifty ml solutions of Cu or Zn sulphates are then added (concentration range of 0 - 500 mg/l).
The suspension are shaken for an additional period of ca 20 hours and than filtered through a Whatman # 1 over # 42 filter paper. In cases when filtration is too slow, the separation is made by centrifugation.
In each batch, the metal concentration in the blank solutions (buffer + metal as added to the substrate) and equilibrium solutions are determined by atomic adsorption.

Calculation of the results.

Amount adsorbed = A = [C(t=0) - C (t=final)]/10 (mg)
Specific amount adsorbed = A/m = (A/10)x1000 (μg/g)

Appendix 3.

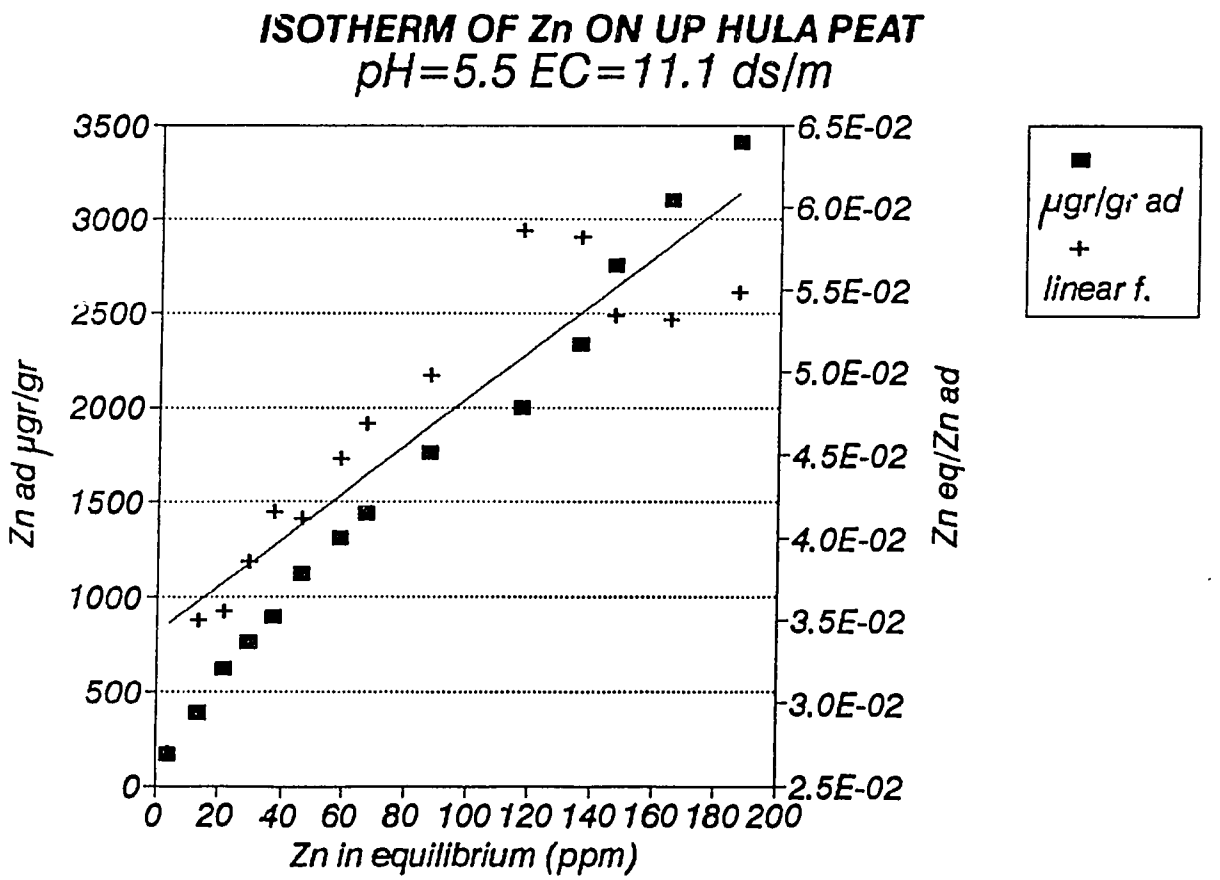


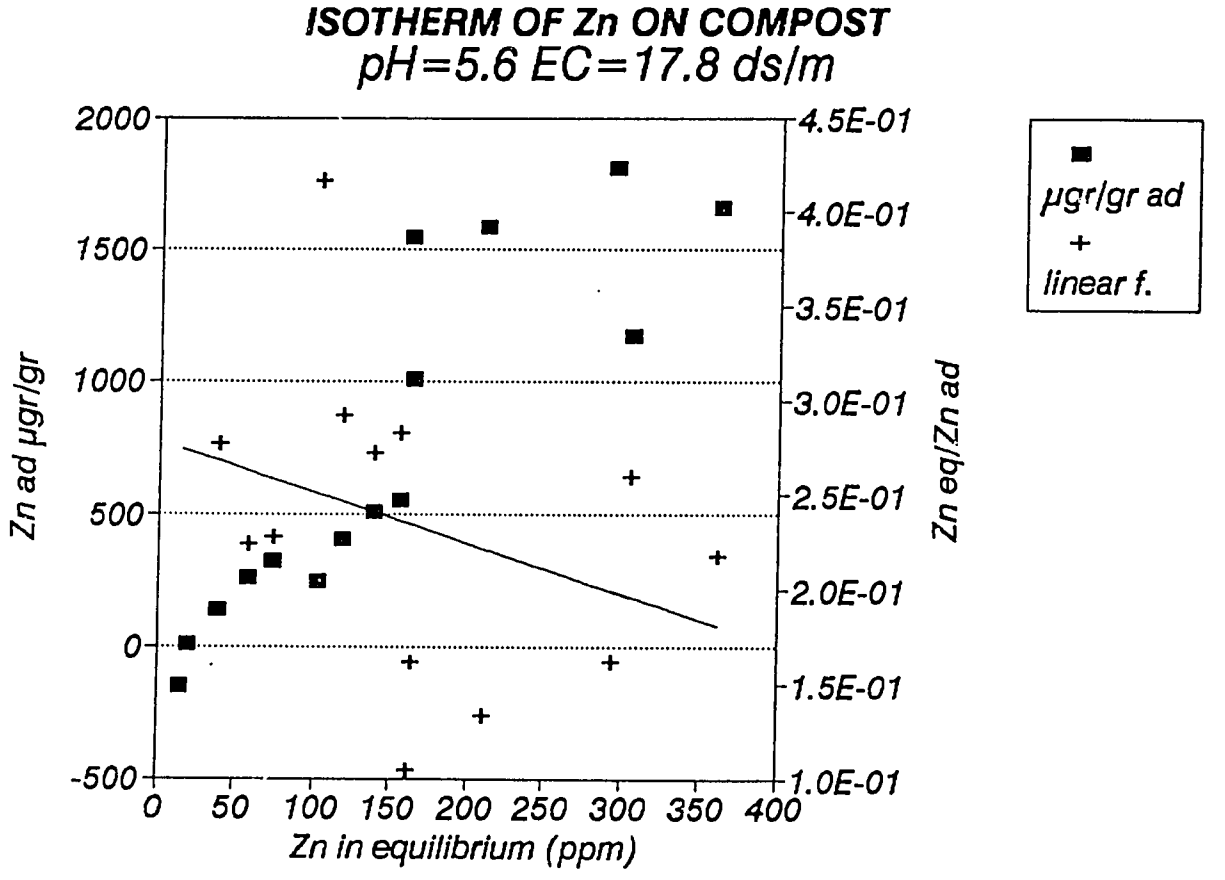
Regression Output:

Constant	0.011262	b=	4752	µgr/gr
Std Err of Y Est	0.003376	K	1.87E-02	
R Squared	0.873553			
No. of Observations	15			
Degrees of Freedom	13			

X Coefficient(s) 0.00021
Std Err of Coef. 2.22E-05

Regression Output:		b=	7020 µgr/gr
Constant	0.034225		
Std Err of Y Est	0.004423	K	4.16E-03
R Squared	0.803544		
No. of Observations	14		
Degrees of Freedom	12		
X Coefficient(s)	0.000142		
Std Err of Coef.	2.03E-05		

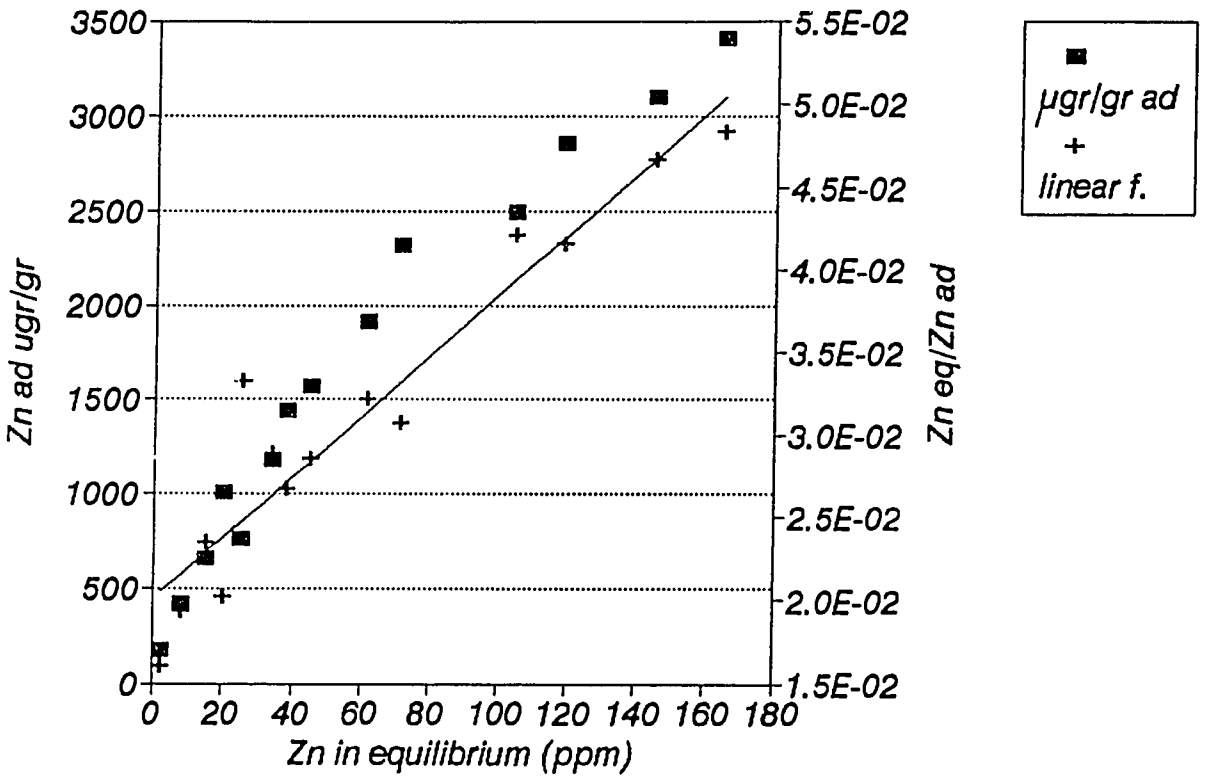




Regression Output:		b=	-3703	ugr/gr
Constant	0.278567			
Std Err of Y Est	0.080979			
R Squared	0.107946	K	-9.7E-04	
No. of Observations	13			
Degrees of Freedom	11			
X Coefficient(s)	-0.00027			
Std Err of Coef.	0.000234			

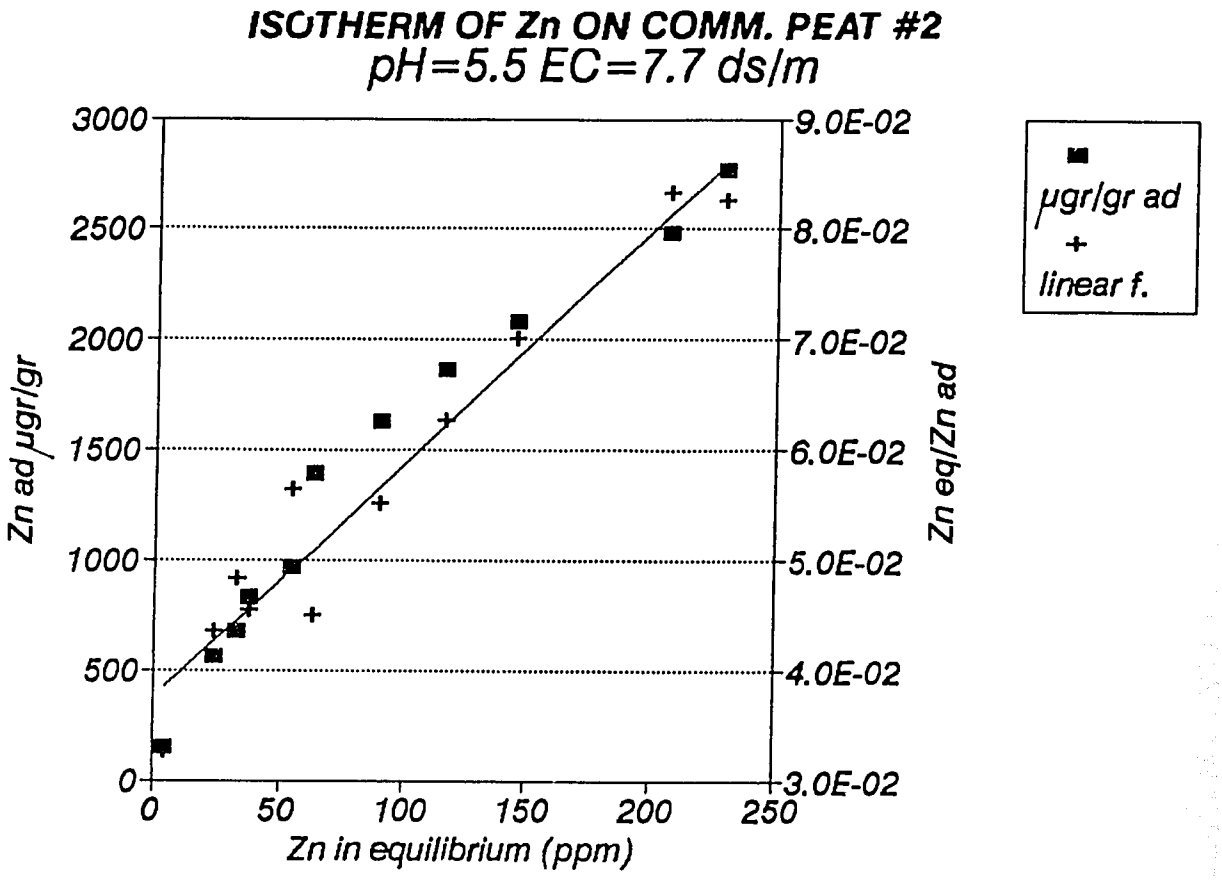
ISOTHERM OF Zn ON COMM. PEAT #3 (*)

pH=5.3 EC=7.3 ds/m



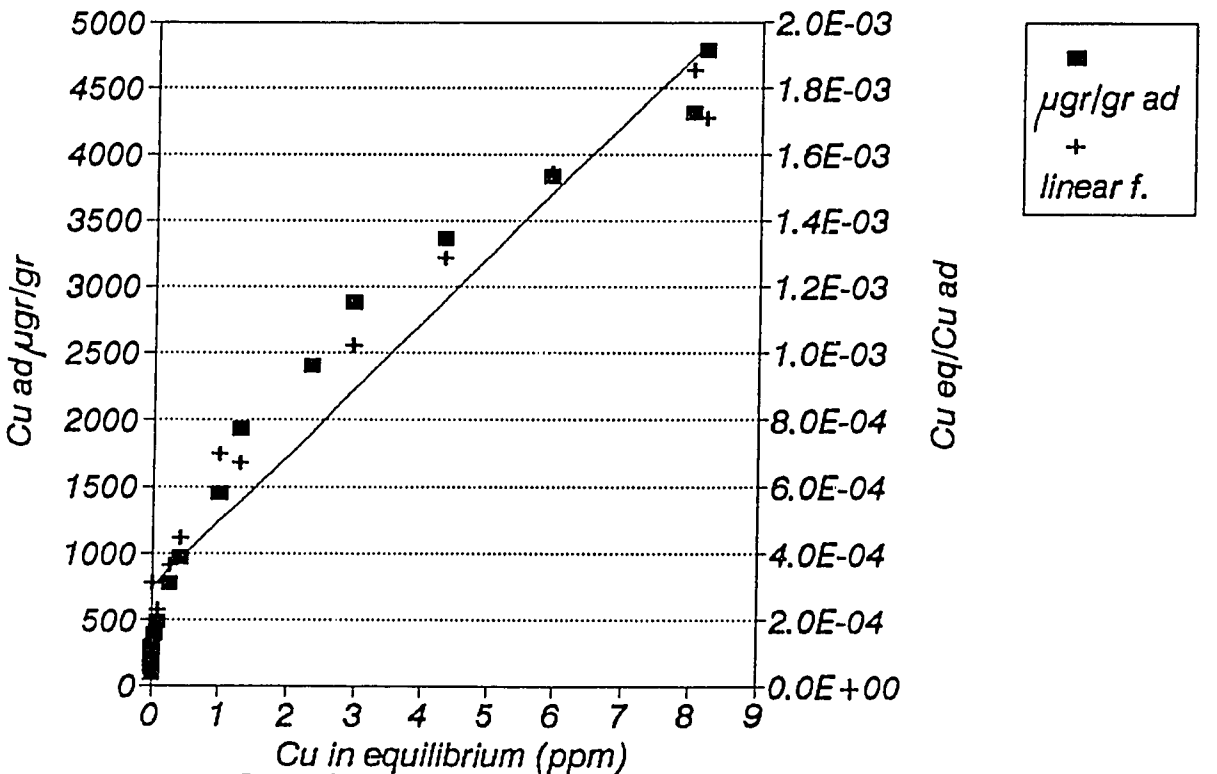
(*) COMM = COMMERCI

Regression Output:		b=	5440	µgr/gr
Constant	0.020064			
Std Err of Y Est	0.003374	K	9.16E-03	
R Squared	0.898929			
No. of Observations	14			
Degrees of Freedom	12			
X Coefficient(s)	0.000184			
Std Err of Coef.	1.78E-05			



Regression Output:		b=	4723	µgr/gr
Constant	0.0375			
Std Err of Y Est	0.004209	K	5.65E-03	
R Squared	0.940547			
No. of Observations	11			
Degrees of Freedom	9			
X Coefficient(s)	0.000212			
Std Err of Coef.	1.77E-05			

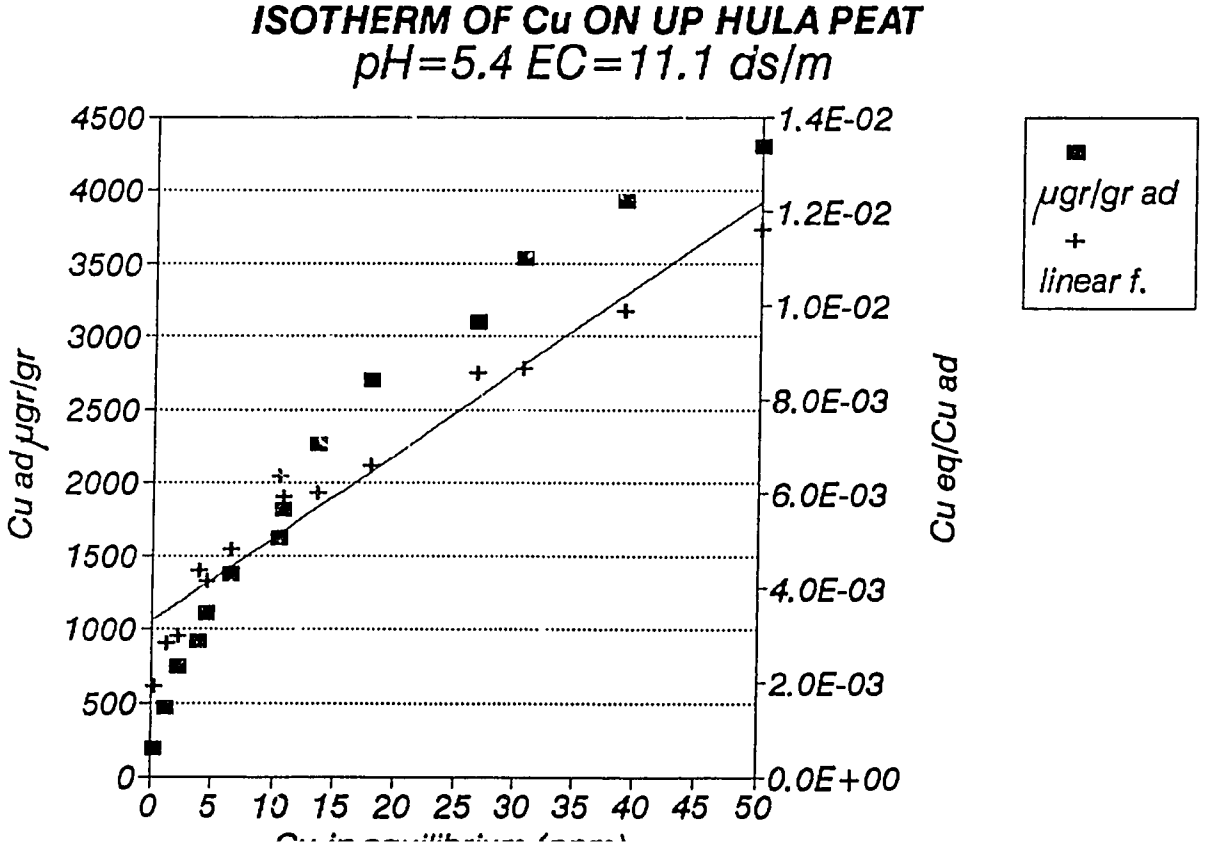
ISOTHERM OF Cu ON BOT. HULA PEAT
pH=5.5 EC=17 ds/m

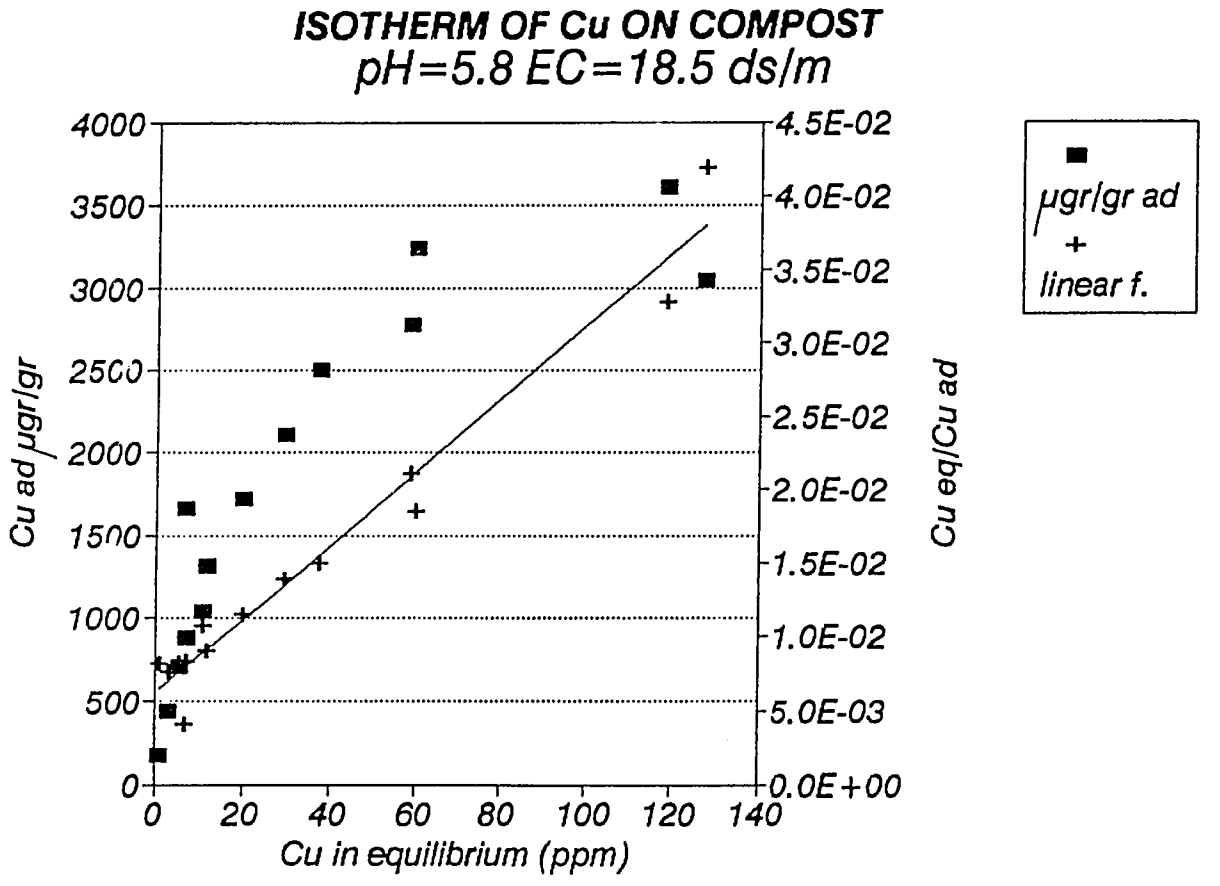


Regression Output:

Constant	0.000294	b=	4994	µgr/gr
Std Err of Y Est	0.000157	K	6.81E-01	
R Squared	0.937572			
No. of Observations	15			
Degrees of Freedom	13			
X Coefficient(s)	0.0002			
Std Err of Coef.	1.43E-05			

Regression Output:		b=	5602 µgr/gr
Constant	0.003274		
Std Err of Y Est	0.000719	K	5.45E-02
R Squared	0.940597		
No. of Observations	14		
Degrees of Freedom	12		
X Coefficient(s)	0.000179		
Std Err of Coef.	1.3E-05		





Regression Output: b= 4000 µgr/gr

onstant	0.00616		
td Err of Y Est	0.00209	K	4.06E-02
Squared	0.964269		
o. of Observations	14		
egrees of Freedom	12		

Coefficient(s)	0.00025
td Err of Coef.	1.39E-05

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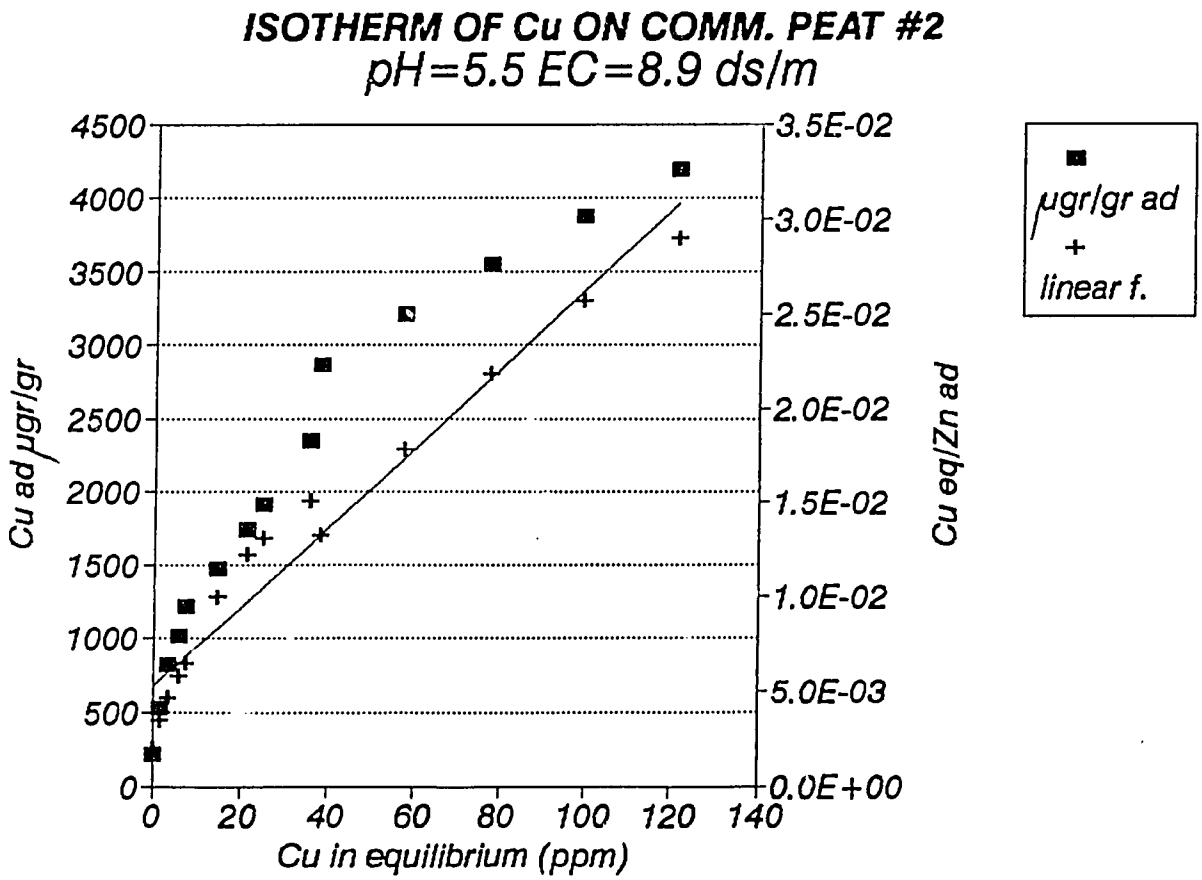
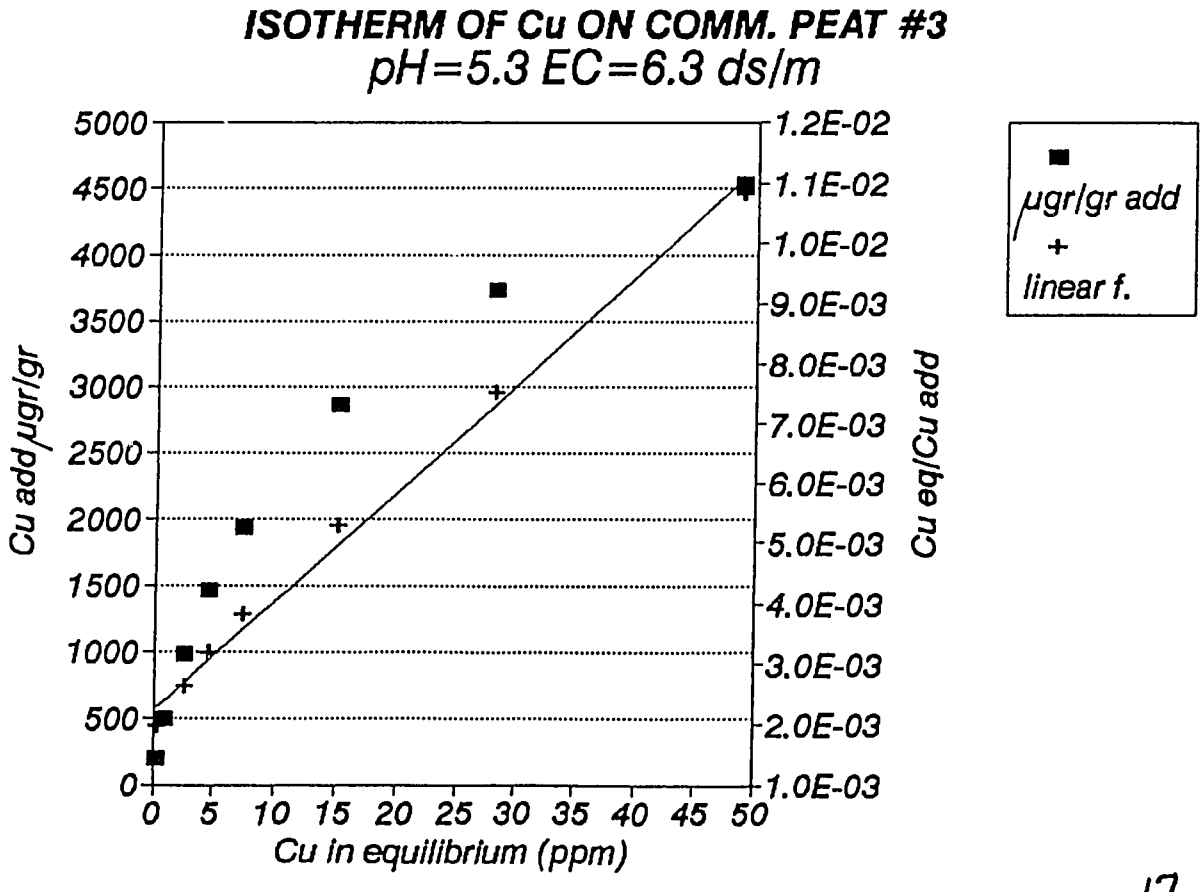
Regression Output:		b=	4747	µgr/gr
Constant	0.005202			
Std Err of Y Est	0.001914	K	4.05E-02	
R Squared	0.951643			
No. of Observations	14			
Degrees of Freedom	12			
X Coefficient(s)	0.000211			
Std Err of Coef.	1.37E-05			



Regression Output:		b=	5525	µgr/gr
Constant	0.002218			
Std Err of Y Est	0.000291	K	0.082	
R Squared	0.992427			
No. of Observations	8			
Degrees of Freedom	6			
X Coefficient(s)	0.000181			
Std Err of Coef.	6.45E-06			



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Number of Pages: 3 April 5, 1994

Dear Yoram:

RE: CDR Grant No. TA-MOU-C12-050

Thank you for your fax messages of 5.12.1993, 5.03.1994 with some of your results (isotherms of Cu on peats #1 & #2, Bot Hula Pear and compost) and of 4.04.1994. Indeed, the communication was not perfect up to now, but I can assure you that since now it will be adequate, though except a copy of a request for periodic advance ve have not received yet even a penny. In fact, a half-year advance in equal instalments is not the most convenient form of payment, considering the planned and accepted budget for 3 years.
Simultaneously with this fax, I am sending a proforma invoice of Perkin Elmer AG for Atomic Absorption Spectrometer Model 3300 with accessories, total 39039 US $ with 8% Special Discount for Prepayment and validity of quotation until 26.06.94. It would be a pity to loose 3395 US $ of discount. The money should be transferred by you directly to the PE account (see page 2 of the invoice). The rest of the budget can be transferred to our Institute account according to the schedule, i.e. 17,000 US $ in the first year and 10,500 US $ in the following two years in any instalments, e.g. quarterly or half-year's, according to your convenience. Please, do consider this my request. I hope that you will arrange the payments properly and with your usual efficiency, and thoroughly rely on you in this respect.

Now, the results and plans on our side:

I. Selection of peats for sampling and investigations.

From database comprising 50807 peat deposits in Poland, in this 8876 highmoor and transitory types and 41931 lowmoor deposits (numbers of peat-bogs registered in database enclosed, Fig. 1), lowmoor peats showing higher pH range (pH 5.5-6.5) than highmoor ones have been selected for adsorption studies:

1. Sphagnum Moss peat from the Pilica and Vistula River basin; ash content (AC) 25.5, decomposition rate (DR) 45;
2. Hypnum Moss peat from the Pilica and Vistula River basin; AC 16.2, DR 60;
3. Sphagnum/Hypnum Moss peat from the Wiercica and Warta River basin; AC 18.0, DR 35-60
4. Sedge peat from the Pisa River basin; AC 9.6, DR 30
5. Rush peat from the Pisa River basin; AC 9.6, DR 40
6. Rush-Sedge peat from the Warta River basin; AC 38.6, DR 33
7. Sedge/Hypnum Moss peat from the Negocin lake; AC 19, DR 40
8. Hypnum/Sphagnum Moss peat from the Niegocin Lake; AC 12, DR 35
9. Hypnum Moss/Rush peat from the Warta River basin; AC 22.9, DR 32
10. Sedge peat from the Warta River basin; AC 23, DR 30

Attempt of peat sampling during February appeared unsuccessful because of a snow cower and frosts. The next planned term is the first half of April.

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II. Phase and chemical composition.[1]

After sampling, phase and chemical composition of sampled peat will be estimated, with a special regard to the binding phases (ion exchange capacity, carbonates, Mn-oxides, amorphous Fe-oxides, sulphides, organic matter and lithogenic crystallites). In Polish lowmoor peats of pH 5.5-6.5, CaO content ranges usually from 2 to 6 %. At CaO>6%, pH of substrate increases, occasionally up to 7.5-8 pH. In carbonatic peats containing considerable amounts of $CaCO_3$, pH ranges from 7.1 to 7.4. Ca occurs usually in organic matter and is bound with adsorbed humic compounds. Considering nature of peats, their binding capacity depends mainly upon chemical composition of organic matter that comprised humic acids and their salts, fulvic acids, lignin and other products of organic matter decomposition. In lowmoor peats, concentrations of C and N in organic matter is higher than in highmoor ones and amounts 50-60% C, 2-3% N, while O and C content increases with peat age and decomposition rate. Concentration of H is 5-6% and close to constant, while S content ranges in lowmoor peats from 0.4-1%, up to 2% S (in highmoor peats S 0.1-0.2%, max. 0.5%). N content in lowmoor peats is also higher (2-3.5%) and usually decreases with the depth. The typical structure of organic matter (N-organic) in lowmoor peat: N-humic insoluble 30.43%, N-humic soluble 9.36%, N-amide 13.38%, N-amine 27.83%, N-free aminoacids 0.03%, N-unidentified 17.68%, N-NH_4 0.93%, N-NO_3 0.33%. (in highmoor peats content of N-humic soluble and N-amide als distinctly lower, while other N forms are more abundant). Humic acid content increases with peat age, depth and DR.
Lowmoor peats contain higher amounts of lignin. Concentration of fulvic acids is changeable (5.5-25.2%)and usually decreases with depth.
Chemical composition of ash is changeable. Ash of lowmoor peats contain considerable amounts of Ca, Fe and some other alkaline species. Ash of lowmoor peats comprises CaO (3-6%), MgO (0.3-0.45%), K_2O (0.07-0.2%), Na_2O (0.1-0.2%), P_2O_5 (0.05-1%, of organic or mineral origin); Fe_2O_3 up to>3%, sometimes up to 20% at high AC, usually in surface layers of peat-bog; SiO_2 contents depends on the sand and clay admixture sometimes is up to 40%; Al_2O_3 increases proportionally to AC, in lowmoor peats up to 2.5%. Besides, Polish peats contain considerable amounts of Ti and Mn, mean concentrations of B, Cu, Zn and low contents of Co and Mo.
Phase and chemical composition of the selected samples will be estimated after sampling.

III. Binding of heavy metals in peats

Considering phase and chemical composition of Polish lowmoore peats, organic/sulphidic fraction F5 seems to be the main binding phase, though carbonates (F2) and Fe-oxides (moderately reducible phase F4) can also play an important role. *Per analogy* with weathered coal mining wastes [2], a probable order of binding strength for investigated metals is Cr > Cu > Zn > Cd, and the same order with respect to bound amounts, either at separate or simultaneous binding. The mobilization capacity is expected in adverse order, having in mind chemical fractionation of metals. Chromium is bound predominantly in F4 and to lesser extent in F5 phase and does not compete with other metals in adsorption fractions, therefore its binding strength and capacity supposed to be the highest. Copper will be probably adsorbed in high amounts in carbonatic fraction F2, successfully competing with zinc, and in oxidizable fraction F5, while Cd is expected to be bound mainly in the most labile exchangeable fractions, and to show strong susceptibility to remobilization due to strong competition of Cu and Cr also in carbonatic F2 and reducible F3 and F4 fractions (example Fig. 3). As shows very high mobility under a wide range of pH-Eh, and its mobility can be probably reduced due to binding in sulphidic fraction at low Eh. The adsorption efficiency is supposed to be higher at acidic pH of input solutions, while at highly alkaline pH of input solution, solubilization of humic acids could be expected. In these cases, highmoore acidic peats could be more efficient. These assumptions need to be proved by experiments, that will comprise adsorption-desorption batch and column experiments, as well as chemical fractionation of metals by sequential extraction. Batch experiments and chemical fractionation for separate and simultaneous binding is being planned to be carried out by the end of August. More time-consuming column experiments will be continued.

IV. Mechanism of metal binding in peat.

Besides phase approach, mechanism of binding also will be investigated (inert bonding, precipitation, adsorption, co-precipitation, coatings, flocculation) after the determination of full adsorption capacity of substrate with respect to studied metals.

V. References

1.J.K. Frankiewicz (1980): Peat properties. In: World raw materials. Peat. Wyd. Geolog., Warsaw, 24-46
2.I. Twardowska, B.Jarosinska (1992): Barrier capacity of weathered coal mining wastes with respect to heavy metal and organic contaminants. In: D.W.Tedder (Ed): Emerging Technologies for Hazardous Waste Management. 1992 Book of Abstracts, ASC, Washington, DC, Vol.II, 649-651

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Root research

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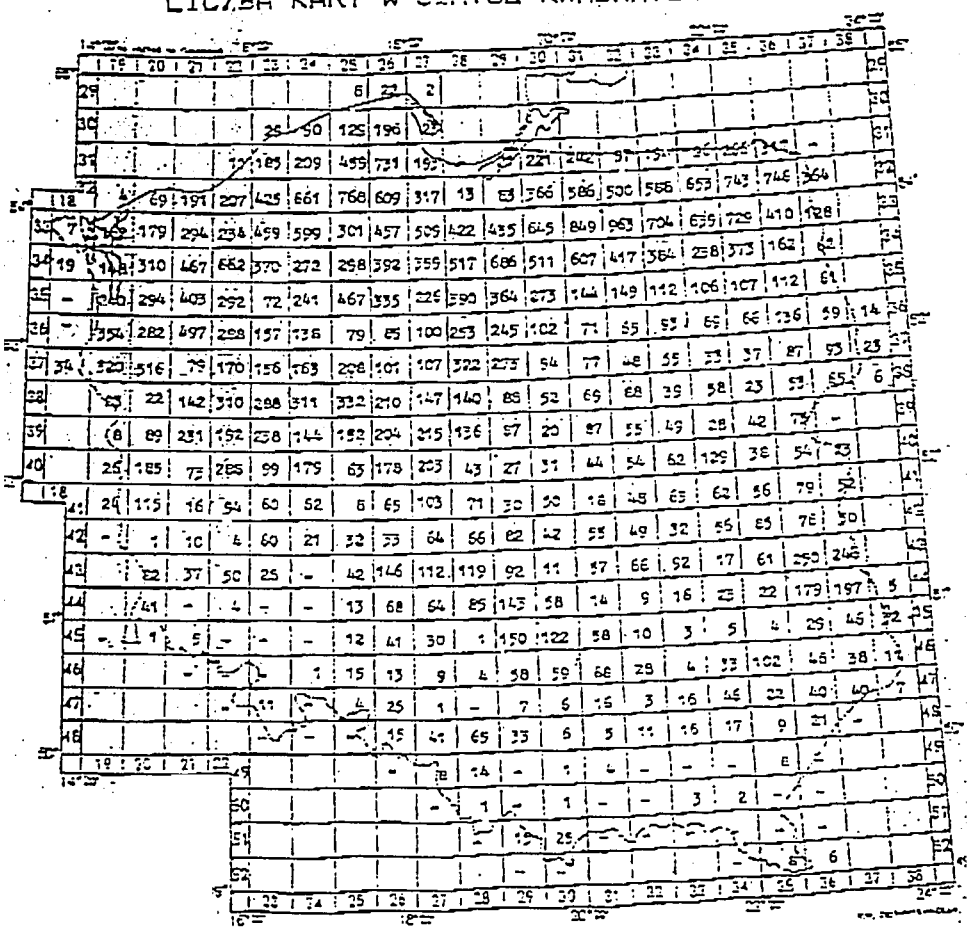

Fig. 1. IMUZ Database: peat-bogs of Poland

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