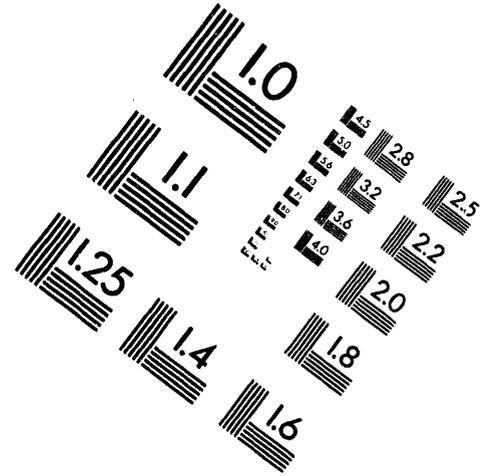
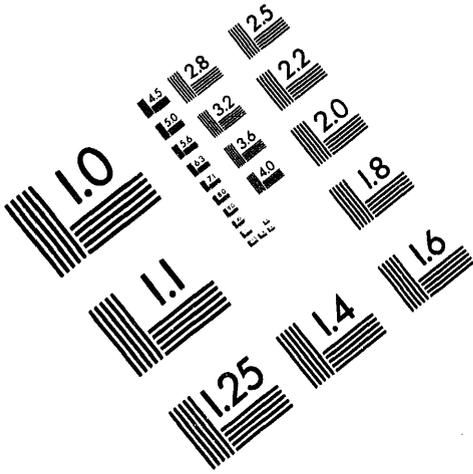




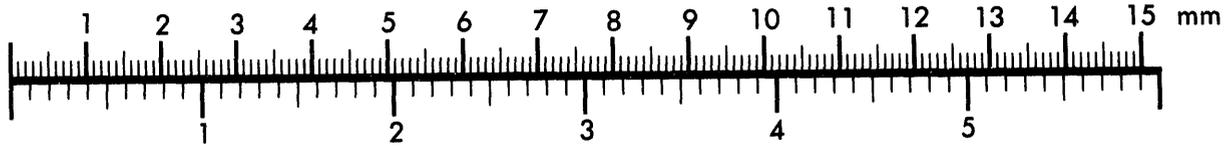
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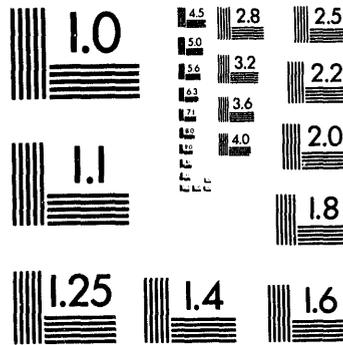
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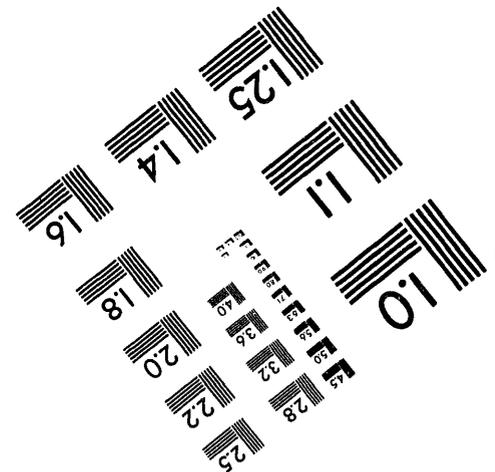
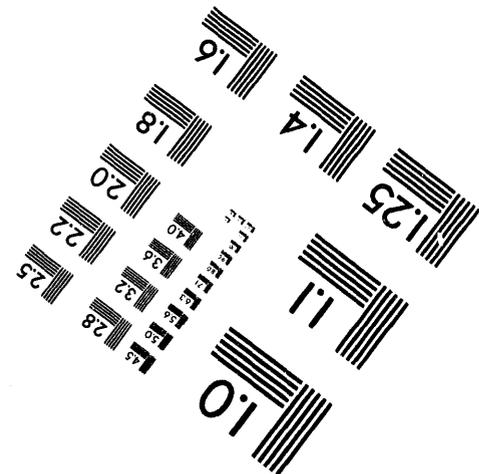
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QUARTERLY TECHNICAL REPORT:

Title: WETLAND TREATMENT OF OIL AND GAS WELL WASTEWATERS

Contract No. DE-AC22-92MT92010

Institution: University of Michigan, Department of Chemical Engineering

Date: December 28, 1993

Contract Date: May 25, 1992

Anticipated Completion Date: May 24, 1994

Government Award:

Project Director: Prof. Robert H. Kadlec

Project Manager: Dr. Keeran R. Srinivasan

PIs: Prof. Robert H. Kadlec and Dr. Keeran R. Srinivasan

Technical Project Officer (COR): Dr. Brent W. Smith

Reporting Period: August 25, 1993 - November 24, 1993.

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## I Executive Summary:

During the first quarter of the above contract, all the elements of Task 1 were completed. The first quarterly report (1) presented an overview of a wetland and its increasing use in industrial waste water treatment. An idealized, reaction engineering description of wetlands was presented to demonstrate how the various processes that occur in a wetland can be modeled. Previous work on the use of wetlands to remove BOD, TSS, Phosphorus and Nitrogen was reviewed. Recent literature on the application of wetland technology to the treatment of petroleum-related waste water was critically evaluated and an outline of the research plans for the first year was delineated. Further, our literature search (nominally completed under Task 1) unearthed more recent studies (some unpublished) and a summary was included in the second quarterly report (2). In the second quarterly report, results of our efforts on the construction of a laboratory-type wetland were also reported. Initial studies on the use of wetland amendments such as modified-clays and algae cells were presented and discussed (2). In the third quarterly report (3), adsorption of heavy metals ions such as Cu(II) and Cr(VI) onto soils drawn from the laboratory-type wetland was shown to be weak. Secondly, it was shown that modified-clays did adsorb Cr(VI) ions strongly at pH 4.5. Further, studies on the pH dependence of the adsorption of  $\beta$ -naphthoic acid, (NA), a well-documented contaminant in many oil and gas well waste waters (4), onto modified-clays were undertaken and it was shown that uptake of NA by modified-clays was of the high affinity type at pH 4.5 and 7.0, but weak at pH 9.0. Adsorption of heavy metal ions,  $\text{Cu}^{2+}$ , and Cr(VI) onto algae, a proposed wetland amendment, was carried out and the results were presented and discussed in the fourth quarterly report (5). Uptake of NA by the soil component of the laboratory-type wetland was monitored as a function of pH. The adsorption of NA onto modified-clays was studied in greater detail and these data were described and analyzed in an earlier quarterly report (5). Studies on the dynamics of uptake of phenol and NA by laboratory-type wetlands (LWs) were initiated and preliminary results indicated that both phenol and NA were sorbed onto components of LWs (6). It was also observed that phenol volatilization from supernatant water contributed to phenol disappearance. This was attributed to high water temperature during the Summer months when these studies were conducted. On the other hand, there was minimal loss of NA through evaporation even during Summer months(6).

- The dynamics of the uptake of Cu(II) and phenol by laboratory-type wetland systems (LWs) have been studied and the results are presented and discussed.
- In continuation of our earlier work on phenol uptake by LWs, the effects of (1) addition of peat (2) the depths of supernatant water and (3) the initial concentration of phenol have been considered. Based on published literature, peat is known to be a potent adsorbent of toxic organics and heavy metals (7). Thus, addition of peat to a wetland is expected to enhance its performance. Supernatant water depths and the initial phenol (nominal) concentrations have been varied to provide insights into phenol losses through evaporation and its effect on phenol mass balance.

## II. Tasks 3A and 3B: Dynamics of the Uptake of Toxic Organics and Heavy Metals by Laboratory-type Wetlands (LWs).

In a previous report (2), we had described the design and the construction of a laboratory-type wetland. Briefly, 18-gallon plastic containers containing 4 cattails/container were prepared in a suitable soil matrix and grown at the Botanical Gardens operated by The University of Michigan.

Uptake experiments were conducted in the following manner:

Fig. 1 Dynamics of Cu (II) uptake by Laboratory-type Wetlands

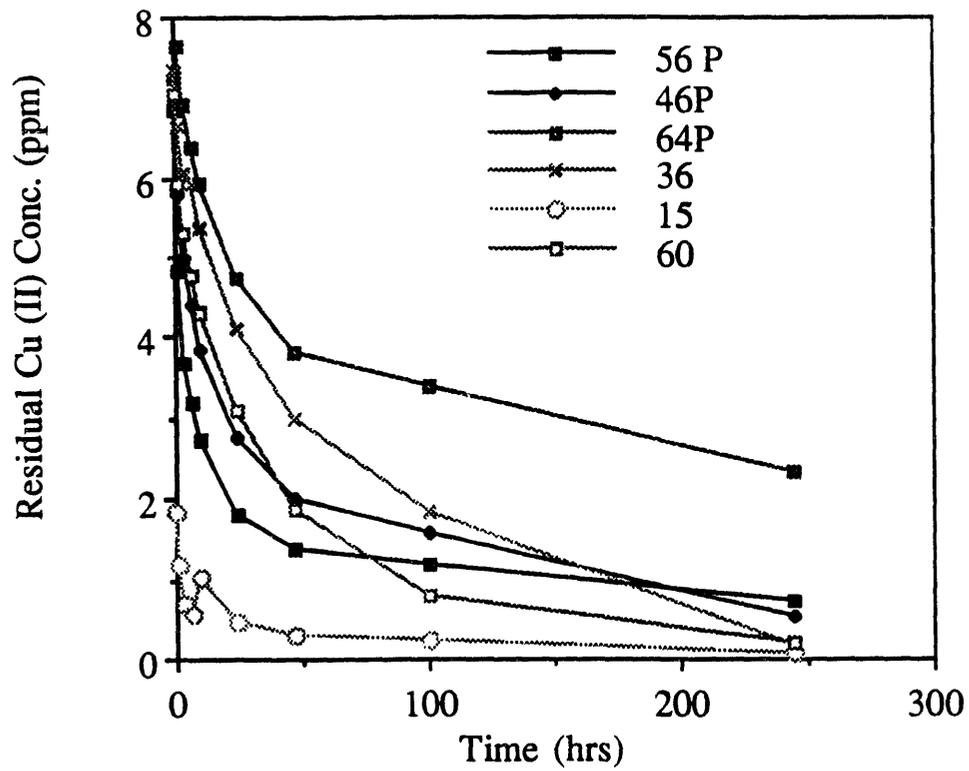
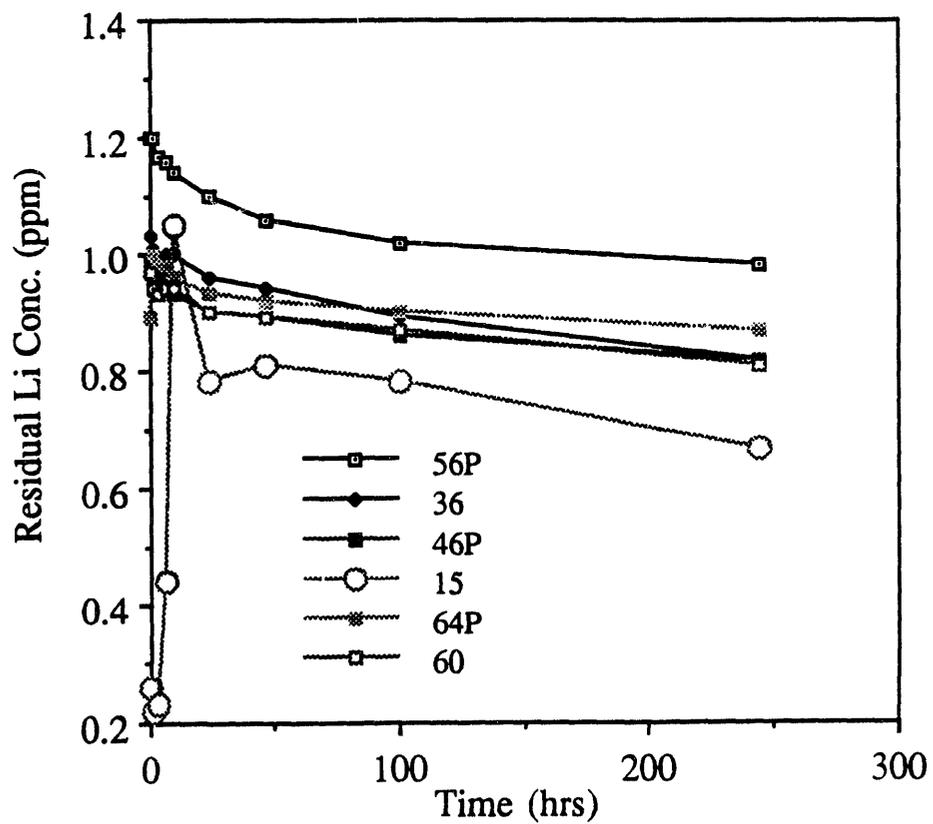


Fig. 2 Uptake of Li Tracer by Laboratory-type Wetlands



- (1) Removed the overlying water and replaced with fresh tap water. In some cases, 2 -3 gallons of peat in the form of a thick paste were layered before adding tap water. Water depth was set to be either 3 or 7 inches from the surface of the soil matrix.
- (2) After 24 -hr equilibration, the height of the water column was monitored again and the overlying water was spiked with **Cu (II)** or **phenol** to a pre-determined nominal concentration. Following the addition of the toxic organic or the heavy metal, the water was mixed manually with a paddle, and was left undisturbed thereafter. In the case of **Cu(II)** uptake experiments, **Li** ions were mixed in with **Cu(II)** ions. Since **Li<sup>+</sup>** is a known to be a conservative tracer its concentration in the supernatant water can be used as a guide to determine the approach to steady state conditions.
- (3) Collected water samples prior to the start of the experiment and periodically during the experiment. The temperature, water depth and the pH were noted.

The concentration of phenol in the supernatant water was determined spectrophotometrically using the aqueous-phase 4-aminoantipyrine method (8). We had previously used steam distillation followed by UV absorbency to quantify phenol concentration in supernatant water. The latter method proved to be time-consuming because of the large number of samples that needed to be analyzed. Therefore, direct assay by the 4-aminoantipyrine method without any pre-treatment was attempted. Phenol concentrations obtained by this method were compared with those obtained by the steam distillation method and the agreement between the two values was within 4%. All the data reported herein were obtained using the aqueous-phase 4-aminoantipyrine method.

Concentrations of **Cu(II)** and **Li<sup>+</sup>** were measured using Perkin Elmer AA Spectrometer. The combined results of **Cu(II)** and phenol uptake by the LWs are shown in Figs 1 - 6.

### **Cu(II) Uptake:**

**Cu(II)** uptake experiments were studied in triplicate, i.e. three LWs per experiment. The effect of peat addition was also monitored in triplicate. Water depth was maintained at 7 inches and the initial concentrations of **Cu(II)** and **Li<sup>+</sup>** were nominally 10 and 1.2 ppm respectively. pH was between 5.5 - 6.0 and did not change during the course of the experiment. The results are shown in Fig. 1.

It can be seen that **Cu(II)** uptake shows a tri-phasic behavior. There is an initial phase during which a portion of **Cu(II)** is rapidly removed followed by a second phase lasting upto 50 hours when **Cu(II)** removal is gradual. These two phases may correspond to partial hydrolysis and precipitation of **Cu** ions and a slow adsorption of **Cu(II)** onto various components of LWs respectively. Since LWs with or without peat show similar behavior, it appears that peat has minimal effect on **Cu(II)** adsorption. Further work to verify this finding is in progress.

Beyond 50 hours, the rate of removal is quite slow and there is an apparent tendency for the **Cu(II)** concentration to level off. This is attributed to a slow dispersion of **Cu(II)** into the underlying pore water of the LWs.

One of the LWs ( LW # 15; no peat added ) shows a much larger and faster uptake of **Cu(II)** compared to any of the other LWs. Results presented in Fig. 2 for **Li<sup>+</sup>** uptake by the same LW help clarify the anomalous results observed with LW # 15. From Fig. 2 it can be seen that **Li<sup>+</sup>** data also show a similar atypical time profile. Since **Li<sup>+</sup>** is a conservative trace ( data shown in Fig. 2 verify this ) it is concluded that a contamination of this LW may have occurred. Thus, the

Fig. 3 Uptake of Cu(II) by Laboratory-type wetlands:  
Effect of added Peat

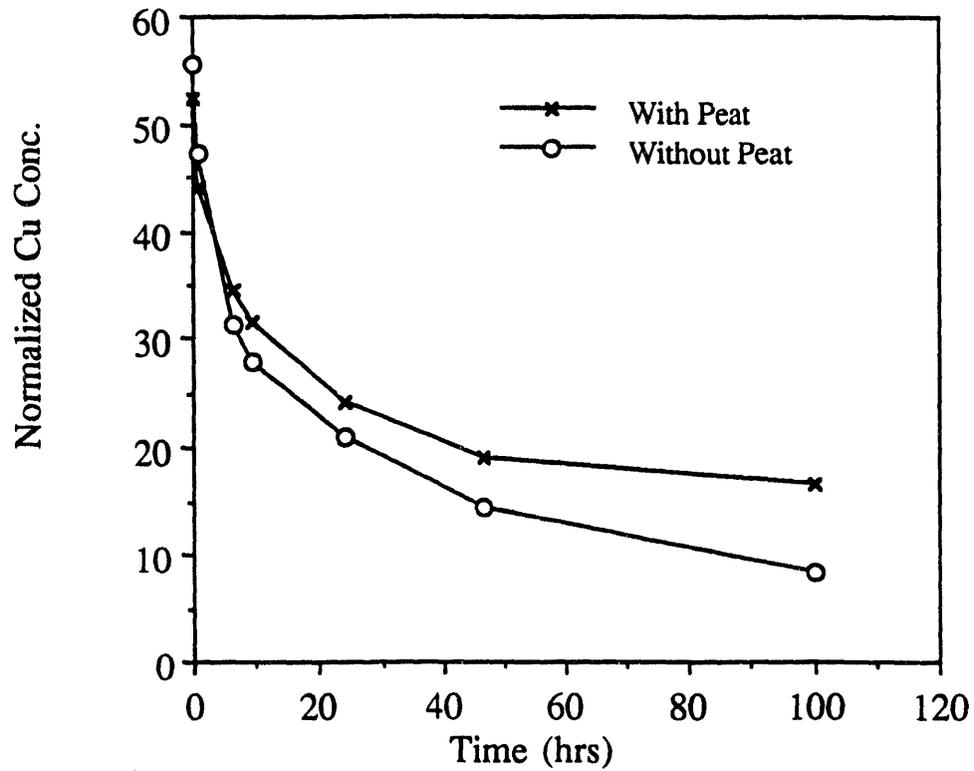


Fig. 4 Uptake of phenol by Laboratory-type Wetlands:  
Effect of water Depth

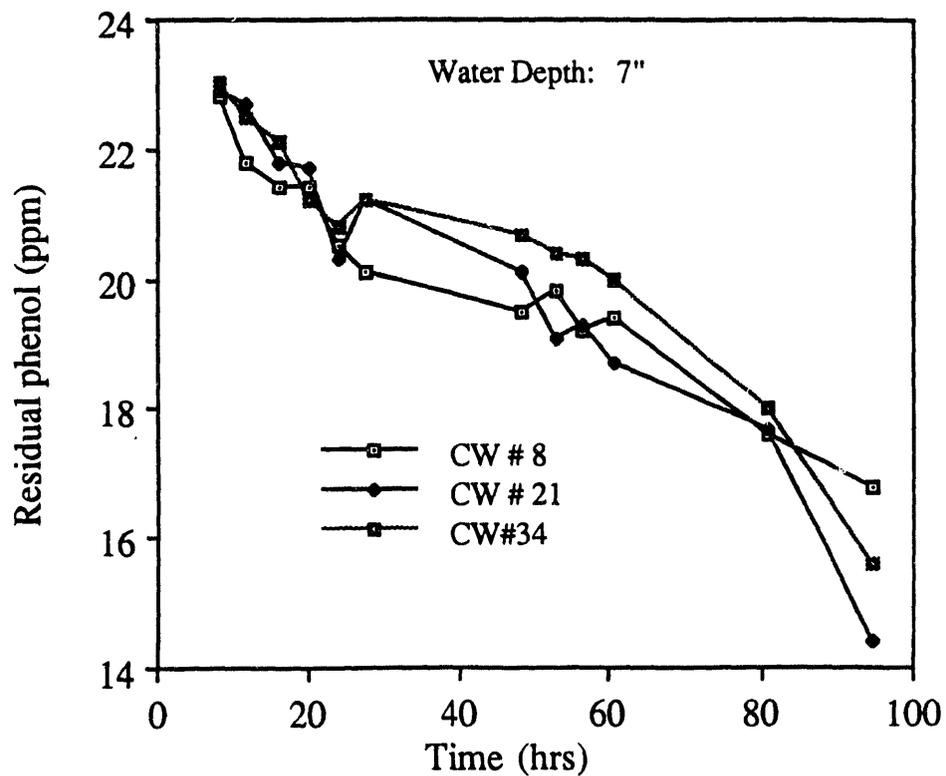


Fig. 5 Uptake of Phenol by Laboratory-type Wetlands in Presence Peat: Effect of Initial Phenol Concentration

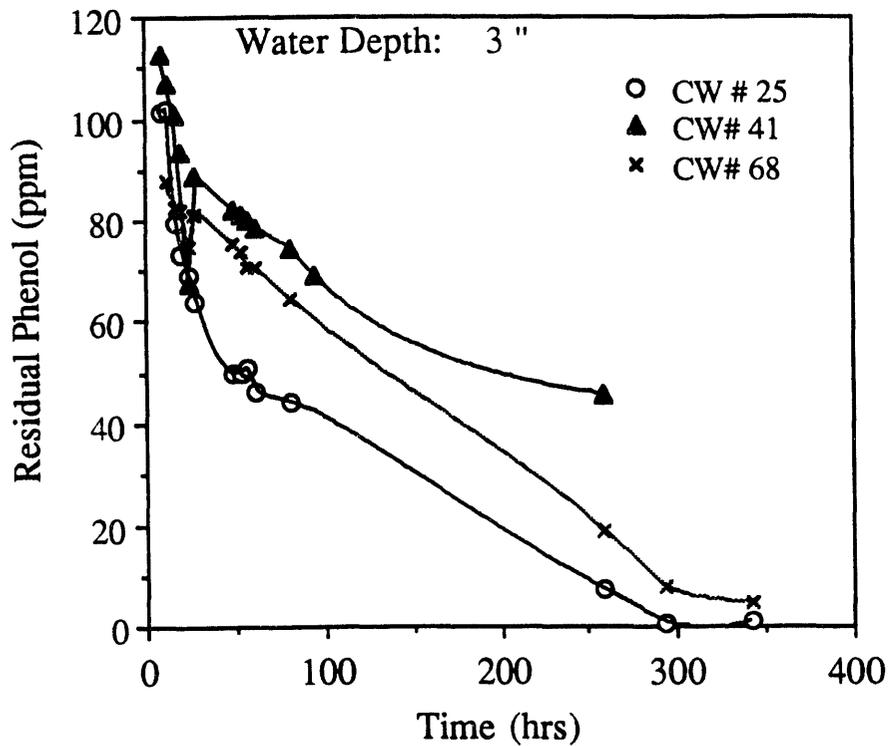
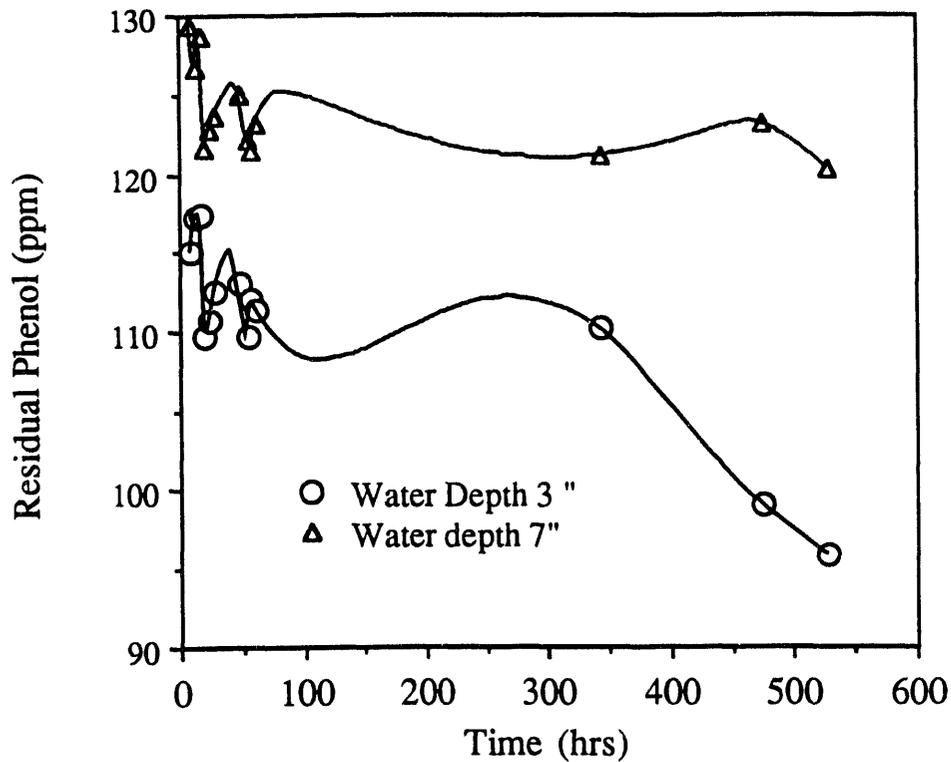


Fig. 6 Uptake of Phenol: Blank experiments



use of  $\text{Li}^+$  tracer is shown to be helpful in sorting out real effects from artifacts when dealing with complicated systems such as LWs.

Fig. 2 also reveals that, for the LWs considered here, it takes about 150 hours for the system to attain steady state. Secondly, it is clear that  $\text{Li}^+$  data can be used to normalize Cu(II) uptake measurements so that the effects of dilution and dispersion of Cu(II) ions through diffusive mass transfer into underlying pore water of the LW can be taken into account. Data from the triplicate set of measurements (with and without peat; Fig. 1) have been averaged and normalized by the apparent  $\text{Li}^+$  "disappearance" data (Fig. 2) and the normalized average results are shown in Fig. 3. The two curves shown in Fig. 3 reveal that:

- (1) Between 75 - 85 % of Cu(II) ions (at an initial concentration of 10 ppm) can be removed by LWs constructed as a part of this study.
- (2)  $\text{Li}^+$  data can be used to normalize heavy metal ion uptake data in complicated systems such as LWs.
- (3) Addition of peat has a minimal effect on Cu(II) uptake by LWs.

### **Phenol Uptake:**

At an initial concentration of 20 ppm (nominal) phenol uptake is quite slow. This can be seen from the results shown in Fig. 4. The lower initial concentration and a lower water temperature may have been responsible for the observed results. Due to higher water depth, the evaporative losses may also have been minimal (see Fig. 6). Thus, a combination of water depth and low ambient temperature has a large effect on phenol removal and its mass balance.

On the other hand, the use of a different set of experimental conditions such as lower water depth, the addition of peat and a higher initial phenol concentration produces dramatic results in terms of phenol removal (Fig. 5). It is apparent from Fig. 5 that shallow waters and high initial phenol concentrations may have caused increased phenol losses through volatilization. However, the major removal mechanism appears to be sorption onto peat and other LW components.

Blank experiments shown in Fig. 6 establish that, as previously reported, phenol losses through evaporation are considerable (between 25 - 35 %), but the major removal mechanism of phenol is sorption of the organic to various components of a LW.

### **III. Future Work:**

Based on the results described above, uptake of Cu (II) and other heavy metals such as Cr(VI) and phenol by laboratory-type wetlands (LWs) will be studied in greater detail. Furthermore, an explanation for the lack of efficacy of peat addition in promoting the retentive capacity of LWs for heavy metals will be sought.

### **IV: SUMMARY**

This quarterly report presents results from studies on the uptake of Cu(II) and phenol by laboratory-type wetlands (LWs) designed and built during the earlier phases of this study. The uptake of Cu(II) follows a tri-phasic behavior attributed to partial hydrolysis and precipitation, sorption onto wetland components and a slow dispersion into underlying pore water of the laboratory-type wetland. The addition of peat was observed to have only a minimal effect on Cu(II) uptake. On the other hand, phenol sorption was favorably modified by the addition of peat. Furthermore, a lower water depth results in slightly higher evaporative loss of phenol, but

the major removal mechanism of phenol has been shown to be through sorption to various components of a laboratory-type wetland.

**V: Report Distribution List:**

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**VI. REFERENCES:**

- (1) R. H. Kadlec and Keeran R. Srinivasan: 1st Quarterly Report, U. S. DOE, PETC, August, 1992.
- (2) R. H. Kadlec and Keeran R. Srinivasan: 2nd Quarterly Report, U. S. DOE, PETC, November, 1992.
- (3) R. H. Kadlec and Keeran R. Srinivasan: 3rd Quarterly Report, U. S. DOE, PETC, March, 1993.
- (4) J. R. Gulley and P. G. Nix: " Wetland Treatment of Oil sands Operation Waste water " ( A private Communication from authors to R. H. Kadlec, PI).
- (5) R. H. Kadlec and Keeran R. Srinivasan: 4th Quarterly Report, U. S. DOE, PETC, July, 1993.
- (6) R. H. Kadlec and Keeran R. Srinivasan: 5th Quarterly Report, U. S. DOE, PETC, October, 1993.
- (7) P. Eger and K. Lapakko: " Nickel and Copper Removal from Mine Drainage by a Natural Wetland," in *Mine Drainage and Surface Reclamation, Vol.I, Mine Water and Mine Waste*, Bureau of Mines Information Circular 9183 (1988), pp. 301-309.
- (8) Standard Methods for the Examination of Water and Wastewater: 16th Edition, a Publication of APHA, AWWA, and WPCF, Published by APHA, Washington, D. C., (1985) pp. 556-570.

**VII. Publications:** None

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