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Accumulation of Copper in Fluvial Sediments and Yellow Water Lilies (*Nuphar lutea*) at Varying Distances from a Metal Processing Plant

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Several studies have been carried out to demonstrate changes in aquatic biota caused by changes in water quality. A few recent studies have reported the usefulness of aquatic macrophytes as indicators of heavy metal pollution on the basis of the plants' ability to accumulate considerable amounts of metals from the environment (e.g. ADAMS *et al.* 1973, RAY and WHITE 1976,1979; FRANZIN and McFARLANE 1980). On the other hand, many studies have demonstrated processes associated with transport and accumulation of heavy metals discharged from various point sources of pollution (cf. FÖRSTNER and WITTMANN 1979). Analyses of water samples with various extraction and partitioning methods require, however, laborious and time-consuming procedures. Therefore, leaf analyses of aquatic plants are of special interest because these simple procedures result in estimates of the water quality over long periods of time.

The purpose of the present study was to demonstrate accumulation of copper in fluvial sediments and in dominant aquatic vegetation in the vicinity of a point source of heavy metal pollution. In addition, correlations were calculated between the Cu concentrations accumulated in various plant organs and the levels of total and exchangeable proportions of Cu in the substrate.

MATERIAL AND METHODS

Samples for heavy metal analyses were collected from the River Kokemäenjoki in western Finland in August 1977. The actual study site is situated near a base metal purification and processing plant in Pori. The plant has an annual production of purified copper of about 40-50'000 tons, and the amount of Cu discharged into the river averaged 24 kg/d in 1977 (NATIONAL BOARD OF WATERS, FINLAND 1978).

Samples of surface sediments and of the dominant aquatic macrophyte, *Nuphar lutea* (L.)Sm. were collected from seven sampling sites which were situating at intervals of 300 m from each other. The sediment samples were taken with a core sampler from the surface layer (0-5 cm) of the substrate. In the laboratory, the samples were oven-dried (at 60^{o}C for 24 h), gently homogenized, and sieved to pass a 2 mm screen. For analyses of the total copper concentrations, one gram portions of sieved material were acid-extracted with 25 ml of 16 *N* nitric acid boiling to dryness twice.

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The residue was taken to solution with dilute hydrochloric acid (AGEMIAN and CHAU 1976). For analyses of the exchangeable proportions of Cu, five gram samples of sieved material were extracted overnight with 100 ml of 0.5 *N* hydrochloric acid (AGEMIAN and CHAU 1976). Three to five replicates were studied for each sampling site.

Simultaneously with the collection of sediment samples, vegetation samples were collected from monotypic stands of *Nuphar lutea* growing along the shorelines at depths of 40-90 cm. In the laboratory, the plant material was washed with tap water, sorted according to plant organs, and oven-dried at $60^{o}C$ for 24 h. One gram samples of dried and ground material were dry ashed at $450^{o}C$ for 4 h. The ash was dissolved in 20 % hydrochloric acid on a heated plate, and after filtering filled to volume with demineralized water. Four replicates were studied for each sampling site and for each plant organ.

The concentrations of copper in sediments and in plant materials were determined with a Perkin-Elmer model 300 atomic absorption spectrophotometer at the Department of Biology, University of Turku. All results are presented as parts per million of dry weight. Differences in the analytical results between the sampling sites were tested by using an analysis of variance.

RESULTS AND DISCUSSION

Analyses of sediments

The concentrations of copper in the fluvial sediments collected from the River Kokemäenjoki, western Finland, are presented in Table 1. The levels of Cu clearly demonstrate the enrichment of discharged metals in the vicinity of the metal processing plant. The highest concentration of total copper in the sediments was 1020 ppm, a value exceeding the records earlier reported from Northern Europe and being one of the highest values reported in recent literature on heavy metal pollution (cf. FÖRSTNER and WITTMANN 1979). Accumulation of metals takes place only in the narrow shallow water zone within 0-8 m from the shoreline. This is because of strong turbulences and backward currents in the river flow just by the processing plant. These circulations tend to raise into the surface layer considerable amounts of waste waters discharged into the deep channel. Thus the dissolved metals tend to accumulate in the shallow water sediments. In contrast, the levels of copper in the deep water sediments are rather low: the concentrations of total Cu ranged from 17 to 54 ppm. Thus the river tends to carry the bulk of the copper load downstream, finally discharging large amounts of metals into the Baltic Sea (ISOTALO 1979). With increasing distance from the processing plant the levels of Cu accumulated in sediments decreased sharply (cf. Table 1). Thus the levels of Cu at the site just by the plant and at the site 300 m downstream differed highly significantly ($P < 0.001$) from each other as well as from any other sampling site. In addition, the concentrations of Cu for the control sites upstream of the waste discharge point were significantly ($P<0.01$) lower than the values for any sampling site downstream of the plant. Nevertheless, all values recorded in the present study were well above the normal background levels of copper in Finnish soils.

TABLE 1

Concentrations of copper in fluvial sediments near a metal processing plant.

Distance (m) below waste discharge	Cu, total (ppm)		Cu, exchangeable (ppm)	
	Range	Average	Average	% of total
-600	16 - 39	29	17	58.6
-300	31 - 60	55	25	45.4
0	735 - 1020	880	468	53.2
300	266 - 530	412	83	20.1
600	69 - 83	78	51	65.4
900	72 - 164	149	100	67.1
1200	76 - 88	84	49	58.3

The easily extractable proportions of copper in the fluvial sediments ranged from 20 to 67 % of the corresponding total values (Table 1). Thus also the amounts of weakly bound copper being available to primary producers are markedly higher than the background concentrations in non-polluted aquatic environments.

Analyses of *Nuphar lutea*

The pattern of copper accumulation in various plant organs of the yellow water lily (*Nuphar lutea*) is presented in Figure 1. In all organs the levels of Cu were markedly elevated at sampling sites near the metal processing plant, and with increasing distance above and below the waste discharge point the levels of Cu decreased sharply (Fig. 1). Thus, the differences in Cu concentrations of leaves and petioles were significant ($P < 0.01$) between the sampling sites by the plant and the site situating 300 m downstream, and highly significant ($P < 0.001$) between the site by the plant and the rest of the sampling sites. The highest concentrations recorded for leaves and petioles were 98 ppm and 115 ppm, respectively. These values are the highest ones by far reported for *Nuphar lutea* (cf. DYKYJOVA 1979). In contrast, the concentrations of copper in the belowground organs were surprisingly low. This phenomenon seems to indicate certain selectivity in the uptake/exclusion and translocation processes by *Nuphar lutea*.

The accumulation of copper in petioles, leaves and rhizomes of *Nuphar lutea* was clearly proportional to the copper levels in the corresponding surface sediments (Table 2). The levels of total copper in the substrate correlated with the amounts of Cu accumulated in plant tissues with slightly higher coefficients than did the exchangeable proportions of Cu (Table 2) (cf. MUDROCH and CAPOBIANCO 1979).

TABLE 2

Correlation coefficients between copper concentrations accumulated in *Nuphar lutea* and Cu levels in substrate. Significance levels: ** = P < 0.01, *** = P < 0.001.

	Cu, total	Cu, exchangeable
flowers	0.198	-0.102
petioles	0.931**	0.965***
leaves	0.978***	0.942**
rhizomes	0.935**	0.938**

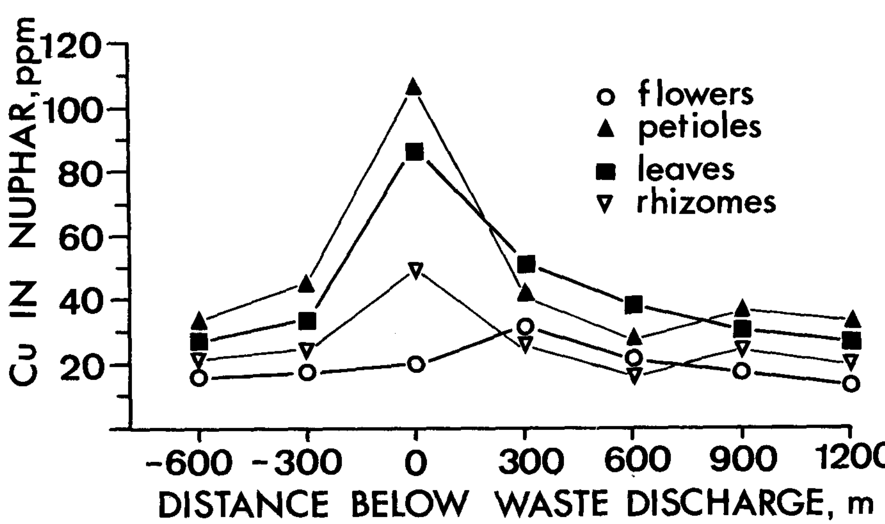

Figure 1. Pattern of copper accumulation in *Nuphar lutea* at varying distances from a metal processing plant.

The fact that the yellow water lilies are able to survive and grow without any visible injuries in the habitats containing very high levels of copper seems to indicate well-developed tolerance to heavy metal pollution. Several studies have reported varying reactions of *Nuphar lutea* against different pollutants. KURIMO (1970) and WIEGLEB (1978) reported that *Nuphar lutea* was indifferent species having no benefits or disadvantages of various forms of eutrophication and pollution aspects. On the other hand, AGAMI *et al.* (1976) showed that *Nuphar lutea* could not survive when transplanted into polluted sections of Israelian rivers. None of these former investigations were, however, associated with heavy metal pollution, and thus the present results extend our knowledge of the usefulness of the yellow water lily (*Nuphar lutea* (L.)Sm.) as a biological indicator of aquatic pollution.

REFERENCES

ADAMS, F.S, H. COLE, Jr. and L.B. MASSIE: Environ. Pollut. 5, 117 (1973).

AGAMI,M., M. LITAV and Y. WAISEL: Aquat. Bot. 2, 203 (1976).

AGEMIAN, H. and A.S.Y. CHAU: Analyst 101, 761 (1976).

DYKYJOVA, D.: Folia Geobot. Phytotax. 14, 267 (1979).

FÖRSTNER, U. and G.T.W. WITTMANN: Metal Pollution in the Aquatic Environment. Berlin: Springer Verlag (1979).

FRANZIN, W.G. and G.A. McFARLANE: Bull. Environm. Contam. Toxicol. 24, 597 (1980).

ISOTALO, I.: Publ. Water Res. Inst., National Board of Waters, Finland 30, 3 (1979).

KURIMO, U.: Ann. Bot. Fennici 7, 213 (1970).

MUDROCH, A. and J.A. CAPOBIANCO: Hydrobiologia 64, 223 (1979).

NATIONAL BOARD OF WATERS, FINLAND: Report 142 (1978).

RAY, S. and W. WHITE: J. Environ. Sci. Health A-11, 717 (1976)

RAY, S. and W. WHITE: Chemosphere 8(3), 125 (1979).

WIEGLEB, G.: Arch. Hydrobiol. 83, 443 (1978).