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Ecological studies in the paper mill effluents and their impact on the river Tungabhadra: Heavy metals and algae

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Abstract. Certain metals have been investigated in paper mills effluent channel and in the river Tungabhadra in relation to their distribution, seasonal fluctuations and their effect, if any, on algae. The concentrations of various metals analysed are in the order of Zn > Cu > Pb > Ni > Co > Mn. In general these metals indicated an increase in their concentration along with the increase in the concentrations of chlorides, total hardness, sulphates and total alkalinity. Blue-greens and diatoms seem to be more tolerant to these ions than Chlorophyceae. *Stigeoclonium* exhibited very good growth at high concentrations of zinc, copper and nickel and at low concentrations of cobalt and lead. *Schizomeris* attained good growth when the lead concentration was high and cobalt was low.

Keywords. Heavy metals; algae; paper mill effluents; river Tungabhadra.

1. Introduction

The term 'heavy metal' although not rigidly defined is generally held to refer to those metals having a density > 5 (Passow *et al* 1961; *cf.* Whitton and Say 1975, p. 287). Although some metals, including heavy metals are needed by living organisms for various metabolic processes (Whitton and Say 1975), the physiological and metabolic roles or requirements of such heavy metals as mercury, lead, cadmium and silver are not properly understood. In contrast to herbicides, pesticides and other potential toxicants, which can undergo breakdown, albeit extremely slowly, heavy metals cannot be eliminated from a water body and they persist in sediments from where they may be released slowly into the water. After their release from sediments, heavy metals may again pose serious hazards to aquatic organisms, including algae (Rai *et al* 1981).

Patrick (1978), Whitton (1970, 1980, 1984), Welch (1980) and Stokes (1983) have carried out lot of work on heavy metals in aquatic ecosystems concerned either with toxicity or accumulation, especially for algae. Rai *et al* (1981) have reviewed the relationships between algae and heavy metals.

In nature, the presence of these metals depends on various environmental conditions. The principal sources of heavy metals have been dealt at length by Williams *et al* (1974). Previous studies have shown higher concentrations of these metals associated with the growth of industrialization, though it is difficult to generalise in view of the differences with the type of industry and specific operation, the same product may result in different amounts of metals being contributed to aquatic environment.

The present paper deals with the analysis of effluents from the Rayalaseema paper mills at Kurnool let out in an open channel and their effect after entering the river Tungabhadra. Attention is focussed on heavy metals and their effect on algae inhabiting both in the effluents and in the river.

2. Material and methods

The river Tungabhadra rises in the Western Ghats on the border of Karnataka and after traversing a course of about 640 km joins the river Krishna at Sangameswar near Alampur in Andhra Pradesh. While flowing through the Kurnool town it receives some domestic wastes and effluents in large quantity from Rayalaseema paper mills. Two sampling sites were selected, one in the effluent channel and another after its entry into the river. The effluent channel is an outlet from paper mills factory which runs for about $1\frac{1}{2}$ km through a small village and finally joins the river Tungabhadra. In the channel certain filamentous algae like *Stigeoclonium tenue* and species of *Oscillatoria* were growing luxuriantly throughout the period of investigation. The river station is highly polluted and the colour of the water is dark brown. The bottom is muddy mixed with some silt. The flow of the water is greatly reduced as the river is very wide and somewhat deep.

Surface water samples were collected from both the sampling sites in polythene cans at monthly intervals. The samples were kept in an ice-box and transported to the laboratory. After returning to the laboratory 250 ml of sample was digested by using concentrated nitric and perchloric acids. The digested solution was diluted to 50 ml with redistilled water and then filtered through a porcelain filter crucible into a thoroughly cleaned 100 ml volumetric flask. Finally the solution was made up to 100 ml. Aliquots of this solution were taken for the determination of different metals. For the estimation of lead, ammonium acetate was used to dissolve the lead sulphate (APHA 1971). Final estimation was done with the help of an Atomic Absorption Spectrophotometer (Perkin–Elmer, 2380).

Algae were collected by following the field technique adopted by Blum (1957) and described in detail by Venkateswarlu (1969). 250 ml of surface water, from both the stations was collected in a wide mouthed bottle of 500 ml capacity. Five uniform sized pebbles (approx. 2″ × 2″), colonized by algae were carefully picked up from the habitat with a pair of clean forceps and transferred to the bottle. After returning to the laboratory these pebbles were scraped with a scalpel and brush. The scraped material was preserved in 4% formaldehyde and the final volume of sample was reduced to 100 ml. This material was used for frequency measurements and species identification. For finding out the frequency of different species of algae, the drop method of Pearsall *et al* (1946) was used. Altogether, 10 slides were prepared and 12 high power fields were counted in each slide. The total number of species occurring in 120 high power fields of the microscope was noted. The percentages and species composition of different groups of algae were calculated. For filamentous algae field observations were considered.

3. Results

The monthly fluctuations in the values of different heavy metals are shown in figure 1.

3.1 *Manganese*

Manganese has been shown to be required for algal growth. Some algal cells become chlorotic and some lose their capacity to evolve oxygen in its absence. It has an important role in some enzymatic reactions in the Krebs cycle. High concentrations inhibit algal growth. In the river Tungabhadra manganese was not detectable for most

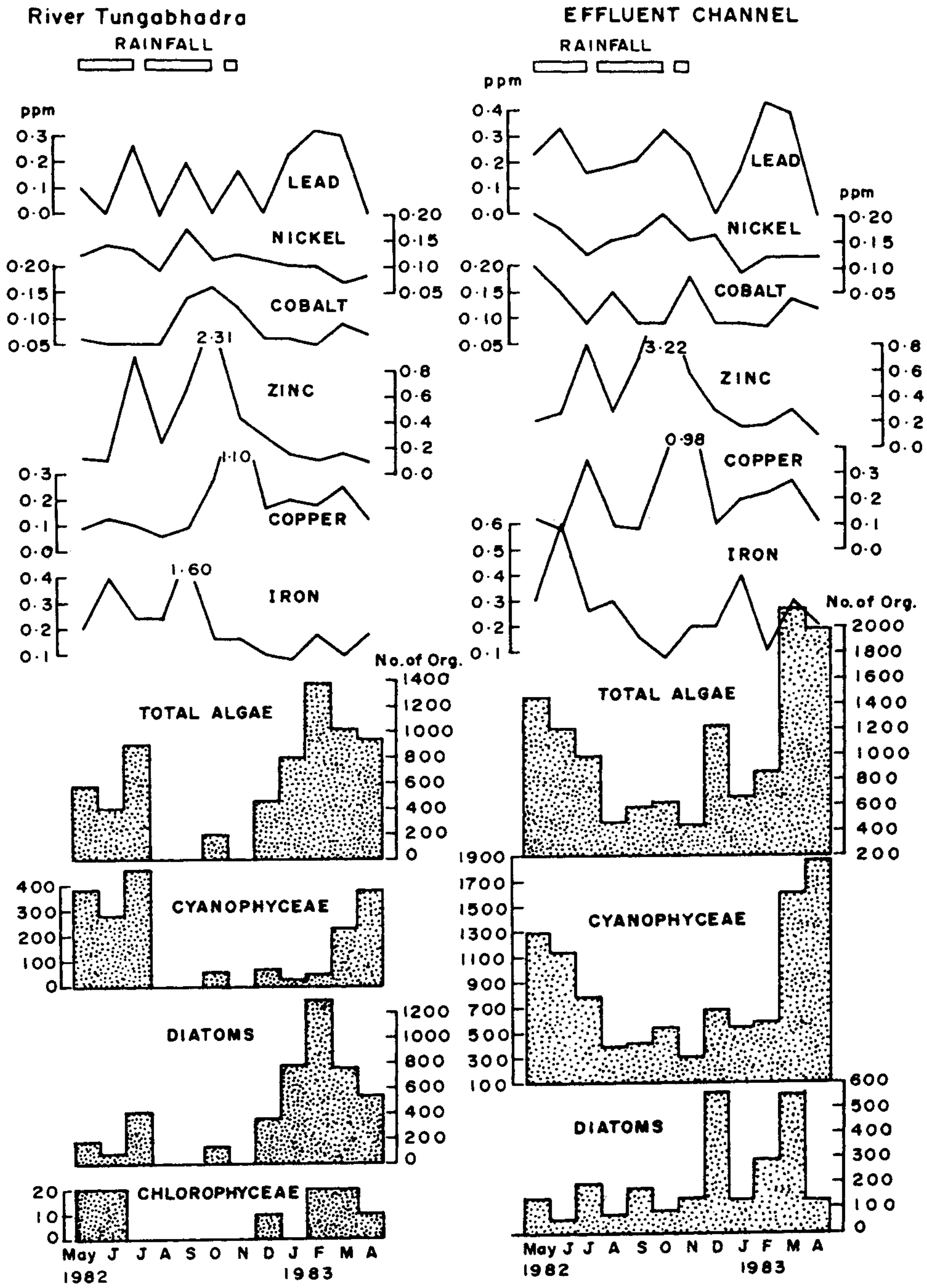

Figure 1. Heavy metals, total algae and different algal groups.

part of the investigation, but it was present in small amounts during the rainy season. This indicates that the contamination was from surface runoff water during floods. In the effluent channel it ranged between 0·03 and 0·08 ppm with an average value of 0·04 ppm.

3.2 *Copper*

Trace amounts of copper is essential for metabolic processes in algae. Higher concentrations are toxic. It inhibits growth as well as photosynthesis of algae (Rai *et al* 1981). Copper showed almost the same average concentrations in both the channel and in the river (0·230–0·247 ppm), recording 0·06 and 1·10 ppm as minimum and maximum respectively. Its high values were observed during winter and low values in the rainy season. On the other hand Kimball (1973) and Namminga and Wilhm (1977) have reported that the concentrations of copper values were low during summer and high in winter.

3.3 *Zinc*

Zinc is an important micro-nutrient for growth and metabolism of algae and plays a vital role in maintaining the integrity of ribosomes. At high concentrations zinc inhibits the growth of various algae (Whitton 1980).

Zinc concentration in the effluent channel was 0·11–3·22 ppm. In the river water it fluctuated between 0·09 and 2·31 ppm. Its high values were recorded during October 1982 and low values during April 1983 in both the habitats.

3.4 *Cobalt*

Cobalt concentration fluctuated from 0·03–0·20 ppm and 0·05–0·16 ppm in the effluent channel and river water respectively. Its highest value was attained in May 1982 in the effluent channel and in October 1982 in the river. Its lowest values were observed during February 1983 at both the stations.

3.5 *Nickel*

The concentration of this metal was high in the effluent channel than in the river. It ranged from 0·07–0·20 ppm. It attained high values during September–October and low values in March in the river water and in January in the effluents.

3.6 *Lead*

Lead is often considered to be a potential pollutant in drinking water. In the present data lead was recorded almost throughout, except on 2 or 3 occasions. It ranged between 0·16 and 0·44 ppm in the river water and effluent channel respectively. It was high during February and low in May and July. Its concentration was very high in the effluent channel than in the river. In the present study lead concentration was quite high in both the habitats, exceeding the limits prescribed by WHO (0·10 mg/l) and EPA and USPHS (0·05 mg/l) for drinking water.

3.7 *Heavy metals and algae*

In the present habitats the heavy metal concentrations are in the order of Zn > Cu > Pb > Ni > Co > Mn. Blue-greens and diatoms seem to be more tolerant to these ions than Chlorophyceae. Chlorococcales were totally absent in the effluent channel which was due to high concentrations of various metals. But in the river they were observed on a few occasions. It is also evident that in the effluent channel the high concentrations of metals were associated with thick massive growths of *Stigeoclonium* whereas in the river, this alga was observed when the metals concentration specially zinc and nickel were high during October. On the other hand when metals concentration was low, *Cladophora* showed good growth in the river water.

3.8 *Heavy metals and benthic algae*

Benthic forms serve as good indicator organisms since they develop in an environment where all sorts of substances come in contact with the substratum. Although various metals occur in different concentrations only the resistant species thrive well in the habitat. The benthic algae in the present habitats were more during winter in the river and in summer in the channel. The algae showed varied responses to metals. Nickel, cobalt and copper showed a direct relationship with total algae in the effluent channel, whereas in the river these metals exhibited an inverse relationship. Zinc showed a direct relationship with total algae in both the habitats but lead gave a direct relationship in the river habitat. Iron and total algae were inversely related in both the habitats (figure 1).

3.8.1 *Diatoms*: An inverse relationship between copper, nickel and cobalt and diatoms was noticed in the river and almost a direct relationship in the effluent channel. A direct relationship between zinc and diatoms was observed in both the habitats. Iron and diatoms were inversely related but lead and diatoms were directly related in the river and inversely in the effluent channel (figure 1). Sometimes direct and sometimes inverse relationships of various metal ions and diatoms could be attributed to the behaviour of the dominant species present in the habitat as only 3 species were found in abundance throughout the period of investigation. *Rhopalodia gibberula* showed a direct relationship with cobalt, copper, nickel and zinc. On the other hand it showed an inverse relationship with lead. *Nitzschia obtusa* var. *scalpelliformis* also exhibited similar relationships in the effluent channel. But *Nitzschia palea* differs somewhat in its tolerance to these metals. With nickel and cobalt an inverse relationship was noticed, whereas with zinc and copper a direct relationship was found (figure 2).

3.8.2 *Cyanophyceae*: Blue-greens exhibited a direct relationship with zinc and an inverse relationship with iron, copper, cobalt and lead. Nickel fluctuated directly with blue-greens in the effluent channel and inversely in the river (figure 1). In the effluent channel certain species gave interesting relationship with these metals. *Oscillatoria chalybea* and *O. ornata* var. *crassa* showed a direct relationship with copper, cobalt and nickel and an inverse relationship with zinc and lead. *Oscillatoria animalis* and *O. subbrevis* behaved inversely with copper but the latter species showed a direct relationship with zinc and lead (figure 2).

3.8.3 *Chlorophyceae*: This group was represented by only two filamentous algae i.e. *Stigeoclonium tenue* and *Schizomeris leibleinii* which were present throughout. In the effluent channel these two species were growing well throughout, but their growth was good during different times. The growth of *Stigeoclonium tenue* was considerable during September, October, December and January, whereas the growth of *Schizomeris*

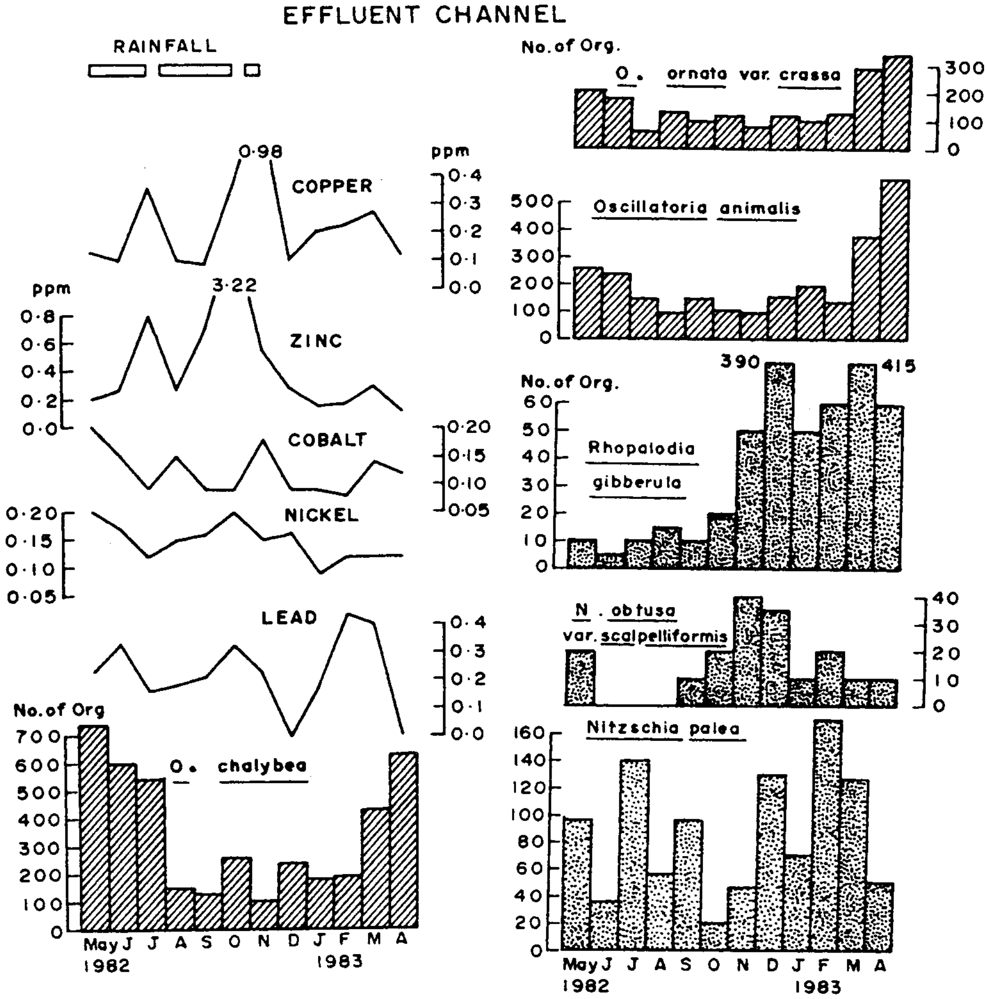

Figure 2. Relationship between heavy metals and certain species of blue-greens and diatoms.

was high during February and March. *Stigeoclonium* gave good response to certain heavy metals. At high concentrations of zinc, copper and nickel and at low concentrations of cobalt and lead its growth was very good. It was also noticed that during October when the zinc concentration was at its maximum the growth of *Stigeoclonium* was in thick masses. On the other hand, *Schizomeris* showed different type of response to metals. This alga attained good growth when the lead concentration was high and cobalt was low.

In the river water this group was recorded in low quantity, hence no definite correlation could be obtained from the data.

4. Discussion

In general the metals analysed indicated an increase along with the increase in chlorides, total hardness, sulphates and total alkalinity. This is in conformity with the observations of Williams *et al* (1974). Bugenyi (1979) observed an indirect relationship between copper and hardness, alkalinity and total dissolved solids. In the present study the alkalinity is due to bicarbonates. The carbonates were either absent or present in very low concentration but did not cause any type of precipitation of heavy metals. This is very well pronounced in the effluent channel where the complete absence of carbonates resulted in the high concentration of these metals as compared to the river water. In the river Tungabhadra apart from dilution, carbonates and somewhat high pH appear to be the factors responsible for the low concentration of these metals. Williams *et al* (1974) reported that calcium carbonate by increasing pH, can remove metals like zinc and copper through adsorption and co-precipitation.

Although algae and heavy metals exhibited some sort of interaction, it may be difficult to attribute that the inter-relationship is exclusively due to these ions. Because of highly polluted nature of habitats the concentration of other pollutants (inorganic and organic) as well plays an important role in the distribution of algae. It is also possible that heavy metals and other pollutants act simultaneously or independently, influencing the flora. Whitton (1984) emphasizes that the influence of metals on algal species and community composition cannot be generalised. Temporal comparisons are rarely possible but spatial comparisons e.g. above and below the point sources of pollution in rivers, have considerable value.

According to Welch (1980) zinc, cadmium, lead, copper, chromium, mercury, silver and nickel are well known toxic heavy metals that can occur in a variety of wastes and cause either acute or chronic effects on organisms. But the toxic effect is generally reduced by several other inorganic and organic compounds which help in the growth and development of algae. Combination of toxicants can display either additive, antagonistic or synergistic effects.

Most of the data on heavy metals and their effects on algae is accumulating specially on diatoms, unicellular and a few filamentous green algae. Several workers have pointed out the tolerance of algal species to certain metals and non-tolerance to others and used them as metal pollution indicator organisms. Patrick (1978) mentioned that algal groups attained dominance at different concentrations of various heavy metals. She reported chromium as toxic to *Scenedesmus* at 5·0 ppm. At lower chromium concentrations diatoms dominated and at higher concentrations the blue-greens dominated. A well illuminated flowing water site with abundant growths of *Stigeoclonium tenue*, but no *Cladophora* at all, should be treated as suspect for metal pollution (Whitton 1970). In the present investigation it is quite evident that in the effluent channel the high concentrations of metals were associated with thick massive growths of *Stigeoclonium* whereas in the river, *Stigeoclonium* was observed when the metals concentration specially zinc and nickel were high during October. On the other hand when the metals concentration was low, *Cladophora* showed good growth in the river water.

5. Conclusions

The paper mill effluents recorded higher concentrations of heavy metals than the river water. In general the metals indicated an increase along with the increase in other ions such as chlorides, total hardness and total alkalinity. There would be some organic and inorganic dissolved compounds in natural waters which act as chelators, bind metal ions and reduce the toxicity of metals. This may help in the growth and development of certain algae. Benthic algae showed good response to certain metals and thus serve good indicators of metal pollution. *Rhopalodia gibberula*, *Nitzschia palea*, *Oscillatoria chalybea*, *O. ornata* var. *crassa* and *Stigeoclonium tenue* are important.

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