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THE DISTRIBUTION OF COPPER IN PORTO NOVO WATERS *

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ABSTRACT

The distribution of dissolved ionic copper has been studied at 14 stations situated in the various aquatic biotopes in and around Porto Novo. The copper concentration in these waters varied from 0·05 to 0·14 μg. at/1. A significant negative correlation ($r = -0{\cdot}88$; $P = > 0{\cdot}001$) was obtained between copper concentration and salinity.

IT is well known that copper is an important trace element for plant and animal life. Copper occurs in chloroplasts[1], possibly to increase its stability. It is essential to certain algae, and phytoplankton concentrate copper from sea-water by adsorption and transfer it to other members in the trophic levels of various food chains[2]. It is present in the haemocyanin of Mollusca and Arthropods. The copper complexes serve as cofactors in oxidation-reduction cycles. Copper is present in proteins (haemocuprein and hepatocuprein of mammalian liver) and a copper metalloprotein has been purified from *Chlorella ellipsoidea*[3]. Copper is also essential for marine sedentary organisms for growth, settlement and attachment, (*e.g.*, Oyster, Balanus). Prytherch[4] made pioneer studies on the role of copper in oyster populations. Copper is also reported to be required for a variety of purposes like the hardening of exoskeleton, egg encasements, blackening of blood after injury, etc. In contradistinction to the trace amounts of copper which are essentially required for healthy life processes, its toxicity in greater amounts has also been repeatedly emphasized.

The concentration of copper in river water is about 5 μg/1 and in sea-water 3 μg/l[5] with considerable variations. It is estimated that the total transport of all rivers and glaciers (into the sea) is about 1·0 million m^3/sec[6]. Due to the unique geochemical balance sea-water maintains a relative constancy in chemical composition preventing a build up of lethal doses of toxic elements. Copper occurs in sea-water in various forms as in the dissolved organically-bound state and in dissolved ionic form and in particulate matter[5,7-9]. The present account reports the distribution of dissolved (ionic) copper in neritic, estuarine, backwater and in the water of the adjoining mangrove environment in and around Porto Novo.

Figure 1 shows the location of the stations in the study area where the samples were collected. The survey was conducted on 29–31 January, 1972 and covered a total of 14 stations (14 surface and 12 bottom samples were estimated). Collections were made using the laboratory boat ('Medusa') and a canoe. Surface samples were collected using a clean plastic bucket and the samples were transferred immediately to high density polyethylene containers. Bottom samples were collected using a Meyer-type bottom water sampler. Since the depth was shallow (between 45 to 500 cm) it was possible (excepting the neritic stations) to send this and open the bottle at the bottom and to close it immediately before hauling up. Care was taken to see that the metal frame enclosing the bottle did not have any contact with the contents of the bottle. Samples were transferred at surface immediately to the plastic bottles. Water samples were filtered on Whatman No. 1 filter-paper and copper was estimated following the diethyl-dithiocarbomate method as recommended by Strickland and Parsons[7].

In the present account the term dissolved ionic copper is used in the sense of Foster and Morris, which Strickland and Parsons call, "soluble" and reactive to diethyldithiocarbomate. It is known that a significant and appreciable amount of dissolved copper is strongly bound to organic matter which has to be irradiated with a high-energy ultraviolet lamp for complete oxidation of dissolved organic matter and then estimated as total dissolved copper. The actual concentration of dissolved and organically bound copper is obtained by difference which is called by Foster and Morris as "organically associated copper". The values reported in the present study are accurate to within $\pm$ 0·001 μg at/l, based on a series of ten replicate estimations.

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The concentration of copper varied from 0·054 to 0·144 μg at/l. The stations may be grouped as those belonging to neritic, estuarine, backwater and the mangrove regions. The concentration of copper at these stations of all the regions is shown in Fig. 2 *b*.

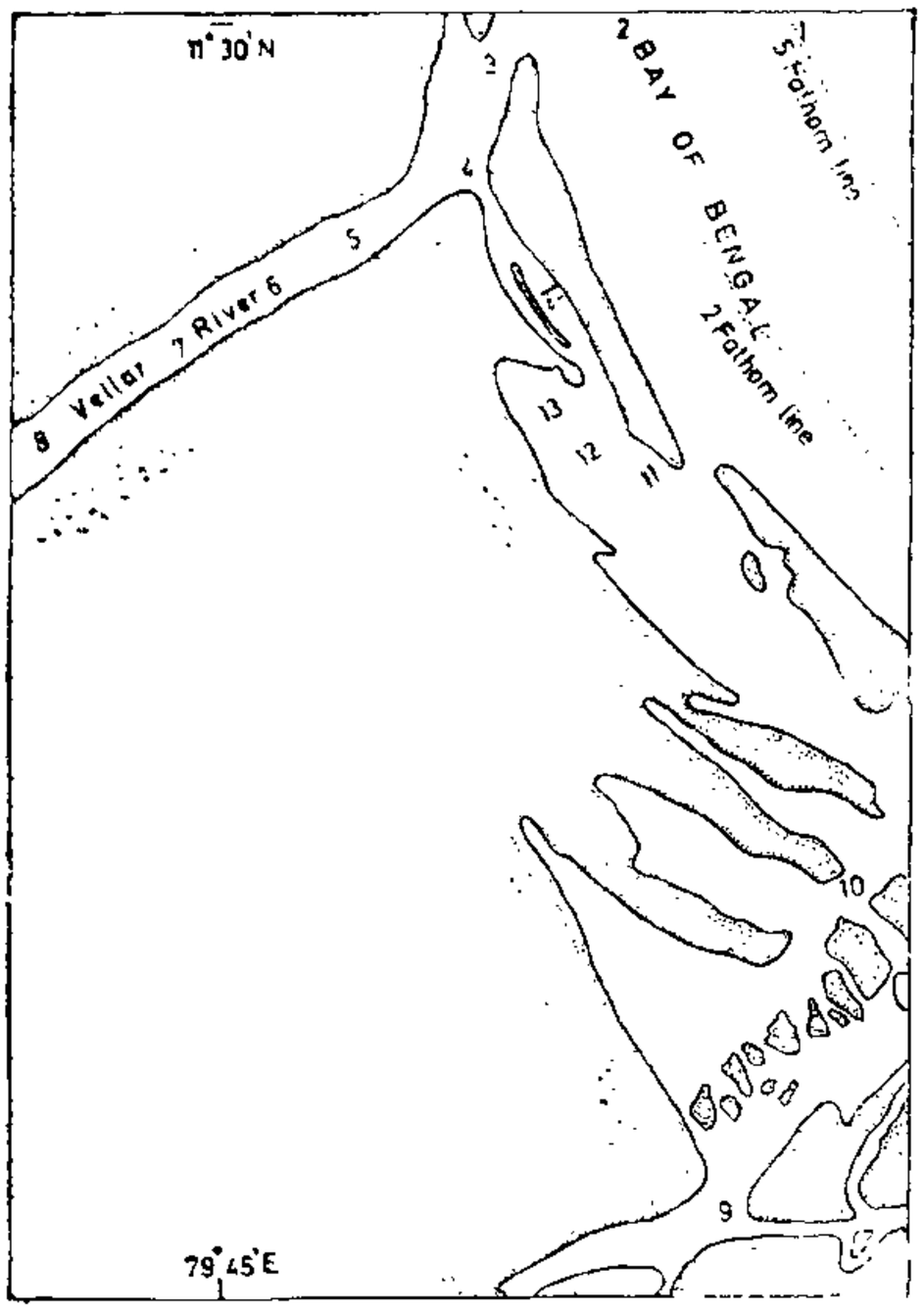

FIG. 1. Map showing the location of stations in the study area.

The depths at the stations varied from a minimum of 45 cm (sta. 13) to a maximum of 900 cm (sta. 1) and the temperature varied from 23·5° (sta. 13) to 27·0° C (sta. 8). Minimum vertical gradient in the copper concentration between surface and bottom water was 0 at (stas. 3 and 12) and the maximum was 0·018 μg at/l (at stas. 4, 10 and 13). [A similar vertical salinity gradient with a minimum value of 0 (stas. 3, 4, 5, 11, 12 and 13) and a maximum of 2·7‰ (sta. 6) was noticed]. However, too much significance should not be attached to this vertical difference in copper concentration, as it is rather imperative that samples should be collected with all-plastic material and detailed seasonal studies are needed before arriving at definite conclusions. It could be observed that a good negative correlation existed between salinity and copper concentration. Except stations 7 to 9 (*see* Fig. 2 *a*), all stations had high salinity values ranging from 26·00 to 30·70‰. The inverse relationship ($r = -0{\cdot}88$) $P = > 0{\cdot}001$ between salinity and copper was highly significant. (The relationship between salinity and copper concentration is shown in Fig. 3).

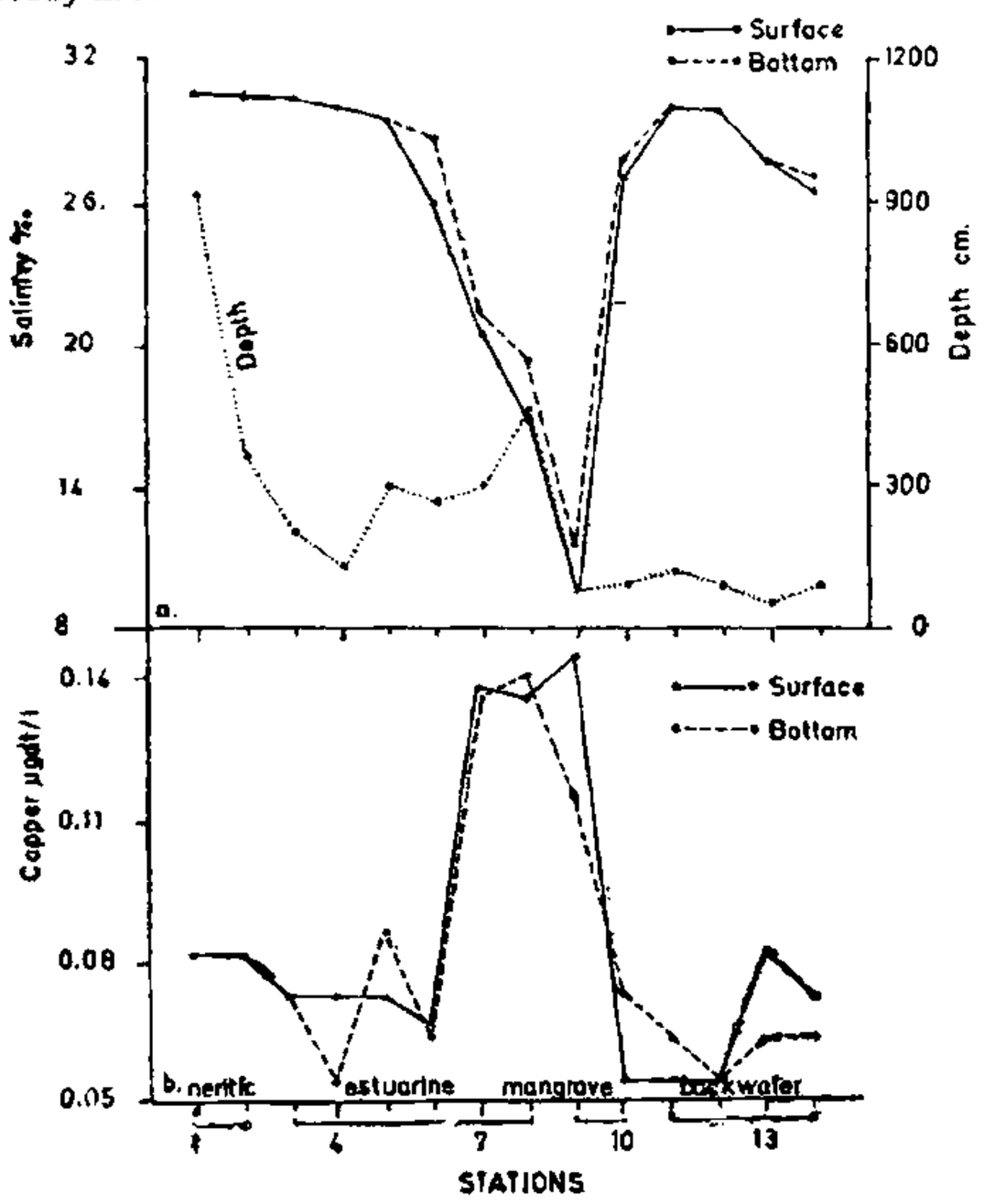

FIG. 2. (*a*) The distribution of salinity at different stations. (*b*) The distribution of dissolved ionic copper at different stations.

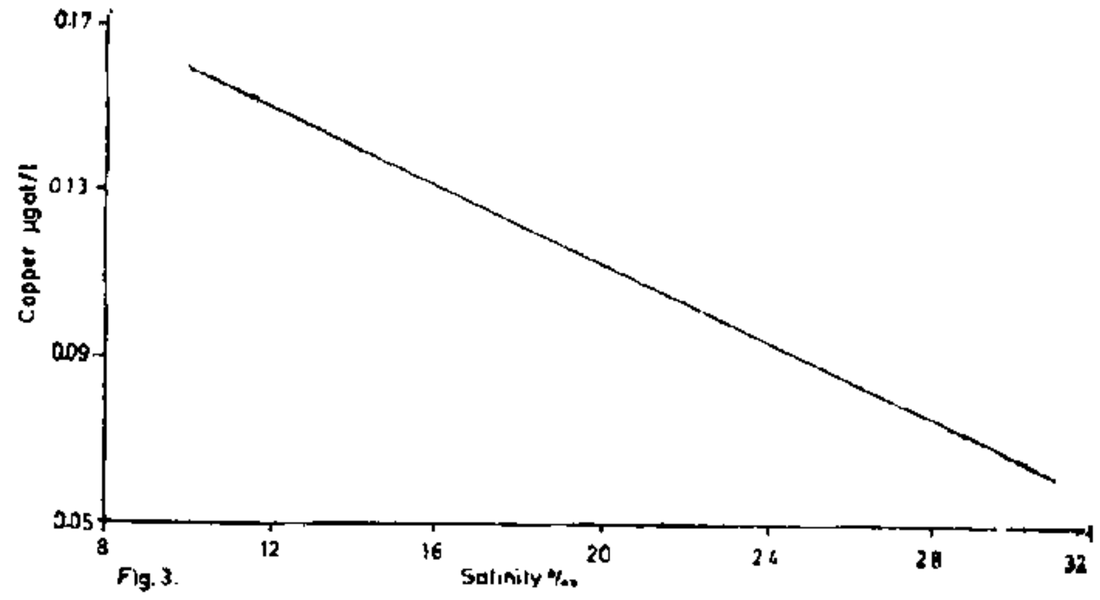

FIG. 3. The relationship between salinity and the concentration of dissolved ionic copper.

The copper concentration of sea-water has been reported by various investigators since Dieulafait's[10] first studies in the Mediterranean sea (*see* Chow and Thompson)[11]. Several authors have also commented upon the existence of an inverse relationship between the concentration of copper and salinity, and increase in copper concentration in sea-water in relation to depth (Atkins[12]; Prytherch[4]; Riley[13]; Alexander and Corcoran[9,14]; Slowey *et al.*[15]; Foster and Morris[8]), and also in the phytoplankton cultures by Mandelli[16]. In the waters of the Florida Current (U.S.A.), the

dissolved ionic concentration of copper in the upper 50 metres was 1·6 μg/l (Alexander and Corcoran[9]). They also found that in the Florida tropical waters the ionic copper concentration was always less than 2 μg/l. (Alexander and Corcoran[14]). Near Aransas Pass, off Texas coast (U.S.A.), at 10 metre, total copper varied between 0·88 to 1·19 μg/l. (Slowey *et al.*[15]). They also found that the "chloroform-extractable copper" concentration was between 0·10 to 0·15 μg/l. In the Menai Straits (U.K.), a seasonal variation of dissolved ionic copper ranging from 1·83 to 3·31 μg/l was noticed (Foster and Morris[8]). They also found that in the 6 different river waters in the vicinity of the Menai Straits, the concentration of copper was between 3·6 to 1,600 μg/l. They concluded that the distribution of dissolved ionic copper was "predominantly controlled by run-off from the surrounding land areas".

In the present study, the values generally agree with observations reported elsewhere (Riley[13]; Buch[17]; Morita[18]; Barnes and Rothschild[19]; etc.). It is, however, difficult to draw strict comparisons in view of the techniques employed and the forms of copper estimated. The values were higher than those reported for the Florida waters and the Menai straits. The salinity range here was rather very wide from 9·60 to 30·70‰, whereas in the Menai Straits salinity values were rather constant (ranging from 32·02 to 33·94‰). and in the Florida waters, the samples were collected from rather deep (700 metres) sea[9]. As stated already, there exists an inverse relationship between salinity and copper concentration, and increase in copper concentration in relation to depth.

The high concentration of copper in coastal and estuarine waters has also been commented upon as owing to human activities[16]. The data collected here permit only a general picture to be drawn. This is, region-wise, as follows in the different aquatic biotopes of Porto Novo (based on average values for the regions and arranged in an ascending order of concentration of copper): backwater → neritic → estuarine → mangrove regions. This study needs to be supplemented by further intensive regional and seasonal investigations of not only dissolved ionic copper, but also of the other forms of copper as well, to draw valid conclusions.

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