EFFECTS OF CHLORINATED COOLING WATER DISCHARGES ON THE CHEMISTRY OF ESTUARINE WATERS

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ABSTRACT

The increasing tendency towards locating power plants at coastal and estuarine sites is in a large measure due to the practically unlimited amounts of cooling water available in these regions. This has also stimulated systematic investigations on the impact of the discharges on the chemistry of the receiving waters. A case in point is the use of chlorine for pretreatment of cooling waters. Available data indicate that chemical species which result from chlorination of seawater differ significantly from those of freshwaters. In the present paper, these differences are discussed in relation to estuaries which contain varying proportions of freshwater and seawater. A critical account is given of the models proposed to explain the reactions, behaviour and persistence of chlorine in discharge plumes in estuaries.

Key-words: Chlorination, estuary, chemistry.

Estuaries are among the natural waters which receive discharges of cooling water from steam electric plants after the water is used for condensation of excess steam and removal of waste heat. In recent years there has been a pronounced trend towards greater use of estuarine, brackish and marine waters for industrial cooling; this is because, available freshwater resources are not adequate to cope with the increasing demand (Loef and Ward, 1969). The present paper discusses some consequences of this trend on the chemistry of estuarine waters with special reference to the distribution of halo-organics and haloamines in the waters.

Discharge of chlorine containing effluents

In the majority of cases cooling water is pretreated with chlorine (as aqueous solution of the gas or as hypochlorite) to eliminate biofouling on the surfaces of condensers and heat exchangers. This gives rise to a host of environmental and epidemiological problems since chlorine is not selective in its reactions and combines with a number of organic and inorganic constituents of the receiving waters.

It is estimated that man-made chemicals are increasing at the rate of about 250,000 per year; these chemicals most of which are synthetic organics, find their way into the ultimate sinks, viz., the natural waters (Metcalf and Pitts, 1969). The organics themselves may be present in ppm or ppb concentrations but the cumulative effects of their reactions with chlorine are such as to produce significant amounts of chloroorganics (including nucleosides, purines, pyrimidines, aromatic acids and phenols). Many of the chloroorganics are potential carcinogens which are transmitted to human populations directly or
indirectly through uptake by aquatic plants and animals (Jolley, Jones, Wilson, Pitt and Thompson, 1977).

Decay of chlorine in receiving waters

The distribution of residual chlorine in the receiving waters is essentially a function of stream flow (Pereira, Terlecky and Yaksick, 1974), water-temperature differences (Hostgaard-Jensen, Klitgaard and Pedersen, 1977) and morphology of the receiving waters (Mattice, 1980).

Pereira, Terlecky and Yaksick (1974) developed a model to predict free residual chlorine (FRC) concentrations in a flowing stream receiving a continuous input of chlorinated waste water. They were able to arrive at a simplified expression inter-relating FRC, stream flow and rates of FRC depletion due to chlorine demand and chlorine gas escape.

Hostgaard-Jensen, Klitgaard and Pedersen (1977) included chlorine demand reactions in the model to predict decay of total residual chlorine in a power plant discharge plume. Laboratory and field-derived values for decay constant of chlorine were found to differ, leading the authors to attribute the differences partly to the action of light on the decay of chlorine.

Lee (1979) conducted a study to determine the persistence of chlorine in the Delaware River Estuary system. Rate constants of chlorine decay were determined for both measured chlorine concentrations and chlorine levels calculated on the assumption that the dilution factor is solely responsible for the observed decrease in chlorine. The inference was made that there are a number of factors which cause chlorine to disappear faster in natural waters than under laboratory conditions.

Salinity-dependent reactions of chlorine

Apart from physical processes of dispersal, the fate of chlorine in receiving waters is determined also by the chlorine-demanding chemical species present. In an estuary which is a "region where river water mixes with and considerably dilutes seawater" (Ketchum, 1951), chemical reactions of chlorine depend additionally on the salinity, pH and concentrations of the reactants in the water. A case in point is the reaction of humic acids with chlorine to produce trihalomethanes (Jolley, Jones, Wilson Pitt and Thompson, 1977); humic polymer molecules undergo a change from predominantly uncoiled configuration in freshwater to increased coiled configuration with increased ionic strength and pH in estuarine waters (Reuter, 1977). These observations acquire added significance in the light of the reported association of humic acids with the primary films responsible for biofouling (Loeb and Neihof, 1975) and the successful use of chlorine as antifoulant.

A second salinity-dependent characteristic of estuarine waters is associated with the bromide content of seas and estuaries. In contrast to the chlorine-containing compounds in chlorinated freshwaters, bromo-organics and
bromo-amines compete with their chlorine counterparts in determining the toxicity of coolingwater discharges in estuaries. This aspect of estuarine and marine chemistry has been emphasised by Trofe, Inman and Johnson (1980) who have determined rate constants for reaction between bromide ion and the biotoxic chloramine species, NH₂Cl. Data on distribution of halogen species have been useful in computer simulation of chlorinated cooling water discharges in natural waters including estuaries (Lietzke, 1976; Eraslau, Lietzke, Fischer and Kalmaz, 1977).

Haloorganics and haloamines in hypochlorinated coastal waters of Bombay

In the course of water chlorination studies tests were carried out for the presence of haloorganics and haloamines in coastal seawater treated with a sodium hypochlorite. In one set of experiments chlorinated seawater (100 ml) was equilibrated with diethyl ether in the ratio 1:1 for half an hour. The ether phase was scanned spectrophotometrically in the UV ranges (200-400 nm) in a Shimadzu model UV-190 double beam spectrophotometer. An absorbance maximum was observed at wavelength corresponding to chlorobromo-amine (Fig. 1).

![Absorbance Spectrum](image)

**Fig. 1.** UV absorbance spectrum of NH BrCl in ether phase.

Fluorescence spectra of hypochlorinated and nonchlorinated (filtered) seawater were studied in an Aminco-Bowman Spectrofluorometer (1 cm cell, excitation wavelength 370 nm and emission wavelength 410 nm). The observed decrease in fluorescence is attributed to the reduction in the amount of soluble
humic acid as judged by reference to appropriate humic acid standards (Table I).

Table I. Effect of chlorination on soluble humic acid in coolant seawater at CIRUS, Trombay.

<table>
<thead>
<tr>
<th>Date</th>
<th>No.</th>
<th>Seawater sample</th>
<th>Nonchlorinated sample</th>
<th>Chlorinated* samples</th>
<th>% Reduction of fluorescence due to chlorination</th>
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</thead>
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<td></td>
<td></td>
<td>EX</td>
<td>EM</td>
<td>EX</td>
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<tr>
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<td>42 x 0.001</td>
<td>30 x 0.001</td>
<td>22 x 0.001</td>
</tr>
</tbody>
</table>

* Chlorine dose, 10 mg/l; Contact time 1 hr.
Intrinsic fluorescence data given here are averages of experiments in triplicate.

For the detection of halophenols phenol was added to artificial seawater prior to treatment with sodium hypochlorite. A benzene extract of the chlorinated seawater was examined in a gas chromatograph equipped with an electron capture detector. Use was made of a glass column (4 mm i.d., 60 cm length) packed with 10% Apiezon L and 3% H₃PO₄ coated on Chromosorb WAW/60-80 mesh at 183°C. In addition to a peak with retention time of 70 second (due to solvent benzene) a second peak was obtained with a retention time of 242 seconds, tallying with that of standard tribromophenol and confirming the role of the bromide ion in the chemistry of saline waters.

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REFERENCES


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