tropics are sparse[24–26] and more effort is needed for wider coverage.

We have highlighted the need to recognize that in hot and humid environmental conditions, the temperature and humidity can have a significant additive contribution to the damaging UV-B effect. Besides, future climate change may further exacerbate the cumulative contribution to UV radiation damage dosage on humans. This effect will be particularly serious in the tropical–equatorial region, where existing UV-B levels are higher than those at mid and higher latitudes, and protective mechanisms against sunlight are far less effective due to outdoor activities at wrong times (Figure 2), e.g. physical education lessons in schools. This is important for human health to most populations in the tropics and should be taken into account while evaluating the UV-B and climate impact in immune deficiency, viral infections and overall health considerations in the context of present and future climate scenarios.

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Chlorination by-products and their discharge from the cooling water system of a coastal electric plant

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Chlorination is one of the most widely used techniques for controlling biofouling in power plant cooling water systems. It often leads to the formation of chlorination by-products (CBPs). Amongst these, trihalomethanes (THMs) are more predominant, relatively long-lived and have possible toxicity to organisms. Thus, THM levels in the coastal marine environment are of great concern. This communication discusses the concentration levels of THMs at various points in the cooling water system of a coastal nuclear power station located on the Bay of Bengal coast. The studies revealed the

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formation of bromoform in predominant quantities and dibromochloromethane in small quantities. The present values are comparable with those reported from other power stations elsewhere.

Keywords: Atomic power station, biofouling control, chlorination by-products, trihalomethanes.

INCREASING demand for electricity for industrial and domestic purposes has necessitated the establishment of more power plants, especially in developing countries. The upcoming plants are often located near coastal regions because of easy availability of water for cooling[1]. Cooling water requirement for fossil/nuclear-fired power plants[1] is of the order of 30–45 cubic m/s/1000 MWe. As sea water is normally used as a coolant for steam condensation, a wide range of fouling organisms colonize the system surfaces. Biofouling interferes with the coolant water flow and significantly affects the heat transfer efficiency[2]. The conditions inside a typical cooling system are favourable for the growth of sessile organisms, which flourish within the intake pipes and conduits, with the flow conditions providing an abundance of food[1]. In general, biofouling is caused by macroscopic organisms like mussels and barnacles, and also by bacteria (microfouling). However, both types of biofouling are inter-related, with development of a biofilm often preceding settlement of macroinvertebrate larvae[2].

In order to control biofouling, the sea water at source is usually chlorinated, with typical applied chlorine doses in the range 0.5–1.5 ppm, while the resultant residual oxidant in the coolant water is generally in the range 0.1–0.2 ppm. Chlorine reacts with organic matter present in coolant water, leading to the formation of several chlorinated by-products (CBPs). Discharge of these contaminants into the sea is of environmental concern due to: (i) large diversity of chloro compounds and (ii) toxicity of some of the by-products[2,3]. Though the organochlorinated by-products represent a small fraction of the added chlorine, they are relatively more persistent than residual chlorine, and thus pose a potential hazard to marine life because of their possible mutagenicity[4–7]. Sea water contains about 65 ppm of bromide and during chlorination bromine is formed by the oxidation of bromide, leading to the formation of organobromine compounds. As a result, THMs in chlorinated sea water mainly consist of bromoform ($CHBr_3$) and dibromochloromethane ($CHBr_2Cl$)[8]. Bromoform has a slow and progressive formation, being the final product in the oxidation of organic substances[1]. Accordingly, majority of monitoring studies have focused on these two compounds. Despite the widespread use of chlorine in cooling systems in coastal power plants in India, so far no published report is available on the quantity of THMs released into the recipient water bodies. This communication reports the distribution of THMs in the cooling system and discharge water of a nuclear power plant, the Madras Atomic Power Station (MAPS), Kalpakkam (12°33′N; 80°11′E) located on the Bay of Bengal coast, India.

MAPS was commissioned in the year 1984. The plant consists of two pressurized heavy-water reactors and employs a once-through cooling system for steam condensation. Sea water, pumped at a designed rate of 35 cubic m/s, was used for cooling the main condensers and auxiliary systems like the process sea water heat exchangers. Sea water was drawn through a 468 m long submarine intake tunnel. From the intake point, the water flowed through the tunnel to a forebay pump house (FPH), from where it was pumped to the condensers and other auxiliary heat exchangers (Figure 1). The intake well was dosed with about 1 ppm chlorine on a continuous basis so as to produce a residual level of 0.1–0.2 ppm, measured at the FPH. Apart from this continuous low dose chlorination, a weekly booster dose resulting in a residual level of 0.4–0.6 ppm was also practised. The combined outfall from the condenser and process sea water heat exchangers was discharged on the shore through an outfall structure. The discharged water flowed through a naturally formed discharge canal of 0.2–1.5 km length (length depends on the season) before it finally mixed with the coastal water, designated as the mixing point (MP). The shore at this point was sandy with weak tidal currents, but was influenced by wave-induced longshore currents that reversed direction in accordance with monsoonal reversal.

Surface sea-water samples were collected at monthly intervals from five stations, namely intake point, FPH, condenser cooling water pump outlet (CCWP), process sea water pump outlet (PSWP) and MP during the period October 2005–September 2006. The sampling point at the intake was located outside the intake well and, therefore, was devoid of any chlorine and notionally representative of the ambient water body. Duplicate samples of 500 ml surface water were colleted from each station using pre-

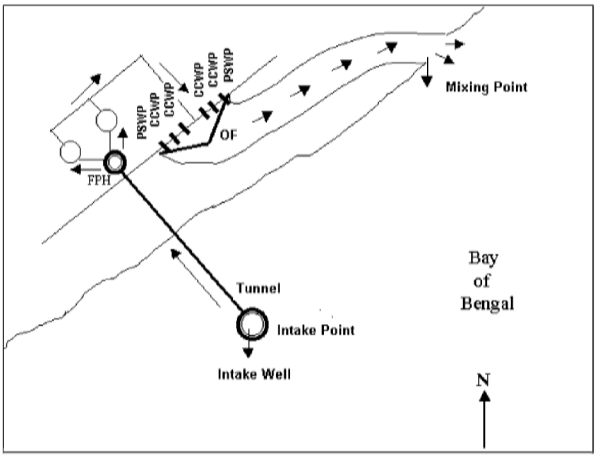

Figure 1. Simplified schematic (not to scale) showing sampling locations. FPH, Forebay Pump House; PSWP, Process Sea water Pump Outlet; CCWP, Condenser Cooling Water Pump Outlet; OF, Outfall.

Table 1. Concentration of total residual oxidants (TRO) and trihalomethanes in the cooling water system of MAPS during October 2005–September 2006 (mean ± SD)

	Intake*		FPH			CCWP*		PSWP			MP*	
Month and year	TRO mg/l	$CHBr_3$ µg/l	TRO mg/l	$CHBr_3$ µg/l	$CHBr_2Cl$ µg/l	TRO mg/l	$CHBr_3$ µg/l	TRO mg/l	$CHBr_3$ µg/l	$CHBr_2Cl$ µg/l	TRO mg/l	$CHBr_3$ µg/l
October 2005	BDL	BDL	0.45	365 ± 1.68	59.99 ± 1.35	0.4	291 ± 0.77	0.55	295 ± 0.95	BDL	BDL	BDL
November 2005	BDL	BDL	0.25	193 ± 1.87	BDL	0.1	183 ± 1.35	0.15	195 ± 0.85	BDL	BDL	BDL
December 2005	BDL	BDL	0.2	80.6 ± 1.65	BDL	0.2	74.6 ± 0.11	0.3	91.8 ± 0.02	BDL	BDL	BDL
February 2006	BDL	BDL	0.1	18.7 ± 0.83	BDL	BDL	BDL	0.1	18.5 ± 0.32	BDL	BDL	BDL
March 2006	BDL	BDL	0.2	23.6 ± 1.49	BDL	0.1	23.3 ± 0.31	0.15	23.9 ± 0.03	BDL	BDL	15.8 ± 0.31
April 2006	BDL	BDL	0.15	54.7 ± 0.81	BDL	0.1	20.7 ± 0.44	0.1	65.7 ± 0.01	BDL	BDL	19.1 ± 0.02
May 2006	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
July 2006	BDL	BDL	0.1	73.2 ± 1.10	BDL	0.1	87.5 ± 0.23	0.1	87.5 ± 0.54	BDL	BDL	20.6 ± 0.01
September 2006	BDL	BDL	0.45	195 ± 1.76	12.6 ± 1.54	0.42	201 ± 0.46	0.42	201 ± 0.91	25.7 ± 0.01	BDL	53.9 ± 0.04

BDL, Below detection limit. *No $CHBr_2Cl$ detected at these stations.

washed glass bottles with Teflon-lined screw caps. One millilitre of 0.1 M sodium thiosulphate was added to each sample and the bottle was closed without headspace in order to prevent loss of volatile organic compounds. The samples were stored at 4°C.

Standards of chloroform ($CHCl_3$), dibromochloromethane ($CHBr_2Cl$), bromodichloromethane ($CHBrCl_2$) and bromoform ($CHBr_3$) were obtained from Sigma–Aldrich, USA. Analytical grade solvents, *n*-hexane and methanol were procured from Ranbaxy, India. A standard stock solution of each compound containing 0.1 mg/10 ml was prepared in methanol. Intermediate standard solutions were obtained by dilution of the standard stock solution using methanol. Blank chromatograms were obtained by injecting pure solvents.

Due to low levels of THMs usually present in chlorinated sea water, a concentration step was used prior to the analysis. Two main methods available for the concentration of THMs in water are purge and trap technique and liquid–liquid extraction technique[9]. In the present study, the latter US EPA method 551.1 (ref. 10) was used. The method involved extraction of 500 ml chlorinated sea water with 5 ml of *n*-hexane in a 1 l separating funnel. After 15 min, the organic phase was decanted into a 10 ml volumetric flask. An aliquot of 3 µl extract was injected into a gas chromatograph (Chemito 8510, India), equipped with a ^{63}Ni electron capture detector. The column used was a glass column, 6 mm ID × 2.5 m long, packed with 1.85% OV-17 + 1.95% on Chromosorb W (HP) (80/100 mesh) and operated at 50°C. The injector temperature was set at 150°C, while the detector was set at 250°C. Nitrogen was used as the carrier gas at a flow rate of 40 ml per min. Calibration was performed by means of ten standard solutions (concentration range 100–1000 ppb) prepared by diluting the standard solution. Calibration curves were made for all the four standards mentioned earlier. The minimum detection limits for the compounds were: chloroform – 1.1 ppb, dibromochloromethane – 0.8 ppb, monobromochloromethane – 1.0 ppb and bromoform – 0.8 ppb. The analytical method had an accuracy of 87% and precision (in terms of coefficient of variation) of 1.3% (determined using 50 ppb bromoform, $n = 6$).

Total residual chlorine levels (expressed as total residual oxidants, TRO) in the samples were estimated in the field using the DPD (diethyl-*p*-phenylenediamine) method with recommended DPD-4 tablet and a hand-held Lovibond comparator[1].

The levels of various CBPs detected at the five sampling stations, along with the respective TRO levels are given in Table 1. The TRO levels at the FPH varied from below detection limit to 0.45 ppm, with higher values (0.45 ppm) observed during booster chlorination treatment. Among the CBPs, bromoform and dibromochloromethane were detected at the FPH and the PSWP outfall, whereas bromoform was the only compound observed at the MP. In the FPH, a maximum concentration of 365 ppb bromo-

form was observed in October 2005. At the CCWP outlet, the highest concentration of 291 ppb of bromoform was observed in October 2005, while the highest concentration found at the PSWP outlet was 295 ppb (October 2005). Dibromochloromethane was detected only at the FPH and at the PSWP outfall. Residual levels were below detection limit (<0.1 ppm) at the MP, irrespective of whether low dose chlorination or booster chlorination was used. At the MP, low levels of bromoform (15.8–53.9 ppb) were occasionally detected. Monobromochloromethane and chloroform were below detection limit in all the samples collected. Dibromomethane was detected only in two samples, where the residual chlorine levels were relatively high (>0.4 ppm), i.e. during booster chlorination (Table 1). During this period, concentration of bromoform was also relatively high. For each station, the measured concentrations of total THMs were found to be correlated with the chlorine residual level (Figure 2). This result is in agreement with those reported by Allonier *et al.*[3]. Increased doses of chlorine in cooling water resulted in elevated levels of bromoform in the effluent[11]. Yang[11] observed a maximum concentration of 124 ppb bromoform at the outfall of the Youngkwang Power Station in Korea. Increased concentration of bromoform has been reported to result from higher chlorine doses, with bromoform levels being approximately linear with the added chlorine[2,11]. Other studies have reported that copper could catalyse the formation of THMs by activating a portion of the humic substances that otherwise would be inefficient precursors[3]. MAPS uses condenser tubes made of a copper-containing alloy, aluminium and brass. Copper levels in the discharge water were found to be in the range 1–4 ppb. Therefore, the effect of copper leached from condenser tubes on the formation of THMs does not appear to be significant.

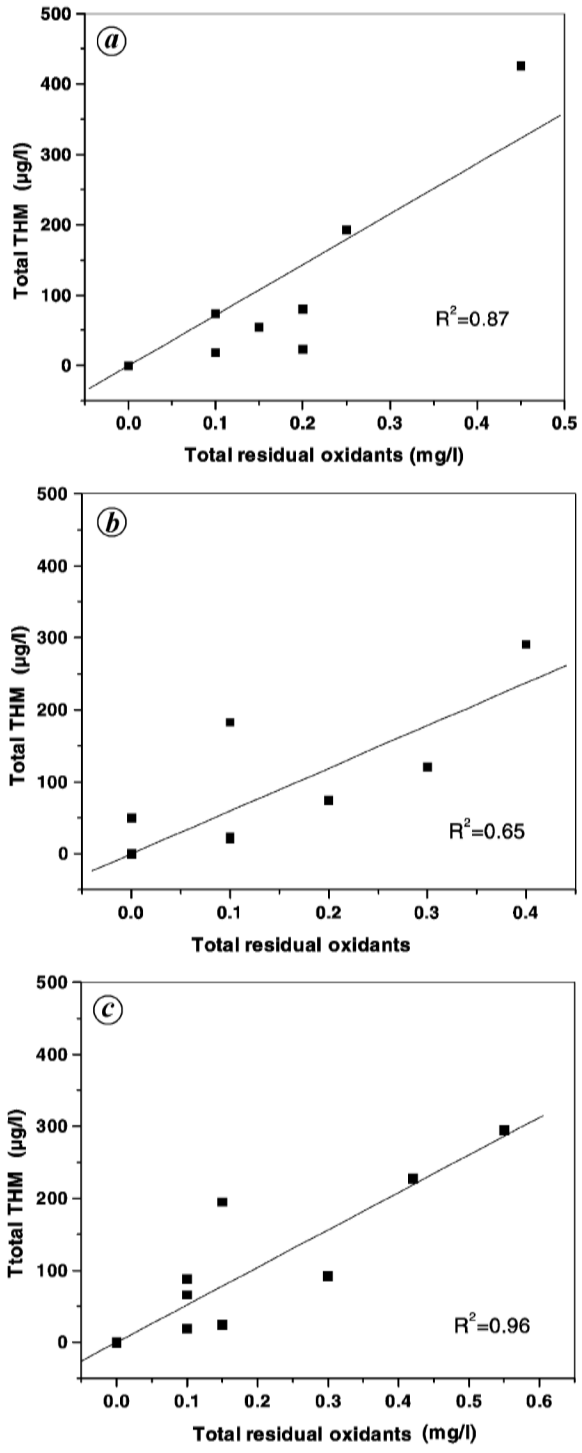

Figure 2. Relationship between chlorine addition (estimated as total residual oxidants) and total trihalomethane (THM) generation and at various sampling points. ***a***, FPH; ***b***, CCWP outlet and ***c***, PSWP outlet.

Among other THMs, only dibromochloromethane (apart from bromoform) could be quantified, albeit at much lower concentration than bromoform. The predominance of bromoform as well as the presence of dibromochloromethane are indicative of the formation of hypobromous acid, and its further reaction as a substituting agent[2]. Among the commonly found THMs, bromoform has the longest half-life (16.9 h)[12]. In the samples collected from the MP, only low levels of bromoform (15–53 ppb) could be detected. Atmospheric exchange and photochemical effects are factors that affect bromoform concentration in surface waters. Since the discharged water forms a canal that runs for a significant distance (0.5–2.0 km, depending on the season)[13] before mixing with the sea, the decrease in concentration of bromoform with distance from the outfall point is understandable. Evaporation and dilution by ambient water may also reduce the bromoform concentration. It has been reported that THMs undergo fast evaporation following discharge, due to the elevated temperature of the effluent[14]. Figure 3 shows that the discharged water has relatively higher temperature (compared to the ambient water) during its transit in the discharge canal of MAPS. Bromoform levels at the MP may further drop as a direct result of mixing with the

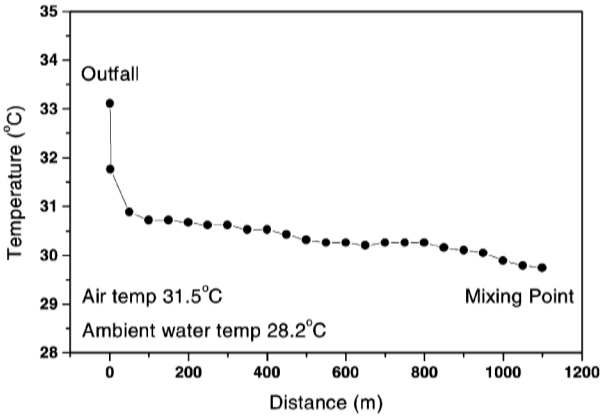

Figure 3. Typical pattern of temperature distribution in the discharge canal as the effluent water travels from the outfall of the power station to the mixing point in the sea (only one out of the two reactor units was operating at the time of sampling).

ambient sea[1]. THMs are generally resistant to degradation[14]. It has been suggested that, owing to the conservative nature of bromoform, it can be used as a tracer to study the spatial spread of condenser effluents in coastal waters[11]. For a given chlorine dose, THM formation may vary with season. For example, in the present case, THM levels in October 2005 and September 2006 were different, even though the observed chlorine residuals were the same. Differences in THM formation could be attributed to qualitative and quantitative differences in organic precursors present in the water.

In India, THM levels in power plant effluents are not regulated by the pollution control agencies. Though THMs have been associated with the occurrence of human cancer, there is not much information on their environmental effects, especially on marine fauna and flora[15]. THMs have been reported to be toxic to organisms, including mammals[16]. In power plant effluents, residual chlorine disappears fast, but THMs remain for longer time. Studies employing long-term chronic exposure of marine organisms to THMs are not available. US EPA stipulates a maximum limit of 100 ppb for THMs in drinking water[17].

In conclusion, THMs formed following chlorination of coolant sea water used in a coastal electric power plant have been quantified and their concentration at the discharge point has been measured. The data show that bromoform was the major THM formed. The concentrations of by-products formed were found to be related to the chlorine residuals measured. The concentrations at the discharge point appear to be similar to those reported elsewhere. The low-dose chlorination presently employed at the power station appears advantageous from the viewpoint of generation of undesirable THM in water.

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