# Stratosphere–troposphere exchange of ozone at Indian Antarctic station, Maitri

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**The frequency of occurrence of stratosphere–troposphere exchange (STE) events and the depth up to which ozone from the stratosphere descended into the troposphere during these events has been examined at the Indian Antarctic research station, Maitri. It is concluded that STE plays a minor role in the tropospheric ozone budget. Stratospheric intrusions at Maitri were associated with pronounced cut-off circulations, which provided a large reservoir of ozone-rich air for eventual transport to the lower troposphere.**

**Keywords:** Exchange events, ozone, stratosphere, troposphere.

The role of stratospheric ozone to protect living organisms and vegetation from the harmful effects of ultraviolet irradiation is well known. Depletion of the ozone layer is a great threat to the human society. However, ozone being toxic to the living system, elevated tropospheric ozone is harmful to living organisms and vegetation. Apart from this, tropospheric ozone is an important contributor to anthropogenic global warming[1]. Thus transport of ozone from the stratosphere to the troposphere can have serious impacts on the air quality and climate. When compared with photochemically induced high ozone episodes produced near the earth's surface, relatively less studies have been reported from the Indian Antarctic research station, Maitri, for the surface episodes which involve downward transport of ozone from the stratosphere. Although these episodes are relatively uncommon, they have been reported to produce transient peak ozone concentrations of around 100 ppbv at sea-level and concentrations in excess of 250 ppbv in mountain regions[2].

Stratosphere–troposphere exchange (STE) involves the transport of atmospheric constituents across the tropopause[3]. It is an important and significant natural source of ozone in the troposphere[4,5]. The mechanisms leading to STE are tropopause folds, cut-off lows and quasi-adiabatic transport along isentropic surfaces[5,6]. Changes in ozone have their largest impact on climate when they occur in the upper troposphere (UT)/lower stratosphere (LS) regions[7]. Shallow exchange events are partially reversible in nature and produce compositional changes in the tropopause region, whereas deep STE events are largely irreversible and have a highly significant impact on atmospheric chemistry, even down to the earth's surface[8].

Several studies suggest that ozone decrease in LS driven by changes in the stratospheric circulation, contribute to an increase in tropospheric ozone. Jenkins *et al.*[9] observed enhanced lower troposphere (LT)/UT ozone due to convective processes over the tropical Atlantic. Thompson *et al.*[10] observed an increase in ozone concentration in UT due to ozone transport from LS. Roelofs and Lelieveld[11] have observed that after ozone descended from the stratosphere, it resided immediately below the tropopause. In the light of these observations, the present communication is aimed to study the frequency of occurrence of shallow and deep STE events and the depth up to which ozone from the stratosphere descended into the troposphere during these events.

Maitri (70°46′S, 11°45′E) is located in the coastal area of Queen Maud Land on a rocky terrain and is devoid of snow throughout the year[12]. Around 100 vertical ozone and temperature profiles from ozonesonde spanning over the period from 1994 to 1998, and 2006 have been obtained from the World Ozone and Ultraviolet Radiation Data Centre (WOUDC), Environment Canada, Toronto. These profiles were measured by the India Meteorological Department (IMD) at Maitri for all standard pressure levels (1–1000 hPa, with an accuracy of 0.5 hPa) at intervals of 15 days. Vertical ozone profiles from 1999 to 2005 are not available with WOUDC. Five-day back trajectories at different pressure levels were retrieved from the European Centre for Medium-Range Weather Forecasts (ECMWF). Vertical pressure velocity at the surface and tropopause and geopotential maps were retrieved from NCEP/NCAR reanalysis[13]. Total ozone column (TOC) was obtained from Total Ozone Mapping Spectrometer (TOMS). Tropospheric column ozone, carbon monoxide (CO) and methane ($CH_4$) data were obtained from Tropospheric Emission Spectrometer (TES) on NASA's Earth Observing System (EOS) spacecraft. TES provides daily global $2.0° \times 4.0°$ gridded data of tropospheric ozone, CO and $CH_4$. Tropospheric column $NO_2$ ($10^{15}$ molecules $cm^{-2}$) was obtained from the Scanning Imaging Absorption Spectrometer for Atmospheric Chartography (SIAMACHY) instrument on the European Space Agency ENVISAT platform.

To achieve uniformity between the vertical profiles, each profile was independently averaged (i.e. ozone partial pressure values (mPa) from 1025 to 975 hPa pressure levels have been averaged and considered as ozone partial pressure value for 1000 hPa) and grouped into 16 pressure levels: 1000, 925, 850, 700, 600, 500, 400, 300, 250, 200, 150, 100, 90, 80, 70 and 50 hPa. The pressure levels (hPa) were equated to their equivalent altitude (km). From the examination of ozonesonde profiles and NCEP reanalysis data from 1948 to 2009, it was estimated that the tropopause height at Maitri is at around 250 hPa (10.5 km from the earth's surface). The vertical ozone profiles were thereafter divided into three sections.

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**Table 1.** General features of the stratosphere–troposphere exchange (STE) events covered in this study

| Total number of profiles | Percentage occurrence of STE events | Number of shallow STE events | Number of deep STE events | Total number of STE events during summer | Total number of STE events during winter |
|---|---|---|---|---|---|
| 100 | 4 | 0 | 4 | 3 | 1 |

**Table 2.** Altitude up to which the stratospheric ozone descended into the troposphere during STE events

| Profile number | Altitude (km) up to which the ozone from the lower stratosphere descended into the troposphere |
|---|---|
| 1 | 0 |
| 2 | 0 |
| 3 | 0 |
| 4 | 3 |

**Table 3.** Summary of the direction of 5-day back trajectory at different altitudes (source: European Centre for Medium-Range Weather Forecasts, UK)

| Profile number | Date of STE event | Altitude (km) from the earth's surface | Direction of 5-day back trajectory at the corresponding altitude |
|---|---|---|---|
| 1 | 7/10/1997 | 0 | Southeast |
| | | 3 | Northwest |
| | | 5.5 | Northwest |
| | | 7 | Northwest |
| 2 | 9/11/1997 | 0 | Southeast |
| | | 3 | Southeast |
| | | 5.5 | Southeast |
| | | 7 | North |
| 3 | 15/1/2006 | 0 | Southeast |
| | | 3 | Southeast |
| | | 5.5 | Northwest |
| | | 7 | Northwest |
| 4 | 15/9/2006 | 0 | Southeast |
| | | 3 | Northwest |
| | | 5.5 | Northwest |
| | | 7 | Northwest |

The regions extending approximately 5 km below and above the tropopause were considered as UT and LS respectively, whereas the region lying below UT was termed as middle and lower troposphere (MLT). The columnar ozone partial pressure (mPa) in these regions was determined and the ozone anomalies were identified. MLT and UT ozone exhibits high natural variability in both space and time[14] and is strongly influenced by the transport of air parcels from one region to another[15]. It is observed from satellite data, that the day-to-day variability in TOC due to natural and anthropogenic factors and transport processes is normally of the order of ± 10 DU within a timescale of 5 days at Maitri. Therefore, the days for which a decrease in stratospheric ozone and a corresponding increase in tropospheric ozone were observed, but the total ozone remained roughly constant (± 10 DU) with respect to the other days (± 5 days), was used for preliminary identification of STE events.

STE events which were restricted only to the upper troposphere and lower stratosphere (UTLS) regions were termed as shallow events, whereas those which influenced not only the UTLS region, but also MLT were termed as deep events (Table 1). Thereafter, all the vertical ozone profiles were grouped into two seasons: summer (October to March) and winter (April to September). These profiles were averaged to obtain a normal ozone profile for each season, which was in turn compared with the ozone profiles for STE events, to determine the depth up to which ozone descended into the troposphere during these events (Figure 1 and Tables 2 and 3). These events were analysed in detail using back trajectories at altitudes where enhanced ozone concentration was observed compared to the normal profile to check the possibility of horizontal transport of ozone precursors (CO, $NO_2$ and $CH_4$) from the areas surrounding these stations in increasing tropospheric ozone. The vertical pressure velocity (Pa $s^{-1}$) at the tropopause was examined to confirm the downward transport of ozone from the stratosphere.

It is observed from the vertical ozone profiles (Figure 1) that the decrease in ozone in the stratosphere (16–25 km altitude range) is higher compared to the amount by which ozone increased in the troposphere. This is because, apart from decrease in stratospheric ozone due to its transport into the troposphere, the polar stratospheric

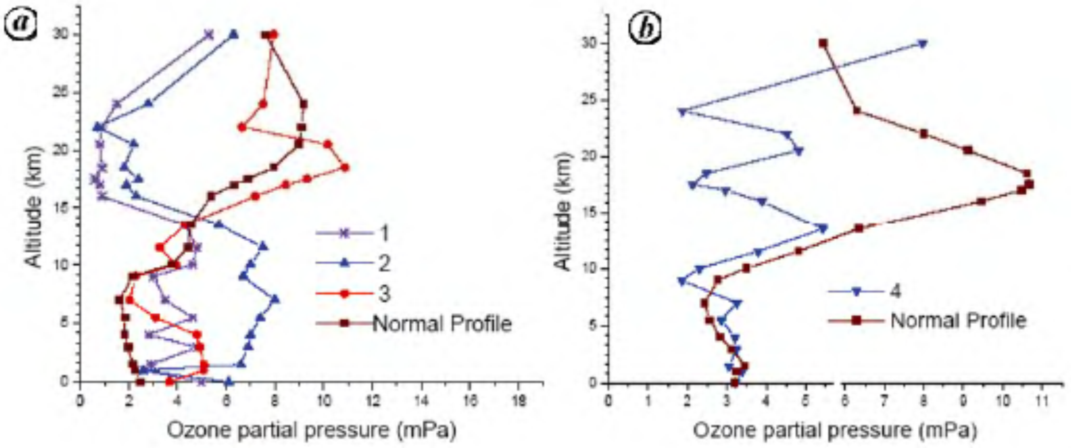


**Figure 1.** Comparison between stratosphere–troposphere exchange (STE) events of ozone with normal ozone profiles during (***a***) summer and (***b***) winter. (Source of data: World Ozone and Ultraviolet Radiation Data Centre, Environment Canada, Toronto.)

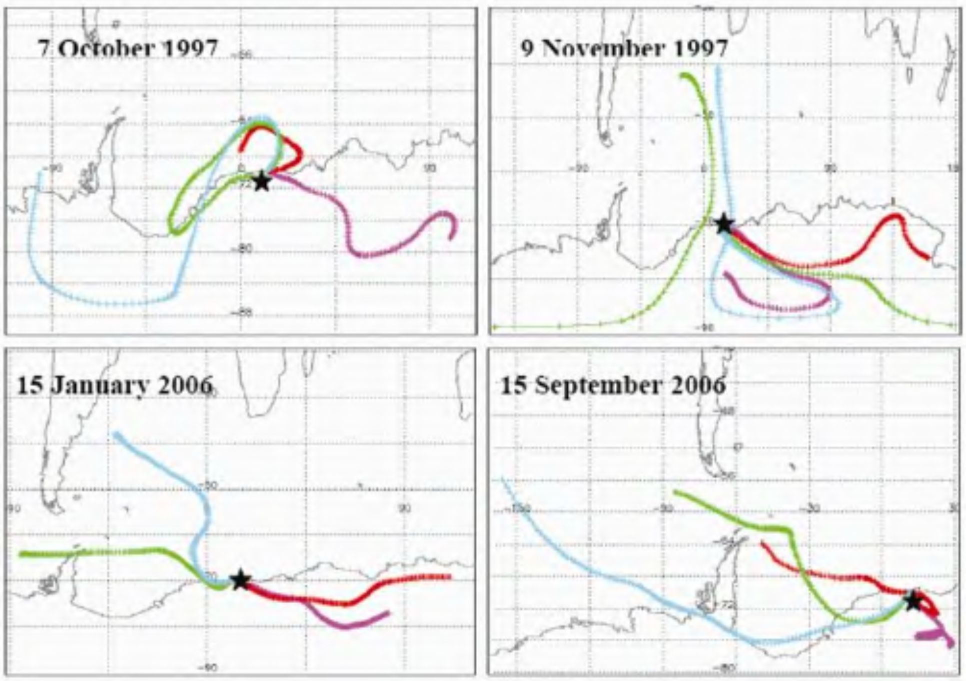


**Figure 2.** Five-day back trajectory at the surface (pink), 3 km (red), 5.5 km (green) and 7 km (green-blue) altitude during the STE events at Maitri (denoted by star). (Source of the trajectories: European Centre for Medium-Range Weather Forecasts, UK.)

clouds that enhance ozone destruction are also located in the 16–25 km altitude range. The back-trajectory analysis at different altitudes in the troposphere indicated the transport of air from the north, northwest and southeast directions during these events (Figure 2). The level of $NO_2$, CO and $CH_4$ at Maitri was observed to be relatively low, whereas it was slightly higher at places lying along the path of back trajectories during these events. One such case is shown in Figure 3. As ozone is destroyed during transport over the sea/ocean due to relatively high insolation and humidity[11], the back trajectories involving transport of air over the sea/ocean are not expected to contribute to the observed enhanced ozone levels. This indicates the possibility of an increase in tropospheric ozone levels at Maitri due to transport of ozone precursors from the surrounding areas.

Since pressure decreases with height, negative values of vertical pressure velocity indicate rising motion in the atmosphere, whereas positive values indicate sinking air. The vertical pressure velocity at the tropopause indicated downward transport of ozone from the stratosphere on all these occasions (Figure 4). The geopotential maps indicated the formation of troughs (upper-level lows) on all these events (Figure 5). Strong troughs are typically

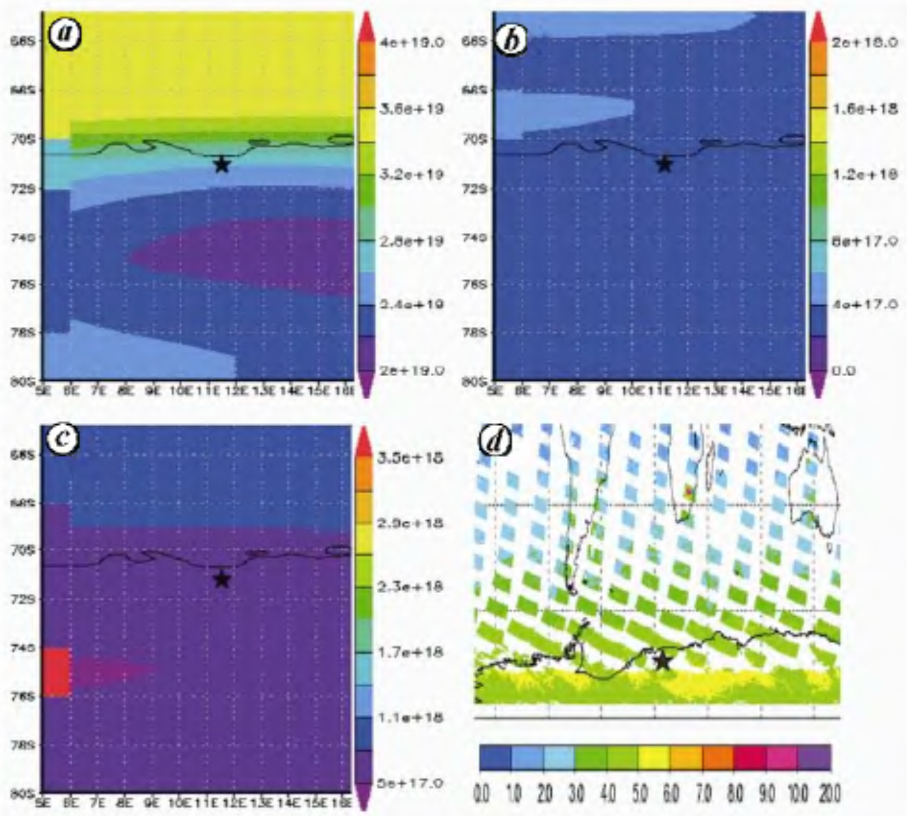

**Figure 3.** Tropospheric column (***a***) methane (molecules $cm^{-2}$), (***b***) ozone (molecules $cm^{-2}$), (***c***) carbon monoxide (molecules $cm^{-2}$) and (***d***) $NO_2$ ($10^{15}$ molecules $cm^{-2}$) during 10–16 January 2006 at Maitri (denoted by star). (Source of data: Tropospheric Emission Spectrometer on NASA's Earth Observing System spacecraft and Scanning Imaging Absorption Spectrometer for Atmospheric Chartography instrument on the European Space Agency ENVISAT platform.)

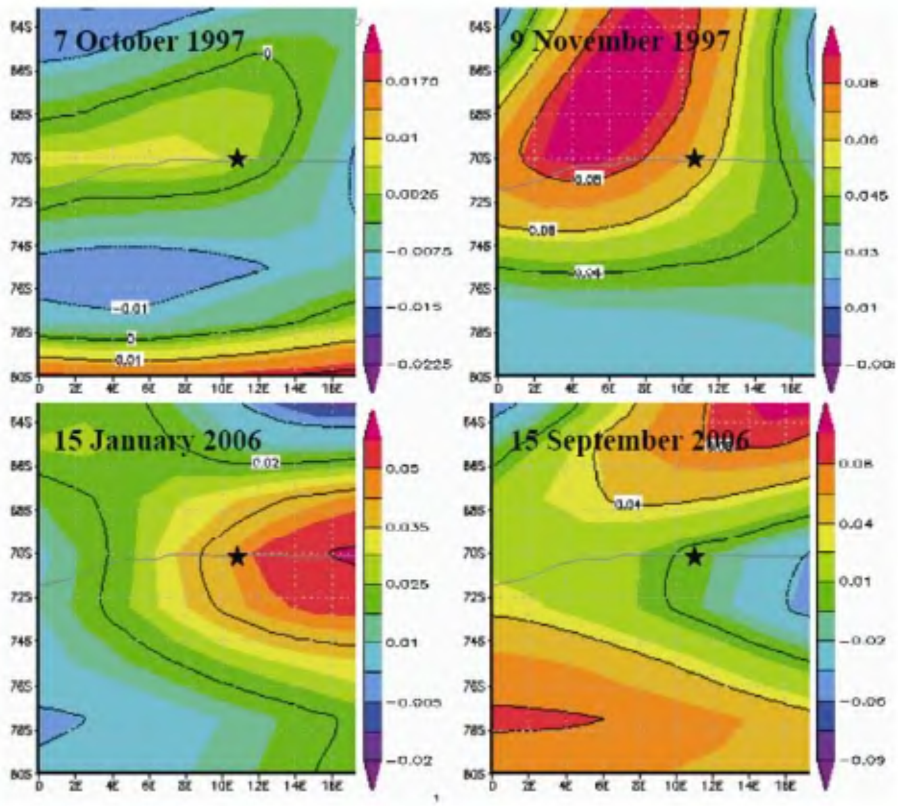


**Figure 4.** Vertical pressure velocity (Pa $s^{-1}$) at the tropopause at Maitri (denoted by star). (Source of data: NCEP Reanalysis; Kalnay *et al.*[13]).

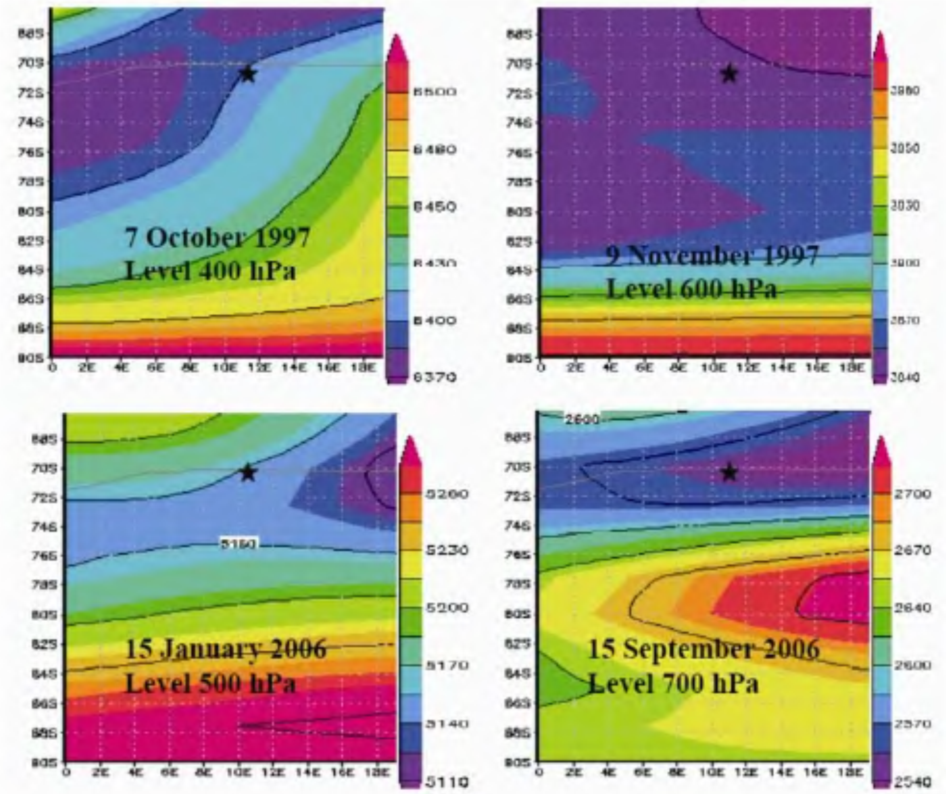


**Figure 5.** Geopotential height (m) maps at different pressure levels (hPa) during the STE events at Maitri (denoted by star). (Source of data: NCEP Reanalysis; Kalnay *et al.*[13].)

preceded by stormy weather and colder air at the surface. These characteristic features suggest that the enhanced tropospheric ozone observed on these occasions may be a consequence of transport of ozone precursors from the surrounding areas, and stratospheric intrusions associated with pronounced cut-off circulations, which provided a large reservoir of ozone-rich air for eventual transport to the ground. Similar results were observed by Davies and Schuepbach[2] at a station on the Dutch coast. Although it is well established that the frequency of occurrence of STE events is higher during winter[16,17], in the present study it appears that the frequency of STE events is higher during summer compared to winter. This is because, fewer vertical ozone profiles were available at Maitri during winter darkness compared to summer.

We can conclude from this study that STE plays a minor role in the tropospheric ozone budget. Stratospheric intrusions observed in this study were associated with pronounced cut-off circulations. However, a deeper analysis of the synoptic situation is essential to indicate strongly the exchange which had occurred. Apart from this, since only two vertical ozone profiles could be obtained per month during summer and few ozone profiles were available during winter, it may be possible that several STE events which had occurred during the data gaps were missed in this study.


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# Reducing biofouling on titanium surface by electroless deposition of antibacterial copper nano films

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**The main objective of this work is to study the antibacterial properties of copper thin nano films on titanium surface deposited by electroless plating technique for biofouling free condenser tube applications. The electroless deposition of copper nano films on titanium substrates was done and Cu films were also post-annealed for 1 h at 600°C under vacuum condition to increase the particle size of the films. Surface characteristics of the films were studied using GIXRD, SEM and AFM. Antibacterial properties of the surface were evaluated by exposure studies in seawater using total viable count and epifluorescence microscopic techniques. Excellent antibacterial activity was exhibited by the electroless plated copper nano film on the titanium surface showing more than two orders decrease in the bacterial density compared to titanium surface with no copper film.**

**Keywords:** Annealing, antibacterial properties, biofouling, copper nano film, electroless plating.

COPPER and its alloys were used as condenser materials to resist biofouling due to copper toxicity. However, in the new 500 MW Prototype Fast Breeder Reactor coming up at Kalpakkam, India, titanium is the condenser material in order to achieve zero corrosion in the steam generator material where a single wall separates sodium and water. Any through wall pitting and leaks can cause catastrophic accidents. Copper ions leaching out from the steam side of condenser materials can cause under deposit corrosion on the steam generator walls.

One of the main challenges in the use of titanium, particularly for heat exchanger tube applications, is its biofouling[1]. Biofouling is the undesirable growth of living organisms on a surface, which will reduce its efficiency and lifetime. The principal methods used to control biofouling are mechanical cleaning techniques to detach the biofoulers and chemical treatment techniques to kill the biofoulers using various oxidizing and non-oxidizing biocides[2]. Since surface properties of the substratum influence initial adhesion and growth of bacterial cells on materials, modification of the surface of the condenser materials like stainless steel, titanium, etc. can further supplement the present treatment programmes. The present study is an attempt to use nanotechnology methods for surface modification aimed at improving the antibacterial properties of these condenser tube materials.

Many of these coatings on the surface provide a barrier between the surface and the environment, and also provide fouling resistance to the surface[3]. This fouling resistance is mostly due to toxic metallic ions on the surface, making it inhospitable to most marine organisms by blocking the respiratory enzyme system of these microorganisms in addition to damaging microbial DNA and the cell well[4].

Copper is known to have excellent toxicity to marine organisms and thereby provide good resistance to biofouling, and hence is used extensively as condenser material in power plants[5]. However, titanium has been chosen as condenser material for the new fast breeder reactor at Kalpakkam to avoid steam-side corrosion problems. Thus this study is focused on exploiting the excellent potential of copper nano coatings on the surface of titanium to con-

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