MONITORING OF OIL SPILL CONTAMINANTS IN WATER SAMPLES FROM ELEPHANTA CAVE IN MUMBAI OIL SPILL

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MUMBAI OIL SPILL AT A GLANCE

A foreign cargo ship, which collided with another vessel about 10 km off Mumbai harbour, tilted further spilling oil for the third day Monday even as Navy and Coast Guard made hectic efforts to contain the leak on Saturday 07 August 2010.

"MSC Chitra had tilted 80 degrees and the total oil spill is nearly 50 tonnes,300 containers carrying oil have tumbled into the water. Several containers contain hazardous chemicals such as sodium peroxide, which have formed a layer over the sea surface, thereby threatening marine life.

The thick oil slick has been sighted two to three kms around the vessel Chitra, with some debris from the ill fated ship floating as far as to the Gateway of India.

MSC Chitra, was loaded with an estimated 2,600 tonnes of oil, 300 tonnes of diesel and 89 tonnes of lubricating oil at the time of the accident.

Oil pollution, especially in the marine environment, is considered as an ecological issue but Arabian Gulf which is the shallowest sea in the world borders major OPEC countries devoid

of natural drinking water resources. Any kind of oil pollution in the sea tends to endanger the vital drinking water sources, i.e. desalination plants, at the first instance.

The presence of oil close to the plant intake system may affect the plant primarily in two ways:

1. Interfere with the plant operation by possible suction of oil constituents into the plant equipments decreasing their performance efficiencies.
2. Adversely affect the quality of the product water making it aesthetically unpleasant and unsafe for drinking purposes.

When oil flows into open sea most of the low boiling point compounds escape to the atmosphere. Only a small percentage of these compounds remain in the seawater in dissolved or dispersed state. Even this amount progressively decreases depending on the aging and weather conditions. After a few days from the spillage higher boiling fractions of the crude oil remains floating either on the surface or a few feet below as undissolved tar balls.

The greatest concern facing the desalination plants is the possibility that some of the crude oil constituents may persist as liquid dissolved in water and find their way into the plant lagoon ending up in process stream. Due to several physico-chemical factors such as the solubility in seawater, boiling points and vapour pressure of the dissolved oil constituents and operational parameters like temperature, vacuum etc., thcrc is a possibility that some of the oil constituents may ultimately find their way into the distillate water. Since some oil constituents are known to be toxic to human health even in small concentrations water containing such compounds will create health hazards.

ECOLOGICAL IMPACT

The impact is felt along the Mumbai coastline, with fish and other marine creatures were found covered with oil. The oil slick was entered the sensitive mangrove belt and damaged the environment there. The shores along the green mangroves were coated with slick black oil. Containers of pesticide were also thought to have spilled over and this is causing alarm to environmentalists.

CAUSE OF THE ACCIDENT

Preliminary investigations suggest that the accident occurred as a result of communication errors. An inquiry is being conducted by the Directorate General of Shipping and a report is expected to be tabled in a month. The captains of the two ships have blamed each other for the mishap. Captain Laxman Dubey of the Khalija-III alleged that he attempted to establish radio contact with the MSC Chitra thrice but received no response.

Captain M Ranjit Martin, who was at the helm of the Chitra, said that it was negligence on the part of Captain Dubey that led to the accident. He claimed that the Khalija-III was not in a good condition after being grounded by Mumbai port authorities earlier in July. The vessel had been moving into the port when it collided with the Chitra. The Geneva headquartered Mediterranean Shipping Company, which owns the Chitra, has stood by its captain on the issue.

TOXIC EFFECTS OF CRUDE OIL CONSTITUENTS IN WATER

There are several compounds or classes of compounds originating from crude oil possessing toxic properties. The most important and well-known among them and their potential health aspects are described briefly below:

1. Mineral Oil:

This constitutes a class of several sparingly soluble (in water) aliphatic and aromatic hydrocarbons of petroleum origin. While some individual compounds from this group may be acutely toxic, a great majority are comparatively harmless. Because of this vast difference in the toxic properties it has been reported as difficult to establish a numerical criterion which would be applicable to all types of oils. Extensive research had shown that tolerance limits of these products to human health far exceed the odour and taste thresholds if they are present in water. In other words, humans tend to refuse to drink water containing mineral oils due to smell and odour reasons at much lower concentrations than toxic threshold levels. World Health Organization (WHO) had set a maximum permissible limit (MPL) of 0.3 mg/L of mineral oil in drinking water in their 1976 standards, but later in I984 this limit was removed. However, API continues to impose an MPL of 0.3 mg/L in the drinking water.

2. Benzene :

This compound is known to be carcinogenic. Children and adults, drinking water containing more than l00ug/L for a life time, are at an increased cancer risk.API has not set any maximum permissible limit for this compound in drinking water. However, WHO suggested a guideline value of l0ug/L in 1984.

3. Toluene :

This is a constituent of crude oil having a significant solubility in water (515 mg/L). It is less toxic than benzene. A daily consumption of upto 700 ug/L through drinking water is considered to be safe for adults. API did not set any safe limit for this compound, however, WHO proposed a guideline value of 1000 ug/L in drinking water.

4. ***Polynuclear Aromatic Hydrocarbons CPAH):***

This is a class of more than 20 organic compounds, some of which are known to be extremely toxic to human health. These compounds have very limited solubility in water but can continuously leach into water from crude oil tar balls over extended period of time. Many PAHs are shown to be mutagenic in bacterial systems and produce skin tumors in some test animals. It has also been presumed that some occupation-associated skin cancers observed in man is due to exposure to some of the PAHs. EPA has set a MPL of 0.2ug/L for these compounds in drinking water. W.H.O. has set a limit of 0.01ug/L for benzo [a] pyrene, one of the wellstudied compounds among PAHs, mainly due to the fact that this compound is associated in water with other PAHs of known carcinogenicity.

5. ***Phenolic Compounds :***

Many phenolic compounds arc known to be present in petroleum crude. They are mostly non-toxic in trace concentrations. But some chlorophenols, produced as a result of chlorination, are reported to be toxic if consumed in small concentrations in drinking water. For example, 2,4,6 - trichlorophenol is a chemical carcinogen that might increase the cancer rate in man if present in sufficient quantities. EPA has set an M.P.L. of 2ug/L for phenolic compounds in drinking water. Many phenols can be detected by their taste and odor at concentrations far below1ug/L.

6. ***Chloroform and Total Trihalomethanes :***

These compounds do not primarily originate from crude oil but could be formed in water on chlorination as a result of reaction between chlorine and some crude oil constituents. Chloroform and some other halogenated compounds, included in the class of total trihalomethanes, are known to have carcinogenic property. EPA has limited the maximum

permissible limit for chloroform and total trihalomethanes in drinking water at 30 and 250ug/L, respectively.

7. *Phthalate Esters :*

Esters of phthalic acid are reported to be a class of contaminants usually found in water originating from wide industrial use of plastic based materials. Though scanty data is available on the toxicity of phthalates in humans this class of compounds have been included in US EPA's priority pollutants list for drinking water. A concentration of 0.1 mmol per Kg body weight per day has been suggested as a threshold value for all phthalates.

Solubility of Some Petrochemical Hydrocarbons found in the Mumbai Oil spill

S.No.	**Compound**	**Carbon no.**	**Solubility(mg/l)**
1-	Benzene	6	1780
2-	Toluene	7	550
3-	Xylene	8	195
4-	Napthalene	10	80
5-	Phenanthrene	14	1.68
6-	Anthracene	18	0.095
Parafins			
1-	Methane	1	32
2-	n-Hexane	6	10.05
3-	n-Dodecane	12	0.0065
4-	n-Octadecane	18	0.0043
5-	n-triacontane	30	0.002

Major findings of the studies are summarised below:

(a) *Mineral Oil :*

Fig. 1 indicates the variation of mineral oil contents in sea water and product water samples during the reported period. While the majority of the samples indicated a mineral oil concentration of close to zero (below detection limit), a few of them had concentrations ranging from 0.02 - 0.1 mg/L.Several samples immediately collected from all intakes and near the mouth of the intake bay did not show a repetition of the results, but one sample collected close to a navy boat anchored in the lagoon showed high levels of both mineral oil and phthalate esters. It was obvious that the source of this contamination was some spillage from the boat. It is known that some lighter fractions of crude oil such as hydrocarbons sparingly dissolve in water. Hydrocarbons with the smallest carbon numbers and their derivatives dissolve the most while those of higher molecular weights dissolve the least. But the low molecular weigh: compounds are the most volatile hence their disappearance from the sea water under the turbulent conditions is quite rapid.It may be seen from that mineral oil concentration in product water were less than 0.03 mg/L in all samples but two. That this was true even during the worst period of the crisis prove that the precautionary measures taken by various pollution control agencies were quite effective. However, one point of concern is tho occurrence of traces of mineral oil in the product water when the same is present in sea water. This may indicate that MSF process is not capable to completely remove the organic contaminants present in sea water. It is difficult to make a quantitative assessment of this problem from the current data, and will require a separate and detailed study most effectively by using pilot plant, since most of the physico-chemical parameters governing an MSF process can not be duplicated in laboratory scale experimental set up.

(b) *Polvnuclear Aromatic Hydrocarbons :*

This class of compounds were specifically monitored using selected ion monitoring (SIM) technique due to their known toxicity and the stringent regulatory control imposed by EPA (MPL = 0.2ug/L) in drinking water.

(c) Benzene and Toluene :

Both benzene and toluene have considerable solubility in water, 1780 and 515 mg/L respectively, and both are present in crude oil in significant quantities. Benzene was detected in sea water twice during this period but it did not appear in the product water However, toluene appeared more frequently in sea water samples at concentrations ranging from 0-0.6ug/LToluene was detected four times in product water as well, the maximum concentration being 0.34ug/L. Though EPA did not impose a maximum permissible limit for both these compounds in drinking water, WHO (1984) had set a limit of l0ug/L for benzene, which is more toxic of the two. Once dissolved, toluene remains in water for longer periods than benzene, since the former has higher boiling point. Frequent appearance of toluene in sea water samples is consistent with this assumption.

(d) ***Phenolic Compounds :***

No phenolic compounds were detected during this period with any consistency. Once when the Mumbai Oil Spill intake sea water was suspected to be contaminated by spillage of diesel oil from Navy boat phenol appeared in small traces in product water (<0.3mg/L). On another occasion on September-10, phenol was detected simultaneously in sea water and product water samples from Elephanta cave at concentrations of 0.31 and 0.l2mg/L, respectively which are significantly lower than the SASO limit of 2mg/L. No phenolic compounds were detected in Mumbai Oil samples during this period.

(e) Chloroform and Total trihalomethanes:

Water when disinfected by chlorination is known to contain several organic
by-products, some of them known to be toxic to human health. They are normally produced by reaction between chlorine and traces of naturally occurring organic compounds of humic and fulvic origin. Halogenated methanes, popularly called trihalomethanes (THMs) are most dominant among the chlorination by-products. It is also probable that some low molecular weight hydrocarbons or their derivatives present in crude oil might react with chlorine when oil-polluted water is disinfected resulting in increased levels of trihalomethanes or other nalogenated hydrocarbons. Therefore concentrations of trihalomethanes in general and
chloroform in particular were monitored both in sea water and product water samples continuously during this period.

Our previous determinations of trihalomethanes in chlorinated seawater in Arabian Gulf yielded an average concentration of about 30ug/L THMs. Fig.5 indicates much higher values during August to September and slightly more than the previous average during September-October in Arabian Sea water samples. This might be indicative of the presence of low molecular weight hydrocarbons originating from oil spills. The THM concentrations were always lower than the detection limit (<5ug/L) in the chlorinated product water. It shows the distribution of chloroform in chlorinated sea water and product water in Arabian Sea. Until Sept. 2010, chloroform concentrations were very frequently higher than the detection limit of 0.lug/L in seawatwer, in keeping with the general trend of THM distribution. THM concentrations both in chlorinated seawater and product water from Arabian Sea were generally slightly higher than found in Elephanta samples .This is consistent with the results of our earlier studies in the plant before the Gulf crisis. However, the concentrations in product water samples were always considerably less than the API limits. Chloroform concentrations remained below the detection limit of 0.lug/L except once in a sea water sample.

The study shows that though there was some increase in the levels of both THM and chloroform in sea water during the crisis period, the actual concentration never exceeded their

permissible levels as per drinking water standards. In product water their concentrations remained below detection limits in all samples from Elepahnta caves and most of the samples from Mumbai Oil Spill.

(f) *Total Organic Carbon (TOC):*

Variation of total organic carbon concentrations in sea water and product water samples from Mumbai Oil Spill. Though TOC concentration by itself is not an indication of the level of toxicity in water samples, any increase in its concentration above the normal level could be indicative of organic pollution. TOC concentrations, as seen from The average value remained close to 1.5-2 mg/L range which is the average level in Arabian sea water as found in our earlier studies. Sudden changes observed in day-to-day values may be due to changes in tidal conditions.

(g) *Phthalate Esters :*

This is a group of a large number of compounds, some of which are widely use in plastic and other industries as plasticizers. A few of them were reported to be found in trace concentrations in drinking water from natural as well as desalination sources. They were assumed to be leached into water from plastic piping and plumbing materials. They are not known to be highly toxic; their tolerance limits reported to vary from 15-350 mg/L in drinking water depending on individual compounds.

A wide variety of phthalate esters were detected in contaminated sea water samples collected from the proximity of the navy boat anchored in the Mumbai Oil Spill intake lagoon. All of them have very high boiling points (greater than 220^{o}C). But surprisingly, trace amounts of several of these esters were detected in the product water samples as well when the intake sea water was contaminated by spills from the navy boats. Though the total concentrations of all these esters detected in product water were always very low (below toxic levels) it is surprising how such high boiling point organics in sea water were carried into the distillates. The Center is currently investigating this problem using laboratory scale experimental set up. However, scaled-up studies on a pilot plant will be essential to fully elucidate this phenomenon as the physico-chemical parameters governing the MSF process cannot be duplicated on laboratory scale set up.

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