*Asian Journal of Chemistry* Vol. 19, No. 1, (2007), 621–626

# Assessment of Sea Water Quality Around Sunken MV Ulla Ship on İskenderun Bay, Hatay, Turkey

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MV Ulla, which was a cargo marine vessel loaded with fly ash, ended its forced voyage at İskenderun Port on February 20, 2000. The ship was abandoned there for 4½ years. Finally, the vessel sunk on September 6, 2004. The load was removed from the vessel in order to comply with related regulations in summer 2005. This paper investigates the sea level metal levels between September 2004 and September 2005. It was found that total chromium during fly ash removal did not pass the upper limit of hazardous waste limits. Furthermore, total suspended solids decreased in recovery ship tanks as a function of time during the recovery process of load.

**Key Words: MV Ulla, Ship recovery, Chromium(IV), İskenderun Bay, Hatay, Turkey.**

## INTRODUCTION

Total load 2200 tons was left out as abandoned ship load of MV Ulla, prior to its sinking on September 6, 2004. Due to technical problems and bureaucratic handicaps, the ship was left to its fate at İskenderun Port. İskenderun is a port and steel production town whose urbanization rate is over 60%. Based on the initial investigations, which were completed by Middle East Technical University (METU) in Ankara, the ship load was tested as hazardous matter taking 21 different parameters into account and only Cr(VI) was detected to be within hazardous waste standards.

In this study, sea water quality was investigated between sunken date and recovery period of MV Ulla sea vessel. Furthermore, the waste character was determined periodically during the recovery of waste from the ship. The recovery operation was started on June 3, 2005. By October 23, 2005, 115 tons of recovered waste and 200 tons of shelled load were transported to the recovery ship and 800 tons of trickling water, that was declared to be non-hazardous, was discharged from the recovery ship.

## EXPERIMENTAL

İskenderun has a population of *ca.* 160,000 residents and the country's second largest steel production plant is located in the north-eastern part of the town. The

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town is situated on 36°35′ N and 36°10′ E coordinates. Another sampling station was chosen as Botaş in Adana Province . Water depth in İskenderun Bay is more or less consistent with 70 m.

Different samples were obtained from the sunken sea vessel and away from the sea vessel to characterize whether a serious environmental contamination was occurring. The sunken sea vessel is 25 m below the sea surface within İskenderun Bay limits.

Periodically taken recovered waste samples were sampled by Hatay Provincial Environment and Forestry Staff from the tanks of Amorito sea vessel. Obtained samples were transferred into Mustafa Kemal University (MKUFAM), Central Laboratory of Science and Research Application, Tayfur Sökmen Campus, Antakya, as soon as probable under standard conditions. MKUFAM Lab completed the sea water analysis.

For water analysis, a 10 mL sample was digested with high purity nitric acid and then filtered through Whatman® quantitative filter paper. For sludge analysis, 1–2 g of wet sample was digested with high purity nitric acid and hydrogen peroxide. Laboratory grade hydrochloric acid was added into the initial digestate and the sample was refluxed. To increase the solubility of metal, this digestate was filtered and the filter paper and residues were rinsed with hot hydrochloric acid and then hot reagent water. Filter paper and residue were returned to the digestion flask, refluxed with extra hydrochloric acid and then filtered again. The digested portion was then diluted to a final volume of 100 mL. At least three replicates for each sample were prepared in order to increase the sensitivity in readings.

All water and solid analyses were completed using Varian® II Liberty Series inductively coupled plasma spectrometer (ICP-AES) located at Mustafa Kemal University.

Also for the chromium(VI) analysis in sea water, a Merck® Spectroquant Nova-60 model instrument and two Merck® kits (1.14758.0001 and 1.14552.0001) were used and results were compared by both ICP-AES and Merck® Spectroquant. The results were found very similar.

## RESULTS AND DISCUSSION

Based on samples obtained by İskenderun Municipality, sea water total chromium was found to increase by almost 12% on surface of direct sunk point with respect to 300 m away from the sunk vessel. Two different sampling points were determined by the Municipality and two different sampling dates were taken into account. Table-1 summarizes total chromium and chromium(VI) concentrations as well as other solid and liquid waste mix quality parameters examined.

It is interesting that the total iron concentration at the ship was *ca.* 4.4 times more than the total lead concentration 300 m away from the vessel. This can he explained by the corroded bottom of the ship. Therefore, it is not very surprising to see such elevated results by iron concentration. Furthermore, about 3.4 times more zinc was found near MV Ulla compared to the zinc level 300 m away from the vessel location. On the other hand, nickel and manganese concentrations in sea water just next to the ship were 0.041 and 0.149 times less than those in sampling station located 300 m away from the abandoned ship. Therefore, near shore areas were more contaminated with nickel and manganese from inland sources. In Table-1, the World Health Organization drinking water guidelines are also included[1].

TABLE-1
ELEMENT CONCENTRATIONS (AS mg $L^{-1}$) IN SEA WATER AROUND MV ULLA

| Sampling date and place | Cr (total) | Cd | Cu | Fe | Mn | Ni | Zn |
|---|---|---|---|---|---|---|---|
| September 8, 2004, centre | 0.0459 | 0.0147 | 0.0504 | 0.1627 | 0.0531 | 0.0017 | 0.0339 |
| 300 m away | 0.0411 | 0.0153 | 0.0552 | 0.0370 | 0.3560 | 0.0410 | 0.0101 |
| September 13, 2004, three different sampling locations | 0.0432 | – | – | – | – | – | – |
| WHO guideline[2] | 0.0500 | 0.0030 | 1.0000 | 0.3000 | 0.1000 | 0.0200 | – |

In Table-2, metal content, in terms of cadmium, chromium and phenols, at two different sea water sampling stations are summarized. These stations are located near highly industrialized and densely populated centres.

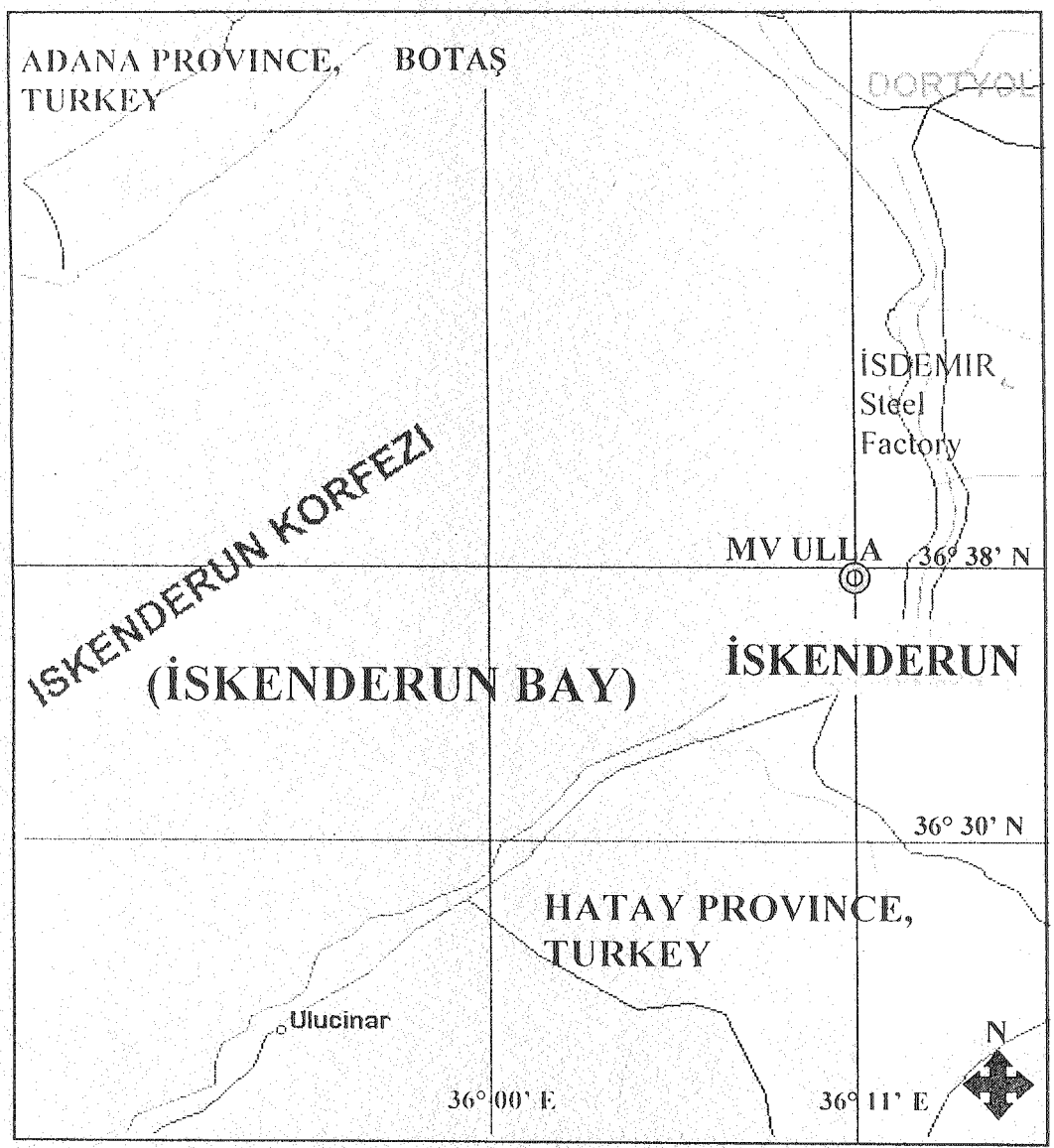


Fig. 1. The location of the sunken sea vessel MV Ulla and two sea water sampling stations (İskenderun and BOTAŞ) (no scale).

TABLE-2
CADMIUM, CHROMIUM AND PHENOL LEVELS (mg $L^{-1}$) IN WATER SAMPLES

| Sampling location | Date: October 18, 2004 | | | Date: November 2, 2004 | | |
|---|---|---|---|---|---|---|
| | Hexavalent Cr | Cd | Phenol | Total Cr | Cd | Phenol |
| Botaş surface | 0.033 | 0.119 | 0.032 | 0.058 | 0.097 | 0.016 |
| Botaş deep | 0.035 | 0.153 | 0.024 | 0.050 | 0.127 | 0.028 |
| İskenderun surface | 0.028 | 0.127 | 0.076 | 0.042 | 0.131 | 0.009 |
| İskenderun deep | 0.010 | 0.137 | 0.020 | 0.044 | 0.149 | 0.018 |
| Regulatory limit | 0.1 | 0.1 | 20 | 0.1 | 0.1 | 20 |

Indeed, 49–78% of total chromium was found to consist of Cr(VI) (hexavalent chromium) based on the initial samples. Under alkaline conditions, this result is notably surprising. When one takes a closer look at Figs. 2 and 3, hexavalent chromium level prior to the second half of August 2005 load in Tanks 3 and 7 of the recovery ship, Amorito, is confirmed to be insusceptible to be treated under hazardous waste category. It should be noted that both suspended solids and oil and grease concentrations are shown in secondary y-axis. Primary (left) y-axis represents only total chromium concentration in Figs. 2 and 3. A parallel drop of total chromium and suspended solids after the second half of August 2005 was observed in both Tanks 3 and 7 of the recovery ship, Amorito. This could be explained by homogenization or more specifically, settlement, of the waste removed from the sunken sea vessel, MV Ulla.

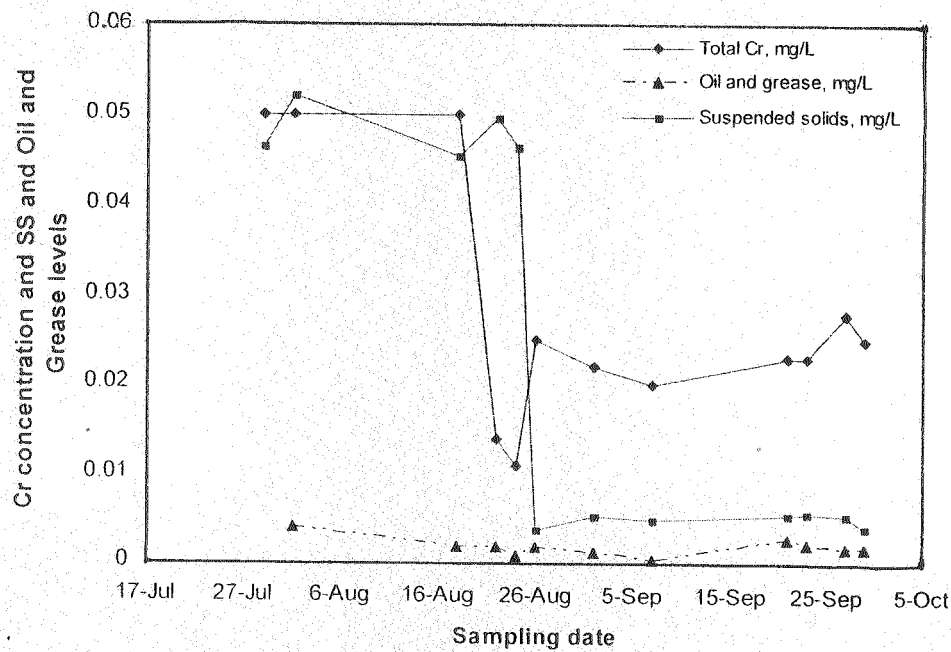


Fig. 2. Pollutant concentrations in Recovery Ship, Amorito, Tank 3.

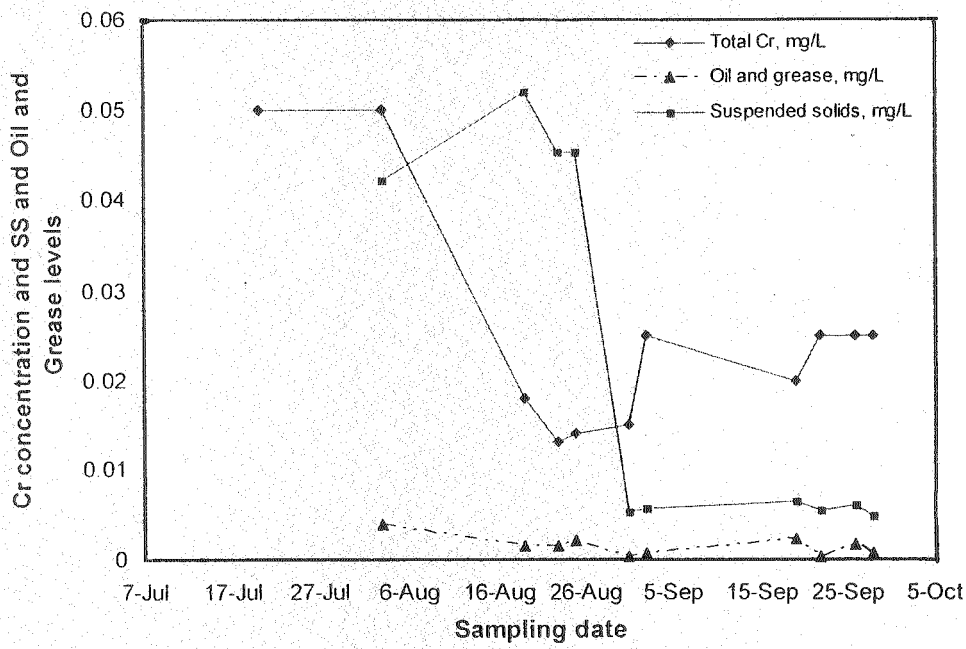


Fig. 3. Pollutant concentrations in Recovery Ship, Amorito, Tank 7.

Based on solid and liquid mix sampled on different days, phenol and cadmium concentrations were found to be more than the regulatory limits. However, the source for phenols and cadmium cannot be considered as the sunken ship. Intensive steel industry and other related branches situated in and around İskenderun may be more responsible for excessive cadmium concentration in sea water. Smelting operations have been noted to add large amounts of metals. In humans, cadmium is noted to be responsible for high blood pressure, liver, kidney and heart diseases and certain categories of cancer[2]. At pH = 8, iron(II), manganese(II) and cadmium(II) are expected to be more soluble than chromium(III)[1].

If chromium concentration in sea water between October 28 and November 2, 2004 is assumed to be unchanged, total chromium at Botaş is estimated to be around 0.050 mg $L^{-1}$. Chromium(VI) can be estimated to be *ca.* 0.035 mg $L^{-1}$ at Botaş on November 2, 2004. Higher values of phenol, with the exception of İskenderun surface on October 18, 2004, detected at Botaş on both sampling sites can be explained by intensive petroleum industry, appropriately shipment port, located there. Phenol's solubility[3] in water is noted to be 80,000 mg/L at 25°C. At Botaş sampling station, both cadmium and phenol concentrations on sea surface were found to be lower than at deep sampling points. This may indicate that sediment is contaminated with certain pollutants associated with petroleum industry. On the other hand, only cadmium was found to be slightly elevated in deep water samples of both sampling dates at İskenderun sampling station.

Anionic and soluble hexavalent chromium is reduced to cationic and insoluble trivalent chromium depending upon site-specific geo-enviro-chemical properties[4]. This transformation is expected to occur mostly during the summer months, if pH is near neutral, due to the fact that organic activity is postulated to be an important factor in this reduction[5].

As a conclusion, the waited ship is thought not to be extremely harmful to the environment during its stay at İskenderun Bay. The recovery operation can be declared as a successful one. To reduce hazards associated with port activities and industrial operations, operations of all types of activities should be carefully fulfilled in order to protect environmental health in the area. It should be underlined that the area is noted to be very active seismically and geohazards pose serious associated risks[6].

## ACKNOWLEDGEMENTS

The authors express their thanks to Hatay Environment and Forestry Provincial Directorate for their help in providing samples. The efforts of İskenderun Municipality are also appreciated. MKUFAM staff, Eng. Mehmet Bayrakçioğlu, Eng. Hidayet Duman and Seher Erişen Misirlioğlu (MSc., Chemistry), should also be appreciated for their help in completing the analyses.

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(*Received*: 10 January 2006; *Accepted*: 30 June 2006) AJC-4987