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Vanadium and Nickel Content of Nowruz Spill Tar Flakes on the Saudi Arabian Coastline and Their Probable Environmental Impact

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The Arabian Gulf is experiencing the worst oil spill in its history. The spill originates from two war demaged Iranian oil wells in the Nowruz oil field. The wells continue to pour approximately 4,000 bbl/day of crude oil into the Arabian Gulf since February, 1983 (Begley et al. 1983). Much of this oil is entering Saudi Arabian waters and washes ashore in the form of tar like falkes. In late March and early April 1983; fish, snake, turtle, and bird kills of different magnitude were noted along the Saudi Arabian coastline (RI-UPM 1983).

A royal decree was issued to stop fishing in the Arabian Gulf fearing that fishes and shrimp from the Gulf may be hazardous for human consumption. In the early days of the spill Saudi Arabian authorities suspected sources other than the Nowruz spill to be causing the kills. Research was initiated to identify the origin of tar like flakes, their environmental impact and the cause of fish, snake, turtle and bird kills. This paper discusses some of the results of this research.

MATERIALS AND METHODS

Tar flakes samples were collected from different locations during April 1983 and are presented in Table 1. To determine the concentrations of vanadium (V) and nickel (Ni), the flakes samples were prepared according to ASTM (1981) except that the flakes were dissolved in Methyl-Iso-Butyl-Ketone (MIBK) in stead of Benzene-Sulfonic acid.

Freshly dead or near dying snakes, turtle and fishes were collected from Saudi Arabian shoreline in April 1983. The specimens were dissected for chemical and pathological analyses. Two grams of muscle and liver tissues from each specimen were digested in 10 ml

concentrated HNO3 (ultrex grade) at 80 C for two hours. The digest was cooled and volume was increased to 50 ml by adding distilled water.

Vanadium and nickel concentrations in the tar like flakes and the acid-digest of fish, snake and turtle specimens were determined using Perkin Elmer Atomic Absorption Spectrophotometer (both flame and flameless techniques were empolyed).

RESULTS AND DISCUSSION

The concentrations of V and Ni in the tar flakes are given in Table 1. Vanadium concentrations in the tar flakes ranged between 31.8 and 160.6 ug/g flakes. Nickel content of the tar like flakes varied between 6.8 and 50.1 ug/g flakes. Statisticall analysis of the data indicated that the flakes collected from different locations differed significantly in V and Ni concentrations ($P < 0.05$). The wide range of V and Ni concentrations found in the flakes was probably the result of washing and weathering of the crude oil. Many of the samples analyzed varied significantly ($P < 0.05$) in V and Ni concentrations when compared with the fresh Nowruz crude oil (Table 2). The concentrations of V and Ni in the flakes or crude oils, as such, are of no significance in identifying the origin of the spill, especially when the oil has been weathered for unknown and different periods. However, the V/Ni ratio has been used as a parameter to identify crude oil origin (ASTM 1981; Deuwer et al. 1975).

The vanadium/nickel ratio of each tar sample was calculated and is given in Table 1. As shown in Table 1, about 80 percent of the tar flakes analyzed had similar V/Ni ratios as that of Nowruz crude. It may be concluded that, based on the V/Ni ratios, the majority of the tar balls were probably formed from the Nowruz crude oil. Futher finger printing of the Nowruz spill using GC, GC/MS and infrared techniques have confirmed these observations (unpublished data).

The concentrations of V and Ni in a queenfish, seven sea snakes and a hawksbill turtle are given in Table 3. The concentrations of Ni in the muscle tissues of sea snakes and queenfish were higher than the liver tissues, whereas the opposite trend was found for V concentrations. The queenfish gut tissue contained appreciable amounts of Ni and V suggesting that death might have been occured due to oil ingestion. Unfortunately, only a few animals could be collected in workable conditions, therefore, the data in Table 3 is inconclusive.

Table 1 Concentrations of V an Ni in tar like flakes samples.

LOCATION	DATE COLLECTED	V (ug/g)	Ni (ug/g)	V/Ni RATIO
Aziziyah beach	02/04/83	86.2	18.7	4.6
Aziziyah beach	03/04/83	38.1	7.9	4.7
Dammam Port	07/04/83	39.9	8.6	4.6
KDP*	11/04/83	31.8	6.8	4.7
KDP	11/04/83	49.3	10.6	4.6
KDP	11/04/83	87.3	20.1	4.4
Al-Khobar Port	11/04/83	78.0	18.1	4.3
Karan Island	12/04/83	78.8	18.0	4.4
Karan Island	12/04/83	130.1	27.8	4.7
Jurayd Island	12/04/83	32.5	3.4	9.6
Karkus Island	13/04/83	63.1	17.3	3.7
Karkus Island	13/04/83	59.9	13.2	4.5
Al-Beni Island	13/04/83	45.5	9.0	4.7
Al-Beni Island	13/04/83	61.9	14.4	4.4
Al-Beni Island	13/04/83	54.4	12.3	4.4
Al-Beni Island	13/04/83	71.7	17.4	4.2
Abu Ali Island	13/04/83	131.3	31.2	4.2
Bird Island	17/04/83	133.1	23.6	5.6
Bird Island	17/04/83	144.4	21.2	6.8
Half Moon Bay	17/04/83	149.2	25.2	5.9
Karkus Island	18/04/83	124.1	20.2	6.1
KDP	18/04/83	150.3	21.2	7.1
Karkus Island	19/04/83	143.2	20.2	7.1
Najran Oil Field	19/04/83	52.4	11.5	4.5
Dammam Port	19/04/83	73.0	17.7	4.1
Aziziyah Beach	19/04/83	86.9	14.7	5.9
Al-Beni Island	19/04/83	114.6	26.1	4.4
Salwa Beach	20/04/83	125.2	23.8	5.3
Salwa Beach	20/04/83	105.5	23.5	4.5
Salwa Beach	20/04/83	106.1	23.9	4.4
Dammam Channel	23/04/83	126.5	21.8	5.8
Nowruz Oil**	-	160.6	36.8	4.4

* KDP Al-Khobar Desalination Plant

** oil sample was collected from about 6 Km from the demaged Nowruz oil well

Table 2 Some selected characteristics of Iranian Nowruz crude oil (AGIP, 1972)

Density at 15 C	0.9296
Gravity (API)	20.63
Total Sulfur (%)	3.85
Calcium & Magnesium (ug/g)	<1
Nickel (ug/g)	34(36.8*)
Vanadium (ug/g)	140(160.6*)
Salt content as NaCl (%)	0.002

* Values taken from Table 1

Table 3 Concentrations of Ni and V in animal specimens (ug/g wet tissue)

Organism	Tissue type	Nickel	Vanadium
Turtle	Muscle	2.59	<1
	Liver	4.93	6.50
Snake A	Muscle	4.60	2.07
	Liver	4.73	5.45
Snake B	Muscle	2.34	1.0
	Liver	1.87	1.0
Snake C	Muscle	5.38	<1
	Liver	2.68	2.44
Snake D	Muscle	1.82	1.10
	Liver	1.89	1.55
Snake E	Muscle	2.90	2.36
	Liver	2.60	5.55
Snake F	Muscle	3.64	2.19
	Liver	2.75	4.94
Snake G	Muscle	1.70	0.93
	Liver	3.19	6.64
Queenfish	Muscle	1.70	0.93
	Liver	0.69	3.95
	Gut	3.37	2.95

As mentioned earlier, several thousands of birds, sea snakes, turtles and fishes have been killed perhaps due to Nowruz oil spill. About 90 percent of the dead or near dying animals, which were observed closely, showed no physical contact with oil. The animal kill dilema is perplexing and may never be resolved. An intensive survey of the available literature of Ni and V toxicity showed that most of the marine animals can withstand concentrations of several mg/l of Ni and V for several days (Eisler 1977; Petrich and Reish 1979; Prosi and Lierde 1979). However, it may be pointed out that several tons of Ni and V have so far been entered the Gulf alongwith oil spill. These elements may ultimately accumulate in marine biota. If this happens, the human population whose diet is composed of a large quantities of marine food from the Arabian Gulf may be exposed to substatially higher levels of these elements. Follow-up studies are recommended to understand the bahavior of Ni and V in the Gulf ecosystem.

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