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# Distribution of Ni, V, and Petroleum Hydrocarbons in Recent Sediments from the Veracruz Coast, Mexico

F. Vazquez, M. Sanchez, H. Alexander, and D. Delgado

Marine and Limnology Sciences Institute, UNAM, D.F. A.P., 70-305, C.P., 04510, Mexico

The coastline of Veracruz is a unique environment due to the presence of extensive coraline systems and of natural oil seeps. Depending on the environmental parameters the coraline systems are higly productive and diverse (UNEP/IUCN, 1988). Changes in these parameters by non-natural processes will cause damage or even the disappearance of these systems (UNEP, 1988). Thus baseline studies in this zone are important in order to establish the natural concentrations of trace metals and the presence of petroleum hydrocarbons originated either from natural oil seeps or accidental spills.

In the present paper the concentrations of nickel and vanadium in seawater and in sediments, as well as petroleum hydrocarbons in sediments are described in order to obtain base line information for the assessment of future man-induced alterations of the study area.

## MATERIAL AND METHODS

The sampling sites are presented in Fig. 1. The stations were divided in five transects. Samples were collected during the PEMARUN-I and II cruises, during November and December 1985, aboard the R/V Justo Sierra. The surface and bottom water samples were collected using Niskin bottles previously cleaned (Kremlin, 1983) and stored in plastic bottles with double distilled nitric acid until their analytical treatment in the laboratory.

Sediment samples were obtained by using a Van Veen grab (0.1 $m^2$). Each sample was carefully taken from the central portion of the grab. For the total content of metals the samples were taken with an acid washed plastic spatula ($HCl:HNO_3$; 1:5), placed in plastic bags and stored frozen. The hydrocarbon sample were

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Send reprint requests to F. Vazquez at the above address

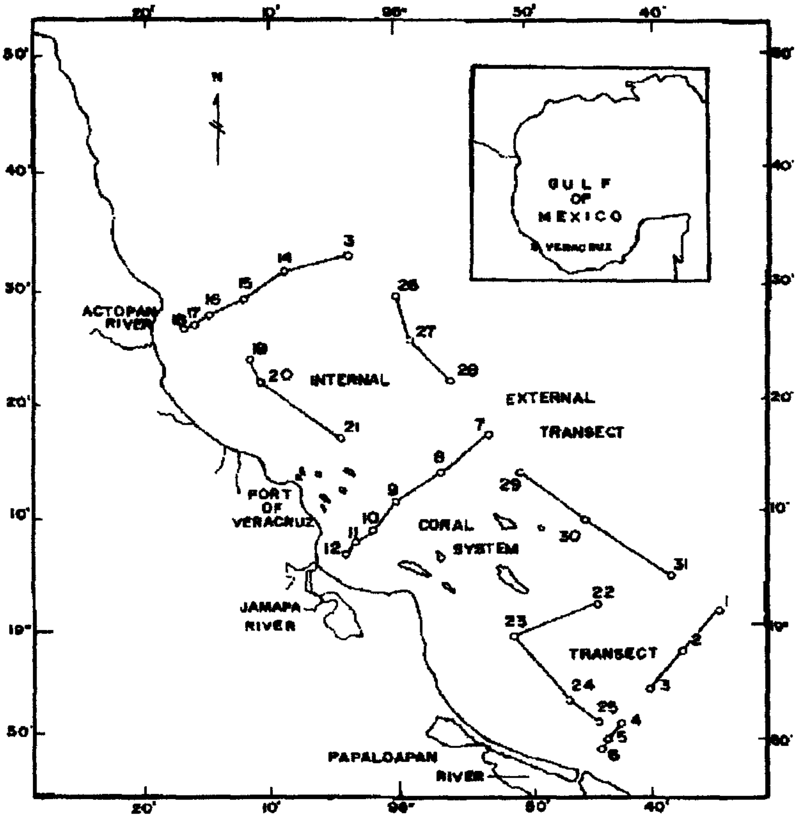

Figure 1. Study area and location of sampling site.

placed in glass jars properly washed and stored at $-20^{o}C$.

The seawater metal concentration was determined using the methods of Kingston et al (1978) and Bruland and Coale (1985) and an atomic absorption spectrophotometer (Perkin Elmer Model 2380, with graphite furnace Model HGA-400). The metals in sediments were digested successively with HCl, $HNO_3$, $HClO_4$, HF and heated (Bruland et al., 1974). Hydrocarbons in sediments were determined by the methods of Clark and Finley (1973) and Botello and Mandelli (1978). The gas chromatography analyses were performed using a Varian 2700 model gas chromatograph equipped with a flame ionization detector The colummns used were packed with 5% FFAP on Gas Chrom-Q (80/100 mesh). The hydrocarbons were analyzed only for the PEMARUN-I expedition.

## RESULTS AND DISCUSSION

Table 1. Trace metals in seawater and sediments,
Veracruz, Mexico.

| Parameter | PEMARUN-I | | PEMARUN-II | | PEMARUN-I | | PEMARUM-II | |
|---|---|---|---|---|---|---|---|---|
| | Ni | V | Ni | V | V | Ni | V | Ni |
| | --------SEAWATER--------- | | | | -------SEDIMENTS-- | | | |
| | | | PAPALOAPAN | TRANSECT | | | | |
| MEAN | 0.027 | 0.030 | 0.028 | 0.036 | 50 | 97 | 42 | 80 |
| MIN. | 0.012 | 0.009 | 0.019 | 0.017 | 43 | 90 | 42 | 85 |
| MAX. | 0.041 | 0.040 | 0.035 | 0.119 | 59 | 102 | 61 | 102 |
| VARIANCE | 0.0001 | 0.0001 | 0.0001 | 0.0001 | 39.7 | 25 | 475.2 | 1552.4 |
| ST.DESV. | 0.012 | 0.009 | 0.005 | 0.036 | 6.3 | 5 | 21.8 | 39.4 |
| | | | INTERNAL | TRANSECT | | | | |
| MEAN | 0.033 | 0.029 | 0.03 | 0.02 | 44 | 93 | 444 | 93 |
| MIN. | 0.015 | 0.210 | 0.023 | 0.003 | 42 | 87 | 42 | 86 |
| MAX. | 0.051 | 0.043 | 0.077 | 0.067 | 47 | 105 | 49 | 105 |
| VARIANCE | 0.0001 | 0.0001 | 0.0001 | 0.0001 | 2.6 | 57.8 | 6.8 | 67.2 |
| ST.DESV. | 0.010 | 0.010 | 0.014 | 0.020 | 1.6 | 7.6 | 2.6 | 8.2 |
| | | | EXTERNAL | TRANSECT | | | | |
| MEAN | 0.034 | 0.030 | 0.03 | 0.02 | 59 | 106 | 28 | 55 |
| MIN. | 0.012 | 0.007 | 0.022 | 0.009 | 55 | 89 | 55 | 108 |
| MAX. | 0.045 | 0.043 | 0.095 | 0.047 | 63 | 113 | 56 | 111 |
| VARIANCE | 0.0001 | 0.0001 | 0.0001 | 0.0001 | 8.4 | 27 | 918.1 | 3564.1 |
| ST.DESV. | 0.009 | 0.011 | 0.020 | 0.012 | 2.9 | 5.2 | 30.3 | 59.7 |
| | | | JAMAPA | TRANSECT | | | | |
| MEAN | 0.035 | 0.026 | 0.03 | 0.02 | 50 | 97 | 50 | 96 |
| MIN. | 0.013 | 0.004 | 0.013 | 0.059 | 43 | 90 | 42 | 89 |
| MAX. | 0.044 | 0.041 | 0.087 | 0.084 | 59 | 102 | 61 | 102 |
| VARIANCE | 0.0001 | 0.0001 | 0.0001 | 0.0001 | 39.7 | 29.2 | 59.3 | 30.3 |
| ST.DESV. | 0.010 | 0.011 | 0.017 | 0.021 | 6.3 | 5.4 | 7.7 | 5.5 |
| | | | ACTOPAN | TRANSECT | | | | |
| MEAN | 0.028 | 0.028 | 0.04 | 0.02 | 43 | 94 | 45 | 94 |
| MIN. | 0.008 | 0.001 | 0.036 | 0.007 | 39 | 86 | 39 | 82 |
| MAX. | 0.046 | 0.042 | 0.057 | 0.039 | 49 | 101 | 52 | 106 |
| VARIANCE | 0.0001 | 0.0001 | 0.0001 | 0.0001 | 13.7 | 38.4 | 27 | 104 |
| ST.DESV. | 0.010 | 0.014 | 0.007 | 0.010 | 3.7 | 6.2 | 5.2 | 10.2 |

The average concentrations of Ni and V in seawater an sediments are shown in Table 1 and for petroleu hydrocarbons in sediments in Table 2.

Nickel in seawater ranged from 0.008 to 0.046 ppb fo PEMARUN-I expedition. Whereas in PEMARUN-II the value ranged from 0.013 to 0.095 ppb (Table 1). Thi difference may be caused by the "north winds" which ar typical of this area, and responsible for this mixtur process (Longhurst and Pauly, 1987). The nicke concentrations were similar in the five transects an with a clear difference between the surface and botto samples. These values are in agreement with other reported previously for marine coastal environments (0. to 6 ppb; Snodgrass, 1980; Jacobs and Emerson, 1985).

Vanadium in seawater ranged from 0.001 to 0.043 ppb fo cruise PEMARUN-I and from 0.007 to 0.119 for cruis PEMARUN-II (Table 1). Along the first expedition th values for the surface and bottom samples were constan within experimental error, and for the second cruise th values showed differences due to the presence of "nort winds" (Longhurst and Pauly, 1987).

The difference in Ni and V concentrations in surface an deep samples may be related to pH values, since tota and free metal trace concentration depends on pH (Stum and Morgan, 1981; Ahrland, 1985).

Nickel concentrations in marine sediments ranged from 8 to 113 and 82 to 111 ppm (dry weight) in PEMARUN-I an II, respectively. The concentrations are higher in th samples taken far away from the coast (100m) due t diagenetic processes (Krauskopf, 1967). Nicke concentrations in marine sediments were quite similar i both expeditions, but each transect had characteristic distribution.

Average concentrations of nickel are comparable wit those reported in previous works (Fig. 2). Our value are in agreement with those reported for Alvarado Lagoo (F in Fig. 2) by Rosales et al. (1986), but are muc higher than those reported for Coatzacoalcos River (I i Fig. 2), and Ostion Lagoon (J in Fig. 2) (Paez e al.,1986) and San Andres Lagoon (G in Fig. 2) (Vázque et al., 1990).

Vanadium concentrations in marine sediments ranged fro 39 to 63 and 39 to 61 ppm (dry weigth) to PEMARUN-I an II, respectively. These values were similar in bot cruises, but each transect had a characteristi distribution.

Standard deviation for the nickel concentrations i marine sediments are high due to the dispersion of th values (Table 1), this is because nickel i

Table 2. Concentrations of petroleum hydrocarbon in sediments of the coastline of Veracruz, Mexico.

| Parameter | T.AL.H. | T.AR.H. | T.H. |
|---|---|---|---|
| PAPALOAPAN TRANSECT | | | |
| MEAN | 103 | 194 | 297 |
| MIN. | 91 | 142 | 233 |
| MAX. | 115 | 233 | 348 |
| VARIANCE | 79 | 918 | 1460 |
| ST.DESV. | 9 | 30 | 38 |
| INTERNAL TRANSECT | | | |
| MEAN | 144 | 215 | 359 |
| MIN. | 119 | 173 | 292 |
| MAX. | 235 | 282 | 517 |
| VARIANCE | 1648 | 1560 | 5887 |
| ST.DESV. | 41 | 40 | 77 |
| EXTERNAL TRANSECT | | | |
| MEAN | 133 | 224 | 357 |
| MIN. | 101 | 177 | 278 |
| MAX. | 188 | 344 | 5342 |
| VARIANCE | 961 | 3757 | 8299 |
| ST.DESV. | 31 | 61 | 91 |
| JAMAPA TRANSECT | | | |
| MEAN | 103 | 194 | 297 |
| MIN. | 91 | 142 | 233 |
| MAX. | 115 | 233 | 348 |
| VARIANCE | 79 | 924 | 1460 |
| ST.DESV. | 9 | 30 | 38 |
| ACTOPAN TRANSECT | | | |
| MEAN | 89 | 152 | 241 |
| MIN. | 66 | 103 | 169 |
| MAX. | 120 | 223 | 343 |
| VARIANCE | 502 | 2144 | 4671 |
| ST.DESV. | 22.4 | 46.3 | 68.3 |

T.AL.H.= Total aliphatic hydrocarbon: n-$C_{14}$ to n-$C_{35}$
T.AR.H.= Total aromatic hydrocarbon: naphtalene (methyl and trimethyl), phenanthrene (methyl), anthracene, fluorene (methyl) and pyrene.
T.H.= Total hydrocarbon

sediments is associate to organic matter and $HS^-$ (Stumm and Morgan, 1981) Vanadium concentrations have low dispersion (Table 1) when compared with nickel values. This is because in both expeditions these concentrations were quite similar.

The analysis of aliphatic and aromatic hydrocarbon in recent marine sediments confirmed the predominance of aromatic compounds. The hydrocarbon source was the

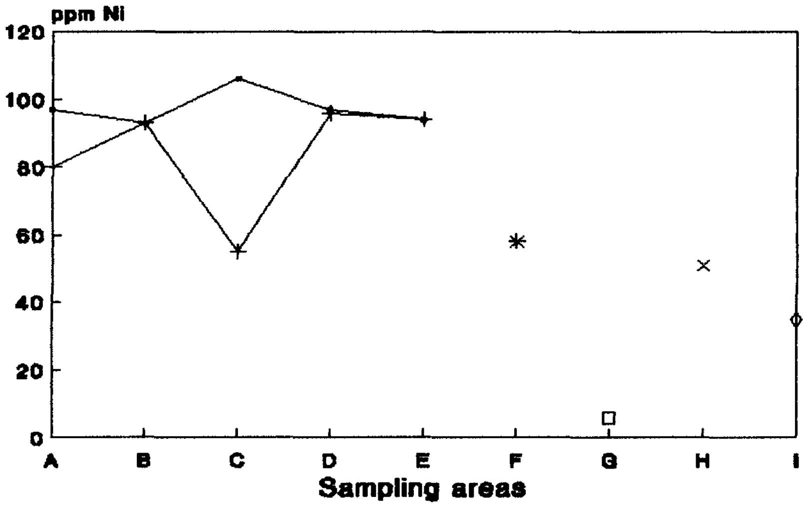

Figure 2. Nickel concentration in marine sediments from Veracruz coast. See text for abbreviation.

natural oil seeps (Table 2). The concentrations of total aliphatics in the sediments of this area ranged from 66 to 235 ppm (dry weight). These values are higher than those recorded (< 70 ppm) for unpolluted coastal areas and deep marginal seas (NAS, 1975; Botello and Mandelli, 1978). Each transect had a characteristic distribution (Fig. 3). Total hydrocarbon levels are in agreement with those reported previously by Botello et al. (1987).

The results presented in this study clearly indicate that Ni and V concentrations in seawater are not affected by oil seeps. While Ni concentration in sediments are derived from oil seeps. Vanadium concentrations in sediments near oil seeps have not been detected.

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## REFERENCES

Ahrland, S (1985) Inorganic Chemistry of the Ocean. In: Irgolic KJ and Martell AE (eds) Environmental Inorganic Chemistry. VCH Publisher, Inc. USA pp 65-88

Bruland KW, Voale KH (1985) Analysis of seawater for dissolved cadmium, copper and lead: an intercomparison of voltammetric and absortion methods. Mar Chem 17: 285-300

Clark RC, Finley JS (1973) Techniques for analysis of paraffin hydrocarbons and for interpretation of data to assess oil spill effects in aquatic organisms. Mar Pollut Bull 4: 172-176

Botello AV, Mandelli EF (1978) Distribution of n-paraffins in sea-grasses, benthic algae, oysters and recent sediments from Terminos Lagoon, Campeche Mexico. Bull Environ Contam Toxicol 28:: 162-170

Botello AV, Villanueva S, Mandelewicz M (1987) Programa de vigilancia de los hidrocarburos fósiles en sedimentos del Golfo de México y Caribe Mexicano: 1978-1984. Carib J Sci 23: 29-39

Bruland KW, Bertine K, Koide M, Goldberg ED (1974) History of metal pollution in Southern California coastal zone. Environ Sci Technol 8: 425-432

Jacobs L, Emerson S (1985) Partitioning and transport of metals across the O2/h2S interface in a permanently anoxic basin Framvaren Fjord Norway. Geochim Cosmochim Acta 49:1433-1444

Krauskopf (1967) Introduction to Geochemistry. Mc Graw Hill, New York pp 721

Kingstom HM, Barnes IL, Brady TJ, Rains TC (1978) Separation of eight transition elements from alkali and alkaline earth elements in estuarine and seawater with chelating resin and their determination by graphite furnace atomic absortion spectrometry. Anal Chem 50: 2064-2070

Kremling K (1983) Determination of trace metals. In: Grasshoff K, Ehrhardt M, Kremling K (eds) Methods of Seawater Analysis, 2nd Edition. Verlag-Chemie, Federal Republic of Germany, pp 189-246

Longhurst A, Pauly D (1987) Ecology of Tropical Oceans. Academic Press Inc. New York, pp 407

Osuna LJI, Botello VA, Villanueva S (1986) Heavy metals in Coatzacoalcos Estuary and Ostion Lagoon, Mexico. Mar Pollut Bull 17: 516-519

Rosales HL, Carranza EA, Alvarez RV (1986) Sedimentological and chemical studies in sediments from Alvarado Lagoon system, Veracruz, Mexico. An. Inst. Cienc. del Mar y Limno. Univ. Nal. Autón. México 13:19-28

Snodgrass WJ (1980) Distribution and behavior of nickel in the aquatic environment, In: Nriagu JO (ed) Nickel in the Environment. John Wiley and Sons, New York, pp 203-274

Stumm W, Morgan JJ (1981) Aquatic chemistry, an introduction emphasizing chemical equilibria in natural waters. John Wiley and Sons, New York, p. 780

UNEP (United Nations Environment Programme) (1988) Implications of climatic changes in the Wilder Caribbean Region (Draft), Part Royal Street, Kingston, Jamaica, pp. 14-20)

UNEP/IUNC (1988) Coral reefs of the world. Volume 1: Atlantic and Eastern Pacific. UNEP Regional. Seas Directories and Bibliographies. IUCN. Switzerland and Cambridge, U.K./UNEP, Nairobi, Kenya, XI Vii, p. 373, 38 maps

U.S. National Academy of Science (1975) Petroleum in the marine environment. Washington, D.C.

Vázquez F, Aguilera G, Delgado D, Márquez A (1990) Distribution of transitional and heavy metals in San Andres Lagoon, Tamaulipas , Mexico. Bull Environ Contam Toxicol

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