



# The effect of an oil drilling operation on the trace metal concentrations in offshore bottom sediments of the Campos Basin oil field, SE Brazil

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## Abstract

The concentrations of Al, Fe, Mn, Zn, Cu, Pb, Ni, Cr, Ba, V, Sn and As in offshore bottom sediments from the Bacia de Campos oil field, SE Brazil, were measured at the beginning and at 7 months after completion of the drilling operation. Concentrations of Al, Fe, Ba, Cr, Ni and Zn were significantly higher closer to the drilling site compared to stations far from the site. Average concentrations of Al, Cu, and in particular of Ni, were significantly higher at the end of the drilling operation than at the beginning. Comparison between drilling area sediments with control sediments of the continental platform, however, showed no significant difference in trace metal concentrations. Under the operation conditions of this drilling event, the results show that while changes in some trace metal concentrations do occur during drilling operations, they are not significantly large to be distinguished from natural variability of the local background concentrations. © 2002 Elsevier Science Ltd. All rights reserved.

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## 1. Introduction

Offshore oil and gas production is a potential source of environmental impacts to the oceans (REF). Apart from accidents during operation, prospecting and drilling, oil fields are of particular environmental significance, since not only oil, but other chemicals, particularly trace metals may be released to the environment during the drilling processes, directly affecting the oceanic biota, which are in general exposed to very low background levels of these substances. The large accumulating capacity of fine bottom sediments for trace metals and other contaminants and the low mobility of the benthic communities, may maximize the effect of pollutants released by drilling and oil exploration operations (Kennicutt II, 1995), although effects upon these biological communities are difficult to detect (Chapman et al., 1991).

The Bacia de Campos oil field is the largest Brazilian oil prospecting and production area, with average output of 1 million BPD of oils and 12,450 m<sup>3</sup> d<sup>-1</sup> of gas. Operations range from a depth of 100–1000 m. In 1997, the PETROBRAS Company, which runs the field, started an environmental monitoring program to investigate the potential contamination of the environment due to oil exploration in the area, in particular the effect of drilling operations upon trace metal concentrations in sediments surrounding the impacted area. The present study shows the trace metal composition (Fe, Al, Mn, Zn, Cu, Pb, Ni, Cr, Ba, V, Sn, As) of bottom oceanic sediments of the Bacia de Campos oil field, SE Brazil, at the beginning and at the end of a drilling operation, in order to verify the potential enrichment of bottom sediments with trace.

## 2. Material and methods

The drilling operation took place at Lat. 22°14'25"S and Long. 40°18'47"W, offshore the Southeastern Brazilian coast (Fig. 1). Four sampling stations were

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established around the drilling site, at 250 m ( $n = 4$ ), 500 m ( $n = 4$ ), 1000 m ( $n = 2$ ) and 3000 m ( $n = 1$ ) distance from the drilling well. Control stations were located 5 km far from the drilling site (Lat.  $22^{\circ}12'47''S$  and Long.  $40^{\circ}15'23''$ ). Sampling cruises occurred twice, 3 days after the start of the drilling “beginning” (January 7–14, 1999), and almost 7 months later (July 23–26, 1999) after finish the drilling operations. Samples were collected using a  $30 \times 30$  cm box corer. Sediments were taken from the box corer using acrylic tubes inserted to a depth of 2 cm in the center of the core. Samples were immediately put in pre-cleaned polyethylene vials, frozen and transported to the laboratory.

At the laboratory, samples were sieved ( $<2$  mm) to exclude shells and eventual organisms, dried ( $40^{\circ}C$ , 72 h) and placed in pre-cleaned polyethylene vials. Total concentrations of Fe, Mn, Cu, Zn, Cr, Ni, Pb, V, Ba, Sn, As and Al, were determined by ICP-AES (Varian Liberty Series II model), after acidic digestion of samples (1.0 g of dried sediment: 10 mL of HF (48%) and 5 mL of  $HNO_3$  (65%) in Teflon bombs at  $110^{\circ}C$  for 18 h, followed by dissolution of the digested sediment with 20 mL of 0.5 N  $HNO_3$  (Kersten and Förstner, 1989; Rantalla and Loring, 1987; Farmer and Gibson, 1981). For As, a 0.2 g of sample was digested in 5 mL of  $HNO_3$

(65%) in closed glass tubes placed in a digester block at  $130^{\circ}C$  for 16 h. The extract was filtered and diluted to 50 mL with ultra-pure Milli-Q water. Ascorbic acid and KI were added to the solution to achieve a final concentration of 10% and 1% respectively. The extracts were then left for 3 h to completely reduce the sample prior to analysis (Magalhães, 1996; Kuldevere, 1989; Weis et al., 1993). Organic carbon and carbonate content in sediments were kindly provided by Dr. Renato Carreira (Universidade do Estado do Rio de Janeiro—UERJ) and Dr. Dieter Muhue (Universidade Federal do Rio de Janeiro—UFRJ) during the internal report to PETROBRAS Company.

All samples were analyzed in duplicate. Whenever difference between duplicates was higher than 10%, the sample was discharged and analyzed again. Simultaneously, 10 sub-samples of a reference standard (Estuarine Sediment 1646a, National Institute of Standard & Technology), were analyzed using the same methodology. For all elements, our results were within the confidence limits of the reference standard (Table 1). The detection limit for each element was established based on Skoog and Leary (1992).

A non-parametric Friedman  $\chi_p^2$  rank two-way analysis of variance was used to compare differences between



Fig. 1. General location of sampling stations in the Campos Basin region (Source: Petrobras Research Center-CENPES).

Table 1

Comparison between certified values and those obtained in the present study

Element (unit in dry weight)	NIST 1646 certified value <sup>a</sup>	NIST 1646 measured values
Al (%)	2.30 ± 0.02	2.38 ± 0.12
Fe (%)	2.01 ± 0.04	1.38 ± 0.12
Mn (µg g <sup>-1</sup> )	235 ± 3.00	212 ± 10.9
Zn (µg g <sup>-1</sup> )	48.8 ± 1.60	46.1 ± 1.96
Cu (µg g <sup>-1</sup> )	10.0 ± 0.34	9.96 ± 0.25
Cr (µg g <sup>-1</sup> )	40.9 ± 1.90	37.4 ± 1.52
Pb (µg g <sup>-1</sup> )	11.7 ± 1.20	10.8 ± 0.61
Se (µg g <sup>-1</sup> )	193 ± 28.0	165 ± 10.8
V (µg g <sup>-1</sup> )	44.8 ± 0.76	39.9 ± 1.63
As (µg g <sup>-1</sup> )	6.23 ± 0.21	5.82 ± 0.25
Ba (µg g <sup>-1</sup> ) <sup>b</sup>	210	204 ± 12.0
Ni (µg g <sup>-1</sup> ) <sup>b</sup>	23	21.2 ± 1.51

<sup>a</sup> National Institute of Standards & Technology Reference Material, Estuarine Sediment.

<sup>b</sup> Non-certified values.

the concentrations measured at the beginning and at the end of the drilling operation. A non-parametric Mann–Whitney test was used to analyze differences between stations of different distances from the drilling site.

### 3. Results and discussion

Bottom sediments of the studied region are composed of fine sands with a low and constant silt and clay content throughout the area (<6.5%). No significant differences were found between particle size distributions in sediments collected at different distances from the drilling site or between samples collected at the beginning and at the 7 months after finish of the drilling operation.

Organic carbon and carbonate contents showed a different profile between stations located at different distances from the drilling site. Organic carbon concentrations ranged from 0.18% to 0.22% and carbonate content ranged from 10% to 20% among stations at the start of the drilling operations. At the 7 months after finish the operations however, a significant increase in carbonate content to values ranging from 27% to 34% was observed for all stations. As a result, organic carbon concentrations were diluted and decreased to values between 0.14% and 0.15%.

Table 2 shows trace metals concentrations in sediments from the stations surrounding the drilling site, at the beginning and at the 7 months after finish of the drilling operation. Concentrations varied differently with distance, depending on the specific trace metal. Highest concentrations of Al, Ba, Mn and Zn, at the finish of the drilling operation, occurred at the two stations closer to the drilling site (stations 250 and 500 m). However, concentrations of Ni, Pb, Sn, V and As showed no clear trend in relation to distance from the drilling site.

Table 2

Trace metals concentrations in bottom sediments sampled during a drilling operation at the Baía de Campos oil field, SE Brazil

	Al	Ba	Cr	Cu	Fe	Mn	Ni	Pb	Sn	V	Zn	As
<i>Stations B</i>												
250 m (n = 4)	4.8 ± 0.2	176 ± 35	11.7 ± 0.7	1.7 ± 0.2	5.2 ± 0.3	82 ± 5	<0.1	4.0 ± 0.5	8.9 ± 1.2	15.7 ± 0.5	9.5 ± 1.3	2.0 ± 0.7
500 m (n = 4)	4.4 ± 0.8	133 ± 33	11.3 ± 0.3	2.3 ± 1.6	4.8 ± 0.2	74 ± 8	<0.1	3.6 ± 1.1	8.5 ± 1.4	15.5 ± 0.7	8.0 ± 0.6	1.2 ± 0.2
1000 m (n = 2)	3.2	112	10.1	1.5	4.1	67	<0.1	4.1	6.6	14.0	7.1	1.5
3000 m (n = 1)	4.3	124	10.0	1.6	4.1	71	<0.1	4.6	7.4	14.9	6.5	1.6
<i>Stations F</i>												
250 m (n = 4)	6.1 ± 0.5	151 ± 17	11.3 ± 1.4	2.7 ± 0.5	5.2 ± 0.5	86 ± 15	3.5 ± 1.1	2.8 ± 1.4	4.6 ± 3.4	16.3 ± 1.8	10.0 ± 1.2	1.5 ± 0.1
500 m (n = 4)	5.5 ± 1.1	150 ± 24	11.4 ± 0.9	2.4 ± 0.3	4.9 ± 0.3	78 ± 10	1.8 ± 2.1	3.2 ± 0.8	8.7 ± 2.5	15.9 ± 1.4	9.3 ± 0.8	1.7 ± 0.6
1000 m (n = 2)	4.8	113	11.0	2.2	4.5	74	3.3	4.0	8.6	16.3	9.3	1.9
3000 m (n = 1)	6.4	120	11.5	2.2	5.0	82	5.5	3.8	9.3	17.0	8.5	ND
<i>Control stations</i>												
250 m (n = 4)	3.2 ± 0.5	63 ± 15	9.5 ± 1.2	1.6 ± 0.3	4.4 ± 0.5	112 ± 18	<0.1	4.1 ± 1.1	13 ± 2.6	15.9 ± 1.7	6.6 ± 0.9	2.0 ± 0.3
500 m (n = 4)	3.3 ± 0.4	61 ± 4.4	8.8 ± 1.2	1.6 ± 0.4	3.8 ± 0.7	97 ± 32	<0.1	3.9 ± 0.5	9.7 ± 4.2	14.5 ± 2.7	6.0 ± 0.9	2.2 ± 0.6
1000 m (n = 2)	3.6	84	10.6	1.5	4.8	112	<0.1	4.2	10	15.0	8.9	2.5

Al and Fe are in mg g<sup>-1</sup> d.w. and all other elements in µg g<sup>-1</sup> d.w. Samples collected at the beginning (B) and 7 months after finish (F) of the drilling operations (ND = not determined).

Table 3

Comparison between trace metals concentrations in bottom sediments during a drilling operation and the concentrations in the region's sediments and average values of other sedimentary materials

	Average sedimentary rocks <sup>a</sup>	Average deep sea sediments <sup>a</sup>	Average sandstone <sup>a</sup>	Campos Basin oil field <sup>b</sup>	Beginning of drilling	Seven months after finish of drilling	Stations above 1000 m
Al	92	–	25	6.8–10.6	4.6	5.8	3.8–6.4
Fe	47	–	10	5.8–6.9	5.0	5.1	4.1–5.0
Mn	850	6700	390	74–88	78	82	67–82
Ba	580	2300	190	165–188	155	151	112–124
Cr	90	90	35	14.0–15.0	11.5	11.4	10.0–12.0
Cu	45	250	15	3.4–6.3	2.0	2.6	1.5–2.2
Ni	68	225	2	6.2–7.7	<0.1	2.7	<0.1–5.5
Pb	20	80	7	5.5–6.7	3.8	3.0	3.8–4.6
V	130	120	20	15.7–17.0	15.6	16.1	14.0–17.0
Zn	95	165	16	24.5–28.9	8.8	9.7	6.5–9.3
Sn	6	–	0.1	8.9–41.3	8.7	6.7	6.6–9.3
As	13	13	1	<0.05	1.6	1.6	1.5–1.9

Al and Fe are in mg g<sup>-1</sup> d.w., all other elements in µg g<sup>-1</sup> d.w.

<sup>a</sup> Förstner and Wittman (1983).

<sup>b</sup> Rezende et al. (unpublished data).

The Friedman rank test applied to the data, showed that only the average concentrations of Al, Cu, and in particular of Ni, were significantly higher at the 7 months after end of the drilling operation than at the beginning, for all stations, particularly at station 250 m, closest to the drilling site ( $P < 0.05$ ;  $P < 0.05$ ;  $P < 0.01$ , for Al, Cu and Ni, respectively). For all other elements and stations, notwithstanding the higher frequency of peak concentrations at the end of the drilling operation, no significant difference was found between sampling periods. When all data were pooled and averaged among stations, as a single population, Al, Cu, Ni but also Zn, showed significantly higher concentrations at the end of the drilling operation relative to the beginning ( $P < 0.05$ ;  $P < 0.05$ ;  $P < 0.01$ ;  $P < 0.05$ ; for Al, Cu, Ni and Zn, respectively). Using the control stations as a regional reference values, surface sediments around the drilling site showed a significant enrichment for Al, Fe, Ba, Cr and Zn in both situation (Mann–Whitney;  $P < 0.05$ ).

During the drilling operation, mud is used to stabilize the well and remove the fragments of drilled rocks (i.e. carbonate, shale and sandstone). This mud is artificially enriched with several minerals such as barite and carbonates. As a consequence it also contains quantities of trace elements such as Ag, As, Cd, Cr, Cu, V, Zn, Hg, Ni and Pb (Phillips et al., 1998). Although we do not know the composition of the mud used in the Bacia de Campos, this may explain the enrichment observed in carbonate content and of several elements studied, when compared with control concentrations or when comparing the values from the beginning and the 7 months after the operations. The concentrations found, however, are lower than reported values for drilling operations offshore California, USA, reported by Finney and Huq (1989) and Steinhauer et al. (1994).

Table 3 compares the average of trace metal concentrations at the beginning and at the 7 months after

finish of the drilling operations with those from the control area, the average concentrations from the Bacia de Campos oil field (Rezende et al., unpublished data), and average trace metal concentrations in sandstone, deep sea sediments and shale (Förstner and Wittman, 1983). Notwithstanding the significant increase in the concentrations of Al, Cu, Ni and Zn, all values fall between, or are even lower than the range reported for sediments of the Bacia de Campos region. Also, probably as a result of the sandy nature of the drilling area surface sediments, concentrations of all elements studied are lower than those found in shale and deep sea sediments.

Concluding, our results shows that drilling operation can increase the concentrations of trace elements in oceanic bottom sediments, as reported for other offshore oil fields. However, at least for the Bacia de Campos oil field, this enrichment is not significantly larger than the natural range of concentrations observed in the sediments of the region.

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