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ECOLOGICAL STUDIES OF THE RECONCAVO, BAHIA, BRAZIL (1976 UNTIL 1990

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OBJECTIVE

To study the effect of the inorganic chemical pollutants in air, sediments, fauna, and human population of the Todos os Santos Bay area in Bahia, Brazil.

IMPORTANCE

The project is interdisciplinary and promotes the development of cooperative research among disciplines previously isolated such as chemistry, biology, geosciences, community health, and statistics. These disciplines work together to solve a significant problem of the community related directly to the development of the region. The project also aims to provide data to the government to use for planning, to locate industries and to establish adequate safe levels for industrial effluents with chemical pollutants in the tropics, particularly strong acids in the air and heavy metals in air and water bodies.

DESCRIPTION OF STUDIED AREAS

The Reconcavo in Bahia comprises the Todos os Santos Bay (1,000 square km, the largest in Brazil), and the land around it, located at 13 South latitude and 38 West longitude. Since 1968, the Reconcavo has been submitted to an intense exploitation of its natural resources and to an exponential industrial growth. Today, this area consists of the second largest industrial park of the country: about 200 industries, dedicated mainly to ferrous metallurgy, manufactured products (tools, weapons, etc.), synthetic fibers, plant oil, cement, ceramic, etc., constitute the Aratu Industrial Center (CIA). On the northeast, about 50 plants of petrochemical products along with one pulp plant, one copper smelter and several fine chemical industries are concentrated in the Camacari Complex. On the northern part, two paper mills, one lead smelter and an oil refinery (250 000 barrels/day) operate independently. The city of Salvador, one of the fastest growing in Brazil, presently with 2 million inhabitants, is a historical and artistical center. The old section is considered to have the greatest concentration of baroque art in the world.

ACHIEVEMENTS TO DATE

A. Related to establishment of infrastructure

Laboratories have been mounted in the Analytical Chemistry Department for trace chemical analysis of substances in water, sediment, biological material, and atmosphere. The chemistry staff has developed considerable expertise in the analytical techniques for inorganic compunds in geological land and biological materials (Raymundo and Tavares, 1980; Santos and Tavares, 1980; Sntos et al., 1980; Tavares and Santos, 1980; Tavares et al., 1987; Tavares, et al., 1988a; Tavares et al., 1989), improving the methodology for determination of mercury by atomic absoption spectroscopy, increasing 2.5 times its sensitivity (Tavares and Kirkwood, 1981), and developing effective procedure for subdivision of humid sediments for the analysis of volatile compounds (Tavares and Tavares, 1981b).

An infrastructure for collecting field samples was established for water, sediment (superficial an profile), bivalves, atmosphere, and human breathing conditions. In the case of water bodies, it has been mounted an analytical infrastructure <u>in locu</u> (until 20 meters deep) for basic physical chemical parameters. In the case of atmosphere, it has been established systems for separatly sampling gaseous and particulated phases (fractionated by size), which allow studies of chemical speciation of S, N, and Cl in the atmosphere (Klockow et al., 1984). Methodology for field sampling and determination of gaseosus hydrogen peroxide in air has been developed (Jacob et al, 1986; Jacob et al., in press). Sampling systems of rain water and fog have been established. A glossary of terms used in environmental analytical chemistry has been elaborated (Klockow et al., in revision).

B. Related to mercury emissions (Hg) in the Tainheiros Inlet

Problem

At the east side of the Tainheiros Inlet bay (5 km2, average depth of 5 m), a chlor-alkali plant released, for 12 years, 10 ton of inorganic Hg into the environment. About 110 thousand people, of very low social-economic level, living near the industry, consumed the contaminated shellfish.

Answered questions

1) How much mercury has been accumulated by the sediments and edible bivalves of the Tainheiros Inlet?

Data have been obtained on the distribution of mercury in sediment and edible bivalves from the Tainheiros Inlet, indicating that most of the sediments in this area could be considered polluted by mercury (Tavares et al., 1977). <u>L.</u> <u>pectinata</u> was found to be the edible bivalve of Todos os Santos Bay which accumulated the most mercury (Tavares et al., 1979), but based on perliminary data, <u>Anomalocardia</u> <u>brasiliana</u> is probably the most useful local indicator species (Peso & Tavares, in preparation). Ingestion of 100 g of edible molluscs from Tainheiros Inlet, randomly fished, exceeds the limit of mercury intake recommended by WHO (Tavares & Peso, 1979).

2) How did these concentrations affect the local consumer population?

The effects of mercury intake on the local population were investigated, proving that the ingestion of molluscs in the area did not result in significantly greater Hg absorption than paired controls (Carvalho et al., 1985), from another area.

3) Did the mercury released in the Tainheiros Inlet affect the levels of this metal in the rest of the Bay?

The mercury concentration of the interdial bivalves of the continental coast of the Todos os Santos Bay was investigated in 1980, showing that the levels are lower than the limit established for consumption by the FDA (1 ppm, wet weight basis) (Silva et al., 1981).

Consequences of these studies

The chlor-alkali industry was relocated, introducing abatement measures.

C. <u>Related cadmium (Cd)</u> and <u>lead (Pb)</u> <u>emissions in the Subaé</u> <u>estuary</u>

Problem

The emissions of Cd and Pb occurred at the north side of the bay, at the bank of the Subaé river. For 21 years, a lead smelter released 400 ton of Cd, and even greater quantities of Pb into the environment. Around 2,000 fishermen and their families live at this estuary consuming local sea and agricultural products. The metallurgy is 1.5 km far from the center of Santo Amaro City, (30 thousand inhabitants). The poor population of this city, located at the industry surroundings, used the industry dross to floor their backyards. Some even used the industry's chimney filters as carpets or blankets in their houses. Both fishermen and Santo Amaro's citizens brethed polluted air.

Answered guestions

1) How much Cd and Pb have been accumulated by sediments and edible bivalves of the Subaé estuary?

Data have been obtained on the concentrations of cadmiun and lead in the sediments and fixed fauna of the Subaé estuary (Souza et al., 1978; Tavares, 1978), demonstrating that the Subaé river and its estuary presented higher concentrations of these metals than the normal concentrations found by other scientists in nonpolluted areas. These high concentrations were associated with the presence of a lead smelter in the area. Oysters from the Subaé estuary contained lead concentrations up to 4 ppm (dry basis) and Cd concentrations up to 140 ppm (dry basis), which is equivalent to approximately 0.8 and 28 ppm repectively (wet basis).

2) How did these concentrations affect the 2,000 fishermen in the area?

It was concluded that the fishermen of the Subaé area have absorbed excessive levels of cadmium and lead (Carvalho et al., 1979; Carvalho, 1980), but no correlation could be established between Cd and Pb absorption and seafood consumption (Carvalho et al., 1983). Mean concentrations of lead and cadmium were higher among fishermen with straight hair than among those with curly hair, but no significant differences were found in relation to hair colour (Carvalho et al., 1984).

3) How was the local agriculture affected by Pb and Cd emissions to the air?

Local vegetables and fruits, within 1,000 m from the lead smelter, presented lead concentrations ranging from 0.01-215 ug/g and cadmium concentrations ranging from 0.004-11.8 ug/g (dry The highest levels were found in the leafy vegetables basis). which are submitted to a greater contact with air, and the lowest levels were found in the local fruits (banana and orange). However, considering the local dietetic habits, the greatest concern is for the constant ingestion of okra, sweet-potato, and sweet cassava, for Cd and only for the last two for lead. The daily consumption of more than 73 g of okra, produced at 200 m from the industry, by a 60 kg weight person, surpasses the limit recommended by WHO/FAO of maximum ingestion of 70 ug of Cd/day. Likely, quantities of 150 g or more of sweet-potato or sweet cassava per day, result in ingestion of 70 ug of Cd/day. Likely, quantities of 150 g or more of sweet-potato or sweet cassava per day, result in ingestion of cadmium and lead higher than the limit proposed by that institution (limit for lead: 430 ug/day for a 60 kg weight person).

4) How was the children population living near the smelter affected by Cd and Pb intake in 1980?

It was proven by determination of zinc protoporphyrin in blood, and lead in blood and hair that, among 617 children living within 900 m from the industry, 10% were lead intoxicated and 17.5% were at high risk of intoxication (Carvalho and Tavares, 1980). Forty five percent of the children presented lead in blood above the tolerance limit of the Center for Disease Control of USA, CDC (2.00 micromol/L), 25% of which were above the critical limit (3.36 micromol/L). Ninety five percent of the children showed cadmium results in blood above normal reference values (0.0089 micromol/L). The average blood concentration was 10 times this value and the range was from 0.004-0.51 micromol/L. Levels of Cd encountered in this study are the highest registered in the literature for environmental exposure.

5) Did the high environmental levels of cadmium cause renal deficiency in the adult population?

Elderly women (population mostly affected in the Cd-Itai itai case in Japan) of Santo Amaro, 131 women aged 50 years or more were studied, as well as 122 individuals from a control area. Prevalence rates of proteinuria and glucosuria among women of Santo Amaro were low and similar to those observed in the reference population showing no signs of renal deficiency (Carvalho et al., 1984).

6) Since anemia is caused by a number of factors, being Pb pollution one of them, which one is considered to be the dominating factor?

A prevalence study of anemia was carried out among children, aged one to nine years old, living near to the smelter, and it was found that variation in hemoglobin levels was significantly associated with malnutrition and with interaction between malnutrition and iron deficiency, but not with lead levels, hookworm infection, and iron deficiency (Carvalho, 1982; Carvalho et al., 1983).

7) How was the lead and cadmium in blood related to nutritional status in a child population?

Multiple regression analysis of 555 children for lead and 396 for cadmium did not show statistically significant associations between Pb and Cd levels in blood and malnutrition, as measured by the wasting (weight/height) index, keeping constant the effects of the variables age, sex, racial group, pica (distortion of eating habits), distance from child's home to smelter, being a child of lead worker, family income, iron status and severe hookworm infection. Neither weight nor height of children with low Pb blood level (<1.68 micromol/L) were significantly associated with the variation in blood lead levels (Carvalho et al., 1986). These findings are not consistent with corresponding strong associations found recently for a large sample of North American children.

8) What was the prevalence of lead intoxication in children aged 1-9 living in Santo Amaro City (where the lead smelter is located) and how was this prevalence associated with the urbanization process? The interation between certain aspects connected with urbanization and industrialization processes and non-occupational lead contamination is strongly associated to the urban space occupation. In turn, this is determined by migration and socialeconomic situation. Factors such as more than six months residence in the area, age below 2 years, home located on the road leading to smelter, black race, and contact with smelter employees, when combined, increased the Pb intoxication risk in children (Silvany-Neto, 1982; Carvalho et al., 1984).

Consequences of this studies until 1980

Based on these studies (Carvalho and Tavares, 1985), the CRA (state environmental institution) forced the metallurgy to undertake measures for pollution control (build a 90 m chimney and install a more efficiente filtration system), remove the population living in an area of 300 m from the metallurgy to other places, and become reponsible for the medical treatment of the affected children.

<u>Other questions answered after 1980 in relation to Cd and Pb in</u> <u>Santo Amaro</u>

9) How was this children population 5 years after the medical treatment and the installation of pollution abatement equipment in the smelter?

According to the CDC criteria, the proportion of children considered in normal conditions with relation to lead remained aproximately the same. However, it was observed a reduction of 21% of the children with indicator levels (ZPP) of lead intoxication, classified as "extremely high" and "moderated high", having this part of the population shifted to the class "slightly high". However, 39% of those who remained in the two first classes where under three years old and though only exposed to the new conditions of the industry. Using the criteria of Pb contents in blood as indicator of absorption of CDC, there was a general reduction of 38%, but around 25% of the children should yet be treated (Silvany-Neto et al., 1989). The reduction of average level of Cd was of 67%, but yet 89% of the population presented values higher than the normal of reference (to be published).

10) Which are the possible causes of persisting cases of Pb intoxication and high concentrations of Cd in the children population, living 1,000 m from the industry chimney?

Social, racial, and personal factors, which affect the absorption of these two metals, were evaluated. It was proved that the fact of being son of worker in the smelter and the presence of smelter dross nutritional condition do not influence on the absorptionintoxication process of these metals. Sex, age, and nutritional condition do not influence on the absorption-intoxication process of these metals. Hookworm infection increases the cadmium absorption, but not the lead one. Belonging to the negro or mixed race increases the Pb absorption-intoxication, and belonging to the white race favours a greater absorption of cadmium. The use of hair as an indicator is useful on situations of great exposure, but hair type and its daily treatment influence the metals levels (Carvalho et al., 1984a; Silvany-Neto et al., 1985; Carvalho et al., 1986; Carvalho et al., 1985; Carvalho et al., 1987; Silvany-Neto et al., 1989; Tavares et al., 1989b). The high contents of the two metals in soil around the dwellings represent one of the factors responsible for the persistence of intoxication cases and the arising of new ones.

11) According to the pervailing winds, the Paraguacú river drains most airborne heavy metals released by industrial activity around the Bay. How much Cd, Pb and Hg enter the Bay via the particulate matter drained by this river?

The concentrations of mercury, cadmium, and lead in the particulate matter of this river showed Hg <0.2-10, Cd <0.1-1.1, and Pb <6-146 microg/g (dry basis) in suspended matter, and Hg 6-35, Cd 10-100, and Pb 1,000-3,300 microg/kg (Tavares and Tavares, 1981a; 1983) in botton sediments.

D. Related to emissions of arsenic (As) in Lamarao do Passé

Problem

The greatest copper metallurgy in Brazil, located at 6 km West from the Camacari Petrochemical Complex, started up operations in 1982. Such kind of industry emit great quantities of copper, arsenic, and SO2 to the atmosphere.

Answered questions

1) Which are the As levels in the atmosphere of Lamarao do Passé?

The As levels were around 5 ng As/m3, from which 85% were present on the form of fine particulates (<2 microns). Such concentrations correspond to deposition in deep lung of 132 ng As/day through breathing (Tavares et al., 1989b).

2) How such levels affected the population of Lamarao do Passé?

Two crosssectional studies of the population were carried out: the first one in 1982, before the start-up of the industry, and the second one in 1986, after 4 years of operation. During this period of 4 years, the average concentration of As in hair of this population increased of 6.7 times (0.08 ppm in 1982 to 0.54 ppm in 1986). The average increase was 11 times. However, on individual basis, it was observed increases up to 92.5 times (9.5% of the population suffered an increase of As levels between 20 to 92.5 times). Factors such as biological and socialeconomic characteristics, personal habits, and location of residence did not influence the As levels in hair. Only the smoking habit favoured higher concentrations of this element (Chaves et al., 1990).

E. Related to emissions of manganese (Mn) in Cotegipe

Problem

Since 1961, a metallurgy of Fe-Mn has operated on the east coast of the Reconcavo with no abatments equipment for atmospheric emissions. A population of 500 people live 1 km far from this industry.

Answered guestions

1) What were the effects of the Mn on this population?

The average content of Mn in hair of the population of Cotegipe was equaled 11.7 ppm. However, no symptoms of intoxication by Mn were observed. No correlations were found between Mn concentrations in hair and the age or time of residence in the area. The smoking habit and the fact of belonging to the negro race showed a tendency to favour higher Mn levels.

2) Which were the benefits introduced by the installation of filters system in the metallurgy?

Without the filtration system the atmospheric average levels in Cotegipe were of 0.56 micrograms/m3. After the installation, the average levels decreased only 14%, that is, to 0.48 micrograms/m3, with similar distribution of particle size. Such levels correspond to deposition of 8.9 micrograms Mn/day in deep lung of each inhabitant through breathing (Tavares et al., 1989b; Carvalho et al., to be published).

F. Related to the quality of the Todos os Santos Bay

Problem

The fast development of the Reconcavo imposed to the bay an intense exploitation of its natural resources, possible change on its fertility, and/or break of life cycles. This leads to a lower productivity, besides the accumulation of industrial and urban chemical products, by edible fauna, with possible transfer to humans. There are no reference data for this bay before the beginning of these ecological disturbances.

Answered guestions

1) Considering the edible bivalves as indicators of pollution of the bay, how is its productivity in the beginning of the 80's in relation to the future?

Two studies were performed giving the only biometric data of native populations of marine fauna existing in this bay (Peso and Tavares, 1980; Peso and Tavares, 1982).

As <u>Anomalcardia</u> <u>brasiliana</u> is the most frequent and dominant species, its ecological condition was determined (Peso, 1980a, 1980b, 1980c; Peso and Verani, 1980a, 1980b).

A small museum was established containing species from the bay for comparison in future years.

The Medo Island was taken as indicator of environmental quality of the bay and the malacofauna was described (<u>Bivalvia</u> and <u>Gastropoda</u>) (Peso, 1979) and <u>Demosporgia</u> fauna (Peixinho and Peso-Aguiar, 1982) in the muddy substrate of the Medo Island of the intertidal zone. This island is probably the best indicator of environmental quality of the Todos os Santos Bay, due to the following factors: central position, total lack of habitation and diversity marine fauna. Present and future data will be compared.

2) The Paraguaca River is the main contributor of nutrients of the Todos os Santos Bay. How much silicate and phosphate enter the Bay via this river?

The balance of silicate (Martins and Tavares, 1981), and phosphate (Martins and Tavares, 1982) of this river proved that there is an internal source of silicate in the river estuary and that its phosphate balance is non-conservative.

3) What industrial activity around the bay was responsible for a catastrophic mortality of bivalves in the Itaparica Channel between September and November of 1977 (continuing until 1980)?

In the assessment of this mortality, the afore-mentioned biometric data were the only information available concerning natural populations in the Bay. Furthermore, the curve of population density for the Medo Island showed that this area was unaffected, indicating that industrial activities in the north (Subaé) and the northeast of the bay (CIA and Camacari Complex) were, most probably, not the cause of the problem (Tavares et al., 1978).

4) Which are the levels of the main organic pollutants in this bay resulting from the industrial (including petroleum refinery), harbours and agricultural activities developed around the bay?

For the first time in South America, levels of aliphatic hydrocarbons (origin: oil spills), PAHs, polycyclic aromatic hydrocarbons (origin: combustion), PCBs, polychlorinated bifenyls (origin: transformers, capacitors, and hydraulic liquids), and DDTs, chlorinated hydrocarbons (origin: pesticides) in shellfish were simultaneously determined indicating the quality of the Todos os Santos Bay. The levels of linear hydrocarbons ranged form 0.1-6.1 ppm (wet basis 80% of H2O) and those of aromatic hydrocarbons ranged from 0.1-9.1 ng eq. criseno/g (wet basis). The highest values were found in the vicinity of the refinery and also near a palm oil plant. The estimated values of DDTs and PCBs are relatively low (lower than 2.5 and 6.6 ng/g, wet basis), but it is observed higher concentrations of DDT in Sao Francisco do Conde and in Tainheiros Inlet, and of PCBs at the east coast of the bay.

- G. Related to the atmospheric quality of the Reconcavo
- Which is the atmospheric destination of the sulphur dioxide, nitrogen oxide and NH3? Does it exist acid rain in the Reconcavo?

The south half of the Reconcavo, very jagged and with a large extension of coast, presents very low levels of these gases in atmosphere, except in exceptional occurrences (Tavares et al., 1984; Tavares et al., 1985). In this region acid rain does not exist, however its ionic content is highly influenced by sea spray particles in atmospheric suspension, indicating that these particles act as purifyers of the atmosphere for these chemical species (Bruynseels et al., 1985). At the north half of the bay, with less contact with the sea, there are acid rain events on the limits of the Petrochemical Complex, probably due to wash-out process (washing of gaseous pollutants when the rain falls) and on the northwest direction of the Petrochemial Complex (Rocha et In all Reconcavo and even in the country side of the al., 1985) state (270 km far east from Salvador) or in coastal "remote" areas there is an enrichment of nitrate in sea spray particulates of between 0.5 and 5 um diameter, the origin of which has not been yet identified (Noqueira et al., 1989).

2) How is the atmospheric chemical transformation and removal processes of SO2 and NOx in other Brazilian regions?

A study was proceeded on the destination of these pollutants in an industrial area in the south of Brazil, in Araucária, Paraná. It was verified that due to the proximity of the source of NH3 to the sulphur and nitrogen oxides into ammonia sulphate and nitrate in the fine particulate mode, and, as final result, reaching the population living in Araucária under this form. As the ammonia sulphate is more toxic than SO2, the population was right concerning its complains and demands, even though the industries argued they were not transgressing the law (the legislation only determines limits for SO2 and not for sulphate). Such studies showed that the legislation is not adequate (Tavares and Rocha, 1988; Tavares et al., 1989c).

3) The majority of the gaseous pollutants are chemically transformed in the atmosphere by photochemical oxidation (SO2, for example, is transformed into sulphuric acid by reacting with hydrogen peroxide). Which is the oxidizing capacity of the atmosphere of the Reconcavo?

Hydrogen peroxide H2O2 was used as indicator of the photochemical activity. It was proved that the Reconcavo presents H2O2 concentrations up to 20 times higher than that of the summer of Central Europe (Jacob et al., 1987; Jacob et al., 1990) and that

Salvador's urban activities (specially the aldehydes resulting from ethanol vehicular combustion) do not contribute in significantly way for its increase. These H2O2 concentrations meet the expected levels for these latitudes and the gradient measured in the Atlantic Ocean from 50 N to 38 S (Jacob et al., 1989). It was demostrated that H_2O_2 is "washed out" by the rain, and in tropics, this process reaches a maximum with a precipitation rate lower or equal to 1 mm/h (Jacob et al., 1990).

4) The use ethanol as fuel produces aldehyde, formaldehydes and acetaldehyde vehicular emissions. Which are the concentrations of these substances in Brazilian urban centers?

The aldehydes levels in Salvador were measured and compared to those of Rio and Sao Paulo. The formaldehyde concentrations in Salvador varied from 6 to 34 ppb and the acetaldehyde from 9.2 to 35 ppb, similar to the levels found in Rio and Sao Paulo. The combustion of gasoline produces aldehydes, mainly formaldehyde as secondary pollutants. Even though the total aldehydes levels in these Brazilian cities are of the same order of magnitude of those of cities such as Los Angeles, the relation aceltaldehyde/formaldehyde is much higher in Brazil (Grosjean et al., 1990).

PRESENT AND NEAR FUTURE STUDIES

- Long range effect (kidney damage) of cadmium and lead in the human population of Santo Amaro
- Biomonitoring of arsenic in the human population of Lamarao do Passé (3rd cross sectional study)
- Development of sampling technique for gaseous cadmium and arsenic in atmosphere and determination of its fractrion around smelters.
- Effects of ethanol and methanol combustion as vehicle fuel
- Photochemical smog in the Reconcavo
- Brazilian contribution to greenhouse effect.

FINANCING AGENCIES

-Rockefeller Foundation (1976-1981) -CNPq (1980-1897) -German Agency for Technical Cooperation, GTZ (1983, 1986, 1990) -Stiftung Volkswagenwerk (1983-1989) -FINEP (1986-1988) -COMCITEC (Government of State of Bahia) (1986-1988)

SENIOR RESEARCHERS OF PEER

Biology: -Marlene Peso-Aguiar (zoology) Medicine: -Fernando M. Carvalho (environmental health) -Annibal M. Silvany Neto (environmental health)

Chemistry: -Vania C. Rocha (chemical analysis) -Tania M. Tavares (project coordinator)

PROJECT BEING ESTABLISHED

A project for graduated education in environmental sciences and resources management shall be established in 1990 at UFBa, with CRA colaboration. The project aims to integrate scientifically the graduated teaching activities (specialization and master degree) of UFBa and enlarge the focus on environment. A new specialization course will be created in the environmental chemistry area, aiming to comply with the demand for training and updating of technicians of governmental and industrial agencies of the north and northeast of the country. The foreseen financing support will be given mainly by GTZ, Germany.

COORDINATORS

UFBa:

- Architecture (Urban Planing): Paulo Rocha
- Biology: Ronan Brito (botany) - Marlene Peso-Aguiar (zoology)
- Medicine: Fernando M. Carvalho (environmental health) - Annibal Silvany Neto (environmental health)
- Chemistry: Vania C. Rocha (analytical chemistry) - Tania M. Tavares (project coordinator)
- CRA: Flora Cerqueira (environmental legislation and management) - Joao Augosto Sampaio (sanitary engineering)

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