

# ENVIRONMENT INTERNATIONAL

Journal of Science, Technology, Health, Monitoring and Policy

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Pergamon Press

New York Oxford Seoul Tokyo

# ENVIRONMENT INTERNATIONAL

A Journal of Science, Technology, Health, Monitoring and Policy

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**Publishing, Subscription and Advertising Offices:** Pergamon Press, Inc., 395 Saw Mill River Road, Elmsford, New York 10523, USA and Pergamon Press plc, Headington Hill Hall, Oxford, OX3 0BW, England.

**Published Bimonthly.** Annual institutional subscription rate (1991): DM700.00; Two-year institutional subscription rate (1991/92): DM1330.00. Personal subscription rate for those whose library subscribes at the regular rate (1991): DM258.00. Prices are subject to change without notice. Notify 8 weeks in advance of address change with a copy of the subscription mailing label. Back issues of all previously published volumes, in both hard copy and on microform, are available direct from Pergamon Press Offices. Subscription rates for Japan include despatch by air and prices are available on application.

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The Item-Fee Code for this publication is 0160-4120/91 \$3.00 + .00

Printed in the USA

 The paper used in this publication meets the minimum requirements of American National Standard for Information Sciences - Permanence of Paper for Printed Library Materials, ANSI Z39.48-1984.

## EDITORIAL

### POLITICAL ENVIRONMENTALISM

The global community has finally accepted environmental protection as a laudable goal. There is no major political party in any industrialized country opposing environmental protection, and there are political parties in many countries that are either partially or entirely devoted to protection of environment. Indeed, there is every indication that environment has a similar status as freedom, patriotism, and economy in the political life of most countries. Therefore, it is not surprising that environmental protection has become politicized.

In contrast to most political issues, environmental protection has a major scientific component. For example, the disposal of high-level radioactive waste requires to conduct a risk assessment and predict the behavior of radionuclides in a given geological setting. It also includes the prediction of migration of radionuclides and their uptake by various foods. Finally, it requires an assessment of effects of low levels of radiation. The combination of all of these leads to the characterization of the potential risks associated with the disposal of high-level radioactive waste. This process is essentially the same for every environmental issue. Therefore, risk assessment is the foundation of the overwhelming majority of environmental decisions. Once the results of a risk assessment are available, a societal decision must be made on what constitutes an acceptable risk. In that process, the costs of various options are assessed, and those options where the cost is associated with the most benefits are chosen.

In most environmental issues, the available scientific information is less than sufficient and often poor to draw a firm conclusion. There are several approaches available to satisfactorily resolve these issues. Occasionally, in the absence of data, assumptions are made based on reasonable expectations. Subsequently, the process of risk assessment is followed using various assumptions to evaluate the sensitivity of the results based on the assumed data. For example, if extremely high or extremely low values would have little impact on the result, one could

confidently assume an intermediate value and proceed with the process. There are other potential approaches to respond to a need when the abundance of data is less than desirable.

Those who are truly dedicated to the protection of the environment must insist upon a scientific process that identifies the problem. Furthermore, they rely upon scientific peer review and the scientific consensus process as prerequisites for the acceptability of a scientific claim.

In the early history of the modern environmentalism, all who were concerned with the protection of the environment were united on the need for legal tools to control the manufacture and distribution of chemicals, the control of emissions from all sources, and strict enforcement of the environmental rules. Gradually, the environmental movement split into two distinct groups: scientific environmentalists who relied upon the best available science and political environmentalists who relied upon politically processed science as the basis for their goals. Political environmentalists argued that the goal of the environmental protection is so noble that one can choose scientific information that supported the preconceived ideology and disregard others. As long as the data supported the goal, it was irrelevant how and why it was chosen. The politically processed science became the workhorse of politically environmentalists.

In contrast to political environmentalists, the scientific environmentalists required the best available science as a prerequisite. They argued that there were insufficient resources to deal with all but the most urgent environmental problems. Therefore, it is imperative that environmental problems are assessed and prioritized so that those requiring the most urgent attention are addressed first.

Whereas during the early years of environmental movement, political and scientific environmentalists were united, it is becoming increasingly evident that these two groups are splitting.

There is a fundamental disagreement between the two groups on what is an environmental issue. Political

environmentalists suggest that only inadvertent exposure to pollutants is an environmental issue and the natural resources should be preserved for their own sake. They give various species of animals and plants about the same importance as the preservation of human life. Scientific environmentalists consider pollutants as undesirable regardless if the exposure is voluntary or involuntary. They believe that humans have an important role to play in the preservation of natural resources. Furthermore, they place human life as a determinant in dealing with preservation of plants and animals.

These distinctions are far from being only of academic interest. Scientific environmentalists regard risk assessment as the most important tool in environmental protection. Political environmentalists do not accept risk assessment as a legitimate branch of science and argue that it is often unprecise and its results are associated with large uncertainties. Recently, a representative of a political environmentalist organization stated that "only industry and some academics like risk assessment". What is being overlooked by political environmentalists is that every measured or computed value has an uncertainty associated with it and that risk assessment is no exception to this rule. Although, uncertainties associated with the results of risk assessment are often large, they provide a statistical limit to a potential adverse effect and as such provide the only available objective information. Scientific environmentalists believe the illicit use of drugs is an important

environmental issue. Political environmentalist have either taken no position on illicit drugs or have accepted them as a personal choice.

Political environmentalists opposed nuclear power and then forced the energy industry to use fossil fuels, thus aggravating the problem of the greenhouse effect. Scientific environmentalists took the opposite view as early as 1970. One should be aware that the term greenhouse effect was coined in the early 1960's and this Journal devoted a major segment of its pages in 1979 to this issue.

The indoor air problem was only recently accepted as an important issue by the political environmentalists. The scientific environmentalists were aware of indoor air pollution at least as early as 1970's during the so-called St. Louis Study. This was confirmed by the Six-Cities Study conducted by a group at Harvard University, and indoor air pollution is now recognized as a major environmental problem.

It is becoming clear that political environmentalism is counter-productive. The expenditure of exceedingly large sums of money for problems that pose smaller risks will inevitably lead to inadequate attention to problems with larger risk. It is urgent that political environmentalists are reminded that their approach is unacceptable. Environmental problems must be addressed correctly, promptly, and consistent with the best available science.

A. Alan Moghissi

# MULTIVARIATE ANALYSIS OF THE RELATIONSHIP BETWEEN METEOROLOGICAL AND POLLUTANT VARIABLES AND THE NUMBER OF HOSPITAL ADMISSIONS DUE TO CARDIO-RESPIRATORY DISEASES

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*EI 88-106 (Received 5 August 1988; accepted 15 December 1990)*

This paper studies the influence of meteorological and air pollutant parameters on the number of hospital admissions due to acute exacerbation in chronic obstructive pulmonary disease (COPD) and heart failure (HF), in the city of Santander (Spain), over a 4-y period. In the multiple linear regression study performed, the variable, which overall shows the strongest correlation with the number of admissions for the two diseases, is the concentration of suspended particulate matter (SPM). Of the meteorological variables studied, the best correlations are with pressure gradient and temperatures: pressure gradient and maximum temperature for admissions due to COPD, and pressure gradient and mean temperature for HF. This behaviour shows seasonal variations with the highest multiple correlation coefficients corresponding to autumn. High pressures, both maximum and minimum, significantly increase the number of admissions for both diseases. Of the pollutant variables, the SPM concentrations reveal a greater relationship with admissions for both diseases than the SO<sub>2</sub> concentration does. It is worth noting that the influence of pollution on the number of admissions is produced at values much lower than those recommended as limits by legislation.

## INTRODUCTION

There is, at the present time, considerable interest in studies whose aim is to determine the influence of climate, weather changes, and atmospheric pollution

on health. Of the atmospheric factors, one which has a strong influence on the human organism is environmental pollution which acts mainly on the respiratory system. While most authors accept that these factors

do have an influence (Groupe Coopératif PAARC 1982a; 1982b; Bates and Sizto 1983; Dorado et al. 1982; Mostardi et al. 1981a; 1981b; Villalbf et al. 1984; Millquist et al. 1984), there are diverse opinions as to which of them is most important concerning their physiological or practical significance. The aim of this paper is to study the possible existence of a correlation between the variables mentioned and certain heart and respiratory conditions, by means of multivariate analysis.

## MATERIAL AND METHODS

### *Study region*

Santander is a mainly commercial and residential city situated by the sea in the north of Spain where the climate is mild and wet. Because of its location and character, Santander has a low-middle pollution level with average annual values of about  $49 \mu\text{g m}^{-3}$  and  $66 \mu\text{g m}^{-3}$  for  $\text{SO}_2$  and suspended particulate matter (SPM), respectively, for the period under study.

### *Hospital admissions*

The number of admissions due to acute exacerbation of COPD (ICD codes 491, 492, and 494) and due to HF (ICD code 428) was analysed for the National Hospital "Marqués de Valdecilla" in Santander. Of the patients admitted at this hospital, only those from the city itself and from the surrounding area (240 000 inhabitants) were taken into account. The study was performed by reviewing the clinical records at the hospital. Over the 4-y period studied, (1979-1982) the total number of admissions due to COPD and HF was 1345 and 517, respectively.

### *Air pollution data*

The data used for the pollutant variables were the daily averaged values obtained at three sampling sites in the city of Santander by the Regional Health Centre which belongs to the National Network for the Monitoring and Prevention of Atmospheric Pollution. One of the three points was situated on the outskirts of the city where traffic is heavy while the other two were located more centrally. The pollution values for the three points correlated well. Sulfur dioxide and SPM concentrations were determined by the acidimetric titration method and reflectometric method for black smoke, respectively. Analysis samples were checked periodically through the quality assurance program, consisting of intercomparison of calibrations performed at different laboratories belonging to the National Network.

### *Meteorological data*

Data for the meteorological variables were supplied by the Regional Meteorological Centre in Santander. The information provided by this centre was collected at a point which is situated centrally in one of the highest parts of the city and approximately 1 - 1.5 km maximum from the pollution sampling points. Daily values were taken in all cases.

### *Data analysis*

Each day represents a single observation. The variables used in the study were as follows:

#### Pollutants:

1.  $\text{SO}_2$  concentration ( $\mu\text{g m}^{-3}$ ): The  $\text{SO}_2$  concentration for the same day as the admission ( $\text{SO}_2$ ) was studied and its powers of 1/2 ( $\text{SO}_2^2$ ) and 1/4 ( $\text{SO}_2^4$ ). The  $\text{SO}_2$  concentration for the previous day ( $\text{ASO}_2$ ) was also studied. The number of days prior to the admission whose combined  $\text{SO}_2$  concentrations reached values of 100, 120, 150, 200, 300, 400 and 500  $\mu\text{g m}^{-3}$  respectively, were termed  $\text{DS}_i$ , where  $i$  has a value of one to seven, depending on the value that the number of days refers to.

2. SPM concentration ( $\mu\text{g m}^{-3}$ ): The SPM concentration for the same day as the admission (SPM) and its powers of 1/2 ( $\text{SPM}^2$ ) and 1/4 ( $\text{SPM}^4$ ) was studied. The previous day's concentration ( $\text{ASPM}$ ) was also studied, as was the number of days prior to the admission whose combined SPM concentration values reached values of 100, 120, 150, 200, 300, 400 and 500  $\mu\text{g m}^{-3}$ , respectively, represented by  $\text{DM}_i$ , where  $i$  has a value of one to seven depending on the value referred to.

#### Meteorological variables:

1. Pressure (mm Hg): The maximum pressure was studied raised to the power of 1/4 ( $\text{PMX}$ ) and 1/2 ( $\text{PMX}^2$ ); similarly, the minimum pressure raised to the power of 1/4 ( $\text{PMA}$ ) and 1/2 ( $\text{PMA}^2$ ). Also included were the differences between the maximum pressures ( $\text{DPMX}$ ) and between the minimum pressures ( $\text{DPMA}$ ) for the two days prior to the admission, the pressure gradient or difference between the maximum and minimum for the same day ( $\text{GRAP}$ ), and its square ( $\text{GRAP}^2$ ).

2. Temperature ( $^\circ\text{C}$ ): Maximum ( $\text{TMX}$ ), minimum ( $\text{TMA}$ ), and mean ( $\text{TMD}$ ) temperatures were studied plus their squares ( $\text{TMX}^2$ ,  $\text{TMA}^2$ , and  $\text{TMD}^2$ ). Also included were the differences between maximum temperatures ( $\text{DTMX}$ ), minimum temperatures ( $\text{DTMA}$ ), and mean temperatures ( $\text{DTMD}$ ) for the

2 d prior the admission, the temperature gradient (GRAT = TMX - TMA), and its square (GRAT<sup>2</sup>).

3. Relative humidity (%): Maximum humidity (HMX) and minimum humidity (HMA) were studied plus their squares (HMX<sup>2</sup> and HMA<sup>2</sup>). Also included were the differences between the maximum humidity (DHMX) and between the minimum humidity (DHMA) for the 2 d prior to the admission, the humidity gradient (GRAH = HMX - HMA), and its square (GRAH<sup>2</sup>).

4. Rainfall (mm): The study includes the quantity of rainfall raised to the powers of 1/3 (PRE) and 2/3 (PRE<sup>2</sup>) and the variable DP<sub>i</sub> which expresses the number of days prior to the admission whose combined rainfall values reached 2, 4, 6, 8, 10, 15 and 20 mm and where *i* has a value from one to seven depending on the rainfall limit referred to.

5. Number of hours of still-air conditions (VHC) and its square (VHC<sup>2</sup>).

6. Number of hours the wind blows from the direction of each quadrant (VC<sub>i</sub>) where *i* = 1 (NE), 2 (SE), 3 (SW), 4 (NW), and their squares (VC<sub>i</sub><sup>2</sup>).

7. Average distance covered by wind (km d<sup>-1</sup>) in 1 d in all directions (VEV) and in the direction of each quadrant (VC<sub>i1</sub> = VC<sub>i</sub> · VEV/24), and its power of 1/3 (VC<sub>i3</sub>).

#### Statistical methods

Statistical analysis of the data was performed using a package of programs from the BMDP series: BMDP1R (multiple linear regression), BMDP2R (stepwise regression), BMDP4F (frequency tables), and BMDP1T and BMDP2T (time series analysis).

The multiple linear regression (MLR) analysis was applied to the number of daily admissions for COPD and HF in relation to all the meteorological and pollutant variables for the same day, and one and two days before admission. A stepwise regression analysis (BMDP2R program) was utilized to assess the relative contribution of the variables. This analysis entered the variables into the equation in the order of their additive contribution to increase the precision of estimating the number of daily admissions as a function of these variables. The most important variable, i.e. the variable with the highest correlation coefficient ( $R^2$ ), was entered first. Then, all variables were each considered in combination with this one and the variable which added the most in predicting the dependent variable was chosen next. This procedure was then continued until no other variable added anything to the precision in accord-

ance with the preset limit. The program also checked that no variable was too highly correlated with one or more of those already in the equation.

Then this MLR analysis was carried out using the BMDP1R program with those variables which had yielded the best  $R^2$ -coefficient values with the BMDP2R program. This was done in two ways, using the total number of data (total model) and using the data grouped seasonally. The purpose of this was to make a comparative analysis between the two regression models by applying a comparison test which would show if there was a reduction of the residuals due to data grouping.

In order to eliminate the seasonal effect of the variables, the time series programs BMDP1T and BMDP2T were used considering lag periods from 1- 48 d. Existence of periodicity conforming to a 7-d cycle was observed. An attempt was made to eliminate this influence in the MLR analysis by using mean differences (data item for the day—mean for the same day of the week for the whole period) or by using the difference between each item and the value from 7 d earlier. The influence of the day of the week variable was also analysed by means of dummy variables.

The data distributions of daily admissions were also analyzed with the BMDP4F program using the  $\chi^2$  test of independence between rows and columns.

#### RESULTS

If all admissions for COPD over the 4-y period are taken, the variables that correlate best with the number of admissions per day are those for the same day. With the BMDP2R program, the SPM concentration was raised to the powers of 1/4 and 1/2, the pressure gradient was squared, the maximum temperature was squared, and the rainfall was raised to the power of 2/3 (Table 1). This relationship is not constant throughout the year and shows marked seasonal variation. The  $R^2$ -coefficient values were 0.0117 in winter, 0.0428 in spring, 0.0291 in summer, and 0.0741 in autumn using the same variables as in the total model ( $R^2 = 0.0489$ ).

For HF admissions, the same day variables with the highest contribution to the  $R^2$  value for the total number of days studied were the SPM concentration raised to the power of 1/4, the pressure gradient and its square, the number of days prior the admission required to give an SO<sub>2</sub> concentration value of 150  $\mu\text{g m}^{-3}$ , the mean temperature, and the rainfall raised to the power of 2/3 (Table 1). Seasonally, the  $R^2$  values were 0.0192 in winter, 0.0219 in spring,



Table 1. Results of multiple linear regression analysis applied to the number of daily hospital admissions total models.

Disease	Variable	Coefficient	Std. Reg. Coefficient	Increase in R <sup>2</sup>	Mean of Variable
COPD	(Y-Intercep.	- 2.13656)			
	SPM4	1.92313	0.639	0.0212	2.7913
	GRAP2	0.107 E-02	0.105	0.0118	25.9736
	TMX2	- 0.669 E-03	- 0.114	0.0088	313.8894
	PRE2	- 0.02369	- 0.065	0.0039	1.6262
	SPM2	- 0.26914	- 0.535	0.0032	7.8988
HF	(Y-Intercep.	0.31682)			
	SPM4	0.10888	0.059	0.0161	2.7913
	GRAP2	0.144 E-02	0.230	0.0137	25.9736
	GRAP	- 0.02676	- 0.146	0.0067	3.8851
	DS3	- 0.00476	- 0.079	0.0045	6.2059
	TMD	- 0.01154	- 0.083	0.0038	14.1655
	PRE2	- 0.01292	- 0.058	0.0029	1.6262

0.0186 in summer, and 0.1093 in autumn using the same variables as in the total model ( $R^2 = 0.0476$ ).

The results of the comparison test between the total and seasonal MLR models were not significant which indicates a better correlation for admissions for both diseases with the total model than with the separate seasons.

There was no increase in the R<sup>2</sup>-coefficient value in the MLR analysis with either the lag-effect correction or the inclusion of the day of the week variable.

The influence of the meteorological and pollutant variables was also studied to determine threshold levels, i.e. the lowest value which separates the data

into two populations so that the admissions for each are significantly different. Table 2 gives the contingency tables with the threshold values for maximum and minimum pressure in relation to the two diseases.

Maximum and minimum temperatures gave no threshold values for COPD admissions but were inversely proportional for the whole range of values as can be seen in Fig. 1. This relationship is less marked for HF admissions.

SPM concentrations did not give a threshold value for COPD admissions either. They were directly proportional even at the lowest concentration

Table 2. Results of the application of the  $\chi^2$  test for comparison of contingency table data distribution for number of days with or without admissions in terms of the grouping variables expressed for each disease with the thresholds indicated.

Disease	Variable	Threshold	With Admissions	Without Admissions	$\chi^2$	p <
COPD	Maximum Pressure	≤ 770 mm Hg	824	634	10.63	0.002
		> 770 " "	48	14		
	Minimum Pressure	≤ 765 mm Hg	773	604	9.08	0.005
		> 765 " "	99	44		
HF	Maximum Pressure	≤ 770 mm Hg	398	1060	5.02	0.05
		> 770 " "	25	37		
	Minimum Pressure	≤ 765 mm Hg	362	1015	17.28	0.0001
		> 765 " "	61	82		

values (Fig. 2). For HF, there was neither a threshold nor proportionality.

The results were similar for SO<sub>2</sub> (Fig. 2) but the proportional relationship with COPD admissions was less marked.

DISCUSSION

In the MLR analysis, the same day's variables are those which yield the best R<sup>2</sup>-coefficient value which agrees with other authors' results (Pershagen et al. 1984). The values are too low to be used as a prediction model and only allow therefore, to state which

variables make the greatest contribution in accounting for the dependent variable, the number of admissions.

In the overall analysis, these variables are the SPM concentration and the pressure gradient for both diseases. For COPD, they are followed by maximum temperature and the rainfall and for HF, the SO<sub>2</sub> pollution for the days prior to admission (via the variable DS3), the mean temperature, and the rainfall. The influence of pollution on both diseases agrees with many other authors' results (Sterling et al. 1967; Bates and Sizto 1983; Dorado et al. 1982; Sheppard et al. 1984; Bethel et al. 1984). The as-

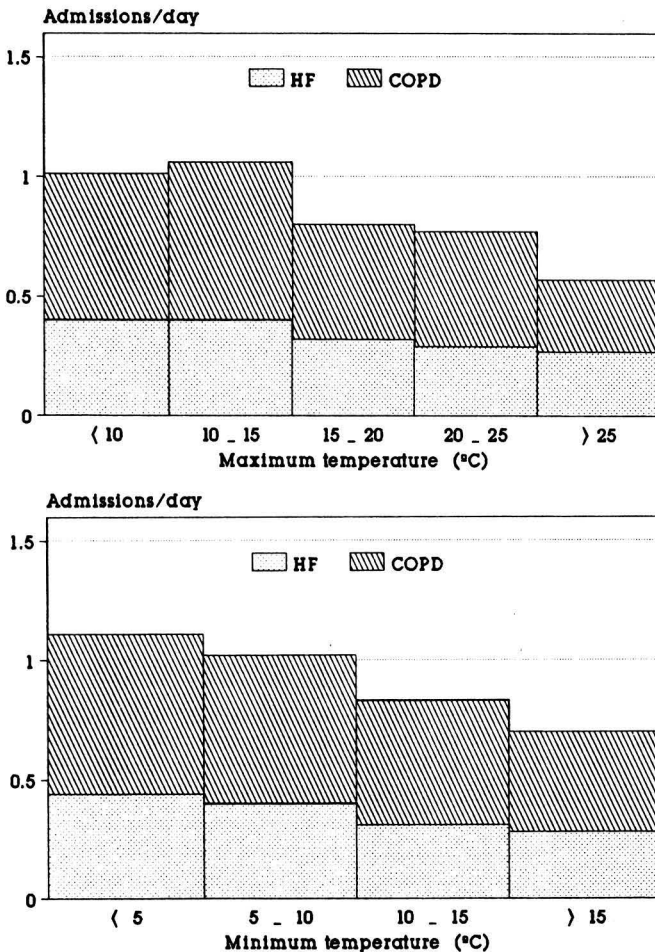


Fig. 1. Average values of the number of admissions due to COPD and HF for the different ranges for maximum and minimum temperatures.

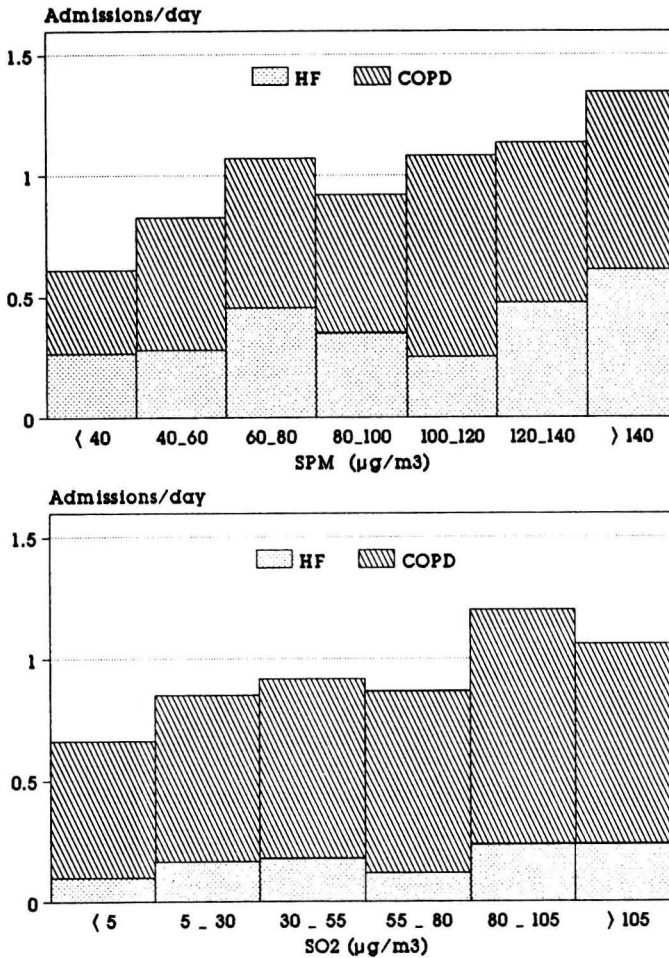


Fig. 2. Average values of the number of admissions due to COPD and HF for the different ranges for the pollutants SPM and SO<sub>2</sub> in  $\mu\text{g m}^{-3}$ .

sociation of low temperatures with COPD has been widely demonstrated (Bates and Sizto 1983; Dorado et al. 1982; Millquist et al. 1984; Chipps et al. 1984; Laborda and Cortada 1983; Sheppard et al. 1984; Bethel et al. 1984) but the influence of pressure has been studied less (Dorado et al. 1982; Chipps et al. 1984; Laborda and Cortada 1983); this is also true for rainfall (Chipps et al. 1984; Laborda and Cortada 1983).

The results from the MLR analysis for daily admissions for each season indicate the existence of a seasonal dependence. The global coefficients,  $R^2$ , for

autumn were higher than for the other seasons, which is in agreement with other authors' findings (Lawter et al. 1970; Goldstein and Cuzik 1983). Lawter et al. (1970) and Wagner et al. (1983) described the relationship between asthma symptoms and the exacerbation of bronchitis and the changes of temperature at the beginning of autumn which might be related to our results. They may also be related to the higher frequency of virus infections of the respiratory tract, such as those caused by rhinovirus and other picornaviruses in early autumn and late spring (Hendley and Gwaltney 1988). This may be due to higher in-

door relative humidity which favours survival of such viruses.

No relationship was found with the day of the week variable in the MLR analysis although the 7-d periodicity of the data seems to indicate a certain influence. This may be due to the lower concentration of pollutants at the weekend. According to some authors (Sterling et al. 1967; Goldsmith et al. 1983) but no others (Goldstein and Cuzik 1983; Freziers et al. 1982), this variable is of great importance.

For some variables, a proportional relationship over the whole range of values was found in our study, which seems to be a common finding. Noteworthy is the continuity of the proportionality and the absence of threshold values separating the data into two groups with significant differences in admission incidence. However, other factors do give threshold values.

The influence of temperature and pollution is evident in spite of the mild climate and benign environment in the area. In the 4 y studied, temperatures of 0°C or below were recorded only on six occasions and maximum temperatures of over 30°C on five occasions, while the pollution values could be described as low-middle.

It is interesting to note that the influence of SPM and SO<sub>2</sub> concentrations on admission incidence for both diseases is significant at values much lower than those given as a guide by international legislation.

In conclusion, through our study an influence was found, though slight, of both meteorology and environment on the number of admissions for the two diseases. The influence of SPM and pressure gradient was most important followed by that of temperatures.

*Acknowledgment* — The authors would like to thank the Director of the National Hospital "Marqués de Valdecilla" for authorising access to the clinical records; Claudia E. M. Onecha, Head of the Clinical Records Archive, and her team for their help in finding the records reviewed; Dr. Angel Pereda of the Regional Health Centre for providing the pollutant concentration data; and Francisco Iglesias, Head of the Regional Meteorological Centre in Santander, Carmen Gozalo, and the whole team at the Centre for their help in compiling the data for the meteorological variables; and Ian Williams for his assistance in the translation of the manuscript.

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# COMPOSITION OF EXTRACTABLE ORGANIC MATTER OF AEROSOLS FROM THE BLUE MOUNTAINS AND SOUTHEAST COAST OF AUSTRALIA

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*EI 9001-005M (Received 29 January 1990; accepted 1 December 1990)*

Extractable organic matter in aerosols from the Australian Blue Mountains and southeastern coast was characterized and compared to a composite sample of the regional vegetation and aerosols collected in New Zealand by Gagosian et al. (1987). The lipid fraction of the aerosols was comprised primarily of *n*-alkanes, *n*-alkanoic acids, and *n*-alkanols, with triterpenoids and phytosterols contributing significantly to the signature. Except for one sample, the aerosols were demonstrated to originate mainly from biogenic rather than anthropogenic sources. Two of the aerosol samples correlated well with the *n*-alkane signature of the plant wax extract. The resemblance was less distinct for the *n*-alkanoic acid and *n*-alkanol fractions. Of the cyclic terpenoids, only triterpenoids were present in the aerosols. Sesquiterpenoids were found in the plant wax sample but not in the aerosols, most probably due to volatilization. Diterpanes were undetected in both aerosol and wax samples. Based on a preliminary comparison, long range transport of these lipids appears to be occurring by the Southern Hemisphere westerlies.

## INTRODUCTION

The lipids (solvent soluble organic compounds  $>C_{12}$ ) found in atmospheric aerosols contain natural products, anthropogenic components and, in arid regions, geological components from erosion of sediments and soils (e.g., Mazurek and Simoneit 1984; Simoneit et al. 1988; Standley and Simoneit 1987; Simoneit 1984a,b, 1985, 1986a, 1989; Simoneit and

Mazurek 1982, 1989). The term "aerosol" is used in this paper to mean aerosol particles collected on fiber filters by a high volume air sampler. The aerosols are unsegregated with respect to particle size. Lipids are useful tracers for determining the origin of organic matter associated with aerosol particles which, in turn, is important for monitoring air quality in urban centers and for tracing long range aerosol transport by global winds. Carbonaceous particles are an important component of visibility-reducing aerosols in urban areas (e.g., Gray et al. 1986; Hildemann 1989) and the associated lipids can be used to estimate contributions from biogenic and anthropogenic

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sources (Mazurek and Simoneit 1984; Simoneit 1984a; Standley and Simoneit 1987).

There has been considerable discussion of the role played by biogenic hydrocarbons in the formation of photochemical smog in the Sydney metropolitan area (Quigley 1984). It is therefore of interest to assess the composition of the biogenic signature from the regional vegetation, the "blue haze", which occurs over the forests around the Sydney metropolitan area, especially in the Blue Mountains lying to the west (Fig. 1). In general, the photochemical smog in Sydney has been found similar in origin and concentration to that in cities of the United States (Nelson and Quigley 1982; Nelson et al. 1983).

Eolian transport and enroute fallout has been invoked as one input mechanism of aerosol organic matter to the oceans (Cachier et al. 1985; Gagosian et al. 1981, 1982, 1987; Gagosian and Peltzer 1986; Lepple and Brine 1976; Simoneit 1977, 1979, 1982, 1986a; Simoneit et al. 1977, 1980; Zafiriou et al. 1985), since the same terrigenous lipids are present in the marine aerosols of major global wind systems (e.g., Cox et al. 1982; Simoneit 1977; Simoneit et al. 1977, 1988). In order to understand the significance

of such major wind systems upon the long-range transport of carbonaceous particles to the remote ocean, it is necessary to examine (1) whether their lipid signature is observed on a continent under the influence of a major wind system and (2) whether this chemical composition can be traced in the ambient aerosols to its source region. Therefore, a general comparison of the compound signatures in these aerosols with those reported for samples from Ninety Mile Beach on the North Island of New Zealand (Gagosian et al. 1987) is also of interest.

## EXPERIMENTAL METHODS

### Sampling

Aerosol particle matter was acquired from rural sites of Southeastern Australia by filtration of the ambient air using a high volume air sampler fitted with quartz fiber filters ( $20 \times 25 \text{ cm}^2$  surface, Gelman Science Inc., Ann Arbor, MI) capable of retaining  $0.3 \mu\text{m}$  particles at a minimum efficiency of  $\sim 99\%$  and those  $>0.3 \mu\text{m}$  with greater efficiency. Prior to sampling, the quartz filters had been sealed in Teflon bags after annealing for three hours at  $560^\circ\text{C}$  in

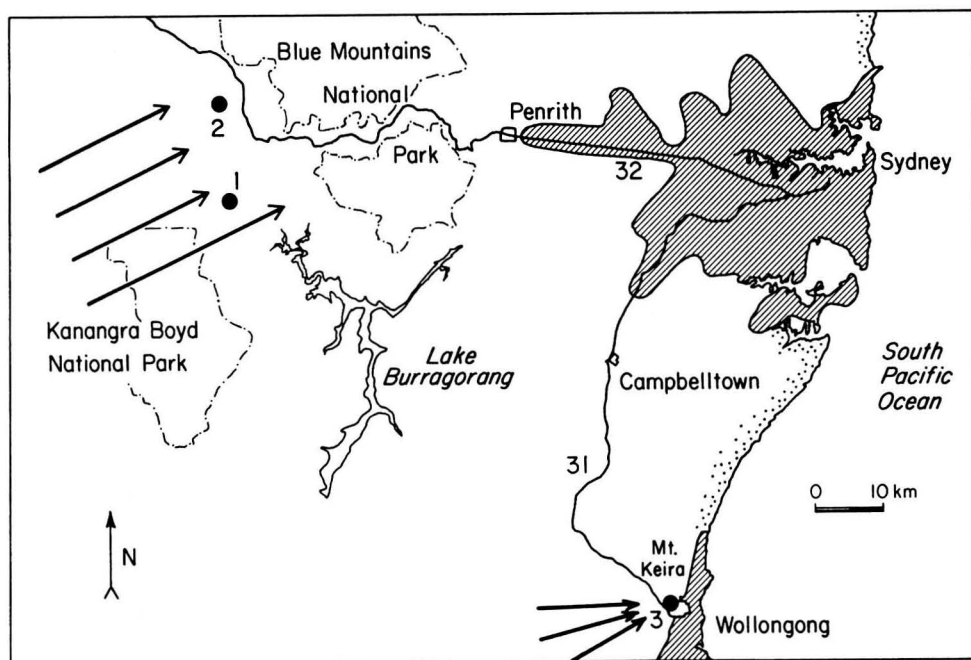


Fig. 1. Location map of the aerosol sampling sites: Station 1—Packsaddlers; Station 2—Mt. Booralee; Station 3—Mt. Keira (arrows indicate wind direction during sample acquisition).

order to pyrolyze and thus remove any adsorbed organic contaminants. After the sampling was completed (usually 12 or 24 h), the collection filters were stored in a freezer and handled as described before (Simoneit et al. 1988; Simoneit and Mazurek 1982).

Representative samples of vegetation were obtained from the area around a sampling site to provide a composite (Table 1). Approximately 12 specimens of *Eucalyptus*, *Acacia*, *Casurina*, *Banksia*, *Peroonia* and grass species were pooled. This plant material was extracted directly by repeated shaking with  $\text{CH}_2\text{Cl}_2$  and the lipid concentrate was then treated in the same manner as filter extracts for separation and analysis.

#### Lipid isolation and separation

Filters were extracted using ultrasonic agitation for two 15-min periods for which 400 mL of distilled-in-glass  $\text{CH}_2\text{Cl}_2$  were used each time. The extractions were carried out within the filter storage jars and the solvent extracts were concentrated to volumes of approximately 5 mL. An 800 mL solvent blank was also concentrated to a total volume of 20  $\mu\text{L}$  and analyzed in order to monitor the solvent residue background.

The extracts were then filtered (glass fiber), concentrated on a rotary evaporator, quantified, and treated with diazomethane to esterify carboxylic acids (Simoneit and Mazurek 1982). The derivatized extract was subjected to thin layer chromatography (TLC) using silica-gel plates (0.25 mm) and eluted with a mixture of hexane and diethyl ether (9:1). The TLC plates had been cleaned prior to use by repetitive elutions with methanol and  $\text{CH}_2\text{Cl}_2$  and before sample application, they were activated in an oven at 120°C for 45 min (Simoneit and Mazurek 1982). The TLC elution regions corresponding to hydrocarbons, esters, ketones, plus aldehydes and alcohols were visualized by UV light and then iodine vapor in conjunction with the coelution of a standard compound mixture (Simoneit and Mazurek 1982). The bands corresponding to these fractions were scraped off the TLC plate, eluted with  $\text{CH}_2\text{Cl}_2$  or ethyl acetate, and concentrated by rotary evaporation followed by nitrogen blow-down. These fractions were then subjected to gas chromatographic (GC) and gas chromatography-mass spectrometric (GC-MS) analyses. All fractions were stored in a freezer. Alcohol fractions were converted to the trimethylsilyl ethers prior to GC and GC-MS analysis by reaction with N,O-bis-(trimethylsilyl)-trifluoroacetamide (BSTFA) plus 1% trimethylchlorosilane: anhydrous pyridine (1:1) for approximately 30 min at  $-70^\circ\text{C}$  under a nitrogen atmosphere.

#### Lipid analyses

The GC analyses were carried out on a Hewlett-Packard Model 5840A gas chromatograph using a 25 m  $\times$  0.20 mm i.d. flexible fused silica capillary column coated with DB-5 (J and W, Inc.). The GC-MS analyses were conducted on a Finnigan Model 4021 quadrupole mass spectrometer interfaced directly with a Finnigan Model 9610 gas chromatograph and equipped with a flexible fused silica capillary column coated with DB-5 (30 m  $\times$  0.25 mm i.d.). The GC and GC-MS operating conditions were as follows: temperature program 35-280°C at 6°C/min, held isothermal at 280°C for 60 min and using helium as carrier gas. Mass-spectrometric data were acquired and processed using a Finnigan-Incos Model 2300 data system. Molecular markers were identified by GC and GC-MS comparison with authentic standards and characterized mixtures. All separations and analyses, except for the alcohol fractions, were carried out during 1980 and 1981. More recently GC-MS analyses were carried out of the alcohol fractions and some reruns of hydrocarbon fractions.

#### Blanks

Procedural and solvent blanks have also been analyzed and quantified in order to assess possible contaminant input and the details have been described earlier (Simoneit and Mazurek 1982; Simoneit 1984a). The major contaminants observed were primarily residual phthalate esters (diethyl, dibutyl, and diethylhexyl), minor amounts of *n*-fatty acids (as methyl esters) ranging from  $\text{C}_{10}$  to  $\text{C}_{22}$ , and traces of *n*-alkanes ranging from  $\text{C}_{19}$  to  $\text{C}_{30}$ , with no carbon number predominance or maximum at  $\text{C}_{25}$ . Polynuclear aromatic hydrocarbons (PAH) were not detectable. The major proportion of the contaminants could be distinguished by their low concentrations and distribution fingerprints (especially the *n*-alkanes and *n*-alkanoic acids). These contaminants did not interfere with the recognition or quantification of the compounds of interest in these samples.

## RESULTS AND DISCUSSION

The sampling locations, extract yields and analytical data for the lipid fractions are given in Table 1. The ambient temperatures at the sampling sites were typically temperate (18-25°C) and the wind direction during sample acquisitions was from the southwest to west (Fig. 1), with speeds ranging from calm to  $\sim 5$  km/h. Visibility was reduced due to haze. Station 1 (Fig. 1) was located at Packsaddlers Pty., Ltd., in a narrow valley (elevation 564 m), with sample ac-



Table 1. Yields and compositional data for the aerosol and plant wax lipids.

Station (cf. Fig. 1)	Sample Location	Total Extract Yield ( $\mu\text{g}$ ) (ng/m <sup>3</sup> )	Total Hydrocarbons		Plant Wax		n-Alkanic Acids		n-Alkanols		Phytosterols (ng/m <sup>3</sup> )	Triterpenoids (ng/m <sup>3</sup> )
			U:R <sup>†</sup> (ng/m <sup>3</sup> )	U:R <sup>†</sup> Pr/Ph <sup>†</sup> (ng/m <sup>3</sup> )	n-alkanes Cmax <sup>§</sup> (ng/m <sup>3</sup> )	n-alkanoic CPI* (ng/m <sup>3</sup> )	n-C <sub>18:0</sub> $\Sigma$ C <sub>18:1</sub> <sup>††</sup> (ng/m <sup>3</sup> )	CPI* Cmax <sup>§</sup>				
1 Pecksaddlers Py.	33°47'20"S 150°13'55"E	625 250	16 1.96	0.81 1.8	7 29	32 16,24	6.3 16,24	32 32	68 13.7	26 26	6 6	6 6
2 Mt. Booralee	33°37'03"S 150°19'05"E	1462 690	80 2.35	5.3 1.2	11.2 29	110 16,26	6.6 16,26	110 12	380 12.2	26 26	22 22	4 4
3 Mt. Keira	34°22'S 150°49'E	415 1020	77 1.73	4.7 1.1	2.0 29	2.8 16,22	21 16,22	3.7 3.7	5.4 10.6	26 26	0.5 0.5	1 1
3 Mt. Keira	34°22'S 150°49'E	865 510	1.6 1.84	1.1 2.0	0.3 29	4.6 16,24	10.6 16,24	6.5 6.5	1.7 19.4	26 26	0.2 0.2	0.4 0.4
3 Mt. Keira	34°22'S 150°49'E	1080 n.d.	- 1.40	1.8 1.8	- 29	- 8.1	16,24 16,24	2.3 2.3	- 14.0	16,26 16,26	- -	- -
1 Carbon Creek	33°47.3'S 150°13.9'E	- 80mg/g	1400 16.0	0 0	n.a. 1400 $\mu\text{g/g}$	29 2650 $\mu\text{g/g}$	17.1 16,26	2.8 2.8	8000 47.5	26 26	4.5 4.5	28 28

n.d. = not determined  
n.a. = not applicable

\*Carbon preference index (Simoneit 1978).

†Unresolved to resolved components, a measure of fossil fuel contamination (Mazurek and Simoneit 1984).

‡Pristane to phytane ratio.

§Carbon chain maximum in homologous series (dominant homolog is underscored).

††Ratio of n-octadecanoic acid to summation of all octadecenoic acids.

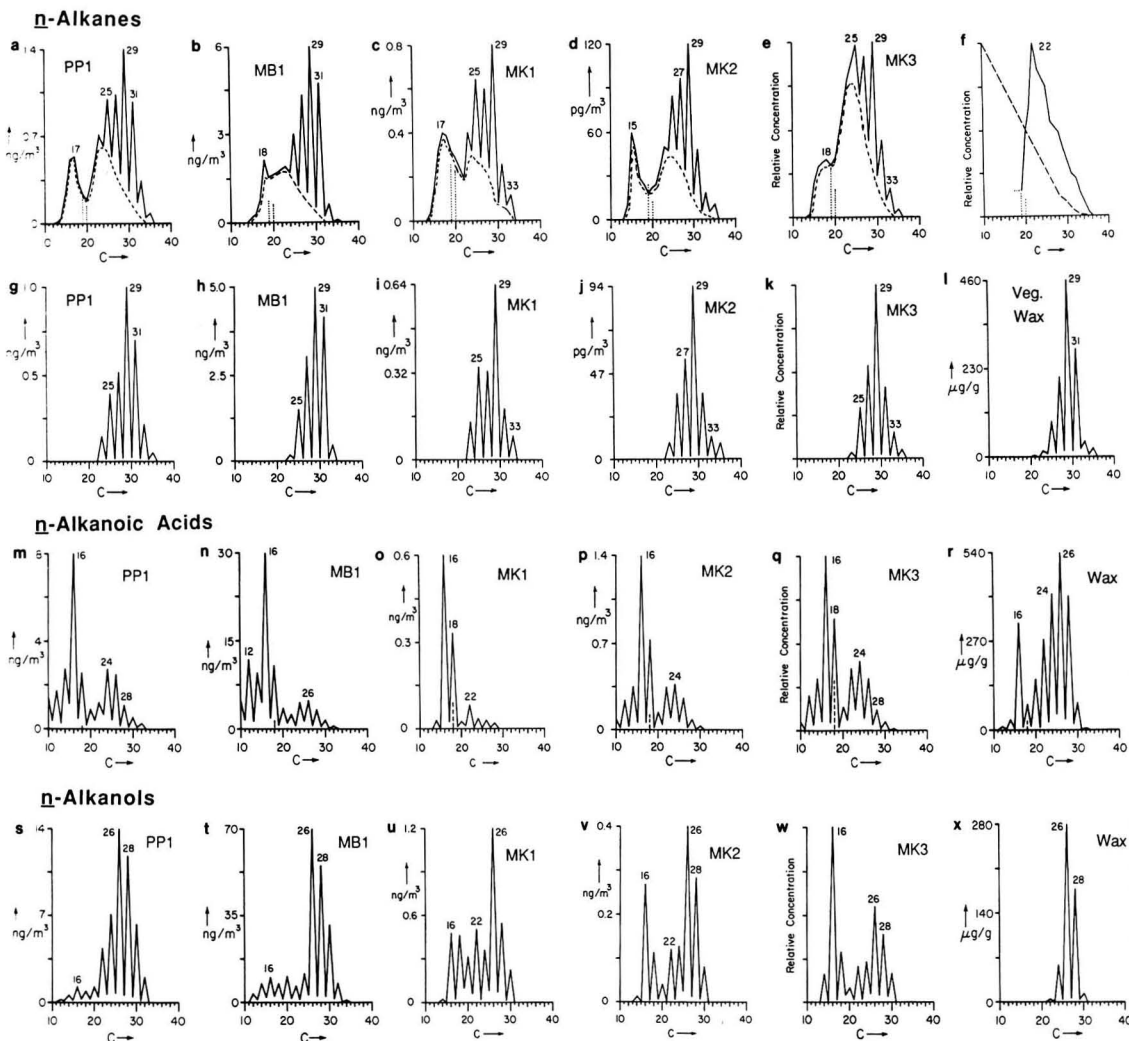


Fig. 2. Distribution diagrams (concentration versus carbon number) of homologous compound series for aerosols, composited vegetation wax and fossil fuels: (a-f) total  $n$ -alkanes (... = pristane and phytane), (g-l)  $n$ -alkanes from vegetation wax, (m-r) total  $n$ -alkanoic acids (--- = total C18 unsaturated acids), (s-x) total  $n$ -alkanols.

Aerosol samples: (a, g, m, s) Packsaddlers; (b, h, n, t) Mt. Booralee; (c, i, o, u) Mt. Keira 1; (d, j, p, v) Mt. Keira 2; (e, k, q, w) Mt. Keira 3. Composited vegetation wax: (l, r, x) Carlon Creek sample. Fossil fuels: (f) Typical crude petroleum (---) and diesel fuel (—).

quisition on 2 September 1979, Station 2 was on Mt. Booralee (elevation 1036 m, with sample acquisition on 14 March 1980), and Station 3 was on Mt. Keira (elevation ~534 m, with sampling on 10, 11 and 25 August 1980 for MK-1, MK-2, and MK-3, respectively).

### Yields

Total solvent-extractable organic matter (lipids) ranged from 250-1020  $\text{ng}/\text{m}^3$  of air, which is of the same magnitude as data reported for aerosols from the rural western United States and Nigeria (Simoneit

and Mazurek 1982; Simoneit et al. 1988). This lipid material consisted primarily of hydrocarbons, fatty acids and fatty alcohols, minor amounts of ketones, and other molecular markers. The highest yields were observed for samples with an urban component (e.g., MB1 and MK1, Table 1). The total hydrocarbon concentrations ranged from 1.6-80 ng/m<sup>3</sup>, with carbon preference indices (CPI) (Simoneit and Mazurek 1982) of <2.4 and with unresolved-to-resolved component ratios (U:R) (Mazurek and Simoneit 1984) of 0.8 to 27 (Table 1). These ranges are also of the same magnitude as reported for aerosols from the western United States and Nigeria. The *n*-alkanoic acid concentrations varied from 3 to ~110 ng/m<sup>3</sup>, with CPI>6 and homolog ranges from C<sub>10</sub>-C<sub>32</sub>. The *n*-alkanols were present at concentrations of about 2-380 ng/m<sup>3</sup>, with CPI >10 and homolog ranges from C<sub>12</sub>-C<sub>34</sub>. Both of these latter fractions are primarily of a biogenic origin, where generally the homologs <C<sub>20</sub> are considered to derive from microbial sources. The term

"microbial" is used in this paper to designate algal and bacterial contributions. In general, the plant wax components dominated over the anthropogenic matter except for sample MK1. It should be noted that the sums of the individual fraction yields do not equal the total extract yield (Table 1). This is due to the significant and variable content of polar material in all extracts as determined by Intrascan analysis and which is not detected in the subfractions.

#### Homologous compounds

The signatures of the homologous compound series present in the aerosol lipid extracts as represented by the CPI, U:R, and the Carbon Number Maximum (C<sub>max</sub>), provide evidence for the incorporation of recent biogenic organic matter into the anthropogenic materials (Table 1) (Mazurek and Simoneit 1984; Simoneit 1986a). The distributions of the homologous compounds in the lipid fractions are shown in Fig. 2. The total *n*-alkanes of the aerosols are mixtures derived

Table 2. Chi-square test for composited vegetation wax and New Zealand aerosols versus the SE Australian aerosols.

Sample	$\chi^2$	$\chi^2$	$\chi^2$	$\chi^2$ Total
	<i>n</i> -Alkanes (C <sub>23</sub> -C <sub>35</sub> ) <sup>1</sup>	<i>n</i> -Alkanoic acids (C <sub>19</sub> -C <sub>33</sub> )	<i>n</i> -Alkanols (C <sub>21</sub> -C <sub>33</sub> )	
<u>Vegetation Wax (Carlton Creek) vs.</u>				
PP1	86	277	898	1261
MB1	21	526	481	1028
MK1	198	316	634	1148
MK2	48	282	361	691
MK3	18	338	672	1028
NZAS-16 <sup>2</sup>	131	-	236	367
NZAS-20 <sup>2</sup>	472	-	4495	4967
<u>New Zealand AS-16<sup>2</sup> vs.</u>				
PP1	117	-	309	426
MB1	59	-	123	182
MK1	324	-	156	480
MK2	110	-	131	241
MK3	63	-	244	307
<u>New Zealand AS-20<sup>2</sup> vs.</u>				
PP1	507	-	114	621
MB1	384	-	77	461
MK1	912	-	231	1143
MK2	523	-	140	663
MK3	353	-	177	530

$$^1 \chi^2 = \sum \frac{(\text{observed} - \text{expected})^2}{\text{expected}}$$

<sup>2</sup> Gagosian et al. 1987.

from natural plant wax and fossil fuel residues (Fig. 2 a-e). The contribution of fossil fuel residues from urban sources is evident in the unresolved complex mixture (UCM in the GC traces) of branched and cyclic hydrocarbons (also termed hump), the relative amounts of *n*-alkanes under the envelope of the dashed line (Fig. 2 a-e) and the presence of minor biomarkers (e.g., pristane and phytane) (Simoneit 1984a,b, 1985). For comparison, the *n*-alkane distributions in typical petroleum and diesel fuel (with no odd carbon number predominance) are shown in Fig. 2 f.

The major compounds that comprise vascular plant wax are *n*-alkanes (C<sub>23</sub> to C<sub>35</sub>, with an odd-to-even carbon number predominance), *n*-alkanols (C<sub>22</sub> to C<sub>34</sub>, even-to-odd) and *n*-alkanoic acids (C<sub>22</sub> to C<sub>34</sub>, even-to-odd), with minor amounts of *n*-alkanals, *n*-alkanones and cyclic biomarkers such as phytosterols and triterpenols (Simoneit 1978, 1986b, 1989; Simoneit and Mazurek 1982; Simoneit et al. 1983; Standley 1987). Plant waxes are evident in the aerosols from the Blue Mountains and the SE coast as the *n*-alkanes >C<sub>23</sub> with an odd carbon number predominance (Fig. 2 a-e). The plant wax alkanes can be separated from the fossil fuel component as follows. Since it is known that *n*-alkanes of petroleum generally have a carbon preference index of one, especially >*n*-C<sub>24</sub>, a subtraction of the corresponding *n*-alkane concentrations of CPI=1 was carried out to determine the distribution signatures of the residual plant wax alkanes. The concentrations of the wax *n*-alkanes were calculated by subtraction of the average concentration of the next higher and lower even carbon numbered homologs:

$$\text{Wax } C_n = [C_n] - \left[ \frac{(C_{n+1}) + (C_{n-1})}{2} \right]$$

Negative values of C<sub>n</sub> were taken as zero. The concentrations of the remaining odd carbon numbered alkanes are plotted as before versus carbon number (Fig. 2 g-k), with the even homologs adjusted to give a CPI of 16 similar to the *n*-alkanes of composited vegetation wax (e.g., Fig. 2 l). It can now be seen that each aerosol sample has a slightly different *n*-alkane distribution derived from vascular plant wax, and the total amounts of this wax are summarized in Table 1. Visual comparison of the alkane distributions of the wax with the aerosols indicates sample PP1 has the closest resemblance (Fig. 2 g vs. l). A  $\chi^2$  test was performed to compare the regional composited vegetation wax with the aerosols of this study and two aerosol samples from the New Zealand study by Gagosian et al. (1987), and then comparing the

two aerosol signatures from New Zealand with those of this study (Table 2). Thus, the  $\chi^2$  test (Table 2) gives the best fits for samples MK-3 and MB-1 (Fig. 2 k,h), ranking PP1 as fourth due to statistical emphasis of minor differences.

The *n*-alkanoic acids can be defined by the *m/z* 74 or 87 (as methyl esters) fragmentograms in GC-MS data and are then plotted in distribution diagrams as shown in Fig. 2 m-r. The *n*-alkan-2-ones and *n*-alkanals (aldehydes) are identified based on the *m/z* 58 and 82 fragmentograms, respectively (not shown due to their trace concentrations), and the *n*-alkanols are identified as the trimethylsilyl ethers in the *m/z* 75 and M<sup>+</sup>-15 fragmentograms of GC-MS data. The *n*-alkanol series are summarized in the distribution diagrams of Figure 2 s-x.

The *n*-alkanoic acids of the composited vegetation are not obvious in the aerosols, and this is supported by the  $\chi^2$  test (Table 2). The *n*-alkanoic acids of the aerosols range from C<sub>10</sub> to C<sub>32</sub>, with a strong even carbon number predominance and C<sub>max</sub> at C<sub>16</sub> (major) and C<sub>22</sub>, C<sub>24</sub>, or C<sub>26</sub> (Fig. 2 m-q), whereas the wax from the composited vegetation has a major C<sub>max</sub> at C<sub>26</sub> and minor at C<sub>16</sub> (Fig. 2 r). The predominance of *n*-alkanoic acids <C<sub>20</sub> in the aerosols may reflect an enhanced microbial component, which is present to a lesser degree in the composited vegetation wax. The presence of unsaturated acids as mainly C<sub>18:1</sub> should be noted (Fig. 2 m-r). These compounds are indicators of recent biogenesis and are present in varying amounts in the aerosol samples. They are very unstable and are rapidly oxidized and degraded in the environment (Simoneit and Mazurek 1982; Kawamura and Gagosian 1987). Their abundance relative to the saturated homologs in the aerosols may indicate a decomposition rate, provided their initial production and introduction are uniform for the region. The concentration ratios of saturated versus unsaturated fatty acids (cf. *n*-C<sub>18:0</sub>/ΣC<sub>18:1</sub> in Table 1) range from 2.3 to 32 for the aerosol samples. This is higher than the values observed for aerosols from the Atlantic Ocean (*n*-C<sub>18:0</sub>/ΣC<sub>18:1</sub> = 0.4-3.3) (Simoneit and Mazurek 1982) and within the range reported for Harmattan aerosols from Nigeria (*n*-C<sub>18:0</sub>/ΣC<sub>18:1</sub> = 0.6-230) (Simoneit et al. 1988) and rural aerosols in the Western United States (*n*-C<sub>18:0</sub>/ΣC<sub>18:1</sub> = 1.4-56) (Simoneit and Mazurek 1982). The higher values for samples PP1, MB1 and MK2 probably reflect decomposition of C<sub>18:1</sub> during aerosol aging, since the value of this ratio for the composited vegetation wax of Australia is 2.8 and for other vegetation samples 3-7 (Simoneit and Mazurek 1982; Simoneit et al. 1988).

The *n*-alkanols of the wax from the composited vegetation (Fig. 2 x) are recognizable in the aerosol samples, although admixed with lower homologs ( $>C_{20}$ ) from microbial sources and additional input from higher plants (Fig. 2 s-w). The *n*-alkanols of the aerosols range from  $C_{12}$  to  $C_{32}$ , with a strong even carbon number predominance and  $C_{max}$  at  $C_{26}$  (major) and  $C_{16}$  (major for MK3), whereas the wax from the composited vegetation contains only the homologs from  $C_{22}$  to  $C_{30}$  with  $C_{max}$  at  $C_{26}$ . The best match of the vegetation wax is with sample MK2 (Table 2). This sample also has the best chi-square

fit with the vegetation wax for all three lipid fractions (Table 2).

#### Anthropogenic components

The overprint of petroleum hydrocarbons from anthropogenic emissions (mainly vehicular) over the natural components in aerosols has been documented for various air basins, e.g., Lake Tahoe and Los Angeles (Simoneit 1984a,b, 1985, 1986a; Simoneit et al. 1980). An additional diagnostic parameter that can be utilized to assess the magnitude of petroleum contributions to aerosols is the U:R ratio (Mazurek

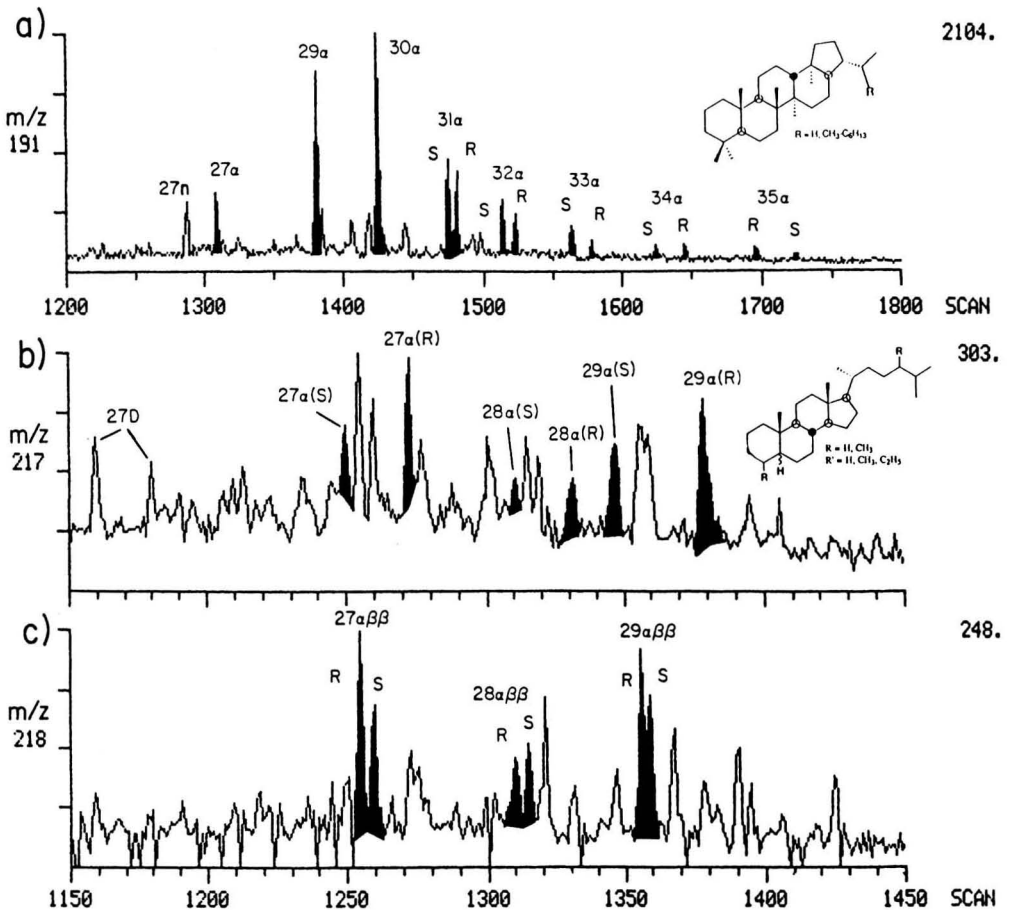


Fig. 3. Typical biomarker signatures from GC-MS data for sample MB1 (numbers refer to carbon skeleton size): (a) m/z 191, key ion for triterpanes (solid peaks are the 17 $\alpha$ (H), 21 $\beta$ (H)-hopane series); (b) m/z 217, key ion for steranes (D = diasterane,  $\alpha$ R/S = 5 $\alpha$ (H), 14 $\alpha$ (H), 17 $\alpha$ (H)-steranes, C-20 R or S); (c) m/z 218, key ion for steranes (solid peaks are the 5 $\alpha$ (H), 14 $\beta$ (H), 17 $\beta$ (H)-steranes, C-20 R or S).

and Simoneit 1984), and such an input component can be confirmed by its fossil fuel biomarker signature (Simoneit 1984a,b, 1985).

The U:R for these samples ranges from 0.8 to 5.3 (Table 1), indicating a typically mixed composition from natural and urban sources (Mazurek and Simoneit 1984). The  $C_{max}$  for all samples is  $n-C_{29}$  derived from vascular plant waxes. The pristane to phytane ratio, Pr/Ph (Table 1), ranges from 1.1 to 2.0. The presence of these biomarkers coupled with their ratios is typical of petroleum. The other petroleum biomarkers in these samples are triterpanes and steranes (Simoneit 1984a,b, 1985). A typical biomarker signature is shown in Fig. 3. The  $17\alpha(H),21\beta(H)$ -hopane series (Structure 1, Appendix 1) ranges from  $C_{27}$  to  $C_{35}$  (no  $C_{28}$ ), with the homologs  $\geq C_{31}$  present as the characteristic C-22 R and S doublets (Fig. 3a) (Seifert and Moldowan 1978, 1979). This pattern fits for petroleum derived from marine source rocks. The steranes are comprised mainly of the regular  $5\alpha(H)$ ,  $14\alpha(H),17\alpha(H)$ -20R, and 20S (II) and the  $5\alpha(H)$ ,  $14\beta(H),17\beta(H)$ -20R and 20S series, ranging from  $C_{27}$  to  $C_{29}$ , with minor amounts of diasteranes (Fig. 3 b,c). These signatures are also consistent with marine-sourced petroleum (Seifert and Moldowan 1978, 1979). The biomarker patterns are not the same for all these samples, indicating various inputs of petroleum products to the aerosols.

#### Natural product biomarkers

The major natural products detectable in the aerosol samples are the phytosterols (III) and triterpenoids (IV-VII) and their yields are given in Table 1. Although sesquiterpanes are present in the wax from the

composited vegetation, they were not detected in the aerosol samples due to their inherent high volatility. Diterpenoids were also not detectable (polyfunctionalized diterpenoids were not elucidated). Phytosterols and triterpenoids are significant components compared to the  $n$ -alkanols (e.g., Fig. 4) in the aerosol samples (4-25% of the alcohol fraction), although they are insignificant in the composited vegetation wax (0.3% of the alcohol fraction). Thus, vegetation waxes upwind from the sampling sites may be richer in phytosterols and triterpenoids than those from the immediate area of the sampler.

The phytosterols (III) range from  $C_{27}$  to  $C_{29}$ , with  $C_{28}$  at low concentrations (Fig. 5). Samples PP1 and MB1 have a  $C_{29}$  dominance and MK1 to MK3 have cholesterol ( $C_{27}$ , III, R = H) dominant. The vegetation wax has an approximately equal content of  $C_{27}$  and  $C_{29}$  phytosterols, which differs from the norm for other plant waxes where generally  $C_{29}$  is  $\gg C_{27}$  (Simoneit et al. 1983, 1988; Simoneit 1989).

The predominant triterpenoids in both the aerosol and plant wax samples are hydroxy acids. The two major compounds are oleanolic (IV) and ursolic (V) acids, based on their mass spectra (Fig. 6) and GC retention times (e.g., Fig. 4) compared with the standards. As the trimethylsilyl ether methyl esters, these compounds have characteristic mass spectra with a molecular ion peak and key fragment ions at  $m/z$  203 and 262 due to ring C scission, with subsequent loss of  $\cdot CO_2CH_3$  (Fig. 6). The minor triterpenoids are alcohols and the major compounds are  $\alpha$ -amyrin (VI) and  $\beta$ -amyrin (VII) based on their mass spectra and GC retention times compared with the standards (Simoneit 1989). In the composited vegetation wax, triterpenoids are more abundant than phytosterols,

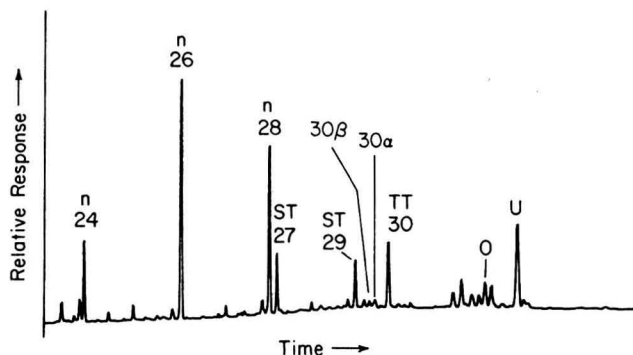


Fig. 4. Partial gas chromatographic trace for the alcohol fraction of aerosol sample PP1 (analyzed as trimethylsilyl ethers,  $n$  =  $n$ -alkanols, ST = phytosterols, TT = triterpenol, O = oleanolic acid, U = ursolic acid,  $\alpha$  =  $\alpha$ -amyrin,  $\beta$  =  $\beta$ -amyrin).

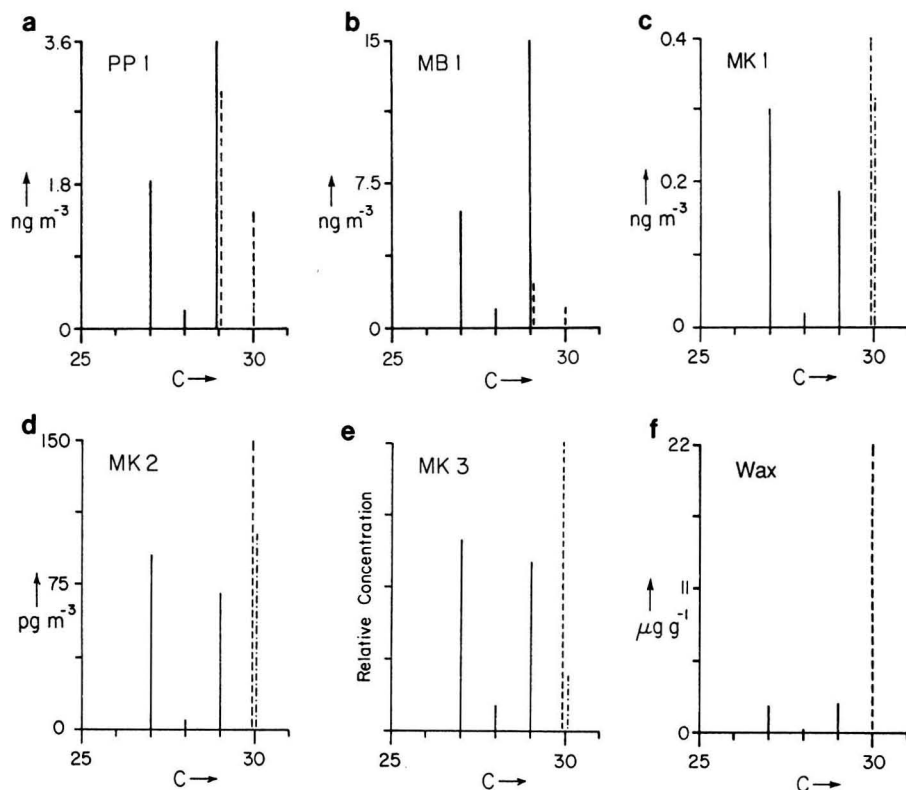


Fig. 5. Distribution histograms (carbon number versus concentration) of the phytosterols (—) and triterpenoids (--- and -.-) in the aerosol and composited vegetation wax samples: (a) PP1; (d) MK2; (b) MB1; (e) MK3; (c) MK1; (f) vegetation wax, Carlon Creek.

whereas the aerosol samples contain equivalent or greater amounts of phytosterols than triterpenoids (Fig. 5). This indicates that triterpenoids may be less stable in aerosols than phytosterols, as proposed earlier (Simoneit 1989; Simoneit et al. 1988, 1991). Nevertheless, both phytosterols and triterpenoids can be used to confirm the plant wax component of the organic matter in aerosols.

#### Long-range transport

Terrestrial aerosols and associated organic tracers can be transported long distances over the oceans (Simoneit 1977, 1979; Gagosian et al. 1981). Data have been published for aerosols collected at a station on Ninety Mile Beach on the northwestern shore of the North Island of New Zealand (Gagosian et

al. 1987). This site is in the westerlies wind regime for the Southern Hemisphere and is located about 1500 km east of Southeastern Australia. It is of interest to check how well the distribution patterns of the *n*-alkanes and *n*-alkanols of the aerosols and composited wax from Australia match the New Zealand aerosols of Gagosian et al. (1987). This comparison makes many assumptions so that any match may be fortuitous and should be taken as a preliminary examination only. The Australian aerosols, taken near the coast, are assumed to be representative of a larger region of the continent, especially the deserts to the west. These aerosols were acquired in the years 1979-1981 during March, August, and September, and the New Zealand samples were taken in 1983 during May to September. We are comparing the same

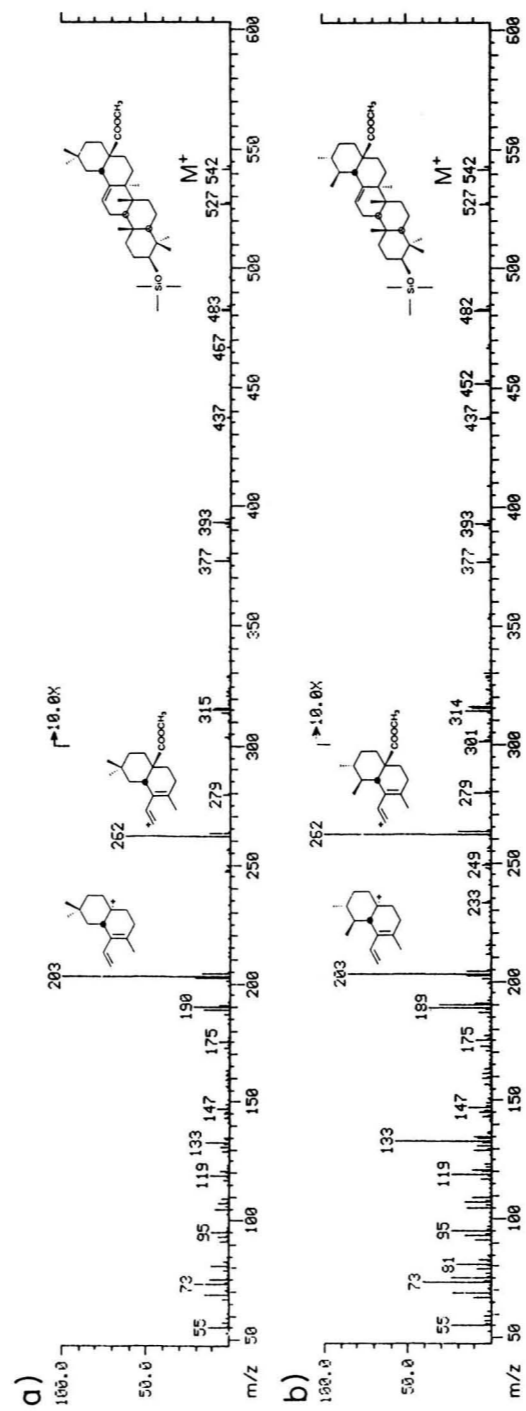


Fig. 6. Mass spectra of (a) methyl oleanolate trimethylsilyl ether and (b) methyl ursolate trimethylsilyl ether (examples from aerosol PP1).



season but not the same year. Nevertheless, samples NZAS-16 and NZAS-20 of Gagosian et al. (1987) fit best with these data and are therefore used for comparison. The anthropogenic component was subtracted from the n-alkanes as described above and the homolog distributions were subjected to the  $\chi^2$  test (Table 2). Both visual inspection and the  $\chi^2$  test

indicate the best fit of the composited vegetation wax with NZAS-16, and this New Zealand aerosol also matches best with aerosol MB1 and secondarily with MK2. NZAS-20, on the other hand, does not fit well with the vegetation wax nor as well with the Australian aerosols (best fit with MB1 and MK3, Table 2). NZAS-16 had a significant continental

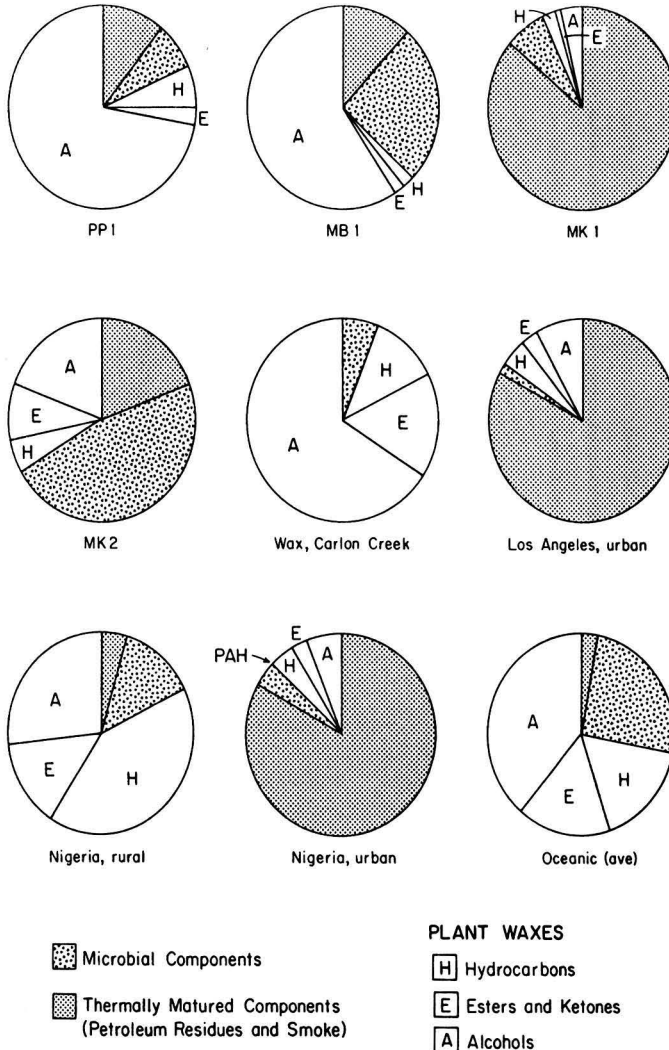


Fig. 7. Pie diagrams summarizing and comparing the partitioning of the lipids of the Australian aerosols and composited vegetation wax with other urban, rural and remote examples (unknown, polar materials are not included).

source component (Gagosian et al. 1987) although weaker than NZAS-20 and was suggested to derive from distant sources outside New Zealand. The isentropic air mass trajectories backward in time for sample NZAS-16 are across New Zealand and those for NZAS-20 graze southeastern Australia prior to transit to New Zealand (Gagosian et al. 1987). Hence, the mixture of terrestrial wax constituents of sample NZAS-20 includes source regions outside the southeast Australian area described here, and the good fit for NZAS-16 may indicate that the distant source of the plant lipids as suggested by Gagosian et al. (1987) is indeed in this region transgressed earlier in the trajectory. A comparison with similar data for aerosols over Cape Grim, Tasmania is not possible, because *n*-alkane concentrations reported there extend only to C<sub>28</sub> (Eichmann et al. 1980).

#### Intercomparison

The apportionment of the various lipid fractions of the aerosols to sources (Simoneit et al. 1988) and comparisons with vegetation wax and aerosols from other urban and rural areas are shown with pie diagrams in Fig. 7. The major identified parts of the lipids in the aerosols of the Blue Mountains (PP1 and MB1) are derived from higher plant wax and compare favorably with wax sampled from that area. Samples MB1 and MK2 have significant microbial lipid components analogous to the rural and/or oceanic examples. The anthropogenic constituents due to mainly petroleum residues and minor amounts of smoke are dominant for sample MK1 and significant for sample MK2. Even though the wind was from the west at Mt. Keira, the anthropogenic components may be derived from cyclonic air movement of coastal urban emissions. Urban constituents in the samples from the Blue Mountains (PP1 and MB1) are minor despite the close proximity of Sydney (~ 50 km to the east). The anthropogenic components especially for the Mt. Keira samples are analogous to those of other urban areas as, for example, Los Angeles and Jos or Ibadan in Nigeria.

#### CONCLUSIONS

The signatures of plant wax and anthropogenic molecular markers were used to determine the sources of aerosols collected in the Blue Mountains and SE coast of Australia. The results were compared to an extract of a composite sample of regional vegetation and aerosols collected in New Zealand by Gagosian et al. (1987). These aerosols were dominated by plant wax components for the most part, with one exception. The *n*-alkanes in MK1 contained more

anthropogenic components as determined by the parameters CPI, U:R, and the Carbon Number Maximum.

The signatures of the aerosols were comprised primarily of hydrocarbons, fatty acids and alcohols, with minor amounts of ketones and other molecular markers. Chi-square tests showed good fits between *n*-alkanes of the composited vegetation wax and the MB1 and MK3 aerosols. There was also a reasonable fit between the *n*-alkanes of these two samples and the New Zealand aerosols described by Gagosian et al. (1987). This demonstrated a reasonable first match between regional vegetation, local aerosols, and aerosols collected downwind. However, the alkanolic acid and alkanol fractions of the SE Australian aerosols did not correlate as well with either the wax sample nor the New Zealand aerosols.

In the distributions of molecular markers, phytosterols and triterpenoids dominated, sometimes contributing up to 25% of the alcohol fraction. Hydroxy acids such as oleanolic and ursolic acids were the major components of the triterpenoid fraction, with a lesser contribution from  $\alpha$ - and  $\beta$ -amyryn. Sesquiterpenoids and diterpanes were undetectable. The former may be absent in the aerosols due to their relatively higher volatility and the latter may be due to a lack of production by the local vegetation. Triterpenoids were prevalent in the molecular markers of the composited vegetation wax sample, whereas the reverse was true in the aerosols. This may be an indication of the lower stability of the triterpenoids.

*Acknowledgment* — We thank Mrs. Norma Carlon, Packsaddlers Pty. Ltd. and Mr. E.J. Hill for permission to sample, Mrs. E. Crisp for assistance with sampling, Ms. X. Chen for technical assistance and Mr. E. Ruth, Mr. R.N. Leif, and Ms. X. Chen for GC-MS data acquisition. We also thank the National Science Foundation, Atmospheric Research Section (Grants ATM 81-16622, ATM 81-18101, ATM-8509184, and ATM-8717988) for financial support.

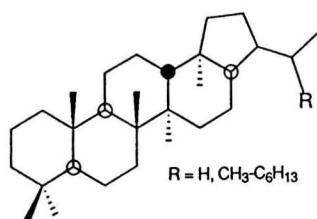
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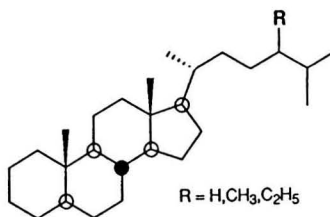
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## APPENDIX 1

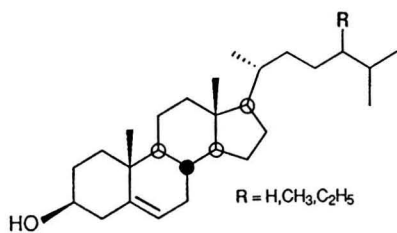
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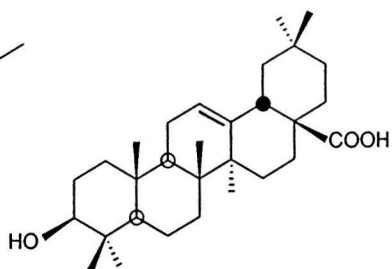
I. 17α(H)-Hopanes



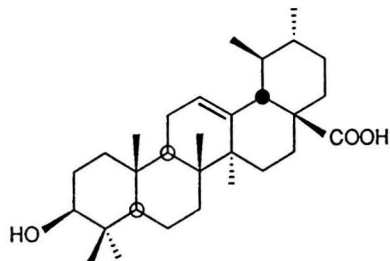
II. Steranes (ααα)



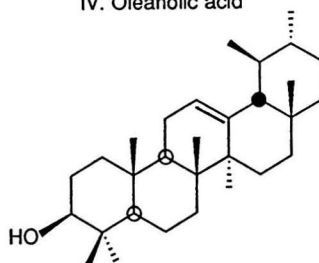
III. Phytosterols



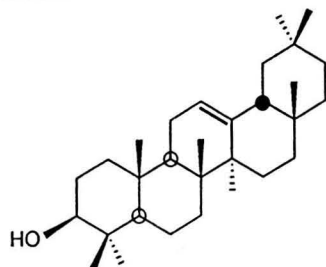
IV. Oleanolic acid



V. Ursolic acid



VI. α-Amyrin



VII. β-Amyrin



# ENRICHMENT FACTORS OF HEAVY METALS IN THE SOUTHERN BALTIC SURFACE SEDI- MENTS DATED WITH $^{210}\text{Pb}$ AND $^{137}\text{Cs}$

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*EI 9002-014M (Received 2 February 1990; accepted 25 December 1990)*

Eight samples of stratified bottom sediments (cores) from the Gdansk Basin, the Bornholm Deep, and the Arcona Deep (Southern Baltic) were collected. The rate of sediment accumulation amounting to 0.1-2.3 mm/y was established by means of the radioactive lead ( $^{210}\text{Pb}$ ) method and confirmed by  $^{137}\text{Cs}$  distribution. The measurements revealed an increase of some heavy metals concentrations in the surface sediments. The enrichment factors for Hg, Cu, Zn, Pb, Cd, Ni, Co, and Cr were found in the ranges of 4.7 - 4.9, 1.1 - 2.7, 1.1 - 2.5, 1.4 - 2.8, 1.0 - 2.2, 1.0, 1.0, and 1.0-1.2, respectively. An increase of metals inflow to sediments caused by anthropogenic factors, modified by oxidative-reductive conditions, is held responsible for the enrichment.

## INTRODUCTION

Two major groups of pollutants introduced into the environment are of special interest due to their influence on biological life in aquatic ecosystems: nutrients and biochemically resistant substances (Förstner and Wittman 1981). The former group may cause mass growth of algae, leading to oxygen depletion in the course of biochemical oxidation of organic matter being formed. The latter group, comprising, for example, polynuclear aromatic hydrocarbons (PAH), polychlorinated biphenyls (PCB), and heavy metals, may be toxic.

Heavy metals, unlike persistent organic chemicals, do not undergo transformation even over long periods of time. Moreover, they tend to be adsorbed on suspended matter and to accumulate in living organisms. Main migration routes of heavy metals in the environment are surface waters and the atmosphere. Metals brought to surface waters are even-

tually deposited to bottom sediments, which, under normal conditions, are considered to be a sink for natural and anthropogenic substances. Next, they can be accumulated by benthic fish and zoobenthos, thus penetrating the food chain. The accumulation rate depends, among other factors, on metal concentration in surface sediments (Förstner and Wittman 1981).

Bottom sediments always contain some concentrations of metals, due to natural pathways of the elements in the environment. Therefore, it is not the mere presence of heavy metals in the sediments, but the enrichment above the natural level that indicates anthropogenic sources of metals. The so-called anthropogenic enrichment factors, which are equal to a quotient of metal concentrations in surface (polluted) and subsurface (background) sediments, are often applied as a measure (Förstner and Wittman 1981; Pempkowiak and Widrowski 1988).

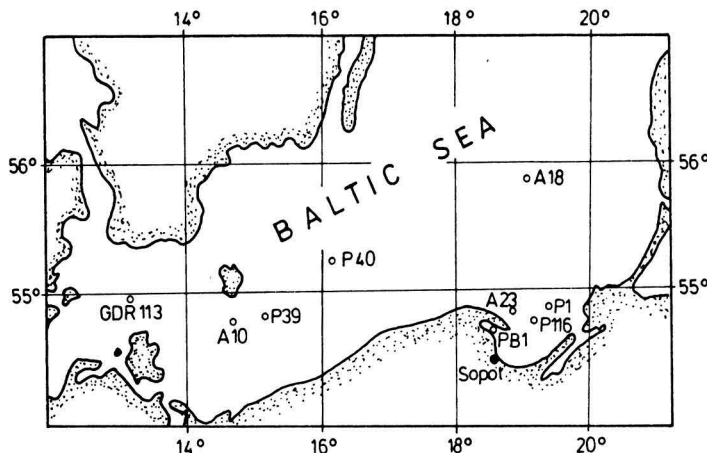


Fig. 1. Sampling sites of investigated sediment cores.

This paper presents the results of an investigation of heavy metals concentrations and the origin in dated sediment cores collected in the Southern Baltic. The age of the sediment layers in the cores was established using the  $^{210}\text{Pb}$  method, and confirmed by the  $^{137}\text{Cs}$  distribution. The profiles of heavy metals in sediments are elucidated on the basis of both, anthropogenic influence and redox conditions in the surface sediments.

## EXPERIMENTAL

Sediment cores were collected by means of a Niemistö type corer (Niemistö 1974) at locations indicated in Fig. 1. Immediately after collection, the cores were cut into slices 1 cm thick and deep frozen. The following analyses of collected material were carried out: moisture;  $^{210}\text{Pb}$  activity (through its granddaughter,  $^{210}\text{Po}$ , after wet digestion of sediment matrix with  $\text{HF} - \text{HC}_{10}_4$  deposition on silver plates from 0.5M HCl and  $\alpha$ -spectrometry);  $^{137}\text{Cs}$  activity (after  $\text{HF} - \text{HC}_{10}_4$  wet digestion, coprecipitation with ammonium molybdophosphate, ion separation of Cs from K, and  $\beta$ -counting using low background G-M counters); heavy metals Hg, Cd, Cu, Ni, Co, Cr, Pb, Zn, Mn, Fe (flame AAS using a Video 11E model spectrophotometer Thermo Jarell Ash, after wet digestion with  $\text{HF} - \text{HC}_{10}_4 - \text{HNO}_3$ ). With the same instrument Hg was determined, using the cold-vapour technique. The oxidation-reduction potentials were measured in selected samples immediately after

cutting the cores into slices. A probe composed of a Pt-electrode and a reference saturated calomel electrode (SCE) was connected to a type-517 pH-meter (Elwro Poland) working in the potential mode. Accumulation rates of sediments were calculated from  $^{210}\text{Pb}$  profiles in the cores according to mathematical models described earlier (Robins 1978; Widrowski and Pempkowiak 1986; Pempkowiak and Skiba 1988). Other analyses were carried out using x-ray and thermal analyses according to procedures described previously (Teszner and Pempkowiak 1986).

## RESULTS AND DISCUSSION

In Fig. 2 distributions of both  $^{137}\text{Cs}$  and  $^{210}\text{Pb}$  along selected cores are presented. They are typical of the three classes of profiles that are seen in distributions of the nuclides in the investigated cores. The  $^{210}\text{Pb}$  distributions can be explained in the following manner: intensive mixing (bioturbation, physical factors) in the uppermost layers causes the distribution of  $^{210}\text{Pb}$  activity to be similar to that found in the GDR 113 core; the lack of mixing leads to profiles resembling that in the P1 core; distributions of the type found in the P116 core are caused by a limited rate of mixing to a certain depth (Robins 1978; Pempkowiak and Skiba 1988).

Of the  $^{137}\text{Cs}$  profiles presented in Fig. 2, the lack of maximum concentrations, usually found a short distance below the sediment-water interface, is characteristic (Müller et al. 1980; McCall and Sørensen

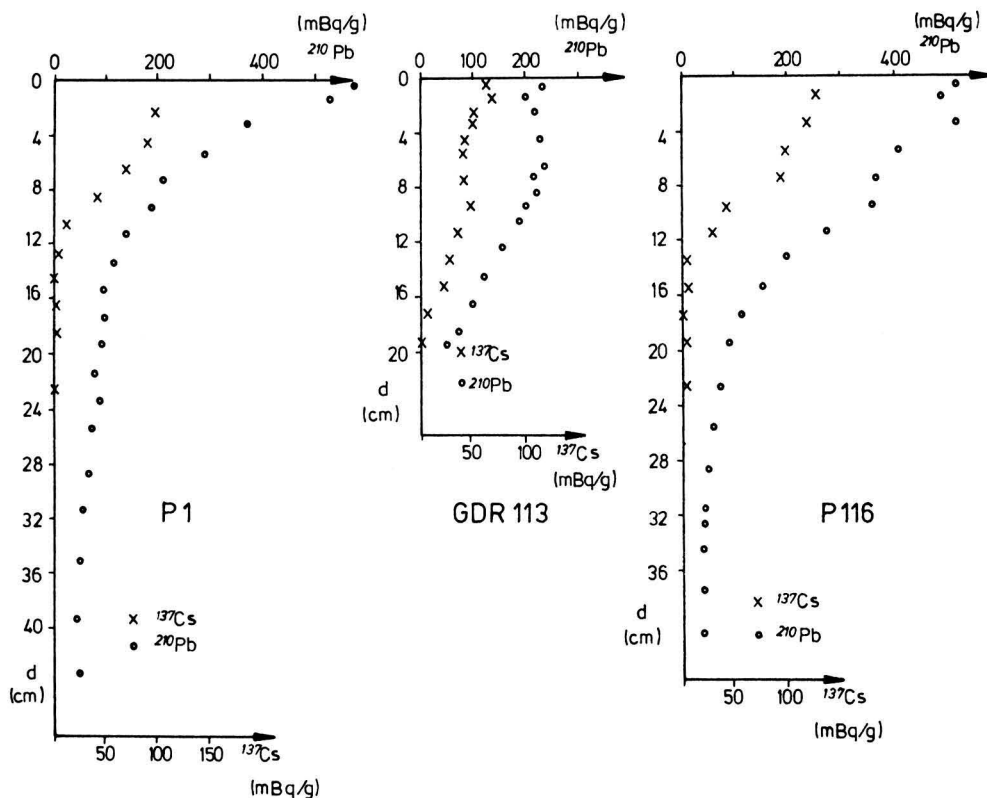


Fig. 2. Typical distributions of  $^{210}\text{Pb}$  and  $^{137}\text{Cs}$  activities in the investigated cores.

1984). Cesium-137 is one of several long-lived isotopes produced during the atmospheric testing of nuclear weapons. As there is no natural occurrence of  $^{137}\text{Cs}$ , the isotope was not present in the environment until the early 1950s. Its maximum occurrence coincides with the peak of testing activity in the early 1960s. Lack of maxima is most likely caused by surface mixing due to bioturbation. However, even in cores where no bioturbation is expected (P1, A23) no maxima are evident. Most likely, the increasing input of  $^{137}\text{Cs}$  from the North Sea, which in the Baltic Sea in the early 1980s exceeded the fallout of  $^{137}\text{Cs}$  by a factor of 1.8 (Pempkowiak and Skiba 1988), and the delayed maximum caused by river run-off (Müller et al. 1980, McCall and Sørensen 1984) could be responsible for the phenomenon.

In Table 1, data characterizing sedimentation regimes in the investigated cores are presented. They were derived from the  $^{210}\text{Pb}$  profiles using the constant rate of supply model or the mixing-constant

specific activity model (Robins 1978; Widrowski and Pempkowiak 1986). In sedimentation environments where mixing takes place, validation of sedimentation rates derived from  $^{210}\text{Pb}$  profiles is necessary (Robins 1978; Pempkowiak and Skiba 1988). For this purpose,  $^{137}\text{Cs}$  distributions are used, applicable to environments with both rapid and slow mixing (DeMaster et al. 1985). They were successfully applied previously in a number of coastal regions (DeMaster et al. 1985; McCall and Sørensen 1984; Wong and Moy 1984; Pempkowiak and Skiba 1988) and were also used in this investigation. On the basis of sedimentation rates and the mixing zone thickness, the expected depth of  $^{137}\text{Cs}$  occurrence was calculated. This was compared with the measured depth of  $^{137}\text{Cs}$ . A good agreement of calculated and measured depths of  $^{137}\text{Cs}$  abundance was found in most cores (P116, P1, GDR 113, A23). When no agreement was found, calculations were repeated as-



Table 1. Rates of sediment accumulation in the Baltic sediments based on  $^{210}\text{Pb}$  and  $^{137}\text{Cs}$  distributions in the sediment cores.

Sampling station	Mixing depth based on $^{210}\text{Pb}$	Mixing coefficient.	Sediment. rate	Accumul. rate	Depth of $^{137}\text{Cs}$ found	
	cm				$\text{cm}^2 \text{ s}^{-1}$	mm $\text{yr}^{-1}$
P1	3		1.95	0.051	10	12
GOR113	10		2.25	0.032	10	19
P39	10		0.47	0.018	12	18
	14*	10	0.38	0.014	16	18
P116	10	1	2.32	0.083	17	15
A23	2		2.08	0.062	9	11
A10	5	10	0.87	0.037	8	18
	12*	5	0.41	0.023	15	18
A17	8	5	1.45	0.073	12	20
	16*	1	0.71	0.030	19	20

\* readjusted to arrive at an agreement between the expected and found depth of  $^{137}\text{Cs}$  occurrence.

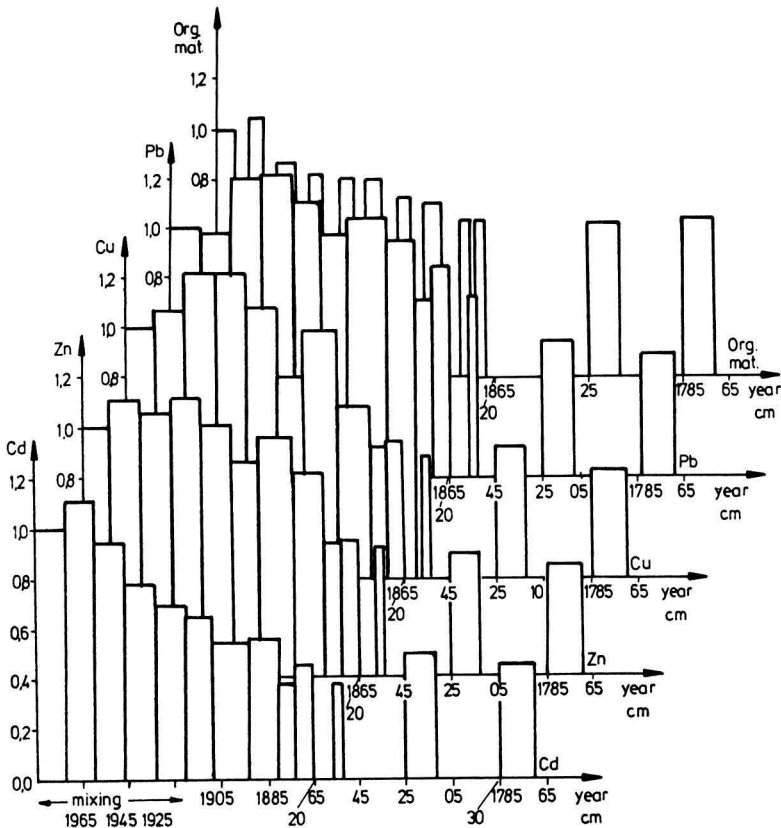


Fig. 3. Relative contents of Cd, Zn, Cu, Pb and organic matter (org. mat.) in successive layers of the P116 core versus the age and depth of the layers (Cd - 1.0 = 1.78  $\mu\text{g/g}$ , Zn - 1.0 = 183  $\mu\text{g/g}$ , Cu - 1.0 = 25.2  $\mu\text{g/g}$ , Pb - 1.0 = 110  $\mu\text{g/g}$ , org. mat. - 1.0 = 13.8%).

suming varying mixing depths until an agreement within 1-2 cm was reached (A10, P39, A17).

Data-characterizing sedimentation regimes (sedimentation rates, accumulation rates, mixing rates) can be used in studies concerning material balances and -the rate of diagenetic processes. In this study, they were used to date surface layers of sediments in order to evaluate the cause for sediment enrichment with metals. Dependencies between concentrations of selected metals in successive segments of the P116 core and the age of the segments are presented in Figs. 3 and 4. It is obvious that the concentrations of mercury, lead, zinc, copper, cadmium, and possibly chromium are greater in the upper section of the core. A distinct increase is observed in sediments deposited during the last 60-70 y. In the case of lead and zinc, the increase started as early as 100 y ago. Concentrations of nickel and cobalt do not change appreciably. Profiles of iron and manganese are irregular, indicating the dependence on other factors, possibly oxidative-reductive conditions (Pempkowiak and Widrowski 1988; Pempkowiak and Widrowski 1990).

Enrichment factors of metals in surface sediments are presented in Table 2. Background concentrations were determined on the basis of  $^{210}\text{Pb}$  profiles. In layers where the so-called supported (Robins 1978) or background activity of  $^{210}\text{Pb}$  occurs, they were assumed to originate from natural sources only (background concentrations). The age of the background layers is estimated to be 200-250 y in areas with surface mixing and about 150 y in sediments with no mixing. Enrichment of surface sediments with heavy metals can be attributed to natural geochemical factors and/or anthropogenic influence (Förstner and Wittman 1981; Brüggmann et al. 1982). The latter explanation is supported by the lack of Ni and Co enrichment. Geochemical factors would lead to the increase of concentration of all investigated metals, including Ni and Co (Förstner and Wittman 1981). Therefore, the enrichments revealed in the Baltic sediments must be attributed to anthropogenic factors. The conclusion is also supported by time sequence of the increase in the metals occurrence. It started in the second part of the 19th century when a rapid increase of heavy metals usage took place (Förstner and Wit-

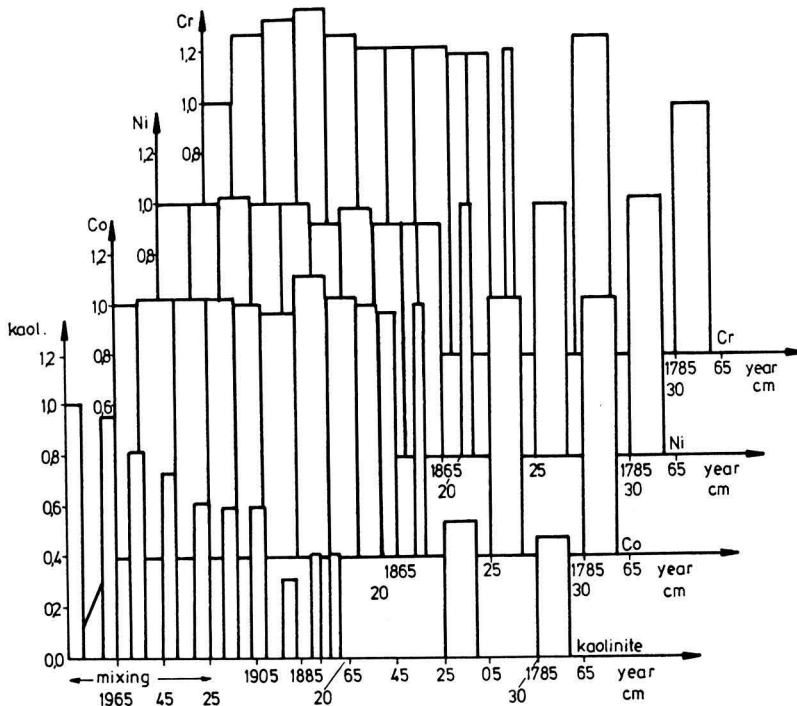


Fig. 4. Relative contents of Co, Ni, Cr, and kaolinite in successive layers of the P116 core versus the age and depth of the layers (Co - 1.0 = 17.0  $\mu\text{g/g}$ , Ni - 1.0 = 51.0  $\mu\text{g/g}$ , Cr - 1.0 = 37.5  $\mu\text{g/g}$ , kaolinite - 1.0 = 27.5%).

Table 2. Enrichment factors of Hg, Cd, Pb, Cu, Zn, Ni, Co, and Cr in the uppermost (2-4 cm) and the background (as indicated) layers of investigated cores.

Station	Average concentration 2-4 cm ( $\mu\text{g/g}$ )								Background layer		Enrichment factor*							
	Hg	Cu	Zn	Pb	Cd	Ni	Co	Cr	cm	year	Hg	Cu	Zn	Pb	Cd	Ni	Co	Cr
GDR113	-	19.0	186	97.8	1.10	47.5	19.5	38.8	-	-								
P39	-	33.9	212	93.8	0.95	50.5	19.8	35.5	18	1650	-	1.4	1.5	2.3	1.3	1.0	1.1	1.0
P40	-	21.3	176	87.5	0.70	49.0	19.5	29.1	7	1790	-	1.3	1.3	1.6	0.9	1.2	1.0	1.1
P1	1.94	30.2	233	103	1.51	52.0	23.7	24.4	32	1790	4.7	1.8	2.5	2.3	2.1	1.0	1.1	1.1
P116	0.75	29.9	199	132	1.78	51.5	17.5	49.0	32	1730	4.9	2.4	2.1	2.4	2.1	1.0	1.1	1.1
A17	0.74	22.5	151	84.5	0.97	47.4	18.4	34.5	34	1740	3.1	1.9	1.8	2.0	1.6	1.1	1.0	1.1

- not determined

\* Enrichment factor = concentration in 2 - 4 cm layer / concentration in background layer

man 1981). The same phenomenon has been observed in sediments of the Japan Sea (Hoshika and Takayuki 1985), the Adriatic Sea (Battiston et al. 1985), the Atlantic and the Pacific Oceans off the coast of the United States (McCall and Størensen 1984; Wong and Moy 1984; Shroeder 1985) and the North Sea (Förstner and Wittman 1981). Szefer and Skwarzec (1988) reported the following enrichment factors of metals in the Southern Baltic: 1.5 (Zn), 1.8 (Pb), 1.4 (Cu), 1.5 (Cd), 1.0 (Co), and 1.0 (Ni). Enrichment factors presented in Table 2 differ from those reported by Szefer and Skwarzec (1988). This can be attributed partly to the fact that these factors were calculated with the background concentrations of metals established only intuitively. Surface concentrations were defined differentially as well (Szefer and Skwarzec 1988). Profiles of trace metals in surface sediments found in this study exhibit decreases of concentrations at the water-sediment boundary or directly beneath it (Fig. 3). This must be caused by natural factors since the load of pollutants introduced into the Baltic Sea has not decreased recently (Bojanowski 1987). Therefore, the enrichment factors presented in Table 2 were calculated assuming layers of sediments with the greatest concentrations of metals (usually 2-4 cm). The enrichment factors presented in Table 2 agree well with the author's earlier findings (Widrowski and Pempkowiak 1986; Pempkowiak and Widrowski 1988; Pempkowiak and Ciszewski 1990).

Decrease of metal concentrations in the uppermost layers of sediments can be caused by increasing in-

flow of neutral sedimentary material (increasing sedimentation rates) within the last twenty years, degradation of organic matter, and by natural processes of migration of metals (Pempkowiak and Ciszewski 1990). The moisture content in the uppermost layers of sediments of the cores is 90%, enabling diffusion of metal ions. The results of measurements of redox potential in some of the cores presented in Table 3 support the last explanation.

Oxidation-reduction potentials are a measure of the quality and activity of reactions involving a change in oxidation states of elements (Seki 1982). Manganese (II) and iron(II) ions, as well as organic matter, act as electron donors in marine environments. In the absence of oxygen nitrates, iron(III), manganese(IV), and sulfates act as electron acceptors (Goth and Yamashita 1966). Theoretically, acceptors undergo reduction in the order of decreasing potentials given by the Nernst Equation. For example, nitrates can be reduced only when all oxygen is reduced. In practice, the sediment redox system rarely approaches a state of equilibrium due to changes in quality and quantity of organic substances. Moreover, usually oxidation and reduction involve several acceptors at the same time. Thus, mixed potentials are formed. It is impossible to assign such potentials to the activity of particular oxidative forms (Goth and Yamashita 1966). However, they allow for the evaluation of the intensity of redox processes in sediments. Reduction of oxygen takes place within the range of potentials from +0.60 to +0.50 V, reduction of nitrates from +0.50

Table 3. Oxidation-reduction potential in surface layers of two sediment cores collected at PB1 station.

Date of sampling	Layer	Organic matter*	Potential
	cm	%	V
6.07.1988	0-2	1.51	-0.13
	3-5	0.48	-0.07
	6-8	0.33	+0.05
4.09.1988	0-2	0.62	-0.06
	3-5	0.46	-0.01
	6-8	0.28	+0.04

\* Organic matter content in the uppermost layer decreased due to rapid oxidation of huge quantities of dead *Pylaiella* deposited to sediment after May's blooming period (Pempkowiak and Ciszewski 1990).

to +0.20 V, Mn(IV→II) from +0.40 to +0.20 V, Fe(III→II) from +0.30 to +0.10 V, and sulfates from 0 to -0.15 V.

The potentials observed in the sediments are in the range from +0.13 to -0.13 V. Anoxic processes must take place in sediments, therefore involving all kinds of inorganic substances, among them manganese(IV). The reduction of Mn(IV) to Mn(II) causes disappearance of manganese dioxide precipitate. This increases the agility of heavy metal ions to be adsorbed on solids in surface layers of sediments and decreases their concentrations due to diffusion. A depletion of heavy metals in surface sediments in many areas (Förstner and Wittman 1981), including the Baltic Sea (Pempkowiak and Ciszewski 1990), has been shown to be caused by this phenomenon.

## CONCLUSIONS

Enrichment of surface sediments in the Southern Baltic Sea with zinc, mercury, copper, lead, and cadmium, but not with chromium, nickel, and cobalt is observed. Dating of the sediments by means of  $^{210}\text{Pb}$  and  $^{137}\text{Cs}$  reveals that the enrichment started about one hundred years ago. These findings point to anthropogenic factors as the cause for the phenomenon. There is a slight but detectable decrease of concentrations of trace metals as well as manganese in the uppermost layers of sediments. This is caused by a change of oxidative conditions in water to reduced conditions in sediments. The change causes reduction of man-

ganese (IV→II), increased agility of metal ions, and their diffusion resulting in decreased concentrations.

*Acknowledgment* — This work was financially supported by the Polish Academy of Sciences Grant C.P.B.P. 03.10.2.

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## MERCURY IN SEAFOOD: A PRELIMINARY RISK ASSESSMENT FOR KUWAITI CONSUMERS

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*EI 9004-057M (Received 13 April 1990; accepted 19 January 1991)*

Fish is a significant source of high quality protein in Kuwait, whose population was believed to be at relatively high risk from hazards associated with the ingestion of mercury. In an effort to determine if a health hazard exists among fish consumers in Kuwait, fish consumption and mercury residues in fish from Kuwait are evaluated in this study. The concentration levels in edible portions of Kuwaiti fish ranged from not detected to a record maximum of 1.57 mg/kg. The most unfortunate group of consumers preferring to eat the highest polluted fish will be exposed to a total intake of 8.1  $\mu\text{g}$  Hg/d. To assess the risk of mercury to Kuwaiti fish consumers, a safety factor of 10 was incorporated in the minimum level currently known to be associated with adverse effects (300  $\mu\text{g}/\text{d}\cdot\text{person}$ ). Kuwait fish consumption data do not indicate any cause for concern from methylmercury poisoning for the average Kuwaiti consumer. At the current, relatively low fish consumption rate the acceptable daily intake has never been exceeded even at the worst, extreme consumption scenarios. All of the fish and shrimp consumers in Kuwait could easily double their current intake and still remain below the mercury acceptable daily intake of 30  $\mu\text{g}$  Hg/d-person.

### INTRODUCTION

Kuwait is blessed with having a good resource of high quality protein harvested from the Gulf. A good number of fish and shrimp species is of significant commercial value. Extensive research on the potential contamination of seafood resources in Kuwait indicated that mercury is the only contaminant to exceed the USFDA (1987) regulatory levels in few cases. None of the other trace contaminants including benzo-a-pyrene at the very low detected levels (Morel et al. 1989) represent any threat to the public health in Kuwait. Recently, there has been some concern

about the hazards associated with mercury ingestion that occur from the consumption of contaminated fish in Kuwait. These hazards consist primarily of damage to the central nervous system, specifically cerebral and cerebellar lesions, and deleterious effects on the developing fetus (USFDA 1974).

According to Wallace et al. (1971), all forms of mercury entering the aquatic environment, either as a result of human activities or from natural geologic sources, may be converted to methylmercury or other organic mercury compounds, which can be concentrated by fish and other aquatic species. The mercury bioaccumulation in fish is due to its relatively long half-life and was estimated by Stopford and Goldwater (1975) to be two years. Fish may concentrate mercury either directly through the water or through components of the food chain.

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The hazardous nature of mercury residue in fish can be best illustrated by the Minamata Bay (1953-1960) and Niigata (1965) poisoning episodes in Japan (Takizawa 1979). A more dramatic poisoning episode occurred in Iraq (1971-1972) as a result of ingestion of home-made bread prepared from wheat seed that had been treated with alkylmercury fungicide intended for planting (Clarkson et al. 1976).

Acute poisoning episodes result in dramatic effects. However, subclinical effects of mercury on particular subgroups of population are also of public health importance and constitute a threat that is more difficult to evaluate. Populations in which fish is a significant source of high quality protein (such as in Kuwait), can be at higher risk to dangers associated with the ingestion of mercury.

In an effort to determine if a health hazard exists among fish consumers in Kuwait, fish consumption and mercury residues in fish from Kuwait are evaluated in this study. The risk assessment approach implemented by Tollefson (1989) has been adopted in this assessment.

Fish consumption data were obtained from the annual Fisheries Statistics Bulletin (1985-1988) published by the Ministry of Planning in Kuwait. The most recent surveys of mercury in Kuwaiti commercial fish were obtained from those generated at the Kuwait Institute for Scientific Research (KISR) by Zorba and Litherathy (1987), Shunbo et al. (1986), Shunbo et al. (1985), Anderlini et al. (1982), and Zorba et al. (1981). These exposure data of mercury residue are sufficiently thorough and valid to ensure a high degree of certainty in the results of this assessment (Zorba and Litherathy 1987).

The estimated exposure levels experienced by the earlier victims of mercury poisoning epidemics and the pharmacokinetics of mercury in humans were used to estimate body levels.

To assess the risk of mercury to Kuwaiti fish consumers, a safety factor of 10 was incorporated in the minimum level currently known to be associated with adverse effects. The risk to populations known to consume large quantities of fish or to have special fish species preference, was also evaluated. The approach of this assessment of risk for Kuwaiti consumers from the ingestion of mercury in fish is consistent with that advocated by the National Research Council (1983).

## RISK EVALUATION

Any chemical can be toxic to humans if enough is ingested. The U.S. Food and Drug Administration (USFDA 1987) has set an action level for methylmer-

cury in fish and seafood at 1.0 mg/kg fresh weight. Due to the difference in consumption patterns of various groups of population, most governments have tried to place a limit on the daily intake of methylmercury for the protection of public health. As defined by Margolin (1980), the acceptable daily intake (ADI) is the amount of a food additive or residue that, in the opinion of a regulatory agency, can be safely consumed daily over a long period of time. ADI is expressed in terms of mg of residue per kg of body weight of the consumer. Since the form of mercury in edible fish is almost entirely methylmercury (Westoo 1966), all calculations will be based on such a fact.

Based on the survey of relevant references (FAO/WHO 1972; Clarkson et al. 1973; Skerfving 1974; Clarkson 1977), a threshold value at which symptoms of toxicity associated with methylmercury are first noticeable would be reached with a minimum daily intake of 300  $\mu$ g mercury present as methylmercury in the diet of a person weighing 70 kg. Below this range of intake, no symptoms can be seen and dose-response relation cannot be established. However, because of the potential hypersusceptibility of the fetus (Marsh et al. 1980), it would be prudent to lower the minimum daily intake of methylmercury. In order to cover for this area of uncertainty, a factor of 10 will be used to provide a sufficient margin of safety. Such a safety factor has been shown to be satisfactory (USFDA 1974). Thus, the maximum tolerable level for the public is estimated to be  $300/10 = 30$   $\mu$ g methylmercury daily in the diet. This would adequately protect prenatal life and populations chronically exposed to methylmercury (Tollefson 1989).

## EXPOSURE ASSESSMENT IN KUWAIT

Our assessment will be centered on the Hg intake from fish consumption in Kuwait. According to Simpson (1974), food sources other than fish and shellfish contribute insignificantly to the total amount of methylmercury intake in humans.

To determine the intake of fish and shrimp in Kuwait, fish market statistics were examined to provide data on average seafood consumption patterns by species. In this assessment, six species of shrimp were considered. The selected species represent more than 70% of the total fish consumption in Kuwait. The consumption patterns of commercially developed shrimp and fish species are given in Table 1. The projected number of consumers is derived from the Central Statistical Office (1986) census. An estimated correction factor of 0.8 was used to account for popula-

Table 1. Monthly consumption of seafood in Kuwait (1981-1988 average).

Shrimp and Fish Species	Monthly Consumption (gm)				
	Mean	±	Std.	Range	
				Minimum	Maximum
Shrimp	42.0	±	20.0	20.3	- 86.0
Zobaigy (Pampus Argenteus)	42.0	±	6.1	33.1	- 55.0
Suboor (Hilsa Lilisha)	11.6	±	2.4	7.4	- 14.4
Nagroor (Pomadasy's Argenteus)	16.2	±	2.0	12.8	- 20.0
Hamoor (Epinephelus Tauvina)	28.6	±	6.3	21.5	- 39.7
Newaiby (Otolithes Argenteus)	8.1	±	2.3	4.8	- 13.1
Hamrah (Lutjanus Coccineus)	10.0	±	5.9	3.1	- 19.0
All Other Species	67.6	±	10.7	52.7	- 67.8
Kuwait Total Consumption	225.0	±	36.0	174.0	- 297.0
USA Total Consumption*	607.2		--	--	--

\* Source: Tollefson (1989).

tion sectors that do not consume fish such as new-borns and low-income classes.

According to Anderlini et al. (1982), the major contributor of mercury pollution in the Kuwait marine environment is the chloralkali plant located in the Northern sector of Kuwait City near the Shuaikh harbor.

Several studies were conducted in Kuwait to determine the level of mercury in edible seafood (Zorba and Litherathy 1987; Shunbo et al. 1986; Shunbo et al. 1985; Anderlini et al. 1982; Zorba et al. 1981). Most of the reported values were much lower than the USFDA action level of 1.0 mg/kg. The concentration levels in edible portions of the fish ranged from not detected to a record maximum of 1.57 mg/kg. Table 2 contains collected data showing the mercury levels that existed in samples of domestic fish and shrimp as measured in Kuwait. The highest ever reported level of 1.57 mg/kg in fresh tissue of hamrah (*Lutjanus Coccineus*) was due to the exceptional long age of this particular sample estimated at 18 y. The average concentration of the same species was always less than 0.4 mg/kg in three separate studies.

Hamoor (*Epinephelus Tauvina*) exhibited one extreme value of 1.075 mg/kg. However, the mean was always below the USFDA 1.0 mg/kg action level. Fig. 1 illustrates the fact that the average concentration of mercury in all fish species has never exceeded the USFDA limit. The consumption pattern illustrated in Fig. 1 shows the fortunate fact that the consumption of low contaminated shrimp and fish is much higher than the consumption of highly contaminated fish. This, in turn, will obviously reduce the health risk associated with fish consumption in Kuwait.

#### RISK ASSESSMENT

In order to define the risk assessment associated with the ingestion of seafood contaminated with mercury in Kuwait, several scenarios were used. These covered not only risks associated with average consumption, but also all the potential extremes in consumption patterns and the likely preference of highly contaminated fish by certain groups of consumers.



Table 2. Mercury levels in commercially developed seafood (mg/kg fresh edible tissues) in Kuwait.

Species	No. of Samples	Reference	Mean	±	Std.	Range
Shrimp	62	a	0.045	±	0.014	NA
Zobaigy	28	b	0.038	±	0.024	ND - 0.097
Suboor	10	c	0.015	±	0.002	0.012 - 0.017
Nagroor	8	b	0.210	±	0.010	0.200 - 0.225
	31	a	0.075		NA	NA
Hamoor	29	b	0.430	±	0.220	0.150 - 1.075
	20	c	0.510	±	0.080	0.150 - 0.775
	10	a	0.700		NA	NA
Newaiby	30	b	0.320	±	0.190	0.100 - 0.900
	24	a	0.125		NA	NA
Hamrah	30	b	0.305	±	0.390	0.025 - 1.575
	70	a	0.375		NA	NA
	70	d	0.410		NA	NA
Other Species		*	0.270			

a Anderlini et al., 1982  
 b Zorba and Litherathy, 1987  
 c Shunbo et al., 1985  
 d Zorba et al., 1981

NA Not Available  
 ND Not Detected  
 \* Average of Tested Species

### Scenario 1: Risk to average consumers

This scenario was based on the fact that the average Kuwaiti citizen will follow the average consumption pattern as reported without any deviation in the amount or diversity of shrimp and fish. This is the most realistic scenario to be considered in our evaluation. The average Kuwaiti consuming an average amount of fish will have a total individual daily intake of mercury calculated as shown in Table 3.

The result indicates that the level of exposure of an average Kuwaiti is around 5% of the acceptable daily intake of 30 µg/d · person as proposed by Tellefson (1989). The majority of the fish consumers in Kuwait can increase their current daily intake by more than 19-fold and still remain below the mercury ADI.

### Scenario 2: Risk to higher-than-average consumers

In this scenario, the potential risk associated with the higher than the average consumption of fish was assessed. In this case four standard deviations will

be added to the average of each consumed species. The total daily intake of mercury in such a case is 2.9 µg Hg/d · person, still below the ADI of 30 µg/d.

### Scenario 3: Risk to group of preference to highly polluted species

In this scenario, we assumed that a certain population group has a special preference to the most polluted fish species. The average total intake will be consumed entirely as hamoor. In this case, the total daily mercury intake was found to be 4.1 µg Hg/d · person. If this group was eating more fish than the average by four standard deviations, then the total daily Hg intake would be 6.8 µg Hg/d · person, still way below the 30 µg Hg/d · person ADI. Again, if another group is unfortunate and will eat only fish with the highest reported mercury level in their particularly favored hamoor, then the total intake would be 8.1 µg Hg/d · person. It would be necessary for this group to increase their currently favored polluted

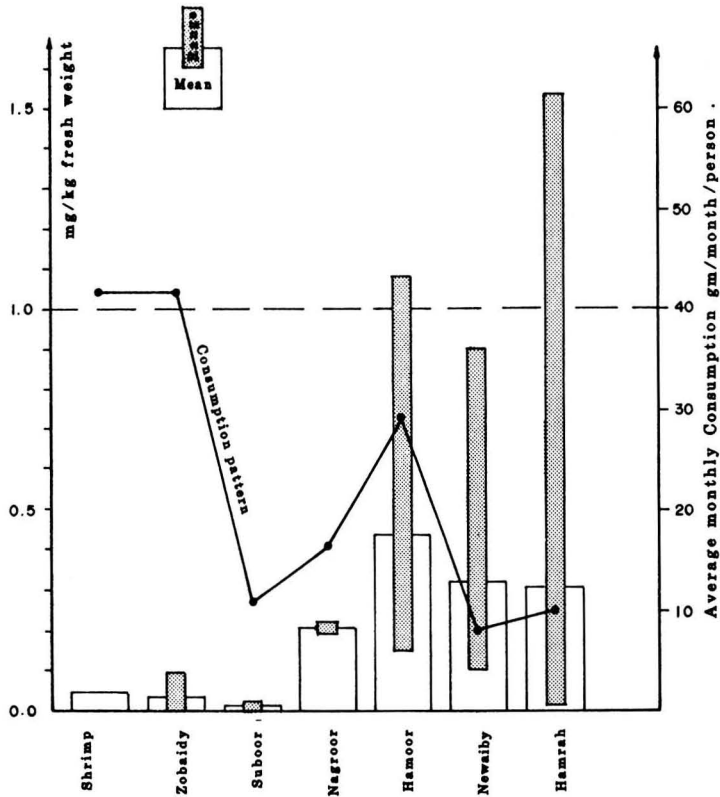


Fig. 1. Consumption pattern of different shrimp and fish species and their relative average and range of mercury concentration in Kuwait.

Table 3. Calculation of the average daily intake of mercury in seafood by Kuwaiti citizens.

Seafood Species	Daily Intake g/d	Concentration of Hg mg/kg	Total Hg $\mu$ g/d
Shrimp	1.40	0.045	0.0630
Zobaigy	1.40	0.038	0.0532
Suboor	0.38	0.015	0.0057
Nagroor	0.54	0.143	0.0772
Hamoor	0.95	0.550	0.5225
Newaiby	0.27	0.222	0.0599
Hamrah	0.33	0.363	0.1198
All Others	2.25	0.270	0.6070
Total $\mu$ g/d.person average intake			1.5080

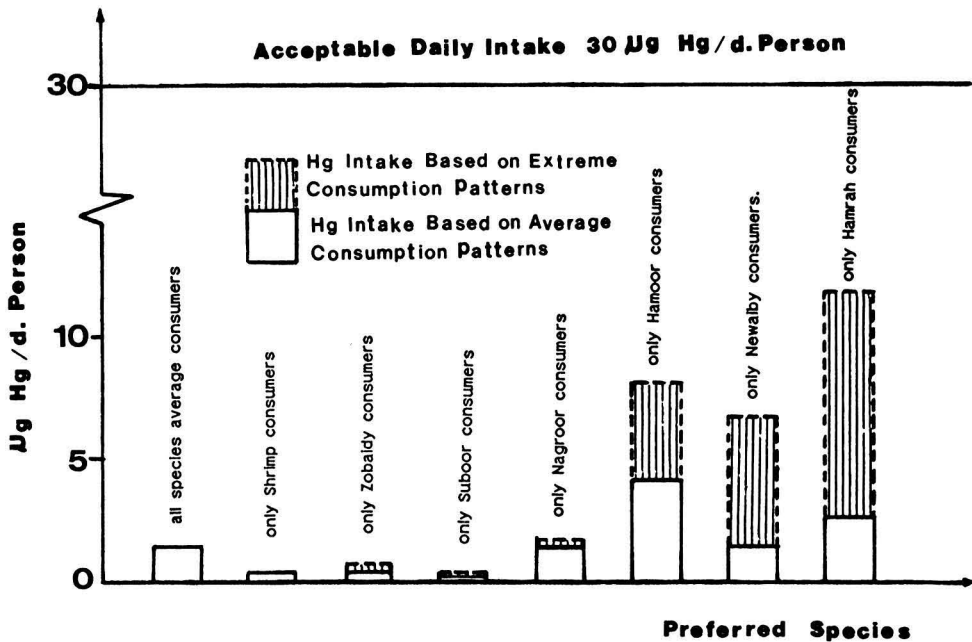


Fig. 2. Mercury daily intake for average consumer group (eating all species), and particularly selective consumer groups (eating one selected species).

fish consumption by 3.7 times to exceed the  $30 \mu\text{g Hg/d} \cdot \text{person}$  ADI. If a particular group has four times the average daily consumption but would be eating only hamoor, then their total Hg intake would be  $13.2 \mu\text{g Hg/d} \cdot \text{person}$ . This is still below the  $30 \mu\text{g Hg/d} \cdot \text{person}$  ADI limit.

Such consumption patterns seem very unlikely; however, they were included to provide answers for any potential argument. Figure 2 illustrates the risk associated with selective consumption as compared to average consumption.

## DISCUSSION

Kuwait fish consumption data do not indicate any cause for concern from methylmercury poisoning for the average Kuwaiti citizen. Despite the fact that very few fish samples have shown mercury levels higher than the USFDA limit, the average concentration is much lower than this limit. At the current relatively low fish consumption rate in Kuwait, the ADI has never been exceeded even at the worst, extreme consumption scenarios. All of the fish and shrimp consumers in Kuwait could easily double their current intake and still remain below the mercury

ADI of  $30 \mu\text{g Hg/day} \cdot \text{person}$ . In brief, it is perfectly safe to state that Kuwaiti fish at the current rate of consumption is totally safe, and no consumption restrictions should be considered at this stage. However, continuous monitoring for fish quality and control of industrial pollution discharges into the Gulf are highly recommended.

*Acknowledgment* — Appreciation is expressed to the Marine Pollution Group at the Kuwait Institute for Scientific Research, Environmental and Earth Sciences Department for making this study possible. The research was sponsored by the Kuwait Institute for Scientific Research.

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# A PRELIMINARY INVESTIGATION INTO THE SPECIATION OF TRACE METALS IN SEDIMENTS FROM THE GULF OF PARIA OFF THE COAST OF TRINIDAD

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*EI 9002-017M (Received 10 February 1990; accepted 10 January 1991)*

Various extractants and extraction procedures were utilized in the speciation of Fe, Mn, Cr, Cu, Ni, Pb, and Cd in several types of tropical marine sediments during a baseline study. Iron apparently existed as amorphous and poorly crystallized compounds while Mn existed mainly as oxides. Unlike copper, the metals Pb, Cr, and Ni appeared to be associated with the organic phases in most of the sediments. Copper and cadmium appeared to be loosely bound.

## INTRODUCTION

The island of Trinidad is located just north of the South American continent (61-61½° W longitude; 10½° N latitude) in the vicinity of the mouth of the Orinoco River (Fig. 1). Recently, the government of Trinidad initiated an industrial expansion program to exploit more efficiently its natural gas reserves (Hall and Chang-Yen 1986). The area, earmarked for the major part of the proposed increased industrial activity, is located along the coast bordering the Gulf of Paria (Fig. 1) which lies on a shallow continental shelf. The contiguous bay is a fishing ground which contributes to the economy of the island. The continued exploitation of this coastal zone is in keeping with a policy being generally adopted by a number of tropical countries (Dean et al. 1986). An investigation, intended to acquire baseline information and to monitor the expected increase in trace metal levels (Lamotte 1983; Grosjean 1983) from industrial effluents, was started just prior to the industrial expan-

sion. The area studied was located in the Gulf of Paria between 12 km and 17 km north of the southern peninsula and extended out to sea as far as the one fathom line. A preliminary investigation was also carried out because of the recognized importance of such studies (Tessler et al. 1979; Lake et al. 1984; Nelson and Donkin 1985; Gibson and Farmer 1986). The sediments were fractionated on the basis of grain size in order to ascertain with what size particles the bioavailable metals were associated (Lake et al. 1984; Carruesco and Lapaquellerie 1985; Thompson et al. 1986).

## MATERIALS AND METHODS

Sediments from 12 sampling sites (Fig. 1) were classified by grain-size analysis (Buchanan 1981). Based on this classification, the sediments were placed in the following categories: mud, sandy mud, clay, sand, and silty sand. A sample of each sediment type

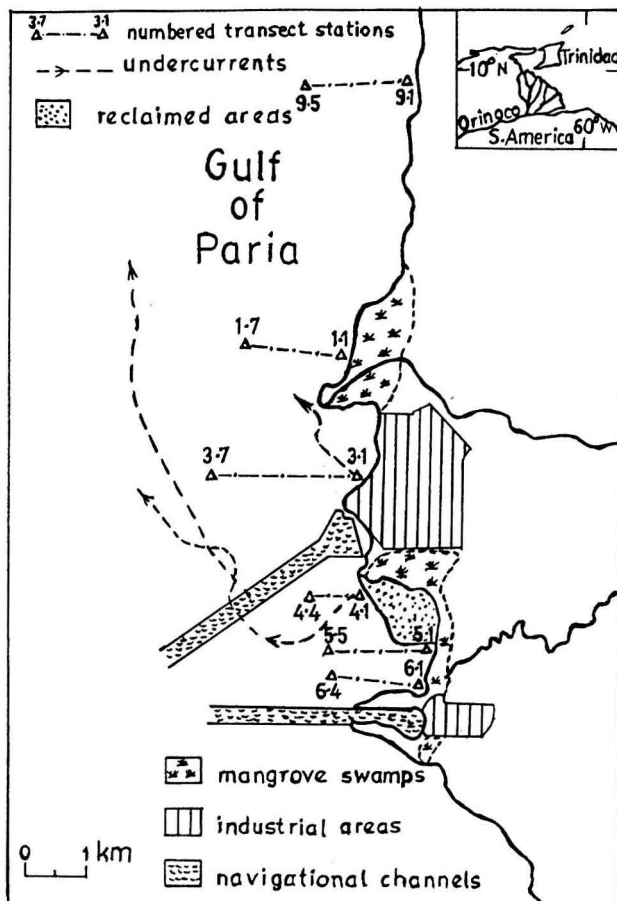


Fig. 1. Map of project area.

was fractionated and subsamples from each fraction subjected to each extractant/extraction procedure.

The sediment samples were first sieved into three fractions: 106-250  $\mu\text{m}$ , 53-106  $\mu\text{m}$  and <53  $\mu\text{m}$  after large shells and stones were physically removed. The sieves were superimposed on each other in order of increasing pore size with the one of the smallest pore size at the bottom. Each sediment was washed through the assembly of sieves with distilled water. Gentle stirring with a plastic spatula was sometimes necessary to facilitate the movement of sediment through the sieves. After settling, the supernatant was removed from each fraction by decantation. This was followed by drying at  $\approx 60^\circ\text{C}$  for 24 h.

#### Extraction procedures

The extractants hydroxylamine hydrochloride ( $\text{NH}_2\text{OH} \cdot \text{HCl}$ ; pH 2), 30% hydrogen peroxide ( $\text{H}_2\text{O}_2$ ; pH 2.5), and a mixture of ammonium oxalate and oxalic acid ( $(\text{NH}_4)_2\text{C}_2\text{O}_4/\text{H}_2\text{C}_2\text{O}_4$ ; pH3) employed in this study were suggested in the "Standard Extraction Method" for the speciation of particulate metals proposed by Salomons and Forstner (1980). Extraction with acidified  $\text{NH}_2\text{OH} \cdot \text{HCl}$  is supposed to remove manganese compounds, exchangeable cations, carbonate-bound metals, and in general easily reducible species. The additional acid-reducible extractive step involving  $(\text{NH}_4)_2\text{C}_2\text{O}_4/\text{H}_2\text{C}_2\text{O}_4$ , suggested by Salomons and Forstner for sediments with

high Fe concentration, was included since it was thought that the presence of an iron and steel complex near to the sampling sites may have resulted in elevated Fe sediment levels. Extraction with acidified 30%  $\text{H}_2\text{O}_2$  is supposed to remove oxidizable and organically bound species while extraction with dilute hydrochloric acid (0.5 M) is supposed to distinguish between detrital and non-detrital metal. Concentrated  $\text{HNO}_3$  digestion is one of the "strong" methods used by Van Valin and Morse (1982) which are designed to attack all solid phases.

Portions of each sediment fraction were digested separately using the following reagents: concentrated  $\text{HNO}_3$ ; 0.5 M HCl; 0.1 M  $\text{NH}_2\text{OH} \cdot \text{HCl}$  (pH 2); and  $(\text{NH}_4)_2\text{C}_2\text{O}_4/\text{H}_2\text{C}_2\text{O}_4$  (pH 3) sequentially; and finally 30%  $\text{H}_2\text{O}_2$  (pH 2.5).

All reagents were either of analytical grade or made using analytical grade reagents obtained from the British Drug Houses, Poole England. All analyses were done in duplicate and suitable blanks were run in each case.

The digestion times and sediment to extractant ratios were optimized for each extractant/extraction procedure using samples of each type of sediment. The times and ratios used in the actual speciation study were therefore assumed to have yielded the maximum extractable metal levels from the samples analyzed.

The type of filter paper used (Whatman No. 541) was checked to ensure that it did not contribute detectable levels of any of the metals studied to the filtrates.

#### *Digestion with concentrated nitric acid*

Approximately 2 g of each dried sediment fraction was digested with 15 mL of concentrated  $\text{HNO}_3$  in a 25 mL PTFE digestion bomb (R. A. Scientific, London, England) for 2 h at 100° C. After cooling, the mixture was filtered with Whatman No. 541 filter paper and the metal levels determined directly on the filtrate by atomic absorption spectrophotometry using a Pye Unicam SP 9 spectrophotometer with automatic background correction.

#### *Digestion with 0.5 M hydrochloric acid*

Approximately 1.5 g of each of the dried sediment fractions was shaken for 12 h with 30 mL of 0.5 M HCl in stoppered flasks on a mechanical shaker. The mixtures were then filtered and the filtrates analyzed as described before.

#### *Sequential procedure*

Approximately 1.5 g of each of the dried sediment fractions was shaken for 12 h with 30 mL of 0.1 M  $\text{NH}_2\text{OH} \cdot \text{HCl}$  (pH 2) in stoppered flasks on a mechanical shaker. The mixtures were then filtered and the filtrates analyzed as described before. The residues were then air-dried and 1.5 g quantities shaken with 30 mL volumes of  $(\text{NH}_4)_2\text{C}_2\text{O}_4/\text{H}_2\text{C}_2\text{O}_4$  for 12 h. The filtrates from these extracts were analyzed in a similar manner to those obtained in the first step of the sequential procedure.

#### *Digestion with 30% hydrogen peroxide*

Aliquots (20 mL) of 30%  $\text{H}_2\text{O}_2$  were added in small quantities at a time to  $\approx 1.5$  g portions of each dried sediment fraction until the initial frothing subsided. The mixtures were then shaken for  $\approx 12$  h in loosely stoppered flasks. The rest of the procedure is similar to those described before.

#### *Precision of extraction methods and detection limits*

The precision of the different sediment extraction methods was determined by the relative standard deviations for replicate determinations on a typical sediment sample. The data are presented in Table 1.

The detection limits for the seven metals analyzed by atomic absorption spectrophotometry using the Pye Unicam SP 9 spectrophotometer are given in Table 2.

## RESULTS AND DISCUSSION

Concentrated  $\text{HNO}_3$  generally extracted higher quantities of metal than the 0.5 M HCl, regardless of the particle size of the fractions extracted (Table 3). For Fe, the 0.5 M HCl almost invariably extracted about half the quantities extracted by the concentrated  $\text{HNO}_3$ . This was assumed to be due to possible attack on the residual phase by the concentrated  $\text{HNO}_3$ . The 0.5 M HCl apparently only removed amorphous or poorly crystallized compounds from the non-clay sediments while the concentrated  $\text{HNO}_3$  attacked more crystalline compounds in addition to the types removed by the HCl. This suggestion is supported by the fact that the sequential extraction scheme involving  $\text{H}_2\text{NOH} \cdot \text{HCl}$  (which removes predominantly amorphous Fe-oxyhydrates) and the  $(\text{NH}_4)_2\text{C}_2\text{O}_4/\text{H}_2\text{C}_2\text{O}_4$  buffer (which removes poorly crystallized Fe-oxyhydrates) (Salomons and Forstner 1980) produced total Fe levels higher than those extracted by the 0.5 M HCl but less than those extracted by concentrated  $\text{HNO}_3$  (Table 3). In the case of the clay, Fe levels from the 0.5 M HCl digests were consistently higher



Table 1. Precision of different sediment extraction methods (n = 5).

MEAN CONCENTRATIONS ( $\mu\text{g g}^{-1}$ ) $\pm$ STD. DEVIATION <sup>a</sup>					
FOR DIFFERENT EXTRACTANTS					
METAL	CONC. HNO <sub>3</sub>	0.5 M HCl	30% H <sub>2</sub> O <sub>2</sub>	NH <sub>2</sub> OH.HCl	BUFFER
Fe	25430 $\pm$ 300	11020 $\pm$ 370	10417 $\pm$ 70	3641 $\pm$ 16	7501 $\pm$ 96
Cu	13.13 $\pm$ 0.24	14.1 $\pm$ 1.2	4.62 $\pm$ 0.19	b	8.43 $\pm$ 0.54
Cr	14.30 $\pm$ 1.00	7.33 $\pm$ 0.27	5.62 $\pm$ 0.32	-	2.53 $\pm$ 0.34
Mn	386.6 $\pm$ 7.1	244.4 $\pm$ 6.0	172.2 $\pm$ 1.5	122.4 $\pm$ 1.1	66.8 $\pm$ 1.8
Ni	16.56 $\pm$ 0.85	6.58 $\pm$ 0.45	5.09 $\pm$ 0.56	-	4.34 $\pm$ 0.76
Pb	26.07 $\pm$ 0.46	12.66 $\pm$ 0.66	5.46 $\pm$ 0.93	-	-
Cd	0.38 $\pm$ 0.10	0.47 $\pm$ 0.05	-	0.76 $\pm$ 0.00	-

a - estimated standard deviation                      b - not detected

(about twice as high) than those obtained from the sequential scheme for all three fractions (Table 3).

Table 2. Detection limits for the metals.

Metal	Detection Limit ( $\mu\text{g g}^{-1}$ )
Fe	0.08
Mn	0.008
Cu	0.008
Cr	0.02
Ni	0.016
Pb	0.04
Cd	0.004

Hydrochloric acid has been shown to attack clay lattices (Van Valin and Morse 1982) which are known to contain significant quantities of crystalline material.

Statistical analysis showed that there is no significant difference at the 95% confidence level between corresponding Fe concentrations obtained with 0.5 M HCl and 30% H<sub>2</sub>O<sub>2</sub> when all the sediment fractions were considered. This suggests that the amorphous and poorly crystallized Fe compounds are organically bound. Hydrogen peroxide is known to dissolve organic phases such and humic and fulvic acids (Salomons and Forstner 1980).

In the sandy mud, sand, and silty sand, especially in the fractions with the larger particles, the NH<sub>2</sub>OH · HCl digests yielded Mn levels comparable to those obtained with 0.5 M HCl and concentrated HNO<sub>3</sub> (Table 4). This was interpreted to mean that the Mn in the sediments existed mainly as MnO<sub>2</sub>. Hydroxylamine hydrochloride is known to dissolve the MnO<sub>2</sub> phase (Agemian and Chau 1976). For the 106-250  $\mu\text{m}$  fractions of these sediment types, NH<sub>2</sub>OH · HCl extracted between 67 and 95% with a combined average of 82% of the quantities extracted by 0.5 M HCl. For the 53-106  $\mu\text{m}$  fractions, it

Table 3. Fe Levels ( $\mu\text{g g}^{-1}$ ) obtained with different extractants.

SEDIMENT TYPE	FRACTION GRAIN SIZE ( $\mu\text{m}$ )	CONC. $\text{HNO}_3$	0.5 M HCl	30% $\text{H}_2\text{O}_2$	$\text{NH}_2\text{OH}\cdot\text{HCl}/$ BUFFER
SANDY MUD	106-250	18662	8718	8274	12025
	53-106	7495	4645	5435	3869
	<53	24904	10417	12243	11611
SAND	106-250	12052	6542	6334	9283
	53-106	8250	5316	4819	7351
	<53	37033	13656	13006	21709
MUD	106-250	15750	5947	7072	10524
	53-106	14289	7853	9424	2144
	<53	27591	12296	15728	12493
CLAY	106-250	33684	18722	17801	14455
	53-106	18573	10686	10712	9698
	<53	27723	13616	11147	10015
SILTY SAND	106-250	17892	4685	3024	12940
	53-106	12556	4627	2306	7840
	<53	24599	9808	8238	7447

extracted between 78 and 219% with a combined average of 133% of the quantities extracted by 0.5 M HCl (Table 4). With respect to the concentrated  $\text{HNO}_3$ , the  $\text{NH}_2\text{OH}\cdot\text{HCl}$  extracted between 63 and 88% with a combined average of 74% for the 106 - 250  $\mu\text{m}$  fractions, while for the 53 and 106  $\mu\text{m}$  fractions, it extracted between 88 and 97%, with a combined average of 91% (Table 4). For some of

the mud and clay fractions, the  $\text{NH}_2\text{OH}\cdot\text{HCl}$  had low extraction efficiencies relative to the 0.5 M HCl and concentrated  $\text{HNO}_3$ , possibly reflecting its inability to remove lattice-bound Mn which is more easily extractable by the HCl and  $\text{HNO}_3$ . Both 0.5 M HCl and concentrated  $\text{HNO}_3$  have been shown to attack silicate lattices. Van Valin and Morse (1982) found about a 4% Al release from certain sediments

Table 4. Mn Levels ( $\mu\text{g g}^{-1}$ ) obtained with different extractants.

SEDIMENT TYPE	FRACTION GRAIN SIZE ( $\mu\text{m}$ )	CONC.	0.5 M	30%	NH <sub>2</sub> OH.HCl/ BUFFER	
		HNO <sub>3</sub>	HCl	H <sub>2</sub> O <sub>2</sub>	NH <sub>2</sub> OH.HCl	BUFFER
SANDY MUD	106-250	233	200	174	168	207
	53-106	117	100	94	103	103
	<53	444	434	426	297	399
SAND	106-250	128	119	105	80	117
	53-106	94	106	90	83	102
	<53	370	302	260	337	485
MUD	106-250	166	130	121	93	143
	53-106	139	120	113	54	54
	<53	276	246	232	193	247
CLAY	106-250	328	329	370	173	257
	53-106	196	178	155	126	161
	<53	294	295	224	156	221
SILTY SAND	106-250	278	259	193	246	285
	53-106	231	102	190	223	237
	<53	449	527	442	355	423

they extracted with 0.5 M HCl. Aluminium release can be used as a measure of attack on clay lattices or aluminosilicate structures. Bradshaw et al. also found that dilute HCl attacked layered silicates.

For a number of fractions, the sequential scheme NH<sub>2</sub>OH · HCl followed by (NH<sub>4</sub>)<sub>2</sub>C<sub>2</sub>O<sub>4</sub>/H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> extracted Mn levels comparable to those extracted by the 0.5 M HCl. The HCl-extractable Mn from these fractions can therefore be categorized as readily to moderately reducible. This might be considered as

further evidence that Mn exists mainly as manganese oxides in the sediments studied.

Manganese oxides are labile forms of Mn which should be readily acid soluble. This can account for the comparable Mn levels extracted with 0.5 M HCl and concentrated HNO<sub>3</sub>.

Copper appears not to be associated with the organic phase in most of the fractions analyzed since their H<sub>2</sub>O<sub>2</sub> extracts did not contain detectable quantities of Cu (Table 5). In the mud and clay samples,

Table 5. Cu Levels ( $\mu\text{g g}^{-1}$ ) obtained with different extractants.

SEDIMENT TYPE	FRACTION GRAIN SIZE ( $\mu\text{m}$ )	CONC. $\text{HNO}_3$	0.5 M HCl	30% $\text{H}_2\text{O}_2$	$\text{NH}_2\text{OH}\cdot\text{HCl}$
SANDY MUD	106-250	2.31	1.94	-	1.93
	53-106	3.43	2.80	-	3.29
	<53	11.00	10.90	5.25	-
SAND	106-250	1.60	1.42	-	-
	53-106	1.33	1.28	-	0.80
	<53	15.21	12.72	-	-
MUD	106-250	9.35	11.06	5.02	2.20
	53-106	7.81	6.85	-	3.75
	<53	23.70	21.92	18.67	4.03
CLAY	106-250	8.98	9.07	5.11	0.70
	53-106	7.21	5.66	-	0.91
	<53	17.77	15.31	8.89	-
SILTY SAND	106-250	5.08	2.21	-	2.08
	53-106	5.62	3.44	-	2.35
	<53	13.30	9.60	6.00	-

there appeared to be some association of Cu with the organic phase. Copper species are known to require acidic extractants for their decomposition (Agemian and Chau 1976). The  $\text{NH}_2\text{OH}\cdot\text{HCl}$  is not sufficiently acidic to effect their decomposition resulting in markedly lower levels in the  $\text{NH}_2\text{OH}\cdot\text{HCl}$  extracts than the 0.5 M HCl and concentrated  $\text{HNO}_3$  extracts. The levels extracted by the 0.5 M HCl and concentrated  $\text{HNO}_3$  are comparable (Table 5) suggesting that the Cu is loosely bound in the sediments since

the respective digestions were done under vastly different conditions.

Lead was almost completely absent from the easily and moderately reducible phases. None of the  $\text{H}_2\text{NOH}\cdot\text{HCl}$  extracts contained detectable quantities (Table 6). However, Pb appeared to be associated with the organic phase in all fractions of the clay and in the <52  $\mu\text{m}$  fractions of the other sediment types except the sand (Table 6). Lead apparently exists mainly as inorganic species with the

Table 6. Pb Levels ( $\mu\text{g g}^{-1}$ ) obtained with different extractants.

SEDIMENT TYPE	FRACTION GRAIN SIZE ( $\mu\text{m}$ )	CONC. $\text{HNO}_3$	0.5 M HCl	30% $\text{H}_2\text{O}_2$	$\text{NH}_2\text{OH.HCl}$	BUFFER
SANDY MUD	106-250	4.36	-	-	-	-
	53-106	-	-	-	-	-
	<53	13.33	18.72	11.56	-	2.90
SAND	106-250	4.32	1.41	-	-	-
	53-106	-	4.43	-	-	-
	<53	20.82	30.90	-	-	-
MUD	106-250	-	2.78	-	-	-
	53-106	6.65	8.54	-	-	-
	<53	15.53	19.67	10.57	-	5.40
CLAY	106-250	13.31	12.65	8.80	-	-
	53-106	8.97	11.51	5.31	-	-
	<53	17.77	18.80	11.97	-	-
SILTY SAND	106-250	6.66	8.03	-	-	-
	53-106	6.61	6.28	-	-	-
	<53	15.62	14.86	8.23	-	-

possibility of an association with the organic phase in the clay and the <53  $\mu\text{m}$  fractions.

When all the fractions were considered, there was no significant difference at the 95% confidence level between the concentrations extracted with 0.5 M HCl and concentrated  $\text{HNO}_3$  for Ni, Cr, and Cd (Tables 7-9). This suggests that these three metals are also loosely held. The acid-extractable Cr and Ni appears to be organically bound since there is no significant

difference between the levels extracted with 0.5 M HCl and 30%  $\text{H}_2\text{O}_2$  (Tables 7 and 8).

The results of this investigation suggest that the metals studied exist in mobile forms in the Gulf of Paria. This could be problematic if there is an accumulation of these metals in the area because of the increased industrial activity there. In a recently conducted monitoring programme, the highest metal levels were found in sediments close to an area with

Table 7. Ni Levels ( $\mu\text{g g}^{-1}$ ) obtained with different extractants.

SEDIMENT TYPE	FRACTION GRAIN SIZE ( $\mu\text{m}$ )	CONC.	0.5 M	30%
		$\text{HNO}_3$	HCl	$\text{H}_2\text{O}_2$
SANDY MUD	106-250	6.21	6.15	6.14
	53-106	5.41	3.31	3.50
	<53	13.66	4.72	7.58
SAND	106-250	4.66	5.94	7.62
	53-106	4.62	5.09	5.85
	<53	18.13	13.77	16.66
MUD	106-250	6.13	4.90	5.95
	53-106	4.99	5.00	6.00
	<53	14.87	12.23	8.65
CLAY	106-250	9.98	9.99	8.27
	53-106	5.81	12.04	4.25
	<53	13.28	10.68	6.67
SILTY SAND	106-250	-	4.15	-
	53-106	-	2.38	-
	<53	11.64	8.79	4.39

already established industries (Hall and Chang-Yen 1986). The Gulf is shallow and is already subjected to a number of stressed conditions (Kenny 1974). During the hot tropical dry season water temperatures greater than  $30^\circ\text{C}$  are common. The situation is aggravated by the discharge of hot water used for cooling purposes by industries on the nearby estate. In addition, there is an annual heavy sediment discharge from the Orinoco River. Thus large increases in the levels

of trace metals would introduce additional stress in the Gulf from which fish, mussels and other filter feeders are extracted for human consumption.

A more comprehensive speciation study can now be attempted in order to acquire information on sediment geochemistry and to more positively identify the metallic species that would be potentially most dangerous.

Table 8. Cr Levels ( $\mu\text{g g}^{-1}$ ) obtained with different extractants.

SEDIMENT TYPE	FRACTION GRAIN SIZE ( $\mu\text{m}$ )	CONC. $\text{HNO}_3$	0.5 M HCl	30% $\text{H}_2\text{O}_2$
SANDY MUD	106-250	2.85	4.28	5.45
	53-106	2.25	2.26	2.33
	<53	10.00	7.27	7.38
SAND	106-250	3.33	3.68	3.91
	53-106	2.81	3.76	3.77
	<53	12.67	11.80	12.15
MUD	106-250	4.48	4.48	5.86
	53-106	7.81	5.98	6.46
	<53	10.00	10.68	10.76
CLAY	106-250	3.33	7.62	5.90
	53-106	1.16	3.15	5.58
	<53	7.80	9.33	8.21
SILTY SAND	106-250	-	2.48	2.31
	53-106	-	2.45	1.49
	<53	4.49	4.32	4.91

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Table 9. Cd Levels ( $\mu\text{g g}^{-1}$ ) obtained with different extractants.

SEDIMENT TYPE	FRACTION GRAIN SIZE ( $\mu\text{m}$ )	CONC. $\text{HNO}_3$	0.5 M HCl	30% $\text{H}_2\text{O}_2$	$\text{NH}_2\text{OH.HCl}$
SANDY MUD	106-250	0.45	1.49	0.89	0.46
	53-106	-	0.17	-	-
	<53	2.90	3.06	3.01	2.66
SAND	106-250	-	-	-	-
	53-106	0.45	-	-	-
	<53	-	0.14	-	-
MUD	106-250	0.60	0.70	-	0.40
	53-106	0.50	0.57	-	-
	<53	0.96	0.84	0.74	0.86
CLAY	106-250	-	0.40	-	0.15
	53-106	0.25	0.55	-	-
	<53	1.21	-	-	-
SILTY SAND	106-250	0.25	-	-	-
	53-106	-	-	-	-
	<53	0.50	0.54	-	0.55

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# NATIONAL SURVEY ON INDOOR RADON IN SPAIN

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*EI 9008-180M (Received 9 August 1990; accepted 4 February 1991)*

A national survey on indoor radon levels in Spain has been carried out by measuring the radon concentration in 1555 randomly chosen houses. Measurements were performed during the winter season of 1988 with complementary measurements in the winter of 1989. Radon in air was determined using modified alpha-scintillation cells under specified conditions in the sampling collection and nuclear track detectors in selected houses. The distribution of indoor radon levels has been found to be approximately log-normal with a geometric mean of  $41.1 \text{ Bq} \cdot \text{m}^{-3}$  and a standard deviation of 3.0. The highest value of the radon concentration found was  $15\,400 \text{ Bq} \cdot \text{m}^{-3}$ . In about 4% of the houses, the radon concentration was found to be in excess of the recently recommended value of  $400 \text{ Bq} \cdot \text{m}^{-3}$ , suggested by the Commission of the European Communities (CEC). Elevated indoor levels were found to be more prevalent in the west and northwest than in the rest of the country. Also shown in this paper is an evaluation of the median effective dose equivalent to the individual in Spanish houses for different regions.

## INTRODUCTION

Radon was first discovered as a product of radium decay in 1900 by Dorn (Dorn 1900). In air, it was first detected by Elster and Geitel in 1901 (Elster and Geitel 1901). Now, it is generally accepted that inhalation of radon progeny led to the increased incidence of lung cancer in underground miners (NRC 1989). These observations, along with measurements of significant radon concentrations in some buildings throughout several countries, have raised concerns over the possibility of a related risk of lung cancer to the public (UNSCEAR 1988; ICRP 1987).

The interest in this main source of natural radiation has initiated, especially in the developed countries, an important number of national surveys in order to evaluate the average radon levels in houses and locate the areas with a potential risk derived from the radon exposure (CEC 1990; Nazaroff and Nero 1988). The objectives of the Spanish national survey on natural radiation included in this paper are:

- 1) To study the distribution of indoor radon in Spanish houses.
- 2) To determine the correlation between factors such as geological nature of the ground, construction design, and household characteristics and the indoor radon measured.
- 3) To assess the dose to the population from the presence of radon and radon progeny in the houses.

## NATIONAL SURVEY DESIGN

The principal sampling strategy in the survey had been to select houses for radon measurements on a population-weighted random basis, taking also the different geologic areas of the country into account.

Figure 1 shows a map of Spain with its different regions and the 55 places selected corresponding for each of them to an average of 30 houses tested. Resulting from this selection, a total of slightly over 1500 houses have been analyzed in the radon survey. For each of these, the occupants were asked to fill

out a questionnaire, giving information on the conditions related to the presence of radon in a house: type and age of the house, building material, and heating and ventilation systems.

For the radon analysis, air was sampled into a 1L Lucite cell developed in our laboratory as a modified design of the original Lucas cell (Lucas 1957). The inside walls of the cell were lined with ZnS(Ag) coated mylar, but the main difference from the traditional one is the ability to open the cell after use by removing the bottom. This modification enables cleaning of the cell if necessary by replacing the ZnS(Ag) sheet, without flushing the cell with clean air or nitrogen, and makes the cell reusable for many times. We checked the cell for leaks by pressurization and by comparing the decay of radon in the cell to the expected, theoretical behavior of radon. In both cases, no leakage was detected.

Previous studies dealt with options for different cell volumes and positions of the ZnS(Ag) sheets (CEC 1988). For practical reasons, standard cells of 1L capacity were chosen with a sensitivity of 3 cpm/pCi. The background of this kind of cell ranged from

0.7 to 1.3 cpm, with counting times of 20 to 30 min, and the resulting lower limit of detection of around  $10 \text{ Bq} \cdot \text{m}^{-3}$ .

The survey was made during the winter period and the sample was collected in the first hours of the morning. This took into account the seasonal and diurnal variation of the radon concentration and provided agreement between the instantaneous measurements with the cells and the time-averaged values. Under these conditions and from data derived from integrated measurements employing passive etched track detectors (Terradex, USA and NRPB, UK) in the same houses, no significant differences were found between the results obtained by the two techniques (Quindos et al. 1990).

## RESULTS AND DISCUSSION

Figure 2 shows the log-normal distribution of indoor radon concentrations in the 1555 houses investigated. Geometric-mean and geometric-standard deviation, as well as the range and number of measurements for each region of Spain, are shown in

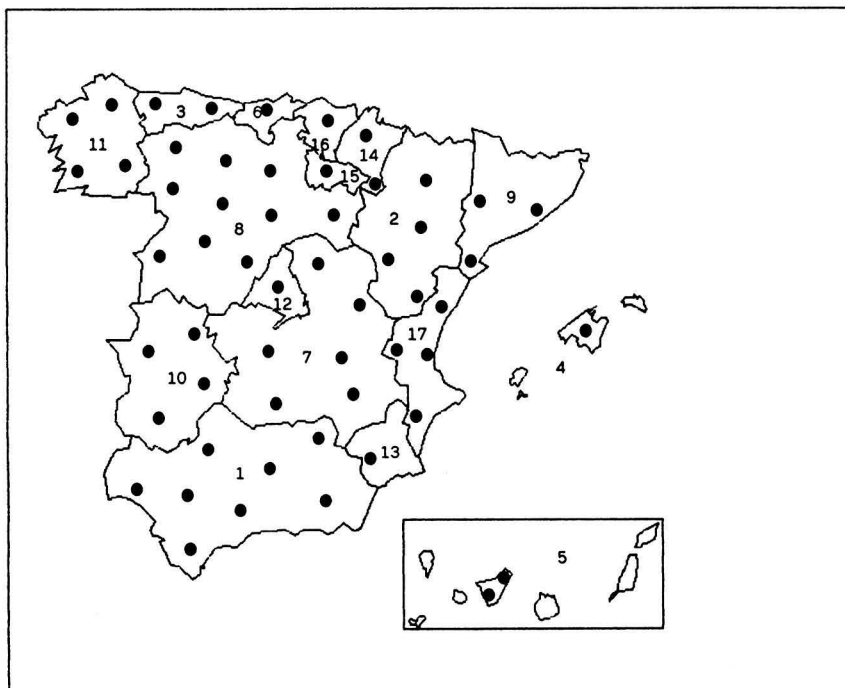


Fig. 1. Geographical distribution of the different regions in Spain, and location of sampling points in the measurement of indoor radon.

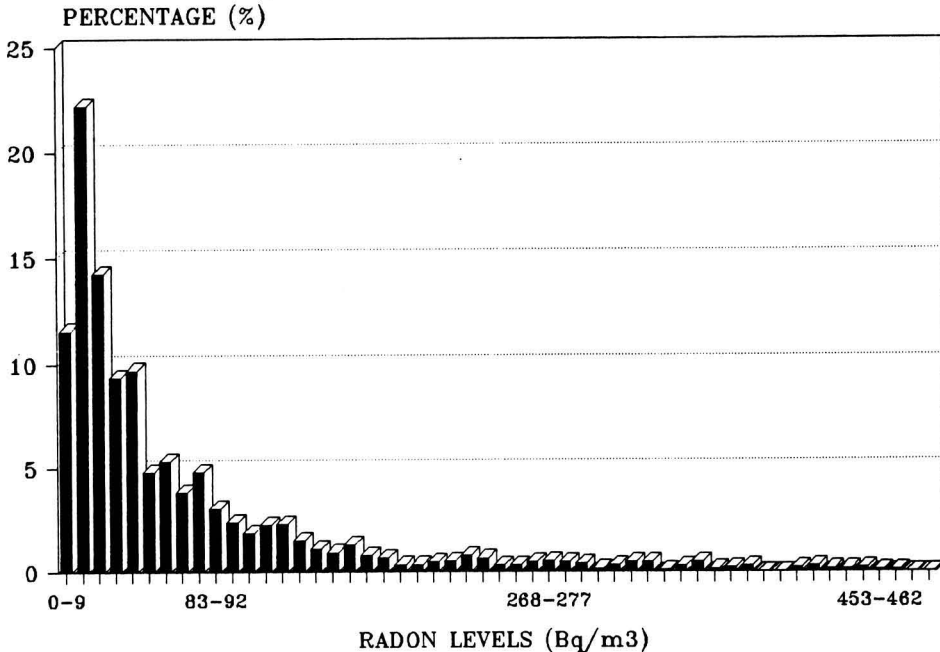


Fig. 2. Log-normal distribution of indoor-radon measurements.

Table 1. The median value was  $41.1 \text{ Bq} \cdot \text{m}^{-3}$  which is similar to that in other countries (APCA 1986). On a regional basis, the median value ranged from  $17.6 \text{ Bq} \cdot \text{m}^{-3}$  in Pais Valenciano to  $117.6 \text{ Bq} \cdot \text{m}^{-3}$  in Galicia. This fact is related to the soil being the primary source of indoor radon, because both areas are typical of non-granitic and granitic areas, respectively.

Figure 3 shows the percentage of houses that fall within certain radon concentrations. About 13% of the houses have levels above the EPA recommended action level and 4% of them above  $400 \text{ Bq} \cdot \text{m}^{-3}$ , as reported by the CEC for existing buildings. Nevertheless, this last percentage increases to 10% when we analyze the data from the granitic area of Galicia and, in general, the west area of the country, along the border of Portugal.

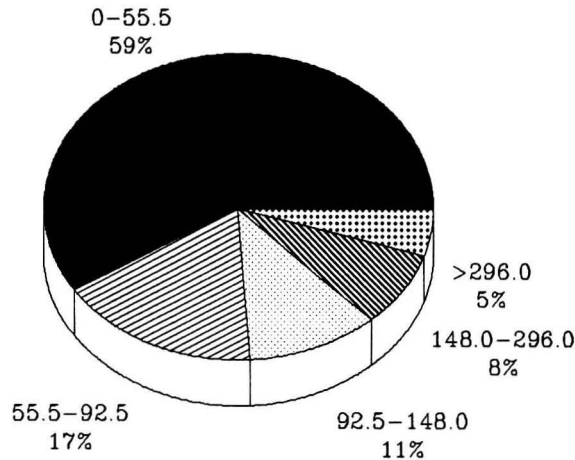
No significant differences ( $p < 95\%$ ) have been found between indoor radon levels for the parameters referred to before, as age of the building, type of construction, ventilation and heating systems, or living habits of the occupants. On the other hand, a significant difference was detected as a function of the

building materials. Figure 4 shows the cumulative frequency distribution of radon concentration in air for the two common building materials used in Spain: stone and brick. Median concentrations of  $49.6 \text{ Bq} \cdot \text{m}^{-3}$  and  $33.9 \text{ Bq} \cdot \text{m}^{-3}$ , respectively, were measured in houses built with these two building materials. This suggests a significant contribution of the building materials as source for radon in the houses. Finally, the present indoor data obtained from the national survey in Spain and the adoption of a dose-conversion coefficient of  $20 \text{ Bq} \cdot \text{m}^{-3}$  (radon gas) per  $\text{mSv} \cdot \text{y}^{-1}$  (ICRP 1984; Vanmarcke and Berkvens 1989) led to a median annual effective dose equivalent of about  $2 \text{ mSv/y}$ . However, for some regions, as we can deduce from the Table 1, the population may receive a higher effective dose equivalent of around  $6 \text{ mSv/y}$  from the natural radiation source.

The results of the present survey in Spain will be used as a data base and source for the development of more specific studies in the regions where high radon levels were detected in order to characterize and evaluate the importance of the sources of radon in houses.

Table 1. Median radon concentrations for the different regions of Spain.

REGION CODE	Region Name	G.M. (Bq.m <sup>-3</sup> )	S.D.	Nº of measurements	Range (Bq.m <sup>-3</sup> )
1	Andalucia	38.3	2.6	219	L.D.-848.4
2	Aragón	46.2	2.8	104	L.D.-921.3
3	Asturias	42.6	2.4	54	18.5-947.2
4	Baleares	27.2	2.1	27	L.D.-160.6
5	Canarias	85.9	3.7	35	14.8-1875.8
6	Cantabria	52.5	2.9	67	L.D.-1972.4
7	Castilla-La Mancha	42.6	2.7	168	L.D.-395.9
8	Castilla-León	70.4	3.7	277	L.D.-15402.7
9	Cataluña	22.9	3.2	78	L.D.-1775.9
10	Extremadura	89.8	2.6	111	L.D.-1258.0
11	Galicia	117.6	2.3	112	18.5-2068.3
12	Madrid	94.9	2.0	29	28.1-492.1
13	Murciana	30.1	2.3	26	L.D.-104.7
14	Navarra	19.8	2.8	49	L.D.-95.8
15	La Rioja	18.5	3.8	26	L.D.-1072.9
16	Pais Vasco	33.1	2.7	49	L.D.-303.8
17	Pais Valenciano	17.6	2.8	124	L.D.-214.2
<b>SPAIN</b>		<b>41.1</b>	<b>3.0</b>	<b>1555</b>	<b>L.D.-15402.7</b>

L.D.: 10 Bq/m<sup>3</sup>Fig. 3. Percentage of houses per interval of concentration of indoor radon (expressed in Bq/m<sup>3</sup>).

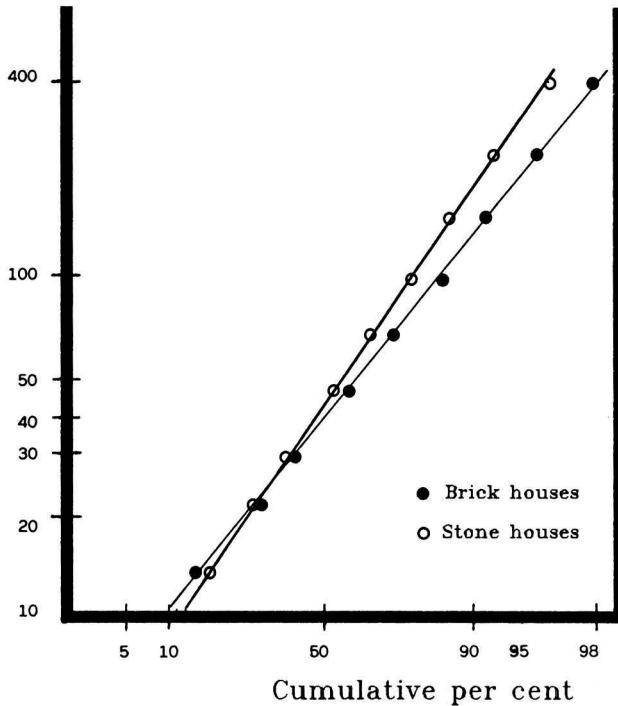
Radon concentration ( Bq.m<sup>-3</sup> )

Fig. 4. Cumulative frequency distribution of indoor-radon concentrations in air for stone and brick houses.

**Acknowledgment** — The national survey of radon in Spanish houses is being jointly funded under contract BI6-0017-E. This work was also supported by DGYCIT (Dirección General de Investigación Científica y Técnica) (CEB-009-TT), FISs (Fondo de Investigaciones Sanitarias de la Seguridad Social) (89/0575), and CSN (Consejo de Seguridad Nuclear) (89/0010), which financial support is greatly appreciated.

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# ZINC AND COPPER LEVELS IN TREE BARKS AS INDICATORS OF ENVIRONMENTAL POLLUTION

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*EI 8911-299M (Received 30 November 1989; accepted 17 July 1990)*

The concentration of zinc and copper in the bark samples of ten tree species at 34 sampling locations, having different pollution levels in Ile-Ife, Nigeria, was investigated. The zinc levels, 13.1-68.9  $\mu\text{g Zn/g}$ , dry weight, detected in different areas on bark surfaces, show correlation with traffic density and bark features suggesting this to have been derived from anthropogenic sources, specifically from motor traffic. Similar analysis on copper gave lower values — 11.1-51.2  $\mu\text{g Cu/g}$ , dry weight, which did not show any correlation either with traffic density or with bark features.

## INTRODUCTION

To determine the nature and deduce the sources of chemical species in the atmosphere are of primary importance in the study of heavy metal pollution. Many of these elements are associated with the natural background aerosol, but certain species such as copper and zinc are mostly of anthropogenic origin. Due to the rapid growth of industrial development in the last few decades, the input of these metals from varied human activities has greatly exceeded the emissions from natural sources. Consequently, an accumulation of toxic metals due to long-range effects, occurs in the various components of the ecosystem.

Many biological materials have been used as sensitive indicators of heavy metal pollution (Huhling and Tyler 1969; Clyde 1971; Little 1973; Garty et al. 1977; Grodzinska 1978; Burton and John 1977; Valkovic et al. 1979; Fatoki 1987). The measured levels of metals in these materials serve as an index of the extent of pollution, and as a basis from which explanations for many ecological phenomenon can be formulated.

The usefulness of tree barks in detecting atmospheric metals was reported by Denaeyer-De Smet (1974), by Barnes et al. (1976), by Osibanjo and Ajayi (1980), by Martin and Coughtrey (1981), and by Tanka and Ichikuni (1982) for various species of trees.

Motor vehicles introduce a number of toxic metals into the atmosphere and they are released adjacent to roadways (Williamson 1973; Moore and Moore 1976). Numerous investigators have demonstrated that lead emissions from motor vehicles produce elevated concentrations of these elements in roadside vegetation (Cannon and Bowles 1962; Quinche et al. 1969; Motto et al. 1970; Fatoki 1987). Likewise, elevated zinc concentrations have been shown in roadside plants (Cannon and Bowles 1962; Lagerwerff and Specht 1970; Connor et al. 1971; Shaklette and Connor 1973; Ward et al. 1977). This contamination of roadside vegetation by airborne zinc is considered to arise mainly from motor traffic due to motor vehicle tire wear and motor vehicle emissions due to zinc-



containing additives in lubricating motor oils (Lagerwerff and Specht 1970; Tanka and Ichikuni 1982). However, this aspect of roadside contamination with zinc has not been much investigated in Nigeria. Thus, an attempt is made in this study to investigate the level of air pollution of zinc and copper in Ile-Ife town, an ancient city of western Nigeria and a tourist centre with Nigerian tree barks as indicators of the metals in the local environment. It appears no such measurement has previously been reported in Ile-Ife.

#### SAMPLE AND SAMPLE LOCATION

The area investigated is shown in Fig. 1. From the visual inspection of the place, no industrial activity is apparent near the vicinity of the sampling locations. Ten species of trees with different bark features (degree of roughness), as shown in Tables 1 and 4, were sampled from 34 locations in

Ile-Ife to represent areas of different traffic density. The sampling points designated  $S_1 - S_{34}$  included locations of high traffic density ( $S_9 - S_{13}$ ,  $S_{16} - S_{18}$ ,  $S_{20} - S_{21}$ ,  $S_{23} - S_{24}$ ,  $S_{26} - S_{33}$ ), and low traffic areas ( $S_1 - S_7$ ,  $S_{14} - S_{15}$ ,  $S_{19}$ ,  $S_{22}$ ,  $S_{25}$ , and  $S_{34}$ ). A suitable place ( $S_8$ ) at the university campus staff residential area, remote from traffic, served as an unpolluted reference point. Trees of about the same age, situated close to the road (about 5 m), were selected, and thin chips of bark were carefully stripped from the trunk with a stainless steel pen knife at an average height of about 2 m above the ground (Barnes 1976).

The bark samples were kept in paper envelopes and then placed in polyethylene bags. Each tree was sampled twice, and analysis was carried out on the duplicate samples to test the reproducibility of the method used. The samples were dried in the oven at about 100 - 120° C for about 3 h to constant weight and then pulverized to uniform size.

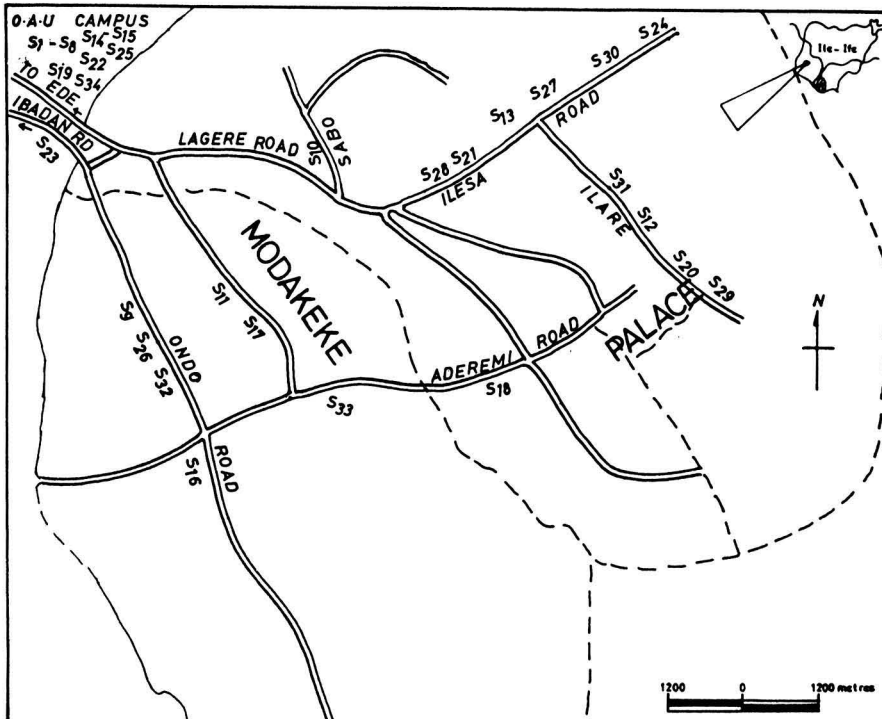


Fig. 1. Map of Ile-Ife showing sampling locations.

Table 1. Concentration of zinc and copper at city high traffic and low traffic density sites for Nigerian *Terminalia catapa*.

Sample Number	Bark Feature	Location	Concentration, $\mu\text{g g}^{-1}$ sample, dry weight of					
			Zn			Cu		
			I	II	Average Concentration*	I	II	Average Concentration*
***S <sub>13</sub>	Rough and hard "	Ilesa Road	69.0	68.8	68.9	51.0	51.3	51.2
S <sub>12</sub>		Ilare	68.0	67.6	67.8	28.2	28.1	28.2
S <sub>9</sub>		Ondo Road	67.2	67.6	67.4	47.6	47.9	47.8
S <sub>11</sub>		Modakeke	57.1	57.2	57.2	33.2	32.8	33.0
S <sub>10</sub>		Sabo	54.2	54.0	54.1	45.8	46.1	46.0
S <sub>5</sub>		Fajuyi Hall, O.A.U.	46.2	45.8	46.0	16.0	16.1	16.1
S <sub>6</sub>		Chemistry Dept. O.A.U.	45.1	45.2	45.2	19.2	19.0	19.1
S <sub>3</sub>		Awolowo Hall, O.A.U.	43.2	43.0	43.1	19.1	19.3	19.2
S <sub>4</sub>		Angola Hall, O.A.U.	36.0	35.8	35.9	19.3	18.7	19.0
S <sub>2</sub>		Mozambique Hall, O.A.U.	34.6	34.2	34.4	22.2	22.1	22.2
S <sub>7</sub>		Secretariat, O.A.U.	34.2	33.5	33.8	25.0	25.1	25.1
S <sub>1</sub>		Morimi Hall, O.A.U.	33.1	33.8	33.5	16.2	15.7	16.0
**S <sub>8</sub>		Road 7 (Residential), O.A.U.	13.0	13.1	13.1	15.2	15.1	15.2

O.A.U. = Obafemi Awolowo University

\* = Average of two replicate analysis

\*\* = Unpolluted reference point

\*\*\* = Sample from Ilesa Road

Table 2. Statistical assessment of zinc and copper contents of bark of Nigerian *Terminalia catapa* collected from two areas of different traffic density level.

Area	Zn	Cu
High traffic density sites (5 samples)		
Means ( $\mu\text{g g}^{-1}$ )	63.1	41.2
R.S.D. (%)	10.9	24.3
Low traffic density sites (8 samples)		
Means ( $\mu\text{g g}^{-1}$ )	35.6	19.0
R.S.D. (%)	29.5	17.7
t-values	2.91	2.26

The t-value with 11 degree of freedom is 1.80 at 90% confidence level. R.S.D. is relative standard deviation.

## EXPERIMENT

About 2 g of each dried sample was accurately weighed into properly cleaned vitrosil crucibles and ashed at a temperature between 450 - 500° C. The ash was dissolved in 5 mL 36% HCl and then mixed with distilled water in a 25 mL volumetric flask. The samples were analysed by atomic absorption spectrophotometry using a Perking Elmer Model 306 instrument operated as per the instrument's handbook. The instrument was calibrated using mixed calibration. Standard solutions were prepared by step-wise dilution from stock standard solution prepared from the pure metal or analytical grade salt of the metal. Stock solutions were 1:1 in HCl or HNO<sub>3</sub>. Results were corrected for reagent blanks and non-atomic absorption. The reproducibility of the method used in decomposing the bark samples was checked by carrying out a duplicate analysis.

## RESULTS AND DISCUSSION

The results of the chemical analysis for the two series of heavy traffic and low pollution areas are presented in Table 1 for bark from *Terminalia catapa*. They reveal the presence of zinc and copper on the bark. High concentrations of the elements were observed in samples taken from high traffic density sites. This is an indication of an enhanced level in the surrounding atmosphere. Furthermore, concentrations of contaminants are low in areas of low traffic density.

Table 2 shows the mean concentrations of elements in the two groups of bark samples. An increasing trend in metal content (Zn and Cu) from high traffic density areas to low traffic density areas is evident from the data. The student t-test was used to demonstrate the significant difference between the two means for both metals (Table 2). The results show the difference between samples taken from high pollution areas and low pollution areas.

Table 3. Correlation coefficient between zinc and copper in Nigerian *Terminalia catapa*.

Element	High traffic density area		Low traffic density area	
	Zn	Cu	Zn	Cu
Zn	-	0.11	-	0.20

Table 4. Concentration of zinc and copper at different city sites for other Nigerian tree barks.

Tree			Concentration, $\mu\text{g g}^{-1}$ sample, dry weight of:					
			Zn			Cu		
Tree Species	Bark Feature	Tree Location	I	II	Average Concentration*	I	II	Average Concentration*
<i>Magnifera indica</i>	Fairly smooth, tough, and thick.	***Ilesa Rd. (S <sub>24</sub> )	67.2	67.1	67.2	31.3	31.0	31.2
<i>Magnifera indica</i>		Ibadan Rd. (S <sub>23</sub> )	60.8	61.0	60.9	25.0	25.1	25.1
<i>Magnifera indica</i>		Road 7 (Non-residential) O.A.U. (S <sub>22</sub> )	40.0	39.5	39.8	18.6	18.9	18.8
<i>Azadiratha indica</i>	Very smooth and light.	***Ilesa Rd. (S <sub>21</sub> )	39.5	40.0	39.8	23.2	23.0	23.1
<i>Azadiratha indica</i>		Modakeke (S <sub>17</sub> )	38.0	38.1	38.1	23.5	23.9	23.7
<i>Azadiratha indica</i>		Ilare (S <sub>20</sub> )	47.0	47.1	47.1	23.1	23.2	23.2
<i>Azadiratha indica</i>		Aderemi (S <sub>18</sub> )	53.7	54.0	53.9	22.7	23.2	23.0
<i>Azadiratha indica</i>		Ondo Rd. (S <sub>14</sub> )	36.2	35.7	36.0	30.0	30.1	30.1
<i>Azadiratha indica</i>		Road 8, O.A.U. (S <sub>19</sub> )	24.0	24.1	24.1	15.0	15.2	15.1
<i>Azadiratha indica</i>		Road 7, (Residential) O.A.U. (S <sub>15</sub> )	18.0	18.3	18.2	11.2	11.0	11.1
<i>Azadiratha indica</i>		Dept. Admin., O.A.U. (S <sub>14</sub> )	15.0	15.2	15.1	11.8	12.0	11.9
<i>Spondias mombin</i>	Rough, thick, and hard.	***Ilesa Rd. (S <sub>28</sub> )	68.2	67.7	68.0	26.2	26.4	26.3
<i>Anthocarpus communis</i>	Smooth and slightly thick.	***Ilesa Rd. (S <sub>30</sub> )	54.2	54.1	54.2	30.7	31.2	31.0
<i>Anthocarpus communis</i>		Ilare (S <sub>29</sub> )	59.7	60.1	59.9	29.0	29.3	29.2
<i>Citrus spp</i>	Smooth, light, soft, and flexible.	***Ilesa Rd. (S <sub>27</sub> )	50.0	50.2	50.1	15.1	15.0	15.1
<i>Citrus spp</i>		Ondo Rd. (S <sub>24</sub> )	45.1	45.0	45.1	15.2	14.9	15.1
<i>Citrus spp</i>		Road 7, (Non-residential) O.A.U. (S <sub>25</sub> )	35.2	35.1	35.2	16.8	15.2	16.0
<i>Spathodia campanulata</i>	Smooth and hard.	Oduduwa Hall, O.A.U. (S <sub>24</sub> )	27.1	27.2	27.2	12.8	13.3	13.1
<i>Cordia millenii</i>	Rough, thick, and hard.	Ilare (S <sub>31</sub> )	61.0	60.8	60.9	17.1	16.9	17.0
<i>Cola millenii</i>	Rough, thick, and hard.	Ondo Rd. (S <sub>22</sub> )	52.3	51.7	52.0	39.2	38.8	39.0
<i>Acacia senegal</i>	Smooth and light.	Modakeke (S <sub>33</sub> )	54.0	54.2	54.1	11.8	12.2	12.0
Mean			-	-	45.1	-	-	21.4
Range			-	-	52.9	-	-	27.9
Relative Standard Deviation			-	-	34.1	-	-	36.4

O.A.U. - Obafemi Awolowo University  
 \* - average of two replicate analysis  
 \*\*\* - sample from Ilesa Rd.

In order to deduce the possible sources of the metal contaminants, one approach taken was to determine the correlation coefficient between elements. As seen in Table 3, the correlation between the samples taken from high traffic density and low traffic density areas is poor. The low correlation coefficient found between Zn and Cu in both groups suggests a non-common source of the metals. Bark samples taken from high traffic density areas show a high concentration of zinc. Also, in both groups of samples, the values of zinc are consistently higher than the values of copper (Tables 1 and 4). These observations, coupled with the fact that zinc additives are often used in lubricating motor oil and tires, could show that zinc in the barks originates from motor vehicle emissions and from motor vehicle tire wear. The sources of copper are probably varied, and may be from sources other than motor traffic. Probable sources of copper in the barks are soil and refuse burning, a common practice.

In areas of similar traffic density, the type of tree appears to have significant influence on the concentration of zinc in the tree barks (Tables 1 and 4). For example, for samples taken at Ilesa Road, values of zinc obtained were *Terminalia catapa* ( $S_{13}$ )  $68.9 \text{ \% g g}^{-1}$ , *Spondias mombin* ( $S_{28}$ )  $68.0 \text{ \% g g}^{-1}$ , *Magnifera indica* ( $S_{24}$ )  $67.2 \text{ \% g g}^{-1}$ , *Anthocarpus communis* ( $S_{30}$ )  $54.2 \text{ \% g g}^{-1}$ , *Citrus spp* ( $S_{27}$ )  $50.1 \text{ \% g g}^{-1}$ , and *Azadiratha indica* ( $S_{21}$ )  $39.8 \text{ \% g g}^{-1}$ , dry weight. This observation can be related to the nature of the barks, since rough barks are known to accumulate metals more than smooth barks (Barnes et al. 1976). *Terminalia catapa*, with a rough, thick surface, was found to accumulate the highest amount of lead on its surface, while *Azadiratha indica*, with a smooth, light surface, accumulated the least amount of lead for all the samples analysed.

This study demonstrates the suitability of tree barks as indicators of environmental metal pollution.

**Acknowledgment** — The authors would like to acknowledge the assistance received from Doyin Jimoh during the collection and analysis of samples.

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# STUDIES ON THE LEVELS OF SULPHUR DIOXIDE, NITROGEN DIOXIDE, AMMONIA, AND HYDROGEN CHLORIDE IN AMBIENT AIR OF HARARE, ZIMBABWE

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*EI 9003-040M (Received 21 March 1990; accepted 21 November 1990)*

The concentrations of sulphur dioxide, nitrogen dioxide, ammonia, and hydrogen chloride, in the ambient atmosphere of Harare were monitored over a period of one year (1988) at four selected sites - university campus, city centre, industrial area, and Msasa, an industrial site in the vicinity of a fertilizer factory. The diurnal variations varied from day to day and sulphur dioxide and nitrogen dioxide levels rose with sunlight hours, reaching peak values about midday which were sustained on some days through till late afternoon. Normally, a decreasing trend is observed by the evening. The profile of the seasonal variation in the average daily concentrations of all the pollutants are shown for the industrial area sampling point. Sulphur dioxide levels were observed, sustained at high levels ( $90-120 \mu\text{g m}^{-3}$ ) during winter extending into spring and lower levels during the rainy season. Hydrogen chloride in the winter and spring was maintained at about  $40 \mu\text{g m}^{-3}$ . Of the four sites, the university area was found to be relatively clean with minimum and maximum daily average levels (in  $\mu\text{g m}^{-3}$ ) recorded during the year, being  $\text{SO}_2$  (2.0-52.6),  $\text{NO}_2$  (2.0-17.2),  $\text{NH}_3$  (1.9-38.1), and  $\text{HCl}$  (9.0-55.1). The order of increasing pollutant concentrations was the city centre, the industrial area, and the Msasa area. In the Msasa area, the pollution originated from the point source, the fertilizer factory. The minimum and maximum diurnal arithmetic means (in  $\mu\text{g m}^{-3}$ ), over the year observed, were  $\text{SO}_2$  (14.0-242.0),  $\text{NO}_2$  (4.5-27.4),  $\text{NH}_3$  (2.0-45.3), and  $\text{HCl}$  (14.8-77.0). The correlation plot of  $\text{NH}_3/\text{SO}_2$  versus  $\text{SO}_2$  gave a slope of  $7.7 \times 10^{-3}$  (corr. 0.69), indicating that high sulphur dioxide levels facilitate the removal of ammonia, possibly through aerosol formation from the ambient air.

## INTRODUCTION

The atmosphere is a complex system from both the physical and the chemical standpoints. The variable atmospheric mixing, the variable radiation, and the nature of pollutants emitted play important roles in determining the nature and rates of chemical transformation in the troposphere. Atmospheric pollution

in particular is a matter of global concern as the problem is not restricted to the boundaries of any single nation or continent.

The prime objective of a study on pollutant levels is the control of the noxious materials in atmosphere. To achieve the objective, it is essential to understand

the sources, sinks, and chemical nature of various pollutants and their effect on materials and life processes. For implementation of controls and achievement of the quality goals, facilities for effective monitoring are crucial.

In the present situation, in most of the African countries, air pollution may not be of serious proportions, but with less stringent restrictions on the pollutant emissions, it may become a threat in the future. Little information is available about the air pollution or air quality studies carried out in the lower troposphere within Africa (Perry et al. 1977; Strauss 1977; Jonnalagadda et al. 1989).

The present communication presents the results of a systematic study carried out by monitoring the levels of four gaseous pollutants, namely, sulphur dioxide, nitrogen dioxide, ammonia, and hydrogen chloride in ambient air at four sampling points in the Harare area of Zimbabwe. Harare, the capital city of Zimbabwe with an estimated population of about one million, is situated in South Central Africa, with a latitude of 18°S, an altitude of 1520 m, and an atmospheric pressure of about 640 mm Hg.

## EXPERIMENTAL

### Sampling

The sampling sites identified had varied surroundings and the descriptions are as follows (Fig.1).

Site 1: University campus—5 km from the city centre and surrounded by thick vegetation.

Site 2: City centre—Traffic island on dual carriage way (two-way street) with three traffic lanes on each side; heavy vehicular traffic.

Site 3: Industrial area—Workington, 9 km from the city centre with varied types of industrial activity and vehicular traffic.

Site 4: Msasa—Industrial area in the vicinity of the fertilizer factory 10 km from the city centre.

Air samples were collected at a level of 1.5 m from the ground. Glasswool was used to trap the particulate matter. Gaseous pollutants were absorbed into appropriate absorbing solutions (10 cm<sup>3</sup>) in separate impingers by cumulative grab-sampling, using flow-regulated suction pumps with flow rates of 1.0-2.0 L/min, i.e., by bubbling the air through for a period of 40 min in each case. Impingers were cleaned from time to time with reverse water flow and using organic solvents and acid.

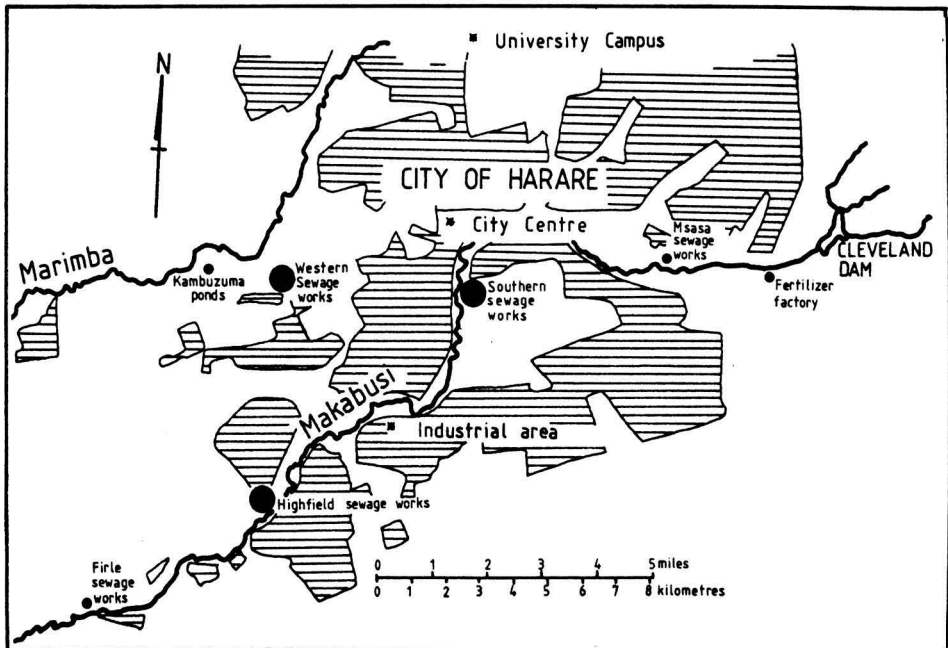


Fig. 1. Map of the city of Harare showing air sampling sites.

## METHODOLOGY AND ANALYSIS:

Throughout the analysis, the day temperature corresponding to every sample was noted and the concentrations of each pollutant were estimated under standard temperature (25°C) and pressure (760 mm Hg) conditions and the values were expressed in  $\mu\text{g m}^{-3}$ .

All the samples except for the HCl determination were analyzed in duplicate and the data presented are the mean values obtained. Analytical results were fairly reproducible and normally values had no more than a 6% deviation from the mean values reported.

### Sulphur dioxide

SO<sub>2</sub> was analyzed by employing the West-Gaeke method. Air samples were bubbled through the impinger containing potassium tetrachloromercurate solution (TCM). The stable dichloro-sulphito-mercurate ion, formed on reaction between SO<sub>2</sub> and the absorbing reagent, was reacted with formaldehyde and acidified pararosaniline at pH 1.6. The pararosaniline methylsulphonic acid formed was monitored at 548 nm. SO<sub>2</sub> was estimated using calibration curves with sulphite as standard. This method is applicable for sulphur dioxide concentrations 0.01-5  $\mu\text{L/L}$ , the lower limit of detection being 0.3  $\mu\text{g SO}_2$  per 10 mL TCM which corresponds to 0.013  $\mu\text{L/L SO}_2$  in 40 L air (Perry et al. 1977; Strauss 1977).

### Nitrogen dioxide

NO<sub>2</sub> was estimated using a modified form of the Saltzman method (Perry et al. 1977; Strauss 1977). Air samples were bubbled through an aqueous solution containing a mixture of sulphanilic acid, acetic acid, and *n*-naphthyl ethylene diamine-dihydrochloride. NO<sub>2</sub> is converted to nitrite and the nitrite ions, in turn, diazotize in solution, giving a red azo dye. The absorbency was measured at 550 nm reference blank and using sodium nitrite as standard for the calibration curve. The lowest detection limit being 0.005  $\mu\text{L/L}$ , the method is reported to be useful in the range of 0.005-5  $\mu\text{L/L}$ .

### Ammonia

The concentration of ammonia in the air samples was analyzed by the Indophenol-blue method. Samples were collected in a 2.5 mM sulphuric acid solution and were reacted with alkaline phenol-hypochlorite and catalyzed by pentacyano-nitrosyl-ferrate. The blue colour developed was measured at its absorption maximum (625 nm). Ammonium sulphate was used as standard. The sensitivity of the method is approximately 0.02  $\mu\text{g} \cdot \text{NH}_4^+$  in the sample solution of 50 mL which corresponds to a detection limit of 1  $\mu\text{g} \cdot \text{m}^{-3} \text{NH}_3$  (Perry et al. 1977).

### Hydrogen chloride analysis

Hydrogen chloride was collected into a 0.001 M NaOH solution and then chloride ion was analyzed by two methods (Perry et al. 1977; Strauss 1977).

1) Ion-selective electrode: The chloride ion in HCl was estimated using ammonium acetate—acetic acid (pH 5) buffer and a chloride ion-selective electrode. Potassium chloride was used as standard. Lowest detection limit was 1  $\mu\text{g} \cdot \text{Cl}^-/\text{mL}$ .

2) Mercuric thiocyanate method: To the absorbing solution acidified with HNO<sub>3</sub>, ferric aluminum sulphate solution was added followed by mercuric thiocyanate in methanol. The absorbency of ferric thiocyanate formed was measured at 460 nm. KCl was used as standard.

## RESULTS AND DISCUSSION

All the four gaseous pollutant samples were collected into their respective absorbing solutions at the chosen site between 0700 h and 1800 h during the day, operating four flow-regulated suction pumps simultaneously. About three to six air samples per day at each site were collected at regular intervals.

While the nitrogen dioxide samples were analyzed on the same day, all the other samples were analyzed within three to four days. Figure 2 illustrates the trends in the levels of sulphur dioxide, nitrogen dioxide, ammonia, and hydrogen chloride on a typical day (11 August 1988) in the ambient air at the university campus. A perusal of the curves show that sulphur-dioxide levels increased with the progress of the day, followed by nitrogen dioxide and also hydrogen chloride, while the levels of ammonia were maintained fairly the same. Figures 3 and 4 show the variation in the levels of the four pollutants on typical days at the city centre (9 August 1988) and the

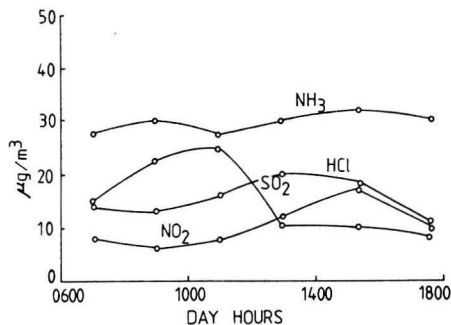


Fig. 2. Typical levels of pollutants in ambient air at the university campus.



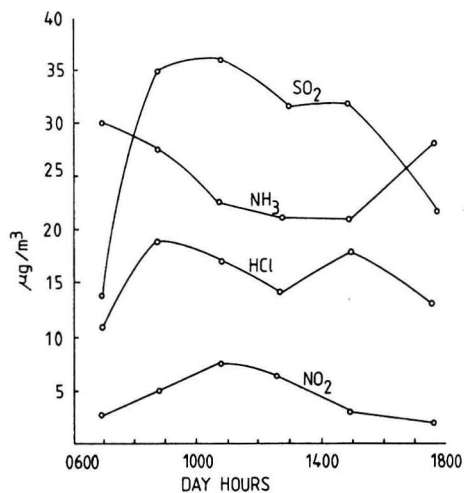


Fig. 3. Typical levels of pollutants in ambient air at the city centre.

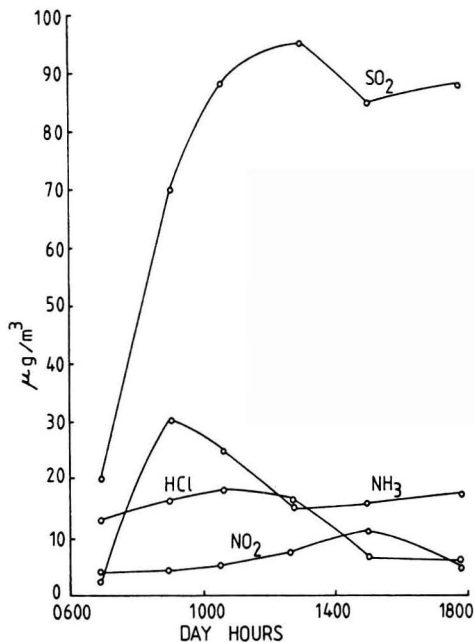


Fig. 4. Typical levels of pollutants in ambient air at the industrial area.

industrial area (10 August 1988) sites, respectively. Although the trends at the two sites are comparable to some extent, the  $\text{NH}_3$  level at the city centre decreased by midday and then registered an increasing trend, whereas the  $\text{NH}_3$  levels at the industrial area increased initially and then decreased in the later part of the day. At the industrial area site, the  $\text{SO}_2$  levels were observed to be quite high on the particular day (11 August 1988) the samples were obtained. In a broad sense, the levels of sulphur dioxide and nitrogen dioxide increased with the sunlight hours, reaching peak values around the midday. On some days, the values were sustained through late afternoon. Normally, a decreasing trend is noticed by the evening. Generally, HCl levels during the day remained the same with small variations. As the level of pollutants at any given site varied with time, day, and season, averaged values of diurnal variation of pollutant over a few days are not provided. But at each site, the arithmetic mean of the diurnal variations of the levels of all the four gases was calculated. Figure 5 summarises the seasonal variations in the levels of sulphur dioxide, nitrogen dioxide, ammonia, and hydrogen chloride at the industrial area site for about one year (January to December 1988). Figure 5 also shows the duration of the seasons. The pollutants had no distinct phase or linear relationship to each other, but in a broad sense, nitrogen dioxide levels were in line with sulphuric dioxide while

ammonia level were out of phase. Using the analytical data presented in Fig. 5, a correlation plot of  $\text{NH}_3/\text{SO}_2$  versus  $\text{SO}_2$  gave a curve with the gradient of  $-7.72 \times 10^{-3}$  (corr. 0.69) (Fig. 6), suggesting that levels of ammonia decrease with the increasing levels of  $\text{SO}_2$ . Further, the concentrations of  $\text{SO}_2$  and HCl were sustained at higher levels in winter months while the values decreased with rains possibly due to precipitation of the pollutants with rain water (Fig. 5).

Further, the diurnal averages corresponding to each pollutant at each site, i.e., the minimum and maximum limits observed during the 12-month period and the annual averages are summarised in the Table.

The observed profiles of pollutant levels for a typical day can be explained considering the interlinked chemistry of  $\text{NO}_x$  and  $\text{SO}_x$  gases in air and their possible sinks (Stern et al. 1973). The increased levels of sulphur dioxide, nitric oxide, ozone, etc., the primary pollutants from automobile exhausts and from the industrial activities during the daylight hours generate nitrogen dioxide.  $\text{NO}_2$  thus formed, in turn, initiates a set of chain reactions resulting in regeneration of NO and other secondary pollutants (Stern et al. 1973; Butler 1979). The ambient concentrations

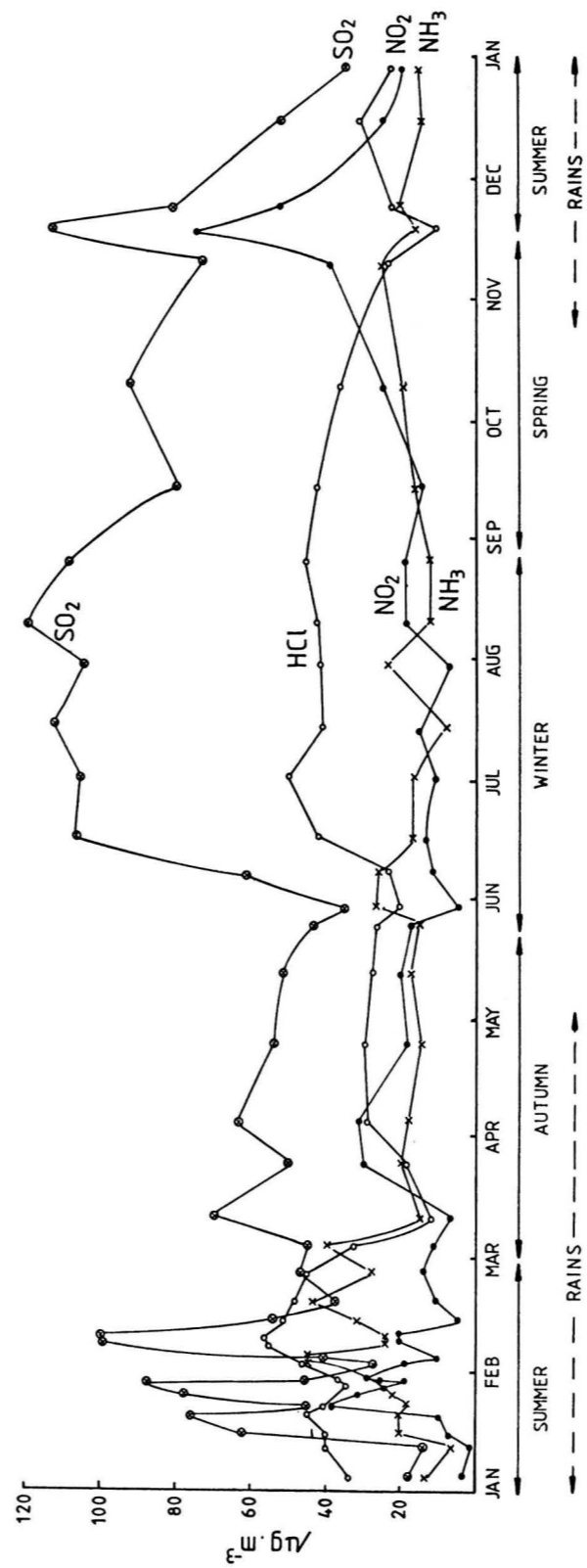


Fig. 5. Seasonal variation in the levels of SO<sub>2</sub>, NO<sub>2</sub>, NH<sub>3</sub>, and HCl at the industrial area site.

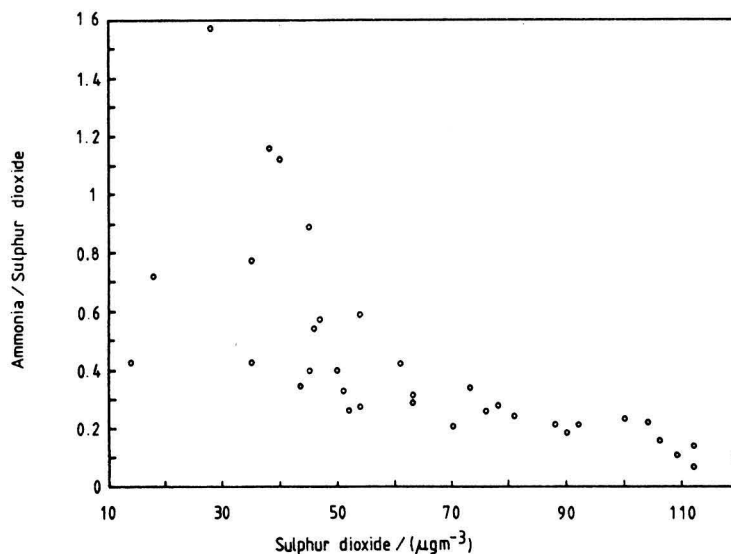
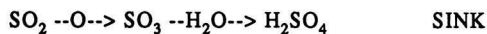
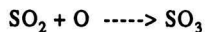
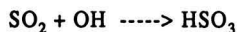
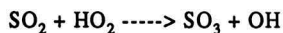
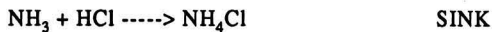
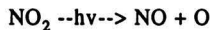
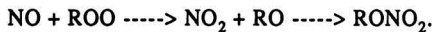
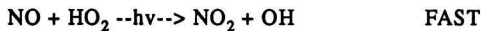
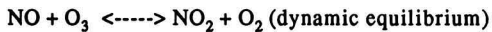


Fig. 6. Industrial area —  $\text{NH}_3/\text{SO}_2$  versus  $\text{SO}_2$  plot.

Table. Gaseous pollutant levels in ambient air of Harare (1988) and air quality limits (in  $\mu\text{g} \cdot \text{m}^{-3}$  under STP).

Pollutant	No Samples*	Mean of Day Samples*		Annual Mean	
		Min	Max	Mean	S.D
<u>I University area</u>					
$\text{SO}_2$	28	2.0	52.6	25.6	23.4
$\text{NO}_2$	18	2.0	17.2	5.0	5.3
$\text{NH}_3$	28	1.9	38.1	8.0	2.8
HCl	27	9.0	55.1	30.6	14.7
<u>II City Centre - Commercial District</u>					
$\text{SO}_2$	40	4.0	142.3	60.1	62.7
$\text{NO}_2$	32	2.0	28.0	12.8	7.3
$\text{NH}_3$	40	2.0	40.9	14.0	10.6
HCl	38	16.5	78.0	34.9	13.0
<u>III Industrial Area</u>					
$\text{SO}_2$	37	14.0	120.2	67.2	28.9
$\text{NO}_2$	37	3.0	75.0	20.4	15.2
$\text{NH}_3$	35	6.0	45.0	24.5	13.8
HCl	36	10.0	56.0	35.6	11.8
<u>IV Msasa - New Industrial Area</u>					
$\text{SO}_2$	15	14.0	242.0	101.1	70.8
$\text{NO}_2$	12	4.5	27.4	13.5	8.9
$\text{NH}_3$	15	2.0	45.3	15.8	16.5
HCl	14	14.8	77.0	40.5	26.3

of NO influence the stoichiometries of the production of O<sub>3</sub> in the troposphere (Crutzen 1988). Important reactions involving NO<sub>x</sub> and SO<sub>x</sub> can be represented as follows (Stern et al. 1973; Butler 1979; Crutzen 1988):



High NO<sub>2</sub> and SO<sub>2</sub> levels are associated with the samples at the city centre and the industrial area where heavy vehicular traffic exists. Low NO<sub>2</sub> levels in the vicinity of the Msasa fertilizer plant, even with significant SO<sub>2</sub> levels, suggest that the detected NO levels mainly originated from the combustion of fossil fuels (automobile exhausts). The lower ammonia levels associated with high levels of HCl or SO<sub>2</sub> levels could be due to their removal through particulate formation, as suggested.

Further, the persistence of high levels of sulphur dioxide and hydrogen chloride during the winter and

spring months could also be due to the prevailing meteorological conditions in the Harare region. Normally, during the winter months, Zimbabwe together with the Botswana region experiences stable atmospheric conditions with inversions within 1 km due to the influence of the atlantic anticyclone systems. This is evidenced by smog or foggy conditions prevalent during the months of May-July. In the months of August, September, and October, conditions are transient in nature with occasional inversions at the heights of about 2 km. Short-term hazy conditions reportedly prevail in the ambient atmosphere during those periods.

Inferences drawn from the present study reflect a generalised situation that prevails in the urban centres of most of the developing countries where the pollution sources may be generally few but enough to impact the surroundings, if proper attention is not paid. Therefore, there is an urgency for developing countries to start implementing environmental pollution control policies more seriously through effective monitoring and impact assessment mechanisms.

*Acknowledgment* — The authors are thankful to the Research Board, University of Zimbabwe, for providing necessary funds. The authors also thank Mr. R. Nyamatora, Mr. S. Makambaya, and Mr. Chikonyora, the officials from the Department of Occupational Health and Safety, for their participation in sample collection. Without their assistance, the project never would have been accomplished.

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# PHYSICO-CHEMICAL CHARACTERIZATION OF CITY SEWAGE DISCHARGED INTO RIVER GANGA AT VARANASI, INDIA

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*EI 8905-183M (Received 24 May 1989; accepted 15 March 1990)*

The Varanasi city sewage discharged into the river Ganga at six sites, Assi ghat, Shiwala ghat, Harishchandra ghat, Chauki ghat, Rajendra Prasad ghat, and Rajghat was analysed for its physico-chemical properties such as temperature, pH, acidity, alkalinity, dissolved oxygen, biochemical oxygen demand, chemical oxygen demand, chloride, electrical conductance, nitrate and phosphate. An analysis of variance reveals significant variation in most of the parameters with respect to months as well as sites. Duncan's multiple-range test shows that a higher concentration of sewage was discharged during May and June. Furthermore, at Rajghat, sewage was the most concentrated with the highest pollution load, whereas sewage at Assi ghat was the least concentrated. The correlation among various parameters is reported.

## INTRODUCTION

The main sources of pollution of the river Ganga at Varanasi are industrial effluents, domestic sewage, and disposal of dead bodies (Sikandar 1986). Pollutants through agricultural runoff also play an important role during the rainy season. A number of large, basic and small industries (Table 1) are situated in and around the city of Varanasi. Most of the effluents from these industries mixed with about 127 m<sup>3</sup>/d sewage generated by 797 000 inhabitants of Varanasi city (Government of India 1985) are discharged through several minor and major nalas (drains) into the river Ganga.

A number of investigations have been conducted on the quality of the sewage entering into different rivers in India such as the river Cauvery at Madras (Ganapati and Alikunhi 1950), the river Hoogly estuary at Calcutta (Basu 1966), the river Yamuna at Delhi (Dakshini and Soni 1979), the river Yamuna at Agra (Sharma et al. 1981), the rivers Ganga and Yamuna at Allahabad (Agrawal and Srivastava 1984), and the river Ganga from Mirzapur to Ballia (Shukla

et al. 1989). However, there is paucity of data regarding the qualitative and quantitative analyses of sewage discharged into the river Ganga at Varanasi city. In order to fill in the gap of knowledge and provide basic ecological data, the present investigation has been performed. Nine sewage discharge points were observed on the 10 km crescent course of the river Ganga. Six perennial discharge points, (a) Assi ghat, (b) Shiwala ghat, (c) Harishchandra ghat, (d) Chauki ghat, (e) Rajendra Prasad ghat, and (f) Rajghat, were selected for regular sampling.

The sewage discharged into the river Ganga at aforesaid sites was analysed for temperature, pH, acidity, alkalinity, dissolved oxygen (DO), biochemical oxygen demand (BOD), chemical oxygen demand (COD), chloride (Cl<sup>-</sup>), electrical conductance (G), nitrate (as nitrogen), and phosphate (as phosphorus). The impact of a pollutant on an aquatic system is associated with its concentration per unit volume as well as the total volume of sewage discharged at a site. Therefore, the pollution load (P) based on some parameters was calculated as follows :

Table 1. Nature and number of industries located in and around the city of Varanasi (Industrial Directory 1981).

Type of industry	Number	Percentage
Metal products (Aluminium, steel, brass, iron and copper)	416	27.7
Chemical and chemical products (Candles, agarbatti, cosmetics, soap, detergent, paints, varnish, ayurvedic medicines, ink, phynayal oils, Pharmaceutical chemicals, etc.)	211	14.0
Electrical	201	13.4
Food products (Ice, cold drink, oil and dall mills, salt products, biscuits, bread, etc.)	54	3.6
Spinning, weaving and finishing of textiles (Hosiery, printing of saris and clothing, cotton and thread processing)	53	3.5
Transportation equipment (Automobile services, truck, bus body, motors, engineering, and motor parts)	32	2.1
Furniture and fixtures	31	2.1
Nonmetallic mineral products except petroleum and coal	26	2.1
Wood and cork work except furniture	18	1.2
Beverages and other consumer products (Zarda, pan masala and surti, etc.)	12	0.8
Leather, fur, rubber and tire etc.	9	0.6
Printing press and paper products	107	7.1
Miscellaneous (Plastic, elastic, silk and saris, fabric, metallic yarn, carpet, brick, cement, tile, surkhi, sport equipment, pens, photostats, sindhur, gulal, etc.)	333	22.2
Total	1,503	100.0

$$P = s \times v,$$

where

P = Pollution load (kg/d),

s = value (kg/m<sup>3</sup>), and

v = volume (m<sup>3</sup>/d) of sewage.

Snedecor's F-test (1934) was applied to find out the factor (site or month) responsible for the variation and its significance in the data obtained through analysis of sewage. The F-test is made from the analysis of variance. F is the ratio of the unbiased estimates of two population variances. Fisher and Yates (1938) designate F as the variance ratio. Duncan's Multiple Range Test (1957) was used to categorise the sites and months on the basis of decreasing or increasing values of sewage quality and pollution load. A correlation analysis has

been done to establish the relationship between various parameters at different sites.

## MATERIALS AND METHODS

Sewage samples were collected in the first week of each month from March 1986 to February 1987. Five replicates, each of two-liter samples, were collected at a time in polythene bottles, between 8:00 a.m. and 10:00 a.m. from each of the sampling sites and were brought to the laboratory for analysis.

Standard methods for the examination of water and wastewater (APHA 1985) were used for the analysis. The temperature was recorded at the site with the help of a mercury thermometer graduated to 10°C with an accuracy of 0.1°C. The dissolved oxygen sewage samples were fixed with the help of a manganous sulphate and alkali-iodide-azide solution (2 mL each) at the site and analysed in the

**Table 2.** Physico-chemical characteristics of Varanasi city sewage discharged into the river Ganga at Assi Ghat (AG sewage), Shiwala Ghat (SG sewage), Harishchandra Ghat (HG sewage), Chauki Ghat (CG sewage), Rajendra Prasad Ghat (RPG sewage), and Rajghat (RG sewage). Note that the values are minimum and maximum.

Parameters	AG sewage	SG sewage	HG sewage	CG sewage	HPG sewage	RG sewage
Temperature (°C)	20.30±0.4 31.30±0.4	21.30±0.4 32.20±0.4	21.60±0.5 33.30±0.4	21.70±0.6 33.40±0.4	22.60±0.6 34.20±0.6	22.80±0.6 34.30±0.6
pH	7.43±0.1 8.07±0.1	7.37±0.6 8.03±0.1	7.10±0.1 7.77±0.1	7.10±0.1 7.97±0.1	7.07±0.1 7.97±0.1	7.13±0.0 7.87±0.0
Acidity (CaCO <sub>3</sub> mg/L)	10.70±1.6 44.80±2.5	10.10±1.3 37.20±1.6	12.5±1.0 62.70±1.8	13.30±1.3 52.50±1.5	10.80±0.9 70.70±1.0	15.50±2.0 72.80±0.8
Alkalinity (CaCO <sub>3</sub> mg/L)	171.00±3.0 402.00±2.0	182.00±3.0 503.00±2.0	171.10±1.0 530.00±5.0	196.00±3.0 522.00±3.0	272.00±3.0 485.00±3.0	273.00±3.0 698.00±8.0
DO (mg/L)	1.50±0.1 3.60±0.6	0.40±0.3 4.60±0.1	1.00±0.2 2.30±0.2	1.40±0.1 3.60±0.1	1.00±0.0 3.40±0.1	0.20±0.1 1.80±0.2
BOD (mg/L)	20.00±1.5 107.00±10.0	86.00±2.0 249.00±10.0	66.00±4.0 298.00±8.0	97.00±3.0 238.00±7.0	105.00±2.0 154.00±4.0	149.00±6.0 330.00±20.0
COD (mg/L)	54.00±15.0 242.00±18.0	180.00±15.0 645.00±18.0	150.00±15.0 689.00±45.0	182.00±14.0 547.00±36.0	169.00±13.0 476.00±34.0	222.00±23.0 876.00±30.0
Chloride (mg/L)	15.00±0.5 31.00±0.5	21.00±0.9 54.50±0.5	28.00±1.3 66.20±0.8	30.80±0.6 95.20±0.8	21.30±1.0 67.80±0.7	46.30±0.8 99.00±0.5
G (uS)	4.50±4.0 542.00±6.0	363.00±7.0 839.00±3.0	484.00±2.0 838.00±3.0	516.00±3.0 842.00±4.0	358.00±3.0 972.00±7.0	516.00±4.0 998.80±8.0
Nitrate (asN) (mg/L)	0.36±0.01 1.55±0.5	0.52±0.01 1.46±0.01	0.61±0.01 1.57±0.03	0.59±0.01 1.44±0.01	0.93±0.01 1.77±0.06	0.69±0.01 2.10±0.01
Phosphate (as P) (mg/L)	0.14±0.02 3.85±0.05	0.50±0.57 4.33±0.29	0.69±0.01 4.39±0.02	0.50±0.20 4.94±0.03	0.71±0.01 55.25±0.13	0.75±0.01 5.90± 9.1

laboratory using Winkler's modified iodide-azide method. The sewage samples were brought to the laboratory in ice boxes and subjected to the analysis of BOD (by incubating diluted sewage samples at 25°C for 5 days in the dark), COD (by the dichromate reflux method using a Ferroin indicator), pH (using a pH meter), alkalinity and acidity (by the potentiometric titration method with the help of a pH meter and diluted H<sub>2</sub>SO<sub>4</sub> and NaOH), chloride (by Mohr's argentometric method using potassium chromate as indicator), conductivity (using conductivity meter), phosphate (stannous-chloride method), and nitrate using the phenol-disulphonic acid colorimetric test (Jackson 1958).

#### Statistical analyses

The data obtained through analysis for various parameters were subjected to a statistical analysis on a computer at the Banaras Hindu University Computer Centre at three levels :

a) Analysis of variance using the appropriate method described by Cochran and Cox (1963). The statistical analysis package provided by International Computer

Ltd. (ICL 1973) was used for this purpose. The model used is :

$$Y = A(I) + B(J) + C(K) + AB(IJ) + E,$$

where

A, B and C stand for the sites, months and replicates, respectively, and (I), (J) and (K) are their respective numbers E is error.

b) Duncan's multiple-range test as described by Federer (1963).

c) Pearson's coefficient of correlation (r) between various parameters at each sampling site using the formula:

$$r = \frac{\sum xy - \frac{\sum x \sum y}{n}}{\sqrt{(\sum x^2 - \frac{(\sum x)^2}{n})(\sum y^2 - \frac{(\sum y)^2}{n})}}$$

where

r is the correlation coefficient, x and y are two variables, and n is the number of samples.



## RESULTS AND DISCUSSION

## Temperature

Temperature is the most important factor which influences the chemical, biochemical, and biological characteristics of the aquatic systems. Temperature also alters the saturation values of solids and gases in water. The present investigation reveals that the temperature varied from a minimum  $20.3 \pm 0.4^\circ\text{C}$  in February (Assi ghat sewage) to a maximum  $34.3 \pm 0.6^\circ\text{C}$  (Rajghat sewage) in July (Table 2). The sewage temperature is mostly governed by the ambient temperature. The temperature values were significantly (Duncan's multiple-range test at 5% level) higher in April to July and lower in October to December (Table 3). The mean temperature was significantly (Duncan's multiple-range test at 5% level) higher in Rajendra Prasad ghat sewage ( $27.8 \pm 3.9^\circ\text{C}$ ) and Rajghat sewage ( $28.0 \pm 3.9^\circ\text{C}$ ) and lower ( $25.8 \pm 3.9^\circ\text{C}$ ) in Assi ghat sewage (Table 4).

## pH-value

Because most of the chemical and biochemical reactions are influenced by the pH, it is of great practical importance. The adverse effects of most of the acids appear below pH 5 and of alkalis above pH 9.5. The sewage pH was slightly alkaline, ranging from  $7.07 \pm 0.06$  in August and November (Chauki ghat and Rajendra Prasad ghat sewage) to  $8.07 \pm 0.06$  (Assi ghat sewage) in May (Table 2). The mean pH values were significantly higher (Duncan's multiple-range test at 5% level) in March to May, September, November, and December with the highest value ( $7.9 \pm 0.1$ ) in April and significantly lower in June to August, October, and January with the lowest value ( $7.2 \pm 0.1$ ) in July (Table 5). Further, significantly higher (Duncan's multiple-range test at 5% level) mean pH values were recorded in Assi ghat, Shiwala ghat and Rajghat sewage and lower in Harishchandra ghat and Chauki ghat sewage (Table 4).

## Acidity

The acidity of water is its quantitative capacity to react with a strong base to a designated pH. Usually

Table 3. Monthly variation in the physico-chemical properties of Varanasi city sewage discharged into the river Ganga at Varanasi (mean values of six sites  $\pm$  standard deviation).

	Temp. ( $^\circ\text{C}$ )	pH	Acidity ( $\text{CaCO}_3$ (mg/L))	Alkal. ( $\text{CaCO}_3$ (mg/L))	DO (mg/L)	BOD (mg/L)	COD (mg/L)	Chloride (mg/L)	G (uS)	Nitrate (mg/L)	Phosphate (mg/L)
March	$26.4 \pm 0.6$	$7.7^* \pm 0.1$	$18.8 \pm 2.4$	$352.0 \pm 26.0$	$2.3 \pm 0.8$	$135.0 \pm 64.0$	$330.0 \pm 140.0$	$49.0 \pm 19.9$	$680.0 \pm 150.0$	$0.84 \pm 0.30$	$2.70 \pm 1.1$
April	$29.9^* \pm 0.8$	$7.9^* \pm 0.1$	$17.8 \pm 5.9$	$410.0 \pm 130.0$	$2.0 \pm 0.9$	$129.0^{**} \pm 25.0$	$350.0 \pm 170.0$	$47.0 \pm 18.0$	$520.0^{**} \pm 34.0$	$0.84 \pm 0.20$	$1.40^{**} \pm 1.1$
May	$32.5^* \pm 1.5$	$7.6^* \pm 0.1$	$33.9^* \pm 7.3$	$377.0 \pm 55.0$	$1.5^{**} \pm 0.8$	$214.0^* \pm 50.0$	$490.0^* \pm 110.0$	$40.0 \pm 17.0$	$650.0 \pm 120.0$	$0.91 \pm 0.30$	$1.21^{**} \pm 0.70$
June	$32.8^* \pm 1.1$	$7.3^{**} \pm 0.2$	$56.6^{**} \pm 13.3$	$410.0 \pm 180.0$	$1.1^{**} \pm 0.7$	$254.0^* \pm 74.0$	$570.0^* \pm 190.0$	$53.0 \pm 18.0$	$700.0^* \pm 180.0$	$0.90 \pm 0.20$	$0.59^{**} \pm 0.20$
July	$30.4^* \pm 0.2$	$7.2^{**} \pm 0.1$	$26.2 \pm 12.1$	$221.0^{**} \pm 61.0$	$1.4^{**} \pm 0.3$	$180.0 \pm 42.0$	$300.0 \pm 90.0$	$32.0^{**} \pm 18.0$	$540.0^{**} \pm 60.0$	$1.14^* \pm 0.50$	$0.66^{**} \pm 0.30$
August	$28.1^* \pm 0.6$	$7.4^{**} \pm 0.2$	$20.3 \pm 7.0$	$215.0^{**} \pm 47.0$	$1.9 \pm 0.7$	$89.0^{**} \pm 38.0$	$165.0^{**} \pm 85.0$	$32.0^{**} \pm 18.0$	$496.0^{**} \pm 65.0$	$1.28^* \pm 0.20$	$0.72^{**} \pm 0.30$
September	$29.4^* \pm 1.3$	$7.6^* \pm 0.2$	$22.8 \pm 15.1$	$395.0 \pm 83.0$	$2.2 \pm 0.8$	$197.0 \pm 65.0$	$380.0 \pm 120.0$	$40.0 \pm 24.3$	$50.0^{**} \pm 210.0$	$1.08^* \pm 0.30$	$1.81 \pm 0.70$
October	$25.0^{**} \pm 0.6$	$7.4^{**} \pm 0.2$	$16.8 \pm 2.8$	$404.0 \pm 33.0$	$2.5^* \pm 1.6$	$168.0 \pm 60.0$	$380.0 \pm 130.0$	$39.0 \pm 14.0$	$570.0^{**} \pm 180.0$	$0.76 \pm 0.20$	$2.61 \pm 0.60$
November	$22.2^{**} \pm 1.1$	$7.6^* \pm 0.2$	$28.3 \pm 3.4$	$420.0 \pm 49.9$	$2.2 \pm 0.5$	$160.0 \pm 67.0$	$360.0 \pm 150.0$	$49.0 \pm 16.0$	$630.0 \pm 140.0$	$0.85 \pm 0.20$	$3.98^* \pm 1.30$
December	$23.2^{**} \pm 0.8$	$7.6^* \pm 0.3$	$33.4^* \pm 3.1$	$506.0^* \pm 375.0$	$1.2^{**} \pm 0.3$	$143.0 \pm 61.0$	$310.0 \pm 140.0$	$62.0^* \pm 21.0$	$780.0^* \pm 190.0$	$0.97 \pm 0.40$	$3.20 \pm 1.50$
January	$22.3^{**} \pm 1.1$	$7.4^{**} \pm 0.2$	$26.9 \pm 18.0$	$360.0 \pm 57.0$	$1.7 \pm 0.5$	$141.0 \pm 60.0$	$290.0 \pm 100.0$	$50.0 \pm 21.0$	$680.0 \pm 160.0$	$1.03^* \pm 0.40$	$2.19 \pm 0.20$
February	$23.1^{**} \pm 1.7$	$7.7^* \pm 0.2$	$17.2 \pm 8.2$	$327.0 \pm 49.0$	$3.0^* \pm 1.0$	$166.0 \pm 92.0$	$380.0 \pm 180.0$	$39.0 \pm 11.0$	$690.0 \pm 140.0$	$0.78 \pm 0.30$	$3.30 \pm 1.1$

\* Significantly higher; \*\* Significantly lower; No mark : nonsignificant variation Duncan's Multiple Range Test at 5% level of significance.

**Table 4. Physico-chemical properties of Varanasi city sewage discharged into the river Ganga at Assi Ghat (AG sewage), Shiwala Ghat (SG sewage), Harishchandra Ghat (HG sewage), Chauki Ghat (CG sewage), Rajendra Prasad Ghat (RPG sewage), (mean values of 12 months  $\pm$  standard deviation).**

Parameter	AG sewage	SG sewage	HG sewage	CG sewage	RPG sewage	RG sewage
pH	7.65 $\pm$ 0.20*	7.65 $\pm$ 0.20*	7.44 $\pm$ 0.20**	7.38 $\pm$ 0.20**	7.56 $\pm$ 0.30	7.60 $\pm$ 0.30*
Temperature ( $^{\circ}$ C)	25.80 $\pm$ 3.90**	26.60 $\pm$ 3.70**	27.00 $\pm$ 3.90	27.10 $\pm$ 4.00	27.80 $\pm$ 3.90*	28.00 $\pm$ 3.90*
Acidity (CaCO <sub>3</sub> mg/L)	20.00 $\pm$ 10.00**	20.80 $\pm$ 9.60**	3.00 $\pm$ 16.00	27.10 $\pm$ 9.50	28.00 $\pm$ 16.00	36.00 $\pm$ 20.00
Alkalinity (CaCO <sub>3</sub> mg/L)	340.00 $\pm$ 78.00	367.00 $\pm$ 97.00	343.00 $\pm$ 94.00	323.00 $\pm$ 82.00	342.00 $\pm$ 68.00	490.00 $\pm$ 150.00*
DO (mg/L)	2.40 $\pm$ 0.90*	1.80 $\pm$ 1.00	1.70 $\pm$ 0.40	2.50 $\pm$ 0.60*	2.10 $\pm$ 0.70	0.90 $\pm$ 0.50**
BOD (mg/L)	46.00 $\pm$ 28.00**	166.00 $\pm$ 57.00	187.00 $\pm$ 56.00	189.00 $\pm$ 50.00	160.00 $\pm$ 42.00	239.00 $\pm$ 56.00
COD (mg/L)	109.00 $\pm$ 50.00**	360.00 $\pm$ 150.00	420.00 $\pm$ 120.00	416.00 $\pm$ 99.00	328.00 $\pm$ 81.00	520.00 $\pm$ 180.00*
G (uS)	518.00 $\pm$ 27.00	640.00 $\pm$ 170.00	580.00 $\pm$ 110.00	640.00 $\pm$ 130.00	560.00 $\pm$ 170.00	310.00 $\pm$ 170.00*
Chloride (mg/L)	22.00 $\pm$ 4.90**	35.00 $\pm$ 11.00**	46.00 $\pm$ 12.00	51.00 $\pm$ 16.00	41.00 $\pm$ 14.00	71.00 $\pm$ 14.00
Nitrate (as N) (mg/L)	0.75 $\pm$ 0.40	0.81 $\pm$ 0.40	0.90 $\pm$ 0.30	0.98 $\pm$ 0.20	1.15 $\pm$ 0.30	1.10 $\pm$ 0.40
Phosphate (as P) (mg/L)	1.40 $\pm$ 1.40**	1.60 $\pm$ 1.20*	2.20 $\pm$ 1.30	1.90 $\pm$ 1.20**	2.40 $\pm$ 1.30*	2.71 $\pm$ 1.50*

\* Significantly higher variation ;

\*\* Significantly lower variation ;

No mark : No significant variation in the parameter between the sites (Duncan's Multiple Range Test at 5% level of significance).

the major component of acidity in natural waters is carbon-dioxide. The acidity values ranged from a minimum of 10.1  $\pm$  1.3 mg CaCO<sub>3</sub>/L (October) in Shiwala ghat sewage to a maximum of 77.8  $\pm$  0.8 mg CaCO<sub>3</sub>/L in Rajghat sewage (Table 2). Significantly higher acidity values in May and December with highest (57  $\pm$  13 mg CaCO<sub>3</sub>/L) in June were recorded. No significant variation in acidity values between

other months was obtained (Table 3). A sharp increase in acidity in May and June may be attributed to the high temperature and, therefore, high microbial activity or discharge of some acidic substances. Acidity values were significantly lower in Assi ghat (20  $\pm$  10 mg CaCO<sub>3</sub>/L) and Shiwala ghat sewage (21  $\pm$  10 mg CaCO<sub>3</sub>/L) and higher (36  $\pm$  20 mg CaCO<sub>3</sub>/L) in Rajghat sewage (Table 4).

**Table 5. Pollution load (kg/d) discharged through city sewage in the river Ganga at Varanasi (average of 12 months).**

Parameters	Assi ghat	Shivala ghat	Harishchandra	Chauki ghat	Ranjendra Prasad ghat	Rajghat*	Total
BOD	365	665	1122	1890	1980	19120	25082
COD	872	1420	2502	4160	3936	41280	54170
Acidity (CaCO <sub>3</sub> )	163	83	179	271	335	2288	3919
Alkalinity (CaCO <sub>3</sub> )	2717	1466	2056	3232	4109	39024	52604
Chloride	174	138	277	506	498	5688	7281
NO <sub>3</sub> <sup>-</sup> (as N)	6.0	3.0	5.4	9.8	13.8	88	214
PO <sub>4</sub> <sup>3-</sup> (as P)	11.2	6.4	13.14	19.0	28.2	216.8	295

\*Significantly high at 5% level (Duncan's multiple range test).

Other sites show no significant variation in the values.

### Total alkalinity

Alkalinity constitutes an important parameter in determining the quality of water. It is the acid-neutralizing capacity of the water that gives primarily a function of the carbonate, bicarbonate and hydroxide content. A variation in alkalinity values was recorded as a minimum of  $171 \pm 1$  mg  $\text{CaCO}_3/\text{L}$  (August) in Harishchandra ghat sewage and a maximum of  $698 \pm 8$  mg  $\text{CaCO}_3/\text{L}$  (July) in Rajghat sewage (Table 2). A significantly higher mean alkalinity value ( $510 \pm 380$  mg  $\text{CaCO}_3/\text{L}$ ) in December and lower in July ( $220 \pm 170$  mg  $\text{CaCO}_3/\text{L}$ ) and August ( $220 \pm 100$  mg  $\text{CaCO}_3/\text{L}$ ) was recorded. No significant variation was noticed among the values of other months (Table 3). Furthermore, the total alkalinity was significantly higher ( $490 \pm 150$  mg  $\text{CaCO}_3/\text{L}$ ) in Rajghat sewage than that of other sites (Table 4).

### Dissolved oxygen

Dissolved oxygen data are valuable in determining the water quality criteria of an aquatic system. In the system where the rates of respiration and organic decomposition are high, the DO values usually remain lower than those of the systems where the rate of photosynthesis is high. Temperature also plays an important role in determining DO in an aquatic body. A high pollution load may also decrease the DO values to a considerable level. The DO values ranged from a minimum  $0.2 \pm 0.1$  mg/L in Rajghat sewage to a maximum  $4.6 \pm 0.1$  mg/L (March) in Shiwala ghat sewage (Table 2). Significantly higher DO values in February ( $2 \pm 1$  mg/L) and October ( $2.5 \pm 1.6$  mg/L) and lower in May to July with the lowest value ( $1.1 \pm 0.7$  mg/L) in June were recorded (Table 3). Lower DO values during summer may be attributed to the high temperature and its consumption due to high growth and activities of microorganisms. Furthermore, DO values were significantly lower ( $0.9 \pm 0.5$  mg/L) in Rajghat sewage and higher ( $2.5 \pm 0.6$  mg/L) in Chauki ghat sewage (Table 4).

### Biochemical oxygen demand

BOD has been used as a measure of the amount of organic materials in an aquatic solution which support the growth of microorganisms (Ciaccio 1971). BOD determines the strength or polluting power of sewage, effluents and other polluted waters and provides data on the pollution load in natural waters. Higher values of BOD indicate a higher consumption of oxygen and a higher pollution load. The BOD values varied from a minimum of  $20 \pm 2$  mg/L (March) in Assi ghat sewage to a maximum of  $330 \pm 20$  mg/L

(July) in Rajghat sewage (Table 2). Usually, higher BOD values in summer and lower in the rainy season were recorded, the mean values being significantly lower ( $89 \pm 38$  mg/L) and  $129 \pm 25$  mg/L) in August and April, respectively, and higher ( $214 \pm 50$  mg/L and  $254 \pm 74$  mg/L) in May and June (Table 3). Furthermore, the mean BOD value was significantly lower ( $46 \pm 28$  mg/L) in Assi ghat sewage. No significant variation in BOD was observed between other sites (Table 4).

### Chemical oxygen demand

COD determines the amount of oxygen required for chemical oxidation of organic matter using a strong chemical oxidant, such as potassium dichromate under reflux conditions. The minimum COD value of  $53 \pm 15$  mg/L (March in Assi ghat sewage) and the maximum of  $876 \pm 30$  mg/L (July in Rajghat sewage) were obtained (Table 2). The mean COD values were significantly higher in June ( $570 \pm 190$  mg/L) and May ( $493 \pm 105$  mg/L) and lower ( $170 \pm 80$  mg/L) in August (Table 3). Furthermore, significantly lower COD values ( $109 \pm 50$  mg/L) were recorded in Assi ghat sewage. The COD values in Rajghat sewage were significantly higher ( $520 \pm 180$  mg/L) than those of Assi ghat, Shiwala ghat, and Rajendra Prasad ghat sewage, whereas no significant variation was recorded between Harishchandra ghat, Chauki ghat, and Rajghat sewage (Table 4).

### Chloride

Chloride is one of the major inorganic anions in water and waste water. The chloride content showed fluctuations within a range of  $15.0 \pm 0.5$  mg/L (September) in Assi ghat sewage to  $99.0 \pm 0.5$  mg/L (January) in Rajghat sewage (Table 2). Usually lower values of chloride during the rainy season at all the sites may be due to a lower chloride content in the supplied water which itself was diluted during the rainy season. Significantly higher values ( $62 \pm 21$  mg/L) in December and lower values in August and October with lowest ( $32 \pm 18$  mg/L) in July were recorded (Table 3). Furthermore, the mean chloride content was significantly lower in Assi ghat ( $22 \pm 5$  mg/L) and Shiwala ghat sewage ( $35 \pm 11$  mg/L) and higher ( $71 \pm 14$  mg/L) in Rajghat sewage (Table 4).

### Electrical conductance (at 25°C)

The electrical conductance is reciprocal to the electrical resistance and the G values show total ions per centimeter. It is a numerical expression of the ability of a water sample to carry an electric current.

The G values ranged from a minimum of  $998 \pm 3 \mu\text{S}$  (September) in Rajendra Prasad ghat sewage to a maximum of  $998 \pm 8 \mu\text{S}$  (December) in Rajghat sewage (Table 2). G values were significantly higher,  $780 \pm 190$  and  $670 \pm 180 \mu\text{S}$  in December and June, respectively, and significantly lower in July to October and April with a minimum ( $496 \pm 65 \mu\text{S}$ ) in August (Table 3). Usually lower G values during the rainy season may be due to a low G value of the supplied water which itself was diluted during the rainy season. Furthermore, the G values were significantly higher ( $812 \pm 169 \mu\text{S}$ ) in Rajghat sewage. No significant variation was recorded in G between all other sites (Table 4).

#### *Nitrate (as nitrogen)*

Nitrate represents the end product of oxidation of nitrogenous matters and its concentration may depend on the nitrification and denitrification activities of micro-organisms. The concentration of nitrate ranged from a minimum of  $0.357 \pm 0.006 \text{ mg/L}$  (April) in Assi ghat sewage to a maximum of  $2.10 \pm 0.09 \text{ mg/L}$  (July) in Rajghat sewage (Table 2). The recorded values were significantly higher in July to September and January with a maximum ( $1.28 \pm 0.20 \text{ mg/L}$ ) in August (Table 3). Furthermore, the nitrate value was significantly higher in Rajghat ( $1.10 \pm 0.43 \text{ mg/L}$ ) and Rajendra Prasad ghat sewage ( $1.15 \pm 0.30 \text{ mg/L}$ ). No significant variation was recorded in the nitrate content between other sites (Table 4).

#### *Phosphate (as phosphorus)*

Phosphate determination is useful in measuring the water quality since it is an important plant nutrient and may play a role of a limiting factor among all other essential plant nutrients (Dugan 1972). The values of phosphate varied from a minimum of  $0.14 \pm 0.02 \text{ mg/L}$  (August) in Assi ghat sewage to a maximum of  $5.87 \pm 0.1 \text{ mg/L}$  (December) in Rajghat sewage (Table 2). Significantly higher phosphate values in December and January with a maximum ( $4.0 \pm 1.3 \text{ mg/L}$ ) in November, and lower values in April to August with a minimum ( $0.59 \pm 0.20 \text{ mg/L}$ ) in June were recorded (Table 3). Furthermore, the phosphate content was significantly higher ( $2.7 \pm 1.5 \text{ mg/L}$ ) in Rajghat sewage. Significantly lower phosphate contents were recorded in Assi ghat, Shiwala ghat, and Chauki ghat sewage with a maximum ( $1.40 \pm 1.4 \text{ mg/L}$ ) in Assi ghat sewage (Table 4).

#### *Pollution load*

The total pollution load discharged in the river Ganga through six nalas (sewage discharge points) was 25 082 kg per day in form of BOD, 54 170 kg of COD per day, 3919 kg of  $\text{CaCO}_3$  per day and 52 604 kg of  $\text{CaCO}_3$  per day as acidity and alkalinity, respectively. The pollution load also contained 7281 kg of chloride per day, 214 kg of  $\text{NO}_3^-$  (as N) per day, and 295 kg of  $\text{PO}_4^{3-}$  (as P) per day (Table 5). A significantly lower pollution load was discharged at Assi ghat (in the form of BOD and COD) and Shiwala ghat (as acidity, alkalinity, chloride,  $\text{NO}_3^-$  (as N), and  $\text{PO}_4^{3-}$  (as P)). However, the highest pollution load was discharged at Rajghat (Table 5), where the highest quantity of sewage is discharged.

Furthermore, the pollution load varied from a minimum of 10 693 kg per day (August) to a maximum of 30 428 kg per day (June) in terms of BOD, 19 820 kg per day (August) to 68 536 kg per day (June) in terms of COD, 2134 kg of  $\text{CaCO}_3$  per day (October) to 6792 kg of  $\text{CaCO}_3$  per day (June) as acidity and from 25 786 kg of  $\text{CaCO}_3$  per day (August) to 60767 kg of  $\text{CaCO}_3$  per day (December) as alkalinity. The chloride, nitrate, and phosphate contents were higher (7387 kg of  $\text{Cl}^-$  per day, 154 kg of  $\text{NO}_3^-$  (as N) per day, and 478 kg of  $\text{PO}_4^{3-}$  (as P) per day in December, August and November, respectively. The lower values were obtained as 3844 kg of  $\text{Cl}^-$  per day in July, 91 kg of  $\text{NO}_3^-$  (as N) per day in October, and 71 kg of  $\text{PO}_4^{3-}$  (as P) per day in June (Table 6).

#### *Analysis of variance*

The analysis of variance (Table 7) reveals that the variation in the values of sewage acidity, alkalinity, dissolved oxygen, chloride, G, and nitrate was significant ( $P < 0.01$ ) between the sites and between the months. However, the variation between the sites was greater than that of the monthly fluctuation. Similarly, temperature, pH and phosphate values showed a significant variation with respect to the sites and the months, but the monthly variation was greater in this case. No significant monthly variation was obtained for the values of BOD and COD. However, they showed a significant variation among the sites.

#### *Correlation analysis*

Only a few parameters at a few sites exhibited significant relationships (Table 8). A positive and significant correlation was obtained between temperature and BOD (in Assi ghat, Chauki ghat, and Rajendra Prasad ghat sewage), between acidity and BOD (in Harishchandra ghat, Chauki ghat, and Rajendra Prasad

Table 6. Monthly variation in the pollution load (kg per day) discharged through city sewage into river Ganga at Varanasi (average of six sites).

Months	BOD	COD	Acidity (CaCO <sub>3</sub> )	Alkalinity (CaCO <sub>3</sub> )	Chloride	Nitrate (as N)	Phosphate (as P)
March	16177	39729	2256	42279	5859	101	3288
April	15509	42242	2134	48470	5603	100	163
May	25649	59147	4067	45272	4770	109	145
June	30428	68563	6792	48837	6339	108	71
July	21585	3575	3150	26559	3844	133	79
August	10693	19820	2438	25786	3853	154	86
September	23702	45739	2739	47440	4796	129	217
October	20109	40015	2014	48450	4680	91	313
November	19189	43084	3397	50429	5893	102	478
December	17212	37676	4610	60767	7387	116	397
January	16956	34958	3230	43153	6038	123	263
February	19928	45061	2066	39257	4701	93	395

ghat sewage), between acidity and COD (in Shiwala ghat, Harishchandra ghat and Chauki ghat sewage), between alkalinity and chloride (in Harishchandra ghat, Chauki ghat, and Rajghat sewage), and between BOD and COD (in Assi ghat, Harishchandra ghat, Chauki ghat, and Rajghat sewage). Seasonal fluctuation seems

to be responsible for this type of correlation. Phosphate showed a positive and significant correlation with alkalinity (in Rajghat and Rajendra Prasad ghat sewage), with DO (in Shiwala ghat, Harishchandra ghat, and Rajghat sewage), with chloride (in Assi ghat and Harishchandra ghat sewage), and with ECE

Table 7. F-variance ratio values obtained through analysis of variance for various physico-chemical parameters of sewage between the sites and the months.

	Sites		Months	
	F Ratio	P	F Ratio	P
Temperature	3.758	0.01	25.725	0.01
pH	14.658	0.01	15.832	0.01
Acidity	7.466	0.01	2.552	0.01
Alkalinity	18,036	0.01	6.604	0.01
DO	26.970	0.01	3.647	0.01
BOD	50.929	0.01	0.780	NS
COD	37.099	0.01	0.641	NS
Chloride	87.269	0.01	2.984	0.01
G	27.884	0.01	4.375	0.01
Nitrate (as N)	13.780	0.01	2.767	0.01
Phosphate (as P)	7.925	0.01	14.947	0.01

(in Chauki ghat and Rajendra Prasad ghat sewage). A negative and significant correlation has also been recorded between temperature and alkalinity (in Chauki ghat and Rajendra Prasad ghat sewage), temperature and DO (in Harishchandra ghat and Rajghat sewage), temperature and phosphate (in Assi ghat, Shiwala ghat, Harishchandra ghat, and Rajghat sewage), and between acidity and DO (in Assi ghat, Shikala ghat, Rajendra Prasad ghat and Rajghat sewage). Some parameters seem to be influenced by the quality of the Ganga water (Sikandar 1986) which is supplied to the city.

The sewage discharged into the Ganga at Varanasi seems to be dominated by domestic wastes because of its neutral pH, lower acidity, alkalinity, chloride, and G values. Significantly higher acidity, BOD, and COD in May and June suggest higher concentration of sewage during this period. A greater variation in sewage characteristics among the sites rather than the months has been noticed. Table 4 reveals the

highest concentration of sewage at Rajghat and lowest at Assi ghat. The sewage characteristics may vary with respect to time and place. However, DO, BOD, and pH values correlate with the values given by Sharma et al. (1979). The range of chloride, G, and nitrate are slightly lower than those reported by Ray and David (1966). These differences may be attributed to the variation in the sewage dilution and its constitution. The range of the phosphate concentration corroborates the values reported by Kothandaraman et al. (1963) and Ray and David (1966).

The Varanasi city sewage is full of organic matter and inorganic minerals. Its total exploitation for beneficial uses through tactful management is needed to reduce the pollution of the Ganga river. A portion of raw sewage from Rajghat is used by local farmers for crop irrigation. Therefore, these farmers are exposed to a wide variety of routinely found disease-producing micro-organisms and protozoans. Helminthic infections and a number of skin and gastrointestinal

Table 8. Correlation coefficient values (r) for various physico-chemical parameters of sewage at different sites.

Parameters	S i t e s					
	Assi ghat	Shivala ghat	Harishchandra ghat	Chauki ghat	Dashawa-medh ghat	Rajghat
Temp:alkal.	-0.37 <sup>NS</sup>	-0.87 <sup>NS</sup>	-0.40 <sup>NS</sup>	-0.48 <sup>*</sup>	-0.50 <sup>*</sup>	-0.03 <sup>NS</sup>
Temp:dissolved oxygen	-0.37 <sup>NS</sup>	-0.28 <sup>NS</sup>	-0.54 <sup>*</sup>	-0.01 <sup>NS</sup>	-0.38 <sup>NS</sup>	-0.57 <sup>**</sup>
Temp:BOD	0.71 <sup>*</sup>	0.36 <sup>NS</sup>	0.34 <sup>NS</sup>	0.48 <sup>+</sup>	0.57 <sup>**</sup>	0.01 <sup>NS</sup>
Temp:PO <sub>4</sub> <sup>3-</sup>	-0.80 <sup>***</sup>	-0.74 <sup>*</sup>	-0.82 <sup>***</sup>	-0.75 <sup>*</sup>	-0.62 <sup>**</sup>	-0.69 <sup>++</sup>
pH:acidity	-0.34 <sup>NS</sup>	-0.38 <sup>NS</sup>	-0.24 <sup>NS</sup>	-0.06 <sup>NS</sup>	-0.59 <sup>**</sup>	-0.77 <sup>*</sup>
Acidity:dissolved oxygen	-0.66 <sup>**</sup>	-0.63 <sup>**</sup>	-0.42 <sup>NS</sup>	-0.06 <sup>NS</sup>	-0.83 <sup>***</sup>	-0.60 <sup>**</sup>
Acidity:BOD	0.46 <sup>NS</sup>	0.37 <sup>NS</sup>	0.73 <sup>*</sup>	0.70 <sup>*</sup>	0.61 <sup>**</sup>	0.06 <sup>NS</sup>
Acidity:COD	-0.62 <sup>**</sup>	0.52 <sup>+</sup>	0.71 <sup>*</sup>	0.69 <sup>++</sup>	0.16 <sup>NS</sup>	0.06 <sup>NS</sup>
Alk:Cl <sup>-</sup>	-0.15 <sup>NS</sup>	0.36 <sup>NS</sup>	0.54 <sup>+</sup>	0.93 <sup>***</sup>	-0.20 <sup>NS</sup>	0.62 <sup>**</sup>
Alk:PO <sub>4</sub> <sup>3-</sup>	0.02 <sup>NS</sup>	0.06 <sup>NS</sup>	0.60 <sup>**</sup>	0.38 <sup>NS</sup>	0.59 <sup>**</sup>	-0.03 <sup>NS</sup>
DO:PO <sub>4</sub> <sup>3-</sup>	0.19 <sup>NS</sup>	0.66 <sup>++</sup>	0.50 <sup>+</sup>	0.28 <sup>NS</sup>	0.19 <sup>NS</sup>	0.48 <sup>*</sup>
BOD:COD	0.93 <sup>***</sup>	-0.01 <sup>NS</sup>	0.89 <sup>***</sup>	0.79 <sup>*</sup>	0.40 <sup>NS</sup>	0.83 <sup>***</sup>
Cl <sup>-</sup> :PO <sub>4</sub> <sup>3-</sup>	0.67 <sup>++</sup>	0.14 <sup>NS</sup>	0.64 <sup>++</sup>	0.44 <sup>NS</sup>	-0.07 <sup>NS</sup>	0.00 <sup>NS</sup>
G:PO <sub>4</sub> <sup>3-</sup>	0.37 <sup>NS</sup>	0.30 <sup>NS</sup>	-0.19 <sup>NS</sup>	0.57 <sup>**</sup>	0.63 <sup>++</sup>	0.07 <sup>NS</sup>

\* Significant at P < 0.01;

\*\* Significant at P < 0.05;

\*\*\* Significant at P < 0.001;

+ Significant at P < 0.1;

++ Significant at P < 0.02;

NS: Non significant;

DO: Dissolved oxygen.

diseases were recorded during the survey by the authors. Some diseases, malformations, and bad taste have also been observed in the vegetable crops like *solanum tuberosum* and *brassica oleracea* var. *botrytis* irrigated with raw sewage. A study from Nagpur (CPHERI 1971) revealed that farm workers had a significantly higher incidence of infection with the nematodes *ascaris lumbricoides* and *ancylostome duodenale*. The gastrointestinal illness, headache, nasal, and eye irritation, chest tightness, fever and skin diseases have also been observed among inexperienced workers exposed to sewage (Clark et al. 1980; Lundholm and Rylander 1983; Clark 1985).

Sludge application on land contaminates the underground water by increasing G and fecal coliform (Higgins 1984; Trout et al. 1976). It causes an increase in the Na, K, Ca, and Mg accumulation of underground nitrate (as nitrogen) as a result of leaching through soil and a decrease in the soil pH to the extent that lime is required (Higgins 1984).

It has been suggested (Govt. of India 1985) that the BOD of effluents or sewage should not be higher than 20 mg/L for its discharge into rivers and 50 mg/L for its use as irrigation water. According to the Indian Standard Institution (ISI 1982), the permissible limits for BOD should not be higher than 100 mg/L for its use as irrigation water for vegetables and crops and COD 250 mg/L for its discharge into rivers. According to these recommendations, present sewage which is discharged into Varanasi neither can be used for the irrigation of crop fields nor can it be discharged into the river. Therefore, prior to its application to the land for crop irrigation or discharge into the river system, its proper treatment is needed.

**Acknowledgment** — The authors are thankful to Prof. R.S. Ambasht, Head, Department of Botany, for providing necessary facilities and to Prof. H.D. Kumar and Prof. J.S. Singh for their valuable suggestions. The authors are also grateful to Environment and Forest, New Delhi, for providing financial assistance.

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## **ASSESSMENT OF NOISE POLLUTION IN FRIENDSHIP TEXTILE MILL LIMITED, UBONGO —DAR ES SALAAM**

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*EI 9002-024M (Received 28 February 1990; accepted 2 December 1990)*

Most of the textile industries in developing countries like Tanzania are facing a big problem of noise pollution. In most of these countries, the industrial hearing conservation programme is not yet established. The assessment of noise pollution in textile industries has been the aim of this study and Friendship Textile Mill (FTM) is chosen as the case study. The investigation was concerned with the noise exposure and its adverse effects to workers at the mill. The findings revealed that about 30% of the FTM employees are working in hazardous environments of above 90 dB, which is the recommended safe limit of noise in the working environment for 8 h used in Tanzania. In this regard, a programme which includes different methods of how to control the problem, has been proposed for conserving hearing at the factory. The methods include the use of hearing protective devices, modification of the noise source, repair of machines, and pre-employment and periodic audiometric testing.

### **INTRODUCTION**

It is common in developing countries like Tanzania to find people working in places like industries with high noise levels that are detrimental to their health (ILO 1976, 1984). The textile industry being one of the major industries in Tanzania has shown a great increase after the independence in 1961. Thus, the increase in textile industries in countries with remarkable noise pollution problems (Kalugendo 1979), reflects the increase in health problems associated with excessive noise exposure, if old technologies and worn-out machines continue to be used.

The Friendship Textile Mill (FTM), located in the Ubungo industrial area, was established in 1965 and employs about 4328 workers. The conveying manufacturing process and batch production use raw cotton chemicals, starch and dye stuff to produce one product. The production is run intermittently for 24 h/d.

Machines are grouped together according to function or process, arranged in separate flow patterns. Open aisles are left to facilitate transportation of materials. The functional layout offers an opportunity for good machine utilization. Mechanization of the process is low with respect to span, level, and penetration. Therefore, operations are labour intensive. The production flow is divided into spinning, weaving, and wet processing. At FTM, a large number of people is expected to work in an environment with noise levels above 90 dB (A). The investigation was conducted to ascertain that the noise levels to which the workers are exposed do not exceed the permissible limit.

The investigation also involved an epidemiological study in order to recognize potential health problems associated with noise exposure of the workers.



## MATERIALS AND METHODS

Noise level measurements were conducted at Friendship Textile Mill between 7 November 1987 and 15 January 1988 whereby 9 to 10 measurements were made at 11 different places in the factory. The measurements were done at one-week intervals and for 2-2.5 h/d. To update the data, the 11th measurement was done on 31 March 1989. Equipment used during the noise level measurements included a precision sound level meter and an Octave Analyzer (Bruel & Kjaer Type 2215). The accessories included the following:

- 1) Sound level calibrator type 4230,
- 2) B & K Free-Field response 1/2 condenser microphone Type 4165,
- 3) four batteries, and so on.

Noise measurements were made in areas normally occupied by workers. The sound level, as well as sound levels in the octave bands between 31.5-16 000 Hz, was measured at all locations. It was not possible to stop work in the various departments to measure the background noise but appropriate background levels of noise were obtained by measuring levels of noise in the administration block which is located close to the mills.

Before the noise level measurements were taken in the factory, areas where the measurements were carried out had to be selected. This was done by observation, considering the unit processes where high levels of noises were generated. Measurement areas were selected as follows:

### Mill No. 1

Six unit processes were selected which seemed to have higher noise levels as compared to other places. The unit processes selected included scutching, card-

ing, roving, ring frames, cone winding, and loomshed.

### Mill No. 2

The type and location of different unit processes were the same as of Mill No. 1 except for the loomshed in which the number of looms was larger. Therefore, in this case, only the loomshed was considered to be a measurement place.

### Mill No. 3

In this mill, four major unit processes, bleaching, dyeing, printing, and finishing, were taking place. From this mill, only three places were selected. These included bleaching, dyeing, and printing.

### Administration block

This place was chosen as the control place.

Noise level measurement at all places were done after checking and calibrating the instrument (Sound Level Meter) as instructed in the manual (Type 2215 B & K).

During the measuring period, the following aspects were observed:

The instrument was held at arm's length in order to minimize reflection from the operator. The position of the microphone was about 1.5 m above the floor in the vicinity of operator's working place, but not directly attached to the operator. A "slow" response type A plus octave instrument was used. Sound levels were recorded by varying frequencies from 31.4 Hz to 16 kHz. The operator observed that the workers did not use hearing protection during the time of the noise measurement.

Table 1. The overall noise level measurement results in dB recorded at Friendship Textile Mill, November 1987-January 1988.

Unit process/sampling place	Sample size	Mean value x	Standard deviation s
Scutching	9	93.3	0.83
Carding	9	91.8	1.37
Roving	10	89.7	1.00
Ring frame	10	92.9	1.53
Cone winding	10	84.9	0.94
Loomshed mill no. I	10	103.0	0.83
Loomshed mill no. II	10	101.2	0.68
Bleaching	9	90.1	2.06
Dyeing	9	90.1	2.06
Printing	10	90.5	1.09
Adminstration	10	67.5	3.05

Table 2. Summary of frequency analysis carried out at 11 different sampling places at Friendship Textile Mill between November 1987 and January 1988.

Unit Process Frequency	Noise Levels dB (A) sample statistics																								
	Scutching		Carding		Roving		Ring Frame		Winding		Come		Loomshed Mill No I		Loomshed Mill II		Bleaching		Dyeing		Printing		Administration		
	X	S	X	S	X	S	X	S	X	S	X	S	X	S	X	S	X	S	X	S	X	S	X	S	X
31,5	56.3	0.94	41.9	1.41	39.8	2.34	48.7	2.61	41.2	2.63	57.2	3.22	55.0	1.16	50.9	0.33	45.1	1.21	43.8	1.01	30.9	3.72	1.01	30.9	3.72
63	66.1	3.14	36.4	1.32	53.6	4.75	65.8	1.99	56.5	3.17	70.4	0.49	69.5	1.32	62.0	0.43	61.9	1.80	62.8	0.98	42.8	1.42	0.98	42.8	1.42
125	83.4	1.22	72.0	1.17	68.9	1.06	80.8	2.52	67.7	1.11	74.1	3.18	72.9	0.71	77.2	1.03	76.7	3.21	75.3	1.59	51.5	2.11	1.59	51.5	2.11
250	91.3	0.50	82.4	0.98	83.2	0.41	85.1	0.57	75.6	0.98	82.4	1.13	80.7	1.60	85.3	2.00	87.1	3.33	86.4	2.42	55.8	2.93	2.42	55.8	2.93
500	92.9	1.63	88.8	1.17	89.4	1.23	91.5	1.78	82.0	1.13	92.0	0.58	89.9	0.88	87.4	1.21	89.0	2.56	87.2	2.86	59.2	3.22	2.86	59.2	3.22
1000	92.3	0.71	91.7	1.09	89.3	0.75	92.8	1.60	84.9	0.94	100.5	0.67	98.9	0.90	88.4	1.24	89.7	1.99	89.0	2.43	60.5	2.93	2.43	60.5	2.93
2000	88.8	1.17	91.2	1.54	85.2	0.67	90.7	1.00	83.5	0.69	101.2	0.83	101.2	0.67	89.1	1.67	88.2	2.53	90.1	1.61	64.7	3.29	1.61	64.7	3.29
4000	81.6	1.38	88.4	1.41	81.2	2.03	88.9	2.79	79.8	0.54	99.1	1.61	97.6	2.05	88.8	2.37	84.1	1.17	88.7	1.92	66.7	5.74	1.92	66.7	5.74
8000	74.7	1.23	81.2	1.09	71.8	0.72	87.2	3.64	74.1	0.72	91.5	0.83	90.0	1.04	86.2	2.85	79.5	2.14	85.2	2.63	60.4	8.52	2.63	60.4	8.52
16000	63.9	0.98	69.3	1.52	61.0	1.11	80.3	3.94	69.9	1.16	79.4	0.97	78.1	0.98	78.0	2.59	71.2	3.52	78.1	3.72	41.7	12.00	3.72	41.7	12.00

X = mean sample S = standard deviation

Table 3. Summary showing computation of actual mean and standard deviation of noise levels (population) in dB (A) from sample statistics of respective unit processes.

Unit Process	N	V (N-1)	t 0.996	$\chi^2$ 0.995	$\chi^2$ 0.005	x	Sample s	Population Actual Noise Level	
								$\mu$	S
Scutching	9	8	3.36	22.0	1.34	93.3	0.83	93.3 + 1.0	0.5 - 2.0
Carding	9	8	3.36	22.0	1.74	91.8	1.37	91.8 + 1.6	0.8 - 3.3
Roving	10	9	3.36	23.6	1.73	89.7	1.00	89.8 + 1.7	0.6 - 2.3
Ring Frame	10	9	3.25	23.6	1.73	92.9	1.53	92.9 + 1.7	0.9 - 3.5
Cone Winding	10	9	3.25	23.6	1.73	84.9	0.94	84.9 + 1.0	0.6 - 2.1
Loomshed Mill no	10	9	3.25	23.6	1.73	103.0	0.83	103.0 + 0.9	0.5 - 1.2
Loomshed Mill no	10	9	3.25	23.6	1.73	101.2	0.68	101.2 + 0.8	0.4 - 1.6
Bleaching	9	8	3.36	22.0	1.34	90.1	2.60	90.1 + 3.1	1.6 - 6.3
Dyeing	9	8	3.36	22.0	1.34	90.1	1.71	90.1 + 1.4	1.0 - 4.2
Printing	10	8	3.25	23.6	1.73	90.5	1.90	90.5 + 2.1	1.2 - 4.3
Administration	10	9	3.25	23.6	1.73	67.6	3.50	67.5 + 3.8	2.2 - 8.0

Key:

N = sample size

V = degree of freedom

t 0.0996 = critical value with 99 % confidence

$\chi^2$  0.996 and  $\chi^2$  0.005 = critical value for which 0.5 % of the area lies in the tail of distribution

x = sample mean

s = sample standard deviation

$\mu$  = mean population

S = population standard deviation

Table 4. Estimates of population parameters (i.e., mean,  $\mu$ , and standard deviation) from sample statistics in Table 3.

Unit process frequency Hertz (Hz)	Noise Level dB (A)											
	Scutching		Carding		Roving		Ring Flame		Cone Winding			
	$\mu$	$\sigma$	$\mu$	$\sigma$	$\mu$	$\sigma$	$\mu$	$\sigma$	$\mu$	$\sigma$	$\mu$	$\sigma$
31.5	56.30 ± 1.12	0.60-2.43	41.90 ± 1.69	0.90-3.65	89.80 ± 2.54	1.52-5.61	48.70 ± 2.83	1.70-6.25	41.15 ± 2.85	1.71-6.30		
63	66.10 ± 3.72	2.00-8.12	56.40 ± 1.57	0.84-3.41	53.60 ± 5.16	3.09-1.14	65.80 ± 2.16	1.30-4.77	56.50 ± 3.43	2.06-7.59		
125	83.40 ± 1.40	0.78-3.16	72.00 ± 1.40	0.75-3.01	68.90 ± 1.15	0.69-2.54	80.80 ± 2.73	1.64-6.04	57.70 ± 1.20	0.72-2.56		
250	91.30 ± 0.58	0.32-1.29	82.40 ± 1.16	0.63-2.54	83.20 ± 0.44	0.27-1.12	85.10 ± 0.62	0.37-1.37	75.60 ± 1.06	0.64-2.35		
500	92.90 ± 1.87	1.04-4.22	88.80 ± 1.40	0.75-3.03	89.40 ± 1.30	0.80-2.95	91.50 ± 1.93	1.16-4.26	82.00 ± 1.22	0.73-2.71		
1000	92.30 ± 0.82	0.45-1.84	91.70 ± 1.30	0.70-2.82	89.30 ± 0.80	0.49-1.80	92.80 ± 1.73	1.04-3.83	84.90 ± 1.02	0.61-2.25		
2000	88.80 ± 1.40	0.75-3.03	91.20 ± 1.83	0.98-3.98	85.20 ± 0.73	0.44-1.61	90.70 ± 1.08	0.65-2.40	83.50 ± 0.75	0.45-1.65		
4000	81.60 ± 1.64	0.88-3.57	88.40 ± 1.68	0.90-3.65	81.20 ± 2.20	1.32-4.86	88.90 ± 3.03	1.82-6.68	79.80 ± 0.59	0.35-1.29		
8000	74.70 ± 1.46	0.79-3.18	81.20 ± 1.30	0.70-2.82	71.80 ± 0.78	0.49-1.73	87.20 ± 3.94	2.37-8.72	74.10 ± 0.78	0.48-1.73		
16000	63.90 ± 1.16	0.63-2.54	69.30 ± 1.81	0.97-3.93	61.00 ± 1.20	0.72-2.26	80.30 ± 4.27	2.56-9.44	39.90 ± 1.26	0.75-2.78		

Table 4. Continued.

Loomshed Mill No I	Loomshed Mill No II		Bleaching		Dyeing		Printing		Administration block		
	$\mu$	$\sigma$	$\mu$	$\sigma$	$\mu$	$\sigma$	$\mu$	$\sigma$	$\mu$	$\sigma$	
57.22 ± 3.50	2.10-7.74	55.04 ± 1.26	0.75-2.78	50.90 ± 0.40	0.21-0.85	45.10 ± 1.44	0.78-3.16	43.80 ± 1.20	0.66-2.41	30.90 ± 4.03	2.42-8.91
70.40 ± 0.50	0.32-1.17	69.53 ± 1.43	0.86-3.16	62.00 ± 0.50	0.28-1.11	61.90 ± 2.14	1.15-4.66	62.80 ± 1.60	0.64-2.35	42.80 ± 1.53	0.92-3.40
75.98 ± 1.50	0.96-1.59	72.60 ± 0.77	0.46-1.70	77.20 ± 1.20	0.66-2.67	76.40 ± 3.80	2.05-8.30	75.30 ± 1.90	1.04-3.83	51.50 ± 2.28	1.37-5.06
82.40 ± 1.22	0.73-2.71	80.70 ± 1.73	1.04-3.83	85.30 ± 2.40	1.28-5.1	87.10 ± 3.96	2.13-8.60	86.40 ± 2.90	1.57-5.80	55.80 ± 3.17	1.91-7.02
92.00 ± 0.58	0.37-1.87	89.90 ± 0.95	0.57-2.12	87.40 ± 1.44	0.78-3.1	89.00 ± 3.04	1.64-6.60	87.20 ± 3.40	1.86-6.86	59.20 ± 3.49	2.10-7.71
100.50 ± 0.73	0.44-1.61	98.90 ± 0.98	0.59-2.16	88.40 ± 1.47	0.79-3.1	89.70 ± 2.36	1.28-5.17	89.00 ± 2.90	1.58-5.82	60.50 ± 3.17	1.91-7.02
103.50 ± 0.90	0.54-1.98	101.20 ± 0.73	0.44-1.61	89.10 ± 1.98	1.07-4.3	88.20 ± 3.00	1.62-6.50	90.10 ± 1.91	1.04-3.83	64.70 ± 3.25	2.13-7.86
99.10 ± 1.74	1.04-3.82	97.60 ± 2.20	1.33-4.90	88.80 ± 2.80	1.52-6.1	84.10 ± 1.40	0.75-3.03	88.70 ± 2.28	1.25-4.60	66.70 ± 6.22	3.37-13.75
91.50 ± 0.90	0.54-1.98	90.00 ± 1.13	0.68-2.49	86.20 ± 3.40	1.82-7.4	79.50 ± 2.50	1.37-5.50	85.20 ± 3.12	1.71-6.30	60.40 ± 9.23	5.54-20.4
79.40 ± 0.97	0.64-2.35	78.10 ± 1.06	0.64-2.53	78.00 ± 3.10	1.66-6.7	71.20 ± 4.18	2.25-9.10	78.10 ± 4.42	2.42-8.90	51.70 ± 13.33	8.00-29.4

Table 5. Data comparison with past studies and research on noise exposure in Tanzania.

Study or research done by:	Kalugendo (former public health consultant - Sungura Textile - DSM)	Saarinen (ILO techn. advisor in industrial hygiene) and Monyo (factories inspectorate team (DSM))	Factories inspectorate team (DSM)	This study
Place/area of research or study	Loomshed at Sungura textile mills	Loomshed in textile industries which are among 74 surveyed industries in Tanzania	Loomshed at Friendship textile mills	Friendship textile mills
Year of research or study	1979	1983	1986	1987/88
Noise exposure dB(A)	105	102-104	100.6 ± 0.2	103.0 ± 0.9

Table 6. Noise exposure versus workers at Friendship Textile Mill.

Noise exposure level dB (A)	No. of workers exposed to noise	Exposure in %	Cumulative %
82	2699	62.75	62.75
82-87	228	5.30	68.65
87-92	132	3.07	71.12
92-97	393	9.14	80.26
97-102	423	9.84	90.10
102-107	426	9.90	100.00
	0	0	100.00
Total	4301	0	100

Table 7. Audiometric test results of 15 workers interviewed at Friendship Textile Mill from loomshed (Mill No. 1) in the weaving department on 28 November 1987.

Name or Sample No.	Age	Years of Employment	Frequency (Hertz)								
			250	500	1000	1500	2000	3000	4000	6000	8000
S1	38	17	95	73	63	70	45	75	70	65	48
S2	33	15	35	28	25	38	33	43	48	45	28
S3	26	7	38	30	25	15	15	23	20	18	10
S4	38	18	45	35	30	25	20	25	25	40	40
S5	32	5	33	23	20	15	15	43	30	38	13
S6	38	13	50	35	30	23	20	25	38	38	53
S7	37	13	38	20	15	13	13	13	13	18	20
S8	37	19	45	28	20	45	48	50	53	58	28
S9	38	20	38	25	25	35	30	33	30	30	15
S10	31	19	46	35	25	25	23	18	15	33	5
S11	32	13	40	25	18	10	20	35	38	23	23
S12	39	19	33	28	15	18	30	48	55	48	25
S13	27	8	35	23	20	15	20	18	33	23	10
S14	34	14	33	23	15	23	25	41	53	53	23
S15	26	9	43	28	23	18	13	13	15	33	18



## RESULTS AND DISCUSSION

Table 1 shows the overall maximum noise levels. The data indicate that the noise levels obtained at each unit did not vary much. Almost all places except for the cone winding and the administration block (control unit) show that noise levels were equal to or above 90 dB. The highest noise levels were recorded at the loomsheds, the ring frame, and the carding area.

Table 2 represents the noise level summary with respect to frequencies. The data indicate that the noise levels were increasing with the increase in frequency up to a certain limit and then started to drop as the frequency increased further. In this case, the high noise levels were in the frequency range of 500 - 4000 Hz. The lowest level was recorded from the administration block.

The statistical analysis method, using  $\chi^2$  is shown in Tables 3 and 4.

Levels of noise so obtained from FTM in 11 different places (unit processes) have been compared with past studies already done in the same or other textile industries in Tanzania (Tuppurainen 1984). The data available range from those recorded in weaving departments (loomshed) from 1979 in Sunguratex up to 1986, as shown in Table 5. No data were obtained concerning the past results of noise levels of other unit processes in the textile mills. The data from this study shows there is a small discrepancy from those data of past studies. The results of a noise level survey in different loomsheds in 1983 were found to be between 102 - 104 dB. The increase might be due to the wornout machines or due to the type of instrument, the calibrations, and method used to conduct the measurements. In this study, about 30% of workers in FTM work in noisy environments where noise levels are equal or greater than 90 dB. The distribution of noise exposure levels to workers at the mill is shown in Table 6.

## AUDIOMETRIC TEST

According to the audiometric tests, results in Table 7 show the development of hearing loss. These included samples Nos. 2, 8, 11, 12, 13, and 14 which is equal to 40% of the total workers examined. Hearing loss due to noise exposure tended to reach a maximum for frequencies in the 3000 - 6000 Hz range for a given exposure. Hearing losses were usual for test frequencies above and below this range.

The response of the exposed subjects at the loomshed to the questions "noise is a problem" and "loss of hearing sensitive" compared with the audiometric measurements confirms the problem. The data collected at the factory dispensary were not significant since the number of patients were mixed (i.e., workers plus non-workers). In addition, these include only data for three years (Table 8). The epidemiological results in this study indicated that the noise levels to which the FTM workers are exposed pose adverse health effects.

*Acknowledgment* — The cooperation of the management and the workers of the Friendship Textile Mill is very much acknowledged. The assistance of Kitenke and of the Department of Factories Inspectorate, Dar es Salaam, and especially of the Monyo is gratefully appreciated.

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# TOTAL BETA RADIOACTIVITY IN THE AIR AND MILK CONCENTRATIONS OF $^{89}\text{Sr}$ AND $^{90}\text{Sr}$ IN BILBAO, SPAIN

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*EI 9004-045M (Received 2 April 1990; accepted 25 December 1990)*

Radioactive contamination increases with the development of human activities. This contamination reaches people by inhalation or by food consumption. The interest and concern about health risks associated with radioactivity has increased since the accidents at the Three Mile Island nuclear power station in Harrisburg, USA, in 1979 and at Chernobyl, USSR, in 1986. The aim of this article is to determine total beta-radioactivity levels in the air and also milk concentrations of the isotopes  $^{89}\text{Sr}$  and  $^{90}\text{Sr}$  in Bilbao, Spain, in order to establish reference levels to future epidemiologic studies. Moreover, this could permit an earlier reaction against accidents similar to those referred. In our study, we have used a Geiger-Müller Counter for both air and milk. Milk samples require a previous treatment which consists of coagulation with 24% trichloroacetic acid (TCA), purification by ion exchange chromatography, and precipitation with ammonium carbonate. Low levels were found in 1989, both in air and milk. They were all lower than registered in 1988 and also lower than EEC recommended limits. Milk concentrations of  $^{89}\text{Sr}$  and  $^{90}\text{Sr}$  were much higher than the total beta radioactivity in the air collected during the same days.

## INTRODUCTION

Development of human activities leads to the progressive increase of environmental irradiation. This contamination occurs by inhaling the air which contains radioactive elements or by ingestion of food, both vegetables and animals.

Radioactive contamination due to nuclear tests has remarkably decreased since 1963 (Lambert 1984), but the risk of radioactive contamination goes on because of other radioactive sources, such as radioactive material treatment, uranium mining, reactor fuel recycling, and also the performance of nuclear power stations, scientific research, and even food preservation. Besides, public interest and worry for health risks associated with contamination due to radionuclides has considerably increased, especially after

two important accidents which happened during recent years, at Three Mile Island, USA, in March 1979 and at Chernobyl, USSR, in April 1986 (Cunningham et al. 1989; Miettinen 1988).

The total activity dispersed in the Chernobyl accident has been estimated at some 750-800 PBq (Bennett 1988). Iodine-131 (half life = 8 d),  $^{137}\text{Cs}$  and  $^{90}\text{Sr}$  have been considered as the most important radionuclides in European Countries affected by radioactive clouds. Strontium-90 substitutes for calcium in osseous tissue and  $^{137}\text{Cs}$  substitutes for potassium in muscular tissue. The latest elements mentioned have longer half lives than  $^{131}\text{I}$  does, 30 y for  $^{137}\text{Cs}$  and 28 y for  $^{90}\text{Sr}$ .

External irradiation from deposited materials and ingestion of radionuclides incorporated into foods



have been considered as the pathways of importance for radionuclides released in the Chernobyl accident, and irradiation from radioactivity in the air and inhalation of airborne material have been indicated as additional pathways (Bennett 1988). Furthermore, it seems that Spain was not in the path of the radioactive cloud (Bennett 1988). However, since then, the interest for continuing radiological research in order to obtain a more complete definition of radiation's harmful effects on health has decreased. There are still many doubts in concern to real dangers of irradiation in low doses (Errera 1985; Miettinen 1988). A constant surveillance of radioactive levels both in the atmosphere and in food could permit to establish reference levels which could be important in future epidemiologic studies. This could also allow an earlier reaction against nuclear accidents similar to those referred (Salo and Daghli 1988).

The aim of this paper is to determine total beta radioactivity in the air and milk concentrations of  $^{89}\text{Sr}$  and  $^{90}\text{Sr}$  in Bilbao, since milk is the main vehicle of these isotopes (Pérez and San José 1986) and also a food of high ingestion in our country.

## MATERIALS AND METHODS

The testing was carried out on 149 air samples which were collected between January and September of 1989. In addition, samples of milk were analysed which were collected between April 2 and August 3 of the same year. All samples of milk came from dairy plants of Bilbao.

Air samples were collected by filtration in our station, and introduced in a Geiger-Müller counter without any previous treatment in order to determine total beta radioactivity. Detection of radioactivity in this type of apparatus is based on the ionisation of the gas which is contained in the detector. This ionisation is caused by the radioactive particles retained by the filter and it is the origin of a number of pulses in the detector. Because of that, it is not possible to discriminate between the different isotopes which can emit beta radioactivity and, in consequence, the total beta radioactivity was obtained. The result is expressed in  $\text{pCi}/\text{dm}^3$  of air ( $1 \text{ pCi} = 3.7 \cdot 10^{-2} \text{ Bq}$ ). However, these data have to be corrected because it is necessary to discount background beta radioactivity.

A method proposed by the Junta de Energía Nuclear (1969) was used to determine the activity concentration of  $^{89}\text{Sr}$  and  $^{90}\text{Sr}$  in milk. This method consists of the coagulation of milk by treatment with 24% TCA and vacuum filtration through Whatman No. 42. This

filtrate is purified by passing through a Dowex WX-8 20-50 mesh size heated ion exchange resin.

Maximum retention of strontium isotopes and also of calcium occurs at pH 1. Since milk is a food with a high level of calcium, this element has to be removed from the resin before strontium is. Thus, a 1.5 M ammonium lactate solution was used. After that, strontium was eluted with 4 M nitric acid. The retention of calcium and strontium could be proved by treatment of the eluate with ammonium carbonate. If calcium is not retained by the resin, the eluate will become turbid. After the purification phase,  $^{90}\text{Y}$  and  $^{226}\text{Ra}$ , which could go with strontium, have to be removed from the eluate. This phase is the final separation which consists of the treatment with an iron-carrier solution in a heated alkaline medium. The two elements are removed from the eluate by vacuum filtration. If there is strontium in the eluate, the treatment with ammonium carbonate in the alkaline boiling medium provokes the precipitation of strontium carbonate which could be removed from the eluate by vacuum filtration. The alkalinity is very important since we have seen that the precipitation of strontium carbonate only happened at  $\text{pH} \geq 9$ . The filter is dried with an infrared-ray lamp in order to obtain the strontium carbonate weight.

Detection of the radioactivity due to  $^{89}\text{Sr}$  and  $^{90}\text{Sr}$  is done by the introduction of the filter prepared as indicated above in a Geiger-Müller counter. To obtain the final data in  $\text{pCi}/\text{L}$  of milk, it has to discount the background radioactivity, the apparatus efficiency (40%), chemical coefficient of strontium (percentage of recovery or efficiency), the efficiency of resin (100%), and the decay coefficient of  $^{90}\text{Y}$  which is determined by the time from the strontium carbonate precipitation to the analysis in a Geiger-Müller Counter.

## RESULTS AND DISCUSSION

The average data found in the air study was  $0.08 \text{ pCi}/\text{dm}^3$  and the standard deviation ( $s_1$ ) 0.086. A minimum of 0.0 and a maximum of  $0.50 \text{ pCi}/\text{dm}^3$ , which was collected on July 4, were observed (Fig. 1). Among weekly results, the maximum was  $0.1464 \text{ pCi}/\text{dm}^3$  which corresponded to the first week of May, and the minimum was  $0.027 \text{ pCi}/\text{dm}^3$  in the week from June 26 to July 2. The maximum monthly average was obtained in July ( $0.1043 \text{ pCi}/\text{dm}^3$ ) and the minimum in January ( $0.063 \text{ pCi}/\text{dm}^3$ ). We found 93.96% of the samples to be within the range of  $0.0\text{-}0.2 \text{ pCi}/\text{dm}^3$ . No beta radioactivity in 11.41% of the samples was found (Fig. 2). In four of the nine months studied, 100% of the samples were within the range of  $0.0\text{-}0.2 \text{ pCi}/\text{dm}^3$ .

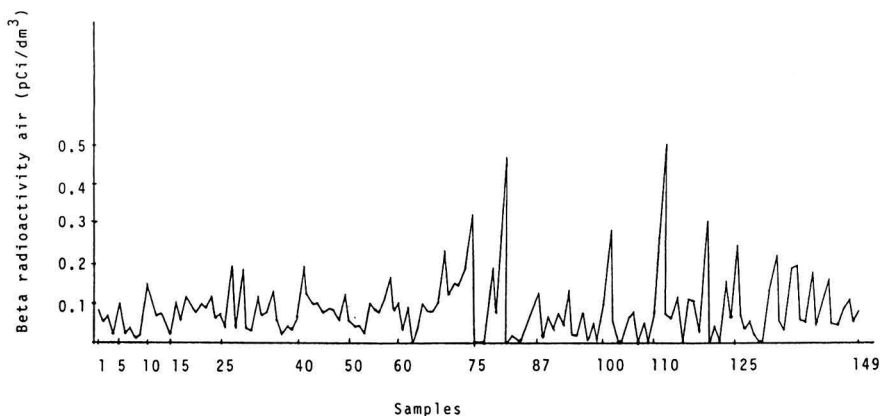


Fig. 1. Total beta radioactivity in the air—daily data.

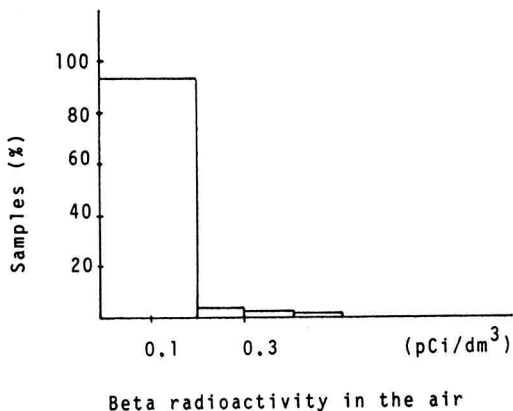


Fig. 2. Total beta radioactivity in the air—total percentage distribution.

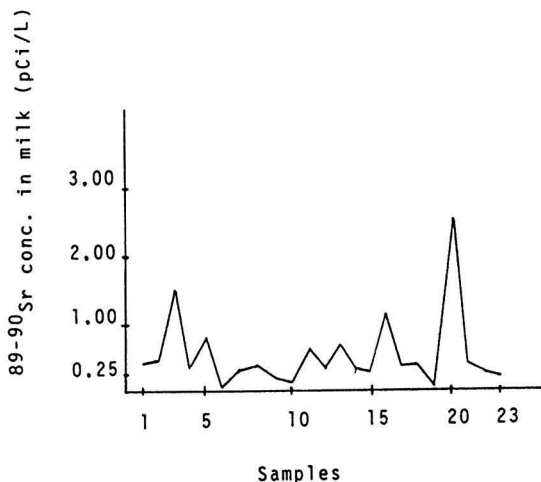


Fig. 3. The <sup>89</sup>Sr and <sup>90</sup>Sr levels in milk from February to August 1989.

The average data found in the milk study was 0.5214 pCi/L and the standard deviation ( $s_2$ ) 0.6120 pCi/L. A minimum of 0.025 and a maximum of 2.505 pCi/L were observed (Fig. 3). Lower levels were observed from June 7 to July 5. While 30.43% of samples contained between 0.30 and 0.40 pCi/L of strontium, 17.39% contained between 0.20 and 0.30 pCi/L (Fig. 4). Strontium was found in all tested samples.

The average percentage of strontium recovery was 57.58%. Maximum recuperation was 90.66% and minimum 9.70% which are clearly separated from the rest. Percentages of recovery higher than 50% were

obtained in 60.86% of samples, ranging between 20% and 90% (Fig. 5).

Contaminant radionuclides enter our organism basically through water and food. Air and milk was collected during 20 d and the obtained values in this period of time were compared (Fig. 6). Total beta radioactivity in the air, in which radioactivity due to <sup>89</sup>Sr and <sup>90</sup>Sr is included, can be observed, since these elements are pure emitters of this type of radioactivity. Radioactive contamination due to <sup>89</sup>Sr and <sup>90</sup>Sr in milk is also represented. As can be seen, levels found in milk are, in all cases, higher than those obtained in the air samples. The ratio of pCi <sup>89</sup>Sr and <sup>90</sup>Sr in

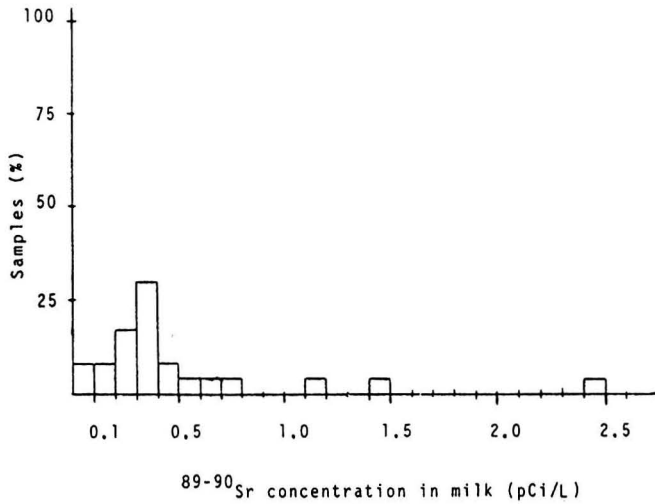


Fig. 4. Milk—Strontium percentage distribution.

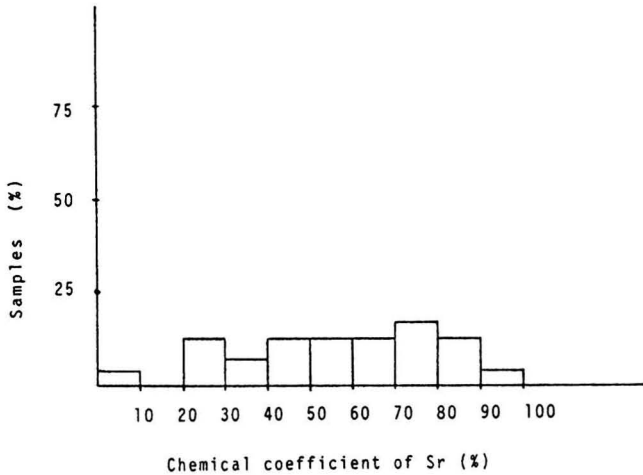


Fig. 5. Milk—Percentage distribution of chemical coefficients of strontium.

milk/pCi beta radioactivity in air was lower than one in four samples. The strontium concentration in milk was four times that of the beta radioactivity in the air collected on the same day. In three samples, strontium concentrations in milk were five times that of the beta radioactivity found in the air. The average ratio pCi in milk/pCi in air was 10.5 and the standard deviation was 16.34. The lack of correlation is clearly seen in Fig. 6 where the air stays at the same level

in spite of the swings in the strontium concentrations in milk.

#### CONCLUSIONS

Total beta radioactivity levels found in the air were very low (CEE 1959). They were highest at the beginning of May and lowest at the end of July. Results were lower, in general, than registered in 1988.

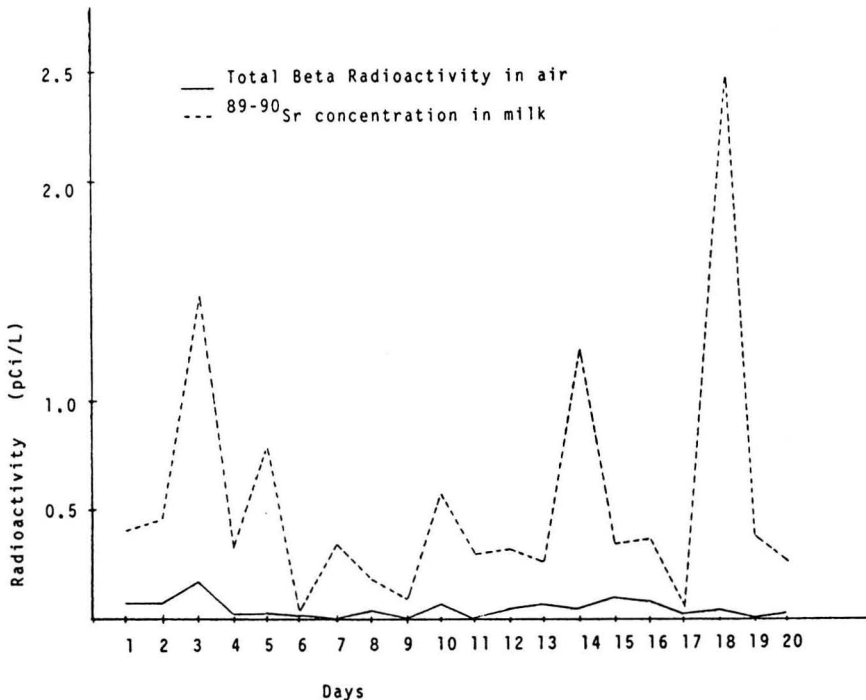


Fig. 6. Comparison between total beta-radioactivity levels found in the air and <sup>89-90</sup>Sr concentrations in milk.

Milk concentrations of <sup>89</sup>Sr and <sup>90</sup>Sr were, in all samples, lower than EEC recommended limits (CEE 1987). Levels of samples collected in June were slightly lower than the rest. Radioactivity due to <sup>89</sup>Sr and <sup>90</sup>Sr in milk decreased with regard to levels found in 1988, the same as total beta radioactivity in the air.

Milk concentrations of <sup>89</sup>Sr and <sup>90</sup>Sr were much higher than those found in the air collected on the same days.

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## LETTERS TO THE EDITOR

### ENERGY AND THE ENVIRONMENT: A RESPONSE

Dear Editor:

In an Editorial of this journal (*Environ. Int.* 17, pp. 1-6, 1991), A. Alan Moghissi raises a series of major environment issues to discuss the links between scientific risk assessments and political decisions. With every respect for the assembled competence behind the statements from the American Society of Mechanical Engineers, the American Association of Engineering Societies and the American Medical Association, on which Moghissi bases his account, it is, however, important to point out that, in actual fact, full scientific consensus does not exist on many of the complex issues associated with the concepts of acid rain, the greenhouse effect, and nuclear power. It seems unwise to assume that the statements from the three national associations to which Moghissi refers will be the last word on these questions.

Sweden's decision to phase out nuclear power gradually while improving energy conservation in the built environment and developing new, environmentally friendly heating technology is put forward in Moghissi's Editorial as an example of wrong political decisions. According to Moghissi, these political decisions have not taken account of the fact that energy conservation in buildings increases the risk of health effects in the form of sick building syndrome (SBS).

It is wrong to conclude that there is some general causal link between energy conservation measures and health and discomfort effects. In the eighties we paid great attention in Sweden to the problems of SBS and the underlying causes of various health and discomfort effects. It is no exaggeration to say the causal links have turned out to be very complex. The choice of unsuitable materials in buildings and finishes is one important factor. Others are unprofes-

sional execution of energy conservation measures and wrongly dimensioned or inappropriately installed ventilation systems. On the other hand, it is not true, as suggested in the article, that there is any general conflict between requirements for healthy buildings and requirements for energy management. Within the Swedish R&D programme, we have developed and analyzed different solutions for ventilation efficiency, filter technique, and heat recovery. In some of our recent demonstration projects, we have shown that it is quite possible to combine the requirements of energy efficiency with health requirements.

Stricter environmental and health requirements coincide largely with requirements for better building design and construction, higher quality in the building process, and more careful selection of building materials. Similarly, for example, our present requirements concerning the comfort, safety, and fuel consumption of motor cars mean that we no longer drive around in Model-T Fords.

In the summary of recent R&D results in the field of healthy buildings, which the Swedish Council for Building Research has just published in English translation (*Buildings and Health*, Swedish Council for Building Research Document 3:1991, distribution Svensk Byggtjänst, S-171 88 Solna, Sweden), we present a strategy for energy conservation in buildings which takes account both of health aspects and of energy conservation. We will make sure that the report is sent to Moghissi and to the Journal's Editorial Board in the hope that there will eventually be space in *Environment International* for a review.

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## ENERGY AND THE ENVIRONMENT: A REPLY

Pettersson (1991) believes that a full consensus does not exist on a number of scientific issues related to energy and the environment. Neither I nor the professional societies mentioned in the Editorial (Moghissi 1991) claimed that a full consensus exists. However, the American Medical Association (AMA) and the American Association of Engineering Societies (AAES) identified areas where there was a consensus and areas where the available scientific information was insufficient to reach a consensus. In fact, the disagreements expressed by Pettersson are overwhelmingly not based on a lack of consensus in the science, but in societal decisions derived from it.

AAES and AMA have a combined membership of over one million physicians, engineers, and scientists, virtually in every branch of science and technology. The members of these groups are chosen solely on the basis of their education and experience and expressly regardless of their political and societal views. Their membership includes those from government (federal, state and local) academia and industry. There is no reason to believe that panels established by these groups would have any specific political or ideological tendencies. In a democracy, the government is chosen on the basis of election of specific parties with identifiable ideologies and platforms.

Because of the inclusion of ideology in the decision-making, governments are uniquely unqualified to make scientific decisions, unless these decisions are based on a clear and unambiguous scientific peer-review and preferably scientific consensus process.

With all due respect to the Swedish (or any) government, its decisions on scientific issues must be considered to reflect the ideology of the political party that happens to be in power. The Swedish decision on energy is an outstanding and clear example of such a process.

Subsequent to the publication of the statements of AAES and AMA, several relevant reports were published. The energy strategy of the U.S. Department of Energy (USDOE 1991), the National Academy of Sciences on policy options related to global warming (NAS 1991), and a report on research needs related to global warming (NAS 1990) are examples of these reports. Although there are certain differences in emphasis among these reports, the conclusions are essentially the same as those reached previously. The

consensus is that it is in the interest of the global community to reduce the emission of carbon dioxide by generating electricity using means other than fossil fuels, particularly nuclear energy; and by reducing energy consumption using energy conservation.

Pettersson blames poor workmanship and the choice of unsuitable materials for the occurrence of the Sick Buildings Syndrome. These are precisely the same reasons given by the proponents of nuclear power during the sixties and seventies for occurrence of nuclear mishaps. The proponents of nuclear power ruled out accidents and used the example of the Model-T Ford to indicate advances of technology much the same as used by Pettersson. The science of risk analysis has clearly shown that a certain level of human error is inevitable. Although human error (poor workmanship, inadequate materials, erroneous installation of equipment, and incorrect judgements in decisions) can be reduced, it cannot be eliminated. Furthermore, the reduction of human error is associated with costs and the curve describing this reduction, starts linearly, becomes quadratic and follows with higher powers as it reaches small levels of human error. There are not only economic, but also human health and environmental costs. Actions taken by the Swedish government and reported by Pettersson are clearly to be welcomed. These actions are consistent with the views expressed in the editorial.

As predicted in the Editorial, Sweden has already taken appropriate steps to take corrective actions. Several major political parties have agreed to keep the energy policy out of the current election campaign.

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## BOOK REVIEWS

*Modelling in Ecotoxicology*, edited by S.E. Jorgensen. Elsevier, Amsterdam; 1990. 360 pp., US\$100.00. (ISBN 0-444-88699-0)

Ecotoxicology is a discipline consisting of toxicology and ecology. It is a science which describes an impact of chemical substances on the living organisms. The large number of chemicals and pathways of natural biochemical processes, often complicated and not well understood, make it impossible to exactly predict the effect of a chemical on an organism.

Consequently, the chemistry and biology of toxic substances in the environment and their fate and effect are extremely complex, and adequate data are needed to cope with the problem. Although, much data have been provided during the last 10-15 years by intensive research in the field.

This book attempts to outline the state of the art of modeling the fate and effects of toxic substances in the environment. Modeling in ecotoxicology differs from modeling in other fields by the great lack of data. The quality of the models is dependent on the parameters used, and parameter estimation methods are crucial for ecotoxicological models.

Models may be physical or mathematical. Physical models contain the main components of the real system. For instance, the study of interactions between a toxic substance and a system of plants, insects, and soil in nature requires the construction of a simplified system which contains only these components. Physical models are often named microcosmos, as they contain all major components of the larger system, but on a smaller scale. However, this book focuses almost entirely on mathematical models which are based on a mathematical formulation of the processes that are most important for the problem being considered.

The field of environmental modeling has developed very rapidly during the last decade due essentially to two factors:

- 1) The development of computer technology which has enabled the handling of complex mathematical systems, and
- 2) a general understanding of pollution problems, including those related to the application of toxic substances.

In the simplest approach, toxic substances are released from a source to the environment (ecosystems) where they may be harmful to living organisms and may change the reactions, the function, or even the structure of the entire system. Complete elimination of all emissions is impossible with a global human population of five billion. But if one can relate an emission with its ecological implications for the environment, it is possible to provide appropriate recommendations. These may include emissions that can be eliminated or reduced to minimize an adverse effect.

The resulting recommendations may be in the form of emission limitations or a ban on the use of a toxic substance. This is a political decision. Although the model may give a rather clear answer, there is always economic cost involved in such decisions. It is possible in some instances to construct models which consider the economy of the problem, but those models are not yet sufficiently developed to give reliable guidelines in more than a few cases. Ecological-economic models will most probably become more developed in the near future. During the next decade, they will be used more widely in environmental management.

The difficult part of modeling is not the mathematical formulation or the translation of the mathematics into a computer language. The introduction of personal computers and applicable software have made it easy to handle these steps of modeling. The more difficult part is to provide the necessary knowledge and be able to estimate which components and processes to include in the model. An ecologist or ecotoxicologist with some knowledge of mathematics and computer science is better equipped to construct ecotoxicological models than a mathematician with some knowledge of ecotoxicology and ecology.

While the first part of the book discusses the methodology of modeling, the second part concentrates on case studies. The case studies have been selected to illustrate the spectrum of applicable models in various directions.

The book illustrates clearly that it is possible to develop simple models useful in environmental management. One of the models relates chromium con-



centration in discharged waste water with chromium concentration in the sediment as a function of the distance from the discharge point, including chromium concentrations in mussels. It is based on two equations—a hydrodynamic equation and one describing the bioaccumulation from sediment to mussels. The model prognosis has been validated with surprising results in spite of its simplicity.

The mercury model is based on a problem similar to the chromium model. Mercury is able to react with the organic matter in the sediment and may bioaccumulate in pelagic and benthic food chains. It implies that a more complex model must be used to solve this problem. The model must account for the release of methyl- and dimethyl-mercury from the sediment and must furthermore consider the relationship between the mass of fish species and the mercury concentration.

A comparison between the chromium and the mercury model illustrates clearly that a profound knowledge of the geobiochemistry of the metal is needed to be able to select the right approximations. Mercury has a more complex geobiochemistry than chromium and it requires a more complex model than chromium under the same environmental conditions.

The copper model differs from the chromium and mercury model by its more simple hydrodynamics. However, a more comprehensive description of the geochemistry of the copper species is needed, and the model is an illustrative example of a geochemical model. It is more complex than the chromium model in the description of the exchange processes of copper between sediment and water but does not contain a hydrodynamic component as the chromium model does.

Another model describes a flow of cadmium and lead from a soil of known composition and pH to cultivated plants. It illustrates the difference between modeling an aquatic and a terrestrial ecosystem. The flow processes in soil are complex and a detailed description of these processes would require detailed knowledge of the permeability of soil at different sites and depths. Consequently, these flow processes have been described simply and the emphasis of the model has been on the factors that are regulating the uptake of heavy metals. These include the solubility of the heavy metal ions. The case study illustrates clearly that it is possible to simplify complex cases, provided the scope of the model is to describe an average situation.

A more complicated system consists of the effect of air pollution on plants to relate the input of cadmium and lead to a soil of known composition and

pH to the cadmium and lead concentration in cultivated plants. The model illustrates the difference between modeling an aquatic and a terrestrial ecosystem. The flow processes in soil require detailed knowledge of the permeability of soil at different sites and depths. Consequently, these flow processes have been described simply and the emphasis of the model has been on the factors that are regulating the uptake of heavy metals, including the solubility of the heavy metal ions. The case study illustrates clearly that it is possible to simplify complex cases, provided the scope of the model is to describe an average situation.

The case study illustrates how complex the effects on the plants are and how much more is needed before the effects of air pollutants can be modeled. Each level in the environmental hierarchy requires its own model, but it may cause difficulties to couple such models to a comprehensive model, as it will involve the use of highly complex models.

The case studies illustrate ecotoxicological problems related to heavy metals, gases, and organic pollutants. They also show the need for information on physical, chemical, and biological processes to make the correct simplifications. They demonstrate the significance of the flow processes in the three spheres, the difference between a distribution and an effect model, and those between models of different scales. The selected case studies should give the reader a good knowledge of the spectrum of models available in ecotoxicology. The book contains tables listing physical-chemical parameters and toxicity data which are needed for modeling.

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*Air Pollution's Toll on Forests & Crops.* James J. MacKenzie and Mohammed T. El-Ashry eds. Yale University Press, New Haven, CT, 1989. 376 pp. (ISBN 0-300-04569) \$38.50 hardcover.

The World Resources Institute is an environmental advocacy group located in Washington, D.C. Its efforts of about two years on the impact of air pollution on forests and crops are summarized in this book. The book contains a great deal of data presented by an international group of respected scientists. The readers will have some difficulties in distinguishing between advocacy and science. Despite this shortcoming, the book provides useful information.

*Aluminum and Health: A Critical Review.* Hillel J. Gitelman ed. Marcel Decker, Inc., New York NY, 1989. 306 pp. (ISBN 0-8247-8026-4) \$79.75 hardcover.

The intent of this monograph is to provide a compendium of what is known about aluminum and its interaction with human biology. The monograph begins by discussing the aqueous chemistry of aluminum. It proceeds with a discussion of techniques for the quantitative estimation of aluminum, an overview of the physiology of aluminum in man, and the content of aluminum in the American diet. Organ systems that have a special relationship to aluminum toxicity are addressed individually. These include the role of aluminum as a possible neurotoxic agent, the interaction of aluminum in calcified tissue, the pulmonary effects of aluminum, and the interactions of aluminum with hematopoietic tissue. Finally, the pharmaceutical uses of aluminum are discussed. This book is recommended as a reference for libraries.

*Biologic Markers of Air-Pollution Stress and Damage in Forests.* Committee on Biologic Markers of Air-Pollution Damage in Trees, Board on Environmental Studies and Toxicology, Commission on Life Sciences, and National Research Council. National Academy Press, Washington, D.C., 1989. 363 pp. (ISBN 0-309-04078-7) \$35.00 softcover.

Forests are subject to stress from natural causes and human activities. The natural causes include competition, predation, pathogens, extremes of weather, and climatic cycles. The human activities include physical disturbance and air pollution, including acids, oxidants, toxic organic compounds, and trace metals. Stresses often occur in combination, and effects of particular stresses on trees and forests are difficult to recognize. Biologic markers, or indicators, associated with the specific air pollutant stress and damage in forests have been sought to improve discrimination among the many anthropogenic and natural causes of stress. This book summarizes the current state of knowledge and research on this topic, and identifies and evaluates promising techniques that might lead to the development of new markers. This authoritative book is highly recommended to all investigators dealing with the subject of impact of air pollution on biota.

*Chemical Modeling of Aqueous Systems II.* Developed from a symposium sponsored by the Division of Geochemistry of the American Chemical Society. Daniel C. Melchior and R.L. Bassett eds. American

Chemical Society, Washington, D.C. 1990. 538 pp. (SBN 0-8412-1729-7) \$89.95 hardcover.

Chemical modeling is a rapidly evolving field with immediate opportunities for application. The present volume summarizes and evaluates the progress and developments in this field during the past 10 years and discusses the directions for further advancement. The 41 papers of *Chemical Modeling in Aqueous Systems II* are grouped into eight chapters. These discuss the new theories used by geochemists to describe the interactions of electrolytes in aqueous systems, thermodynamic data, improvement of information exchange among computer systems, enhancement of the capability to evaluate systems under more drastic conditions, and the need to increase the specific utility of chemical codes for various applications. Other topics include the applications to modeling of equilibrium and mass transfer, transport and coupled codes, surface chemistry, and new concerns and approaches to future chemical modeling. This volume is a basic reference for the major aspects of chemical modeling and is of value to those investigators in environmental chemistry, geology, geochemistry, and chemical engineering. This book is recommended as a reference to libraries.

*Climate Change—The IPCC Scientific Assessment.* J.T. Houghton, G.J. Jenkins, and J.J. Ephraums eds. Cambridge University Press, Cambridge, UK, 1990. 365 pp. (ISBN 0521 40720 6) \$29.95 softcover.

This is the Report of Working Group I of the Intergovernmental Panel on Climate Change, which was set up jointly by the World Meteorological Organization and United Nations Environment Programme in 1988. It is an assessment of how human activities may be changing the Earth's climate through the Greenhouse Effect—potentially the greatest global environmental challenge facing mankind. The topics covered by this assessment include changes in greenhouse gases in the atmosphere, the global climate system and how it is modelled, computer predictions of climate change, observed climate change over the last century, detection of climate change due to human activities, changes in sea level due to global warming, the response of ecosystems to climate change, and research required to narrow uncertainties. Several hundred international scientists participated in the preparation and review of this assessment, making it an authoritative statement. The information has been designed to provide a common guide to policymakers worldwide, and will now form a solid scientific foundation upon which forthcoming negotiations on the response to climate change will be based. This as-

assessment is, therefore, an essential reference for all who are concerned with climate change and its consequences. This book is recommended as a reference for libraries.

*Environmental Bioassay Techniques and Their Application.* Proceedings of the 1st International Conference held in Lancaster, England, 11-14 July 1988. M. Munawar, G. Dixon, C.I. Mayfield, T. Reynoldson, and M.H. Sadar, eds. Kluwer Academic Publishers, Dordrecht, The Netherlands, 1989. 680 pp. (ISBN 0-7923-0498-5) \$239.00 hardcover.

Traditionally, environmental assessment has been mainly geared towards chemical monitoring to develop preliminary guidelines for regulatory purposes. The recognition of the need to base environmental management on experimental assays was an important step towards achieving ecosystem sustainability, and maintaining the integrity and health of the resident biota. In order to obtain a state-of-the-art evaluation of this subject, an International Conference on Environmental Bioassay Techniques and Their Application was convened at the University of Lancaster, Lancaster, U.K., during the period July 11-14, 1988, which was sponsored by the International Association of Sediment Water Science. Approximately 100 papers were presented. A proposal for a refereed publication (not a proceedings) received overwhelming support from the contributors, which resulted in the submission of 90 manuscripts. Additional papers, though not presented at the conference, were included if they were relevant to the theme of the conference. The resulting book is a peer-reviewed, authoritative information resource. It is highly recommended as a reference.

*Lake Restoration by Reduction of Nutrient Loading—Expectations, Experiences, Extrapolations.* H. Sas, ed. Academia Verlag Richarz, St. Augustin, 1989. 520 pp. (ISBN 3-88345-379-X) hardcover.

This book summarizes the result of a survey of major long-term effects induced by nutrient control measures on 18 eutrophied lakes, located in Western Europe. These lakes are: Norrviken, Glumsø, Hylke Sø, Søbygard, Veluwemeer, Schlachtensee, Cockshoat Broad, Alderfen Broad, Lough Neagh, Gjersjøen, Wahnbach-Talsperre, Lake Constance, Lac Léman, Zürichsee, Walensee, Fuschlsee, Ossiachersee and Lago Maggiore. The study was stimulated by the inability of current statistical and other models to demonstrate ecosystem changes during the restoration of these lakes. The publication particularly covers the following aspects of lake restoration prac-

tice: (1) the lag time required for ecosystems to recover; (2) the influence on algal biomass of phosphorus and other important growth factors, like nitrogen, silicon and light; (3) persistence or disappearance of cyanobacteria; and (4) the effect of random annual variability in ecosystem state. Predictive models for all these effects are developed and described. This book is recommended as a reference.

*Managing Troubled Waters—The Role of Marine Environmental Monitoring.* Committee on a Systems Assessment of Marine Environmental Monitoring, Marine Board, Commission on Engineering and Technical Systems, and National Research Council. National Academy Press, Washington, D.C., 1990. 125 pp. (ISBN 0-309-04194-5) \$24.50 hardcover.

This book from the National Research Council presents a comprehensive overview of marine monitoring and provides practical information and a model for revamping the nation's marine monitoring system. It explores current monitoring programs and evaluates whether they do or do not work; examines the benefits and limitations of monitoring, with case studies of successful programs and a 10-step agenda for strengthening monitoring's role in environmental management; describes the critical need for greater coordination among monitoring programs, with case studies of programs in the Chesapeake Bay and the Southern California sight, and an analysis of particulate waste disposal; and recommends steps for designing and developing more effective monitoring programs. This authoritative book is highly recommended as a reference for individuals and libraries.

*Methods of Dendrochronology—Applications in the Environmental Sciences.* E.R. Cook and L.A. Kairiukstis, eds. Kluwer Academic Publishers, Dordrecht, The Netherlands, 1990. 394 pp. (ISBN 0-7923-0586-8) \$94.00 hardcover.

Only recently have tree rings been fully recognized as a valuable tool in detecting environmental changes. For example, tree-ring measurements have been critically important in studies of forest decline in Europe and North America. There are also attempts to use tree-rings analysis for ecological prognosis to solve large-scale regional problems including the sustainability of water supplies, prediction of growth of agricultural crops and adoption of silvi-cultural measures in response to ecological changes. More speculatively, dendrochronological methods are also used for dating and evaluating some astrophysical phenomena and for indicating possible increase in

the biospheric carrying capacity due to increased atmospheric carbon dioxide. Such a wide range of application of modern dendrochronology beyond its traditional field has resulted in the development of various approaches. This has placed heavy demands on methodological unification and improvement. This book is a review and description of the state-of-the-art methods of tree-ring analysis with specific emphasis on applications in the environmental sciences. It is a reference for foresters, climatologists, and broad-profile environmental scientists who are interested in applying the techniques of tree-ring analysis. This book is recommended as a reference for libraries.

*Nitrate Pollution and Politics.* Jobst Conrad. Gower Publishing Company, Ltd., Aldershot, UK, 1990. 82 pp. (ISBN 0-566-07147-9) hardcover.

The book summarizes the debate and politics concerning the pollution of ground and drinking water by nitrate in three countries: Great Britain, the Federal Republic of Germany and the Netherlands. The investigations are based mainly on expert interviews with relevant actors in the nitrate policy and on the analysis of relevant literature. This involved official and unofficial documents, as well as secondary material from various newspapers, journals and the publications of interest groups up until around the end of 1987.

*Practical Applications of Quantitative Structure-Activity Relationships (QSAR) in Environmental Chemistry and Toxicology.* W. Karcher and J. Devillers, eds. Kluwer Academic Publishers, Dordrecht, The Netherlands, 1990. 475 pp. (ISBN 0-7923-0827-1) \$139.00 hardcover.

The intention of this volume is to acquaint prospective users with the scope, potential and the state of the art of present day QSAR methods. The book treats the structural and statistical background of QSAR methods and highlights validated QSAR models for the derivation of physicochemical and biological data. In addition, QSAR methods which have been developed to estimate the distribution of pollutants and chemicals in the environment are presented in detail including bioaccumulation and biodegradation aspects. The present volume combines the lectures presented June 1990 in the frame of the Eurocourse programme at Ispra under the sponsorship of the Institute for the Environment. It is recommended as a reference book for libraries.

*Introduction to Radiation Chemistry* 3rd Edition. J.W.T. Spinks and R. J. Woods. John Wiley & Sons, Inc. New York, NY, 1990. 574 pp. (ISBN 0-471-61403-3) \$89.95 hardcover.

When the first edition of this book appeared, it stood out as the only single-source introduction to the subject of radiation chemistry. Now completely updated and revised, *Introduction to Radiation Chemistry* retains its approach to radiation chemistry while incorporating the current knowledge and research data on the subject. This third edition covers new material on applied radiation chemistry and experimental methods, as well as gaseous and solid systems including new topics related to kinetics and experimental procedures, and a new chapter on aqueous organic systems. The expanded chapter on applied radiation chemistry and radiation processing gives better coverage of chemical reactions initiated by high-energy radiation and their commercial application, recognizing the increasing importance of radiation processing in industry. Additional changes to the third edition include presentation of numerical data in SI units, simplifying most radiation-chemical calculations, and making the book more practical for use in modern chemistry instruction and more readily available to scientists in such related areas as radiation physics and radiation biology. This classical book is highly recommended as a textbook and as a reference.

*Acid Rain and Acid Waters.* Gwyneth Howells. Simon & Schuster International Group, Hemel Hempstead, UK, 1990. 215 pp. (ISBN 0-13-004797-X) £39.95/\$67.95 hardcover.

This book seeks to clarify the present level of understanding of acid rain, contending that there is often insufficient causal evidence to formulate effective legislative measures to prevent the claimed environmental damage occurring. Taking an objective view, the book considers the extent to which natural ecosystems are damaged by man-made activities against a background of long-term ecological change. This book integrates a wide range of scientific disciplines—engineering, atmospheric physics, climatology, chemistry, soil science, biology, ecology, land use and management expertise—and stresses the need for interdisciplinary understanding between scientists and those involved in legislation, industrial innovation, and the economy. For scientists who welcome a searching analysis of a major environmental issue of the last few decades, *Acid Rain and Acid Waters* will provide a source of useful information. The book is highly recommended for libraries and individuals.

*Nuclear Contamination of Water Resources.* Institution of Civil Engineers. Thomas Telford Ltd., London, 1990. 268 pp. (ISBN 0-7277-1527-5).

In the wake of the Chernobyl accident, the vulnerability of the water cycle to radionuclide contamination has been an issue of great concern. The impact of the event throughout Europe has been highly variable and wide-ranging, and has demonstrated the need to evaluate the potential risk to drinking water supplies, soil water and the food chain. This book provides information on the methods of monitoring and on concepts in design to minimize risk and to highlight the possible consequences of a nuclear event. With contributions from engineers and scientists from eight countries, it is a source of information about present radiological standards and monitoring requirements. It also deals with the development of management strategies designed to cope with a nuclear event.

*A Modern Approach to the Protection of the Environment.* Proceedings of Study Week November 2-7, 1987. Pontificia Academia Scientiarum. G.B. Marini-Bettolo, ed. Pergamon Press, Oxford, UK, 1990. 602 pp. (ISBN 008-0408168) \$59.95/£35.00 hardcover.

The study of environmental protection commonly deals with the physical, chemical, biological, and medical aspects of pollutants. There are, however, ethical aspects of environmental protection both in terms of polluting the environment and stopping the development, and thus prolonging poverty. This book contains the presentations by 20 scientists who met on November 2-7, 1987, in a meeting organized by the Pontifical Academy of Sciences and were greeted by Pope John Paul II. The unique perspective of the participants, the emphasis on ethics, and the scientific quality of the presentations make this book an important source of information. It is highly recommended as a reference book for libraries.

*5000 Days to Save the Planet.* Nicholas Goldsmith, Nicholas Hildyard, Peter Bunyard, Patrick McCully, Paul Hamlyn Publishing, London, 1990. 288 pp. (illustrated), (ISBN 0-6--057156-4) £17.95 hardcover.

This is an advocacy book. The authors claim that there are only 15 years left to rescue the earth from absolutely certain extinction. No scientific evidence is provided to indicate the validity of the claim.

*Asbestos in the Natural Environment.* H. Schreier. Elsevier Science Publishers, Amsterdam, 1989. 172 pp. (ISBN 0-444-88031-3) \$89.50/Dfl. 170.00 hardcover.

This book examines non-occupational exposure and environmental effects of asbestos relating to animal and plant growth in the natural environment. Major nutrient imbalances and excess concentrations of trace metals have been identified as main causes for the poor plant response. Given the complexity of the asbestos analysis and the extent of the problem, this book attempts to bring together the multitude of subjects pertaining to asbestos in the natural environment with the aim of contributing to a better understanding of the chemical characteristics of asbestos-rich materials and their effect on plant growth. The book contains a wealth of information and is highly recommended as a reference volume for scientists involved in asbestos studies.

*Ecological Assessment of Environmental Degradation, Pollution and Recovery.* O. Ravera, ed. Elsevier Science Publishers, Amsterdam, 1989. 370 pp. (ISBN 0-444-87361-9) \$155.25/Dfl. 295.00 hardcover.

This book contains the lectures of a course held at the Joint Research Centre, Ispra (Italy) 12-16 October 1987. The course was given in the form of a series of lectures presented by 12 speakers. It was structured to include the terrestrial and aquatic ecosystem concept; the structure, functions, and evolution of the ecosystem in relation to the natural and anthropogenic influences; and the concept of stress, assessment, and restoration of terrestrial and aquatic ecosystems. For the various aspects of the environmental problems, the principles of restoration techniques, the results obtained by their application and the research needs to acquire a better knowledge of the ecological processes were discussed. The lectures were illustrated by several case studies concerning forests, lakes, reservoirs, rivers, soil, and the interrelations between air and terrestrial and aquatic ecosystems. Excluded from the lectures were ecological risk assessment methodologies and applications. The volume is recommended as a reference book.

*Environmental Data Report (UNEP).* Second Edition. United Nations Environment Program. Basil Blackwell, Inc., Cambridge, MA, 1990. 547 pp. (ISBN 0-631-16987-3) \$39.95 softcover.

This report is the response to the need for reliable and readily available information on a wide variety of environmental issues. Examples of data are provided and sources referenced in order to make a wide range of information available for assessment. For example, the data from the GEMS (Global Environmental Monitoring System) Health Related Monitoring projects are included and this will be a regular feature. It is

evident that these networks provide a unique insight into the pollution of air, water, and food at the global level. Examples of other GEMS monitoring projects are also included, such as climate and long-range transport of pollutants. The *Environmental Data Report* will serve as an invaluable reference source for government departments, research organizations and environmental scientists world-wide. It is recommended for libraries and as a textbook for environmental courses.

*Restoration Ecology. A synthetic approach to ecological research.* William R. Jordan III, Michael E. Gilpin, John D. Aber, eds. Cambridge University Press, Cambridge, UK, 1990. 342 pp. (ISBN 0-521-33728-3) £14.95/\$24.95 softcover.

This is a reprinted version of the 1987 edition. The new edition contains no additions.

*Expert Systems for Environmental Applications.* Judith M. Hushon, ed. American Chemical Society, Washington, DC, 1990. 232 pp. (ISBN 0-8412-1814-5) \$49.95 hardcover.

This book resulted from a symposium held in conjunction with the 198th National Meeting of the American Chemical Society, Miami Beach, Florida, September 10-15, 1989. Expert systems in the environmental area have been relatively slowly developed because of disagreements on methods and usefulness of the results. Furthermore, few environmental problems can be solved by a single expert. Often there is a need to involve scientists from many disciplines to identify an optimal problem solution. This 16-chapter book reviews the state of the art in developing expert systems to solve environmental problems. Some chapters describe the process of expert system development and the stages in their life cycles. Other chapters provide specific case studies, such as those in the Intelligent Quality Assurance Planner, a system for prediction of aquatic toxicity, the Citizen's Helper, the system to diagnose performance-limiting factors at publicly owned treatment works, the Activated Sludge Advisor prototype, the Cost of Remedial Action Model, a system for performing risk assessments, and the Defense Priority Model. Some of the systems described can be used on personal computers and others on mainframes with artificial intelligence shells. This volume is recommended as a reference book.

*Drinking Water and Health. Volume 9: Selected Issues in Risk Assessment.* National Academy Press,

Washington, DC, 1989. 268 pp. (ISBN 0-309-03897-9) \$29.95 softcover.

This is the final volume of the National Research Council's landmark series *Drinking Water and Health*. The first part, DNA Adducts, provides an overview of molecular adducts of DNA and their effects on human health, explores the techniques currently in use for detecting them, examines their use in risk assessment, and offers an outlook on future toxicity testing. The second part, Mixtures, explores the issues surrounding multiple-chemical exposure from drinking water, reviews current techniques for assessing the toxicity of chemical mixtures including options for grouping compounds so their toxicity in mixtures can be more reliably assessed. The book describes several alternative approaches to the risk assessment of mixtures. This volume also contains a comprehensive index for all nine volumes of the series. This is a highly recommended book for individuals and libraries.

*The Heavy Elements: Chemistry, Environmental Impact and Health Effects.* Jack E. Fergusson. Pergamon Press plc, Oxford, UK, 1990. 614 pp. (ISBN 008 0348602) £45.00/\$75.00 hardcover, (ISBN 008 0402755) £27.50/\$45.00 softcover.

The intention of this book is to provide a survey of the heavy elements, their chemistry, environmental impact, and health effects. The particular group of ten elements has a number of features in common. These are arsenic, selenium, cadmium, indium, antimony, tellurium, mercury, thallium, lead, and bismuth. The book is divided into four parts. The first is a brief introduction to the criteria used to select the elements, and the history of the discovery and uses of the elements. The second part is on the chemistry of the elements relevant to the rest of the book. In part three the environmental impact of the elements is reviewed. This includes the concentrations in the environment, sources, and chemistry. The final section is a brief introduction to the health effects of the heavy elements.

*Permethrin. Environmental Health Criteria 94.* World Health Organization Publications, Geneva, Switzerland, 1990. 125 pp. (ISBN 92-4-154294-2) Sw.fr. 15.-/\$12.00 softcover.

This book evaluates the design and findings of over 250 studies on human health and the environmental effects of permethrin, a photostable synthetic pyrethroid insecticide marketed since 1977. Because of its strong repellent properties and effectiveness as a stomach and contact insecticide, permethrin is widely

used in the protection of several agricultural crops, in the control of insects in households and on cattle, in aerial application for forest pest control, as a fog in mushroom houses, and as a wood preservative. Public health applications include the disinfection of aircraft, treatment of mosquito nets, and human lice control. The book concludes that most toxic effects are transitory, that the likelihood of carcinogenic effects in humans is extremely low or non-existent, and that permethrin, when used as recommended, is not likely to present a hazard to the general public, exposed workers, or the environment. The volume is highly recommended as a reference book.

*Fenvalerate*. Environmental Health Criteria No. 95. World Health Organization Publications, Geneva, Switzerland, 1990. 121 pp. (ISBN 92-4-154295-0) Sw.fr. 15.-/\$12.00 softcover.

This book evaluates the risks to human health and the environment posed by fenvalerate, a synthetic pyrethroid insecticide widely used for crop protection. Marketed since 1976, fenvalerate is also used in homes and gardens and for the control of insect infestation in cattle. Included are the properties of fenvalerate and identifies appropriate methods for environmental sampling and the analysis of residues, sources of human exposure, concluding that residues in crops grown by good agricultural practice are generally low. Sections are devoted to environmental behavior, metabolic pathways, effects on aquatic and terrestrial organisms, and bioaccumulation. The book evaluates effects on human health as determined from the results of animal experimentation, *in vitro* tests, case studies of accidental exposure, and clinical investigations. The book concludes that exposure of the general population is very low, that the effects of occupational exposure are transitory, and that risks to the environment and human health are unlikely when fenvalerate is applied as recommended. The volume is highly recommended as a reference book.

*D-Phenothrin*. Environmental Health Criteria No. 96. World Health Organization Publications, Geneva, Switzerland, 1990. 64 pp. (ISBN 92-4-154296-9) Sw.fr. 10.-/\$8.00 softcover.

This book evaluates the risks to human health and the environment posed by d-phenothrin, a synthetic pyrethroid insecticide used primarily for the household control of noxious insects, including head lice, and for the post-harvest treatment of stored grain. It contains information on properties and analysis, industrial production and use, and residues in stored

grain. Other areas of concern are photo-degradation and transport, the pathways by which d-phenothrin is metabolized in mammals, and effects on aquatic and non-target terrestrial organisms. An extensive assessment is made on the toxicology of d-phenothrin based on studies in experimental animals, *in vitro* test systems, embryotoxicity, teratogenicity, and neurotoxicity. The evaluation confirms a low toxicity for d-phenothrin and an absence of mutagenic, teratogenic, embryotoxic, oncogenic, and neurotoxic effects observed in the animals and systems investigated. The book concludes that d-phenothrin, when used as recommended, is not likely to pose a hazard to either human health or the environment. The volume is highly recommended as a reference book.

*The Standard Pesticide User's Guide*, Revised and Enlarged. Bert L. Bohmont. Prentice Hall, Englewood Cliffs, NJ, 1990. 498 pp. (ISBN 0-13-840802-5) \$41.00 hardcover.

This is a revised and expanded book first published in 1981 and again in 1983. It is a valuable source of information to those who are new to pesticides or wish to have an understanding of the importance of pesticides in our society. Recognizing that pesticides are an essential tool in helping to control most pests, the information in this book is oriented toward those who apply pesticides. High school and college teachers should find it useful in conveying to their students that pesticides are highly regulated chemicals that deserve respect in their use and for their role in food and fiber production. It is especially useful to commercial pesticide applicators, as well as employees of regulatory agencies. Information or suggestions for the use of specific pesticides for specific pest control problems is not included in this book. Specific control measures and recommendations have been intentionally omitted because they are subject to change and may soon become obsolete. Only current recommendations should be used, along with making sure that you are using the latest pesticide label. The volume is highly recommended as a textbook and as a reference for individuals.

*Environmental Fate of Pesticides*. D.H. Hutson, T.R. Roberts, eds. John Wiley & Sons Limited, Chichester, UK, 1990. 286 pp. (ISBN 0-471917117) £65.00 hardcover.

This volume of *Progress in Pesticide Biochemistry and Toxicology* addresses the fate of pesticides in the environment. The study of environmental fate should lead to an improvement in the ability to predict problems and encourage the development of screen-

ing methods and modeling procedures to identify compounds worth more detailed investigation. The issues of pesticides in ground water, methodologies for the conduct of field studies, the application of hydrogeological principles applied to pesticide movement in ground water, and the fate of pesticides in soil are covered in this volume. Other topics include the theoretical aspects of laboratory studies, field studies, the fate of pesticides in fish and photodegradation of pesticides. This publication is recommended as a reference book.

*The Effect of Pesticides on Human Health.* Scott R. Baker, Chris F. Wilkinson, eds. *Advances in Modern Environmental Toxicology*, Volume 18. Princeton Scientific Publishing Co., Inc., Princeton, NJ, 1990. 415 pp. (ISBN 0-911121-23-X) \$65.00 hardcover.

This book resulted from a workshop, held on May 9-11, 1988, in Keystone, Colorado, which focused on the potential chronic health effects of pesticides. Seventy expert participants collaborated within six working groups concentrating on pesticide exposure, neurotoxicity, carcinogenicity, immunotoxicity, developmental toxicity, and reproductive toxicity. This report combines the deliberations that each of these several working groups developed before, during, and after the Keystone workshop. In addition, it includes a general introduction and overview of the subject and an executive summary that contains several conclusions and recommendations that represent the consensus opinion of the chairs of the working groups. The workshop was sponsored by the Task Force on Environmental Cancer and Heart and Lung Disease, an interagency group established by the U.S. Congress in 1977. This volume is recommended as a reference book.

*Carbon Dioxide and Other Greenhouse Gases: Climatic and Associated Impacts.* Proceedings of a Symposium held in Brussels, 3-5 November 1986. Roberto Fantechi and Anver Ghazi, eds. Kluwer Academic Publishers, Dordrecht, The Netherlands, 1989. 279 pp. (ISBN 0972301919) Dfl. 175.00/\$94.50/£54.55 hardcover.

The book contains the proceedings of a symposium organized by the Commission of the European Communities to discuss the climatic and associated impacts of the accumulation in the earth's atmosphere of carbon dioxide originating from the combustion of fossil fuels and other greenhouse gases. An important climate change is foreseen during the 21st century. This will cause a thermal expansion of the ocean waters and a consequent rise in sea level of about 20

to 165 cm. Vegetal biomass may increase, while at the same time climate difficulties for agriculture are foreseen, together with a geographical shift of crops and forests due to perturbations in mean annual precipitation and temperature patterns. An increased frequency of meteorological anomalies (storms, droughts) is also to be feared. Counteracting measures could include the development of renewable energy sources, reduction in the production of greenhouse gases, intensive reforestation, a better management of land and water resources, the protection and restoration of degraded/threatened soils. The book, thus, deals with the main environmental issue reviewed at the symposium by about 60 leading European and U.S. scientists. It serves as a reference and is recommended as a reference book.

*Pollution: Causes, Effects, and Controls.* Second Edition. R.M. Harrison, ed. Royal Society of Chemistry, Cambridge, UK, 1990. 393 pp. (ISBN 0-85186-283-7) £29.50/\$57.00 softcover.

The first edition of this book arose from collation of the course notes from a Residential School held at the University of Lancaster. The second edition has been expanded. The level of treatment is essentially introductory. The contributions combine to give a broad overview, touching on most of the important areas, and delving deeper into many of them. New chapters deal with radioactive pollution and chemistry and pollution of the atmosphere. The book contains 18 chapters with authors entirely from the U.K. It was apparently peer-reviewed and thus reliance can be placed on its scientific validity. The book is useful as a textbook and is highly recommended.

*Risk Assessment in Setting National Priorities.* James J. Bonin and Donald E. Stevenson, eds. Plenum Press, New York, 1989. 686 pp. (ISBN 0-306-432463) \$125.00 hardcover.

This volume contains the proceedings of the annual meeting of the Society for Risk Analysis held on 1-4 November 1987 in Houston, Texas. Like with most proceedings, the contributions are of varied quality and deal with a large number of topics, not all of them related to the title of the volume. The over 70 contributions represent a spectrum of studies in risk analysis in government, academia, and industry. The book is a library reference book and is recommended.

*Changing Directions.* Ken Dyer and John Young, eds. Proceedings of the Conference on Ecopolitics IV.



University of Adelaide, Adelaide, Australia; 1990. 667 pp., Aus\$40 paperback.

*Dirty Words.* Hannah Bradby, ed. Earthscan Publications Ltd, London, U.K.; 1990. 166 pp., £6.95/\$14.95 paperback.

*Environmental Consequences of Energy Production.* James P. Hartnett, Chairman. Proceedings of the 17th Annual Illinois Energy Conference. Energy Resources Center, The University of Illinois at Chicago; 1989. 211 pp., paperback.

*Discarding the Throwaway Society.* John E. Young. Worldwatch Paper 101. Worldwatch Institute, Washington, D.C.; 1991. 45 pp., \$4.00 paperback.

*An Environmental Odyssey: People, Pollution, and Politics in the Life of a Practical Scientist.* Merrill Eisenbud. University of Washington Press, Seattle, WA; 1990. 276 pp., \$24.95 hardback.

*Environmental Research Groups at the Spanish Council for Scientific Research.* Teresa Mendizábal and Fernando Hiraldo, eds. Consejo Superior de Investigaciones Científicas, Madrid, España; 1991. 177 pp., paperback.

*The Kalahari Environment.* David S.G. Thomas and Paul A. Shaw. Cambridge University Press, Cambridge, U.K.; 1991. 254 pp., £55.00/\$95.00 hardback.

*Ozone Diplomacy—New Directions in Safeguarding the Planet.* Richard Elliot Benedick. Harvard University Press, Cambridge, MA; 1991. 293 pp., \$27.95 hardback/\$10.95 paperback.

*State of the World 1991.* Lester R. Brown et al. A Worldwatch Institute Report on Progress Toward a Sustainable Society. W.W. Norton & Company, New York, NY; London, U.K.; 1991. 246 pp., US\$10.95/Canada\$12.95 paperback.

*Technological Responses to the Greenhouse Effect.* George Thurlow, ed. Watt Committee Report No. 23. Elsevier Applied Science Publishers Ltd., Essex, England; 1990. 98 pp., £45.00 paperback.

*Trees of Life—Saving Tropical Forests and their Biological Wealth.* Kenton Miller and Laura Tangle. A World Resources Institute Guide to the Environment. Beacon Press, Boston, MA; 1991. 201 pp., \$9.95 paperback/\$22.50 hardback.

*Wetlands—A Threatened Landscape.* Michael Williams, ed. The Institute of British Geographers. Basil Blackwell, Inc., Cambridge, MA. 390 pp., \$79.95 hardback.

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**Book:** Henderson, P.m Inorganic geochemistry. New York, NY: Pergamon Press; 1982.

**Regulation:** USEPA (U.S. Environmental Protection Agency). National primary drinking water regulations: fluoride. 40 CFR Parts 141, 142 and 143. Fed. Reg. 50:47142-48933; 1985.

**Proceedings:** Swedjemark, G.A.; Mjörnes, L. Exposure of the Swedish population to radon daughters. Berglund, B.; Lindvall, T.; Sundell, J., eds. Proc. 3rd international conference on indoor air quality and climate. Vol. 2. Stockholm: Swedish Council for Building Research; 1984:37-43.

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