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Editorial

Environment is the sum of all social, economical, biological, physical and chemical factors which constitute the surroundings of the man. It has the components of air, water, land and biota. It is well established that the environment keeps changing with time due to natural events and man made progress vis-a-vis technological developments. Many changes in the environment have adverse effect on man and his health. It is, therefore, essential to monitor and assess the quality of environment. Modern man was awakened in the mid sixties to these changes which gave an impetus to learn about the changing environment, causes and effects, and environmental protection. The efforts are continuing to improve the quality of environment. The Department of Atomic Energy has been in the forefront of many R&D activities and environmental monitoring is not an exception. Scientists and academics in many research institutes and universities in India are striving to bring environmental awareness among students and also contributing in making a data base on environmental quality monitoring and assessment by their R&D activities. It was felt that it would be appropriate to bring a thematic bulletin on "environmental quality monitoring and assessment". IANCAS is fortunate to have an expert like Dr. S. Sadasivan, Head, Environmental Assessment Division, BARC, as guest editor for this issue. He has meticulously chosen the topics and the authors, and I thank him for his efforts. An educative article on Environment is included which is expected to be useful to the beginners in this subject.

I am glad that the concept of thematic bulletin which was conceived in 1993 has resulted in a series of thematic bulletins during last few years. I am optimistic of maintaining quality of the bulletin and frequency of the cation during the tenure of the present managing committee. This is the first bulletin for the present managing committee and I solicit the support from members of IANCAS and other readers with suggestions to improve the quality of bulletins.

A.V.R. Reddy

CONTENTS

Nuclear Analytical Techniques : Environment

__Dr. A.V.R. Reddy__ obtained his M.Sc. in Physical Chemistry in 1974 from Sri Venkateswara University, Tirupati and graduated from BARC Training School in 1976-77. He joined Nuclear Chemistry Section, Radiochemistry Division in 1977 and at present is the Head of the Section. His main areas of research are nuclear fission, nuclear reactions, radiochemical separations and neutron activation analysis. He has about 100 publications to his credit. He is a co-author of the books Fundamental of Radiochemistry, Experiments in Radiochemistry and Introduction to Radiochemistry and edited another 5 books. He has worked for an year on the extension of periodic table in the Institut für Kernchemie, Mainz, Germany. He is a member of IUPAC's (International Union of Pure and Applied Chemistry) Commission on Radiochemistry and Nuclear Techniques since 1996. During 1999-2000, Dr. Reddy as Technical Officer in the Division of Physical and Chemical Sciences, IAEA, Vienna, was looking after the programmes of radiochemistry and nuclear analytical techniques.

Introduction

Environment concerns with water, air, land and their interrelationship viz. human being, fauna and flora. Natural environmental changes may be invisible in a short span of time, but are likely to appear over long periods of time. Rapid industrialisation, deforestation and use of fertilizers, pesticides etc. in modern agriculture, in addition to the urbanisation and vehicular emissions have resulted in serious environmental changes. This reflects in the imbalance of elemental concentrations. The impact of imbalance of elemental concentrations could be understood in the context of health aspects by looking into trace/ toxic element content in our environment. The overall problem of environmental protection is intrinsically linked to man's understanding and interaction with natural biospheric processes. To understand the environmental problem, it is essential to determine the concentration of elements present in varied matrices like water, food, plant materials, minerals, soil, sediments, particulate matter and air and if possible the chemical states of these elements.

The elements are mainly grouped [1] based on their influence on the environment as (i) As, Be, Cl, Mn, Pb, Sb, Se, Tl and V which characterise the overall ecological situation, (ii) indicator elements like Al, Ba, Fe, Zr and REEs that often introduce matter into ecologically important materials and (iii) toxic elements: As, Cd, Cr, Hg, Ni, Pb and others. These elements are present in trace to major concentrations in different environmentally important materials. Various analytical techniques such as inductively coupled atomic emission (ICP-AES), mass spectrometry (ICP-MS), atomic absorption spectroscopy (AAS) and Nuclear Analytical Techniques (NATs) are being used routinely for multi element analysis. Neutron Activation analysis (NAA), Ion beam analysis (IBA) and X-ray fluorescence (XRF) are the oft used Nuclear Analytical Techniques.

There is neither a unique definition nor a sharp boundary for NATs [2]. NATs utilise certain properties of the nucleus itself, in contrast to non-nuclear techniques which utilise the properties of the atom as a whole. The term NATs is frequently associated with the phenomena of ionising radiation and isotopes. Besides nuclear excitations, nuclear reactions and/or radioactive decay, the utilisation of the processes involved in electron inner shell excitations are also regarded as pertinent to NATs. Although mass spectrometry and nuclear magnetic resonance (NMR) are considered as related NATs, they are not discussed here because in these techniques ionising radiation is neither produced nor utilised. On the other hand, Particle Induced X-ray/gamma ray Emission (PIXE /PIGE) as one of

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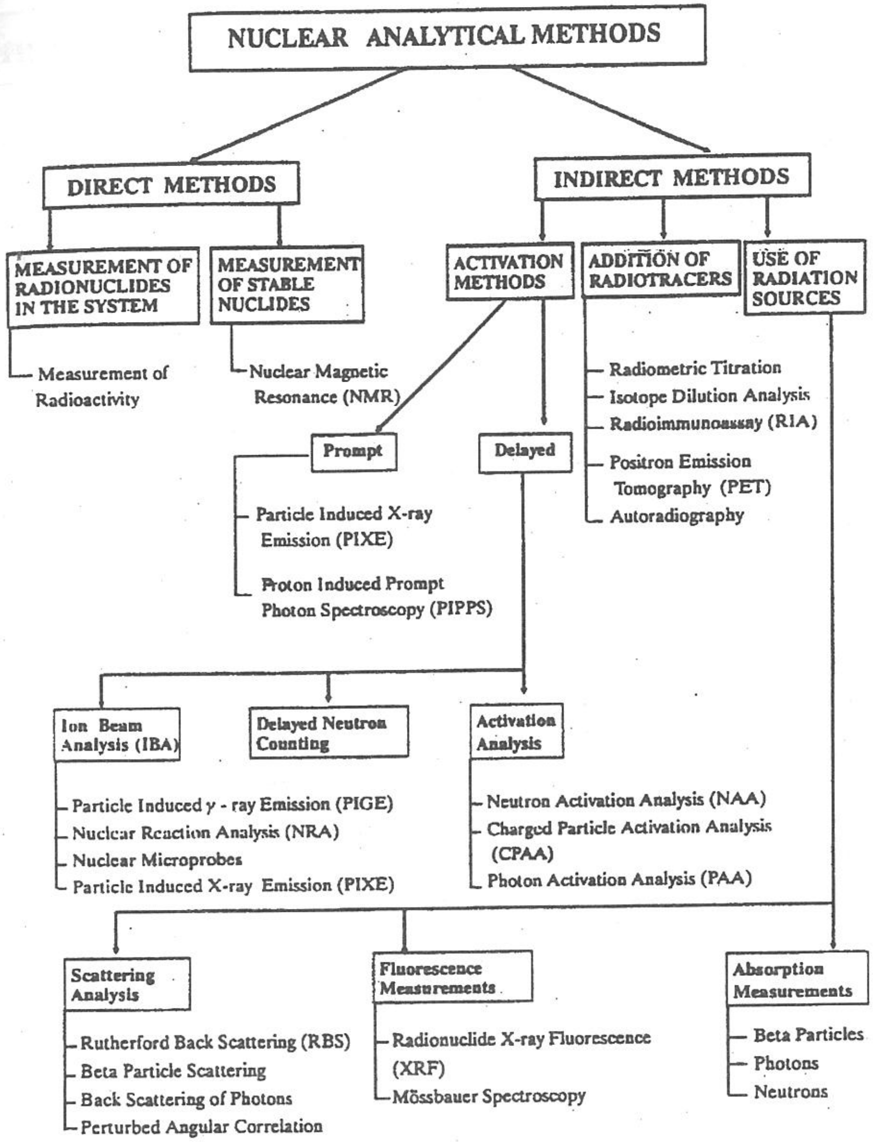

Fig. 1 Nuclear analytical methods

the varieties of ion beam analysis, deals with electron shell ionisation and thus is formally a non-nuclear technique. However, since PIXE requires almost the same equipment as the other ion beam techniques, it is considered as an NAT. NATs are divided broadly into two categories namely direct methods and indirect methods, and a select few are illustrated in Fig. 1 [3]. To have an idea about the effectiveness of NATs vis-à-vis some of the multi element analysis techniques, capabilities are compared in Table 1 [4] and detection limits for a few elements are given in Table 2 [5]. Direct NATs are not covered here as a separate article is included in this issue. Three of the NATs namely NAA, XRF and IBA with a few examples pertinent to environment applications are described below

TABLE 1. Comparison of some analytical methods for trace element analysis [Ref. 4]

Method	Accuracy	Sensi-tivity (S)	Sensi-tivity (L)	Distribu-tion	Multi-elemental	Sample size	Sample type	Routine	Turn-around time	Accessibi lity	Costs (S)	Costs(L)
INAA	+	0	0	-	+	mg-kg	S,L	+	-	-	0	0
RNAA	+	+	+	-	0	mg-g	S,L	+	-	-	-	-
XRF	+	-		-	+	mg	S	+	+	+	+	
TXRF	0	0	+	-	+	mg-g	L	+	+	+	0	+
PIXE	-	0		+	+	mg	S	+	-	-	-	
AAS	-	0	+	-		mg-g	L	+	+	+	0	+
ICP-AES	0	0	+	-	+	mg	L	+	+	+	0	+
ICP-MS	0	0	+	-	+	mg-g	L	+	+	0	-	0
ICP-IDMS	+	0	0	-		mg-g	L	0	+	0	-	-

L = Aqueous solution, S = solid, + : good, 0 : average; - : not so good; TXRF : Total reflection x-ray fluorescence; ICP-IDMS : inductively coupled isotope dilution mass spectrometry.

TABLE 2. Detection limits for some elements in μg [ref. 5]

Element	INAA	XRF	PIXE	ICP-ES	AAS	ICP-MS
As	0.03	4	0.4	3.5	0.2	0.04
Cd	0.6	6	10	1.7	0.003	0.06
Cr	0.03	16	0.8	4	0.01	0.06
Cu	0.03	6	0.3	3.5	0.02	0.32
Fe	6	12	0.5	0.5	0.02	ND
Hg	0.03	7	1	17	2	0.02
In	0.0006	ND	14	40	ND	0.07
Mn	0.001	12	0.6	0.95	0.01	0.1
Mo	0.3	5	1.9	5.5	0.02	0.04
Ni	3	5	0.4	6.5	0.2	0.1
Sb	0.001	8	14	20	0.1	0.05
Sc	0.03	2	0.4	50	0.5	0.79
Sn	1	8	16	17	0.1	0.06
V	0.03	20	1.3	3.5	0.2	0.03
Zn	0.3	5	0.3	1.2	0.001	0.21

Neutron Activation Analysis

Neutron being a non-charged particle interacts with nuclei of almost all isotopes and often produces radioisotopes which are measured to determine the concentration of the isotope and the element. Thus neutron activation analysis (NAA) is based on irradiation of a sample with neutrons from a neutron source like nuclear reactor, and subsequent measurement of the induced radioactivity preferably employing a high resolution gamma ray spectrometer with a HPGe detector. Depending on the requirement, NAA can be carried out either non-destructively (Instrumental NAA) or by performing pre- or post chemical separations (Chemical or Radiochemical NAA). With the advancements in the detector technology, improvements in electronic accessories and development of software for spectral analysis, NAA has become a very capable simultaneous multi-element analysis technique with improved sensitivity. In many cases, more than 30 elements can be determined from a single experiment. Elemental concentrations in a sample can be determined by absolute, relative or k0 standardisation methods [6,7]. In relative method, sample and a standard very similar to the sample, are coirradiated and the activities are measured in identical conditions. On the other hand, single comparator like gold is used in k0 standardisation method obviating the use of multielement standard. In both these methods sensitivities ranging from μg to ng are obtained and they depend mainly on the neutron flux, reaction cross section and detector efficiency. These methods are being used in various fields of research. A few examples that pertain to the environment studies are given here.

To understand the anthropogenic load and to compare with the prevailing pristine environment, compositional characteristation of different sea and lake sediments are carried out. Bottom sediments from Nainital lake were analysed to obtain the multielement profiles as a function of depth [8] and no perceptible anthropogenic load could be observed. Ferromanganese encrustation samples from the Indian Ocean were analysed by k0 NAA method for studying the different oceanic conditions on the trace element distribution [9]. The observed negative cerium anomaly indicated the prevailing reduced environment at the deposition site which is associated with a low concentration of trace elements alongwith REEs. The role played by micro nutrients and trace elements in the biochemical functions of human life and their impact on human life are important. Elemental concentrations of different edible and medicinally valuable leaves alongwith a SRM were determined [10]. A particular leaf variety (neem) from two places were analysed to know the effect of soil and environment on the elemental profiles. Air particulate matter (APM) is an important component to analyse to get the information on different pollutants. NAA is extensively used to measure different elements like As, Se, Br, V and Cd [11]. Prompt gamma ray NAA (PGNA) uses a neutron beam and is an on-line measurement technique. PGNA is used to measure toxic elements like Cd, Hg and and other toxic elements from oil spill and other related matrices [12].

The accuracy and precision achievable in NAA and its totally independent principle compared to other analytical techniques play a very important role in quality control of chemical analysis, namely in the certification of reference materials of chemical composition, including homogeneity testing [11].

X-ray Fluorescence Analysis

X-rays emitted from an ionised atom have energies characteristic of the element involved and the intensity of X-ray is proportional to the concentration of the element and the strength of the ionising source. Thus X- ray fluorescence (XRF) analysis is based on the generation of characteristic X-rays from a sample by an energetic beam of any kind, measuring the intensities to arrive at the concentration of different elements in the sample. In wavelength dispersive XRF (WD-XRF), the intensity is measured with a gas proportional counter or scintillation detector. In the energy dispersive XRF (EDXRF) the characteristic X-ray spectrum is measured with a solid state detector like Si(Li). In many ways, the ED-XRF technology is more related to modern nuclear technology.

In typical environmental samples, some dozen elements can be assessed simultaneously using EDXRF [13]; this is only superseded by neutron activation analysis (NAA), which is inherently much slower, and by ICP-AES or ICP-MS. For quantitative analysis, ED-XRF offers a large dynamic range, from the mg kg^{-1}-level to 100% m/m, and when preconcentration of samples is incorporated, this range can be extended down to the %g kg^{-1}-level [14]. ED-XRF remains the method of choice for the monitoring of aerosols, mostly for heavy metals. A correlated study on the environmental monitoring has been carried out by Nguyen et al by determining concentrations of 22 elements in environmental samples like coal, soil, water and sediment using EDXRF technique [13]

Total reflection x-ray fluorescence (TXRF) is a variation of XRF in which the exciting beam is highly collimated vertically, and it impinges at a very small angle on a flat, polished sample or support (usually quartz or Plexiglas) carrying a minute sample. If the angle of incidence is below the critical angle (a few minutes of a degree), the beam will practically not penetrate into the flat sample or support but be totally reflected. In this way, practically no scattered X-rays are generated, and the background measured by a Si(Li) detector (usually at right angle) well be extremely low, enhancing the detection limits [14]. TXRF has been applied to analyse different waters, such as rainwater, drinking water, river water, seawater and even wastewater [15]. TXRF is capable of determining numerous elements down to detection limits of 0.2 ng m^{-3}. In **Micro-x-ray fluorescence technique**, the incoming beam is collimated and/or focused down to dimensions in the range of a few micrometers by means of optical elements comprising glass capillary, lenses and finds application in environmental studies in characterisation of individual particles with advantageous detection limits, in the order of 10^{-14} g.

Ion Beam Analysis Techniques (IBA)

Close ion-nucleus encounters occur when a sample is bombarded with charged particles like protons, deuterons and alpha particles of a few MeV/u. By detecting the various signals produced during interactions with atoms and nuclei in the sample, the elemental/isotopic composition can be obtained. Ion penetration in solid matrices is normally tens of micrometers. Analytically probed depth vary from sub micrometer to tens of micrometers depending on the radiation detected. The most common techniques are Particle-Induced X-ray/gamma ray Emission (PIXE/ PIGE) [16], Rutherford Backscattering Spectrometry (RBS) [17] and Nuclear Reaction Analysis (NRA) [18]. The analytical characteristics vary from trace element analysis to depth profiling of near surface layers. The first nuclear microprobe was developed in the early seventies but during the last decade the technique has matured and the proliferation of such systems has been very strong (>80 systems world-wide) [19]. The systems needed for collimating, focusing and manipulating the beam are now commercially available in addition to the turn-key based "desktop" versions of a very compact accelerator.

The most common techniques in environmental applications are still PIXE and RBS, due to high cross-section and high accuracy, respectively. The development of the PIXE technique has been closely linked to general environmental problems. e.g., studies on atmospheric particles to understand respiratory human health effects. and for the modeling of climate change is now very important input for global climate development models. By combining these data with data obtained using XRF, INAA and other analytical techniques, very pertinent information for understanding a sustainable global future will be at hand.

The development of a specific technique for using the concept of "geogas" for ore prospecting is based on emission of minute amounts from deep underground deposits to the earth surface [20]. Small particles are collected on thin foils and after several weeks of exposure these foils are analysed using a millimeter ion beam. Composition of the material deposited is determined using PIXE and from this, it is possible to judge the mineral deposits in deep ground. This is a technique with a good potential for the understanding of the rock conditions (rock crack characteristics) in investigation to prepare for underground long-term storage of highly radioactive waste [20].

Conclusions

Nuclear Analytical Techniques are quite useful and effective in environment monitoring in view of capability of multi element analysis in a variety of samples and with good detection limits for a number of elements. Most of the NATs are contamination free and often non-destructive analysis is feasible. Some of the areas which need constant monitoring are surroundings of mining areas, power reactor sites, industrial areas etc. A comprehensive programme of monitoring air, soil, water and plants around these areas could provide valuable information about the impact of pollutants on environment

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Radon and its Progeny : Occurrence, Measurements and Health Effects

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*Dr. **T.V. Ramachandran** has joined the Bhabha Atomic Research Centre after his graduation from Kerala University in 1971. He has worked on natural and fall out radioactivity measurements in soil, food stuffs, coal, fly ash and other environmental samples. Currently he is working on mapping of the country for indoor radon/thoron levels as well as in the monitoring of radon/thoron levels in mixed field environments with emphasis on monazite regions of southern parts of the country using passive detector technique.*

Introduction

Radon and its short-lived progeny concentrations in the atmosphere are the most important contributors to radiation exposure from natural sources to human beings. While the health risks associated with high radon exposures in underground mines have been known for a long time, relatively little attention was paid to environmental radon exposures until the 1970s. Indoor radon exposures could be quite high, in some cases comparable to those experienced by many underground miners. The significance of lung cancer is undisputed among miners with bronchial-epithelial doses in excess of 2000 mSv [1]. Quantification of these risks to general public is based largely on epidemiological evidence and subject to significant uncertainties. In view of the potential health hazard presented by indoor radon, a considerable amount of effort has been devoted to the development of mitigation techniques and strategies, especially in underground mines, that might limit or control exposure to this source of radiation.

Table 1. Physical properties of radon (^{222}Rn) and its short lived decay products

Isotope	Historical name	Half-life	Principal radiation & energy (MeV)
^{226}Ra	Radium	1600 y	α 4.785 (94%) 4.602 (6%)
^{222}Rn	Radon	3.82 d	α 5.490 (100%)
^{218}Po	Radium A	3.11 m	α 6.003 (100%)
^{214}Pb	Radium B	26.8 m	β 0.650 (50%)
^{214}Bi	Radium C	19.8 m	β upto 3.26 MeV
^{214}Po	Radium C'	1.64 μs	α 7.687 (100%)
^{210}Pb	Radium D	22.3 y	β 0.015 (81%)
^{210}Bi	Radium E	5.01 d	β 1.161 (100%)
^{210}Po	Radium F	138 d	α 5.303 (100%)
^{206}Pb	Radium G	Stable	None

% abundance are given in the parentheses of column 4

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Sources

Radon-222 is the decay product of the most prominent radium isotope, ^{226}Ra, which in turn is a decay product from ^{238}U. Table 1 gives the physical properties of radon (^{222}Rn) and its short - lived decay products. Concentration of radon in the atmosphere is governed by the source term, characterised by the exhalation rate and atmospheric dilution processes, which are affected by meteorological conditions. More important physical factors include the soil porosity, soil moisture, soil grain size, and conditions of the soil surface (Table 2). The main mechanism for the entry of radon into the atmosphere is by molecular diffusion. For a porous mass of homogeneous material, the flux density of radon at the surface of dry soil J_D (Bq.m^{-2}.s^{-1}) is given by

$$J_D = C_{Ra}\,\lambda_{Rn}\,f\rho_s\,(1 - \varepsilon)\,L \qquad (1)$$

Where C_{Ra} is the activity concentration of ^{226}Ra in the earth material (Bq.kg^{-1}), λ_{Rn} is the decay constant of ^{222}Rn (2.1 x10^{-6} s), f is the emanation fraction of the earth material (f=0.20), ρ_s is the soil grain density (2700 kg.m^{-3}), ε is the porosity of the dry earth material (0.25) and L is the diffusion length, equal to $(D_e/\lambda_{Rn})^{1/2}$; (D_e = 2.0 E^{-6} m^2.s^{-1}). The J_D calculated using the typical values (Table 2) works out to be 0.033 Bq.m^{-2}.s^{-1}.

TABLE 2. Characteristics of soil with respect to radon emanation [2,3]

Parameter	Typical range	Typical value
Radium content (Bq/kg)	5 - 120	40.00
Emanating fraction, f	0.01 - 0.50	0.20
Effective porosity, e	0.10 - 0.50	0.25
Exhalation rate, Bq.m^{-2}.s^{-1}	0.001 - 0.05	0.03

Even though the major source of radon is from the soil, contributions from other sources like underground water, natural gas, coal and phosphate residues are also reported (Table 3).

TABLE 3. Different sources of global atmospheric radon [4]

Source	Input to atmosphere (T Bq per year)
Emanation from soil	7.40 x 10^7
Ground water (potential)	1.85 x 10^7
Emanation from oceans	1.11 x 10^6
Phosphate residues	1.11 x 10^5
Uranium mill tailings	7.40 x 10^4
Coal residues	7.40 x 10^2
Natural gas	3.70 x 10^2
Coal combustion	3.70 x 10^1

Measurement Techniques

Both active and passive methods are available for the measurement of radon and daughter products. Most important active methods for radon measurements in the air are by collecting the gas in a scintillation flask / ionization chamber or by sucking the gas through two filter samplers. Progeny levels are measured by collecting on filter papers and by measuring radioactivity at suitable intervals. In radon gas estimation progeny concentration in the sampled air is removed by filtration when gas is collected in the scintillation cell. The alpha activity in the sampling cell is computed for the build up and decay of radon gas with respect to post sampling delay. On the other hand, in progeny measurement, filter paper sample is collected and the decay profile is followed in computing individual progeny concentrations. The various techniques commonly used are Ionisation Chamber Counter (ICC), Activated Charcoal Collection (ACC), Double Filter Method (DFS), Electrostatic Method of Collection (ERM), Passive Integrated Method (PRM) and Solid State Nuclear Track Detector (SSNTD). The detection ranges of the methods mentioned are illustrated in Fig. 1 [5].

In comparison to other methods, passive time integrated measurements using SSNTDs are more meaningful for the inhalation dosimetry because of the wide fluctuations in the concentration due to

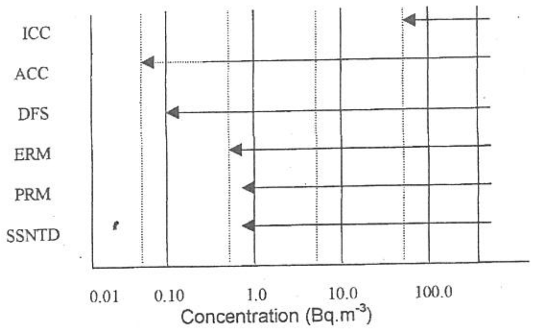


Fig. 1 Detection range of various techniques

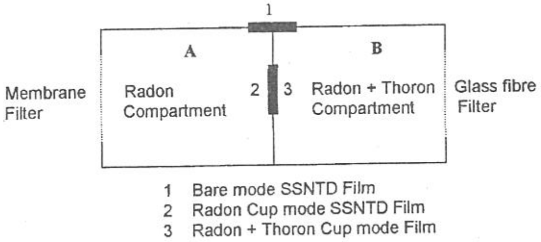


Fig. 2 Twin cup radon-thoron dosimeter

diurnal and seasonal variations. The SSNTD method exploits the fact that alpha particle leaves a microscopic track of damage when passing through certain plastics. The tracks are enlarged by chemical etching and counted under a microscope. The concentration of radon or progeny is obtained using the calibration factors generated from controlled experiments. Of the various types of nuclear track detectors available for use, LR-115 type II (cellulose nitrate) film is commonly used for radon measurements [6-8]. Presently, techniques have been developed using twin cup detector systems for the measurement of radon, thoron and their progeny. Fig. 2 gives the schematic diagram of the SSNTD dosimetric system. The dosimeter is designed for the simultaneous measurement of radon, thoron gases and their progenies.

Health Effects

The hazard from airborne radon is due to inhalation of its short-lived decay products. Due to the low solubility of the inert gas in the body tissues the effective dose equivalent from the inhalation of radon gas is small compared with the radiation dose from inhaled radon decay products. The decay products are trapped in the lung which deposit their alpha particles' energy in the lung tissue. For a given concentration of radon in the air, the concentration of its short lived progeny can vary depending on the removal processes. The amount of alpha-particle energy that potentially could be deposited in the lung is proportional to the number of short lived daughter atoms in the air and the amount of alpha particle kinetic energy each is capable of producing in the decay to long lived ^{210}Pb or ^{208}Pb. Radon freely mixes with the room air and decays to initiate its short lived decay series. They rapidly diffuse, collide with and attach to aerosol particles with in the house air space. The combined effective size of the decay series members and their aerosol particles ranges from 0.05 μm to a few μm in diameter. This portion of the decay products attached with aerosols is called the ***attached fraction.*** Depending on the size distribution and concentration of the aerosol particles (number of particles per unit volume) present in the room air, up to 20 % of the progeny can exist in the ***unattached state.*** Since the unattached radon progeny are positively charged, they often attract to the small polarized molecules in the air [9]. The atoms or ions, which comprise the unattached fraction of the radon decay products, deposit by simple diffusion to the walls of the respiratory tract. Deposition in the lung of the fraction of the radon decay products attached to the aerosol ***(attached fraction)*** is mainly the result of three processes. These are diffusion, impaction and sedimentation. The probability of the deposition of

Table 4. Average concentration of radon and its progeny in air and dose conversion factors

Location	Concentration (Bq.m^{-3})		Effective dose coefficient (nSv per Bq h.m^{-3})	
	Gas	EEC*	Gas	EEC
Out door	10	8	0.17	9
Indoor	40	16	0.17	9

*EEC - Equilibrium Equivalent Concentration;
Eq. Factors : Out door - 0.8, Indoor - 0.4

the attached atoms per unit area of respiratory tract surface is a function of the size distribution of the atmospheric aerosol to which they are attached. On an average, the dose to the bronchial basal cell layer in the lung is about 5 to 8 times higher than the dose to the pulmonary region. Table 4 gives the effective dose coefficients and annual dose to public from inhalation exposure to radon and progeny [10]. From the dose conversion factors (Table 4) the inhalation exposure of personnel can be assessed by knowing (i) the concentration of radon and its progeny concentrations inside as well as out side the house and (ii) the occupancy factor.

Annual inhalation dose (D_A) due to ^{222}Rn and progeny concentrations is given by

$$D_A\ (\mu Sv) = 10^{-3}\ [\ Rn_I\ (0.17 + 0.4 \times 9)\ 7000 + Rn_O\ (0.17 + 0.8 \times 9)\ 1760\ ] \qquad (2)$$

Where Rn_I - is the ^{222}Rn concentration inside the house, Bq/m^3, Rn_O - is the ^{222}Rn concentration outside the house, Bq/m^3, 7000 - Occupancy inside the house (h) and 1760 - Occupancy outside the house (h)

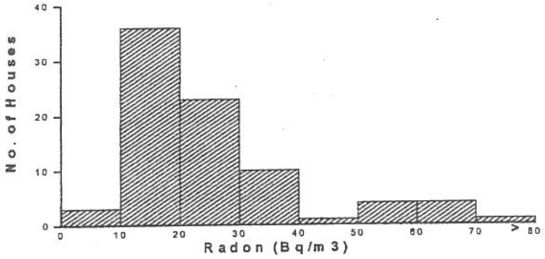
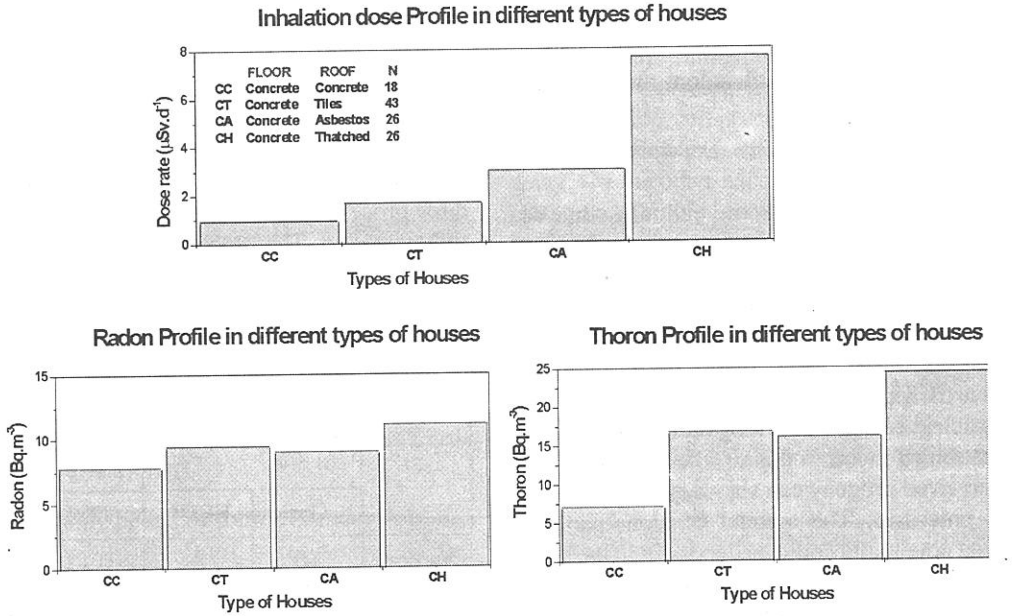


Fig. 3 Frequency distribution of radon.

The International Commission on Radiological Protection (ICRP) has developed a more detailed lung model [11] to calculate the effective dose for exposure to airborne radionuclides. The new dose conversion factor for equilibrium equivalent radon concentration is 6 nSv per Bq.h.m^{-3} replacing the value of 9 nSv used in UNSCEAR 1993.

Results

A sample survey of ^{222}Rn was carried out using cup dosimeter system in 97 dwellings in different parts of the country. The distribution of radon in these houses is shown in Fig.3. The results are comparable with the values reported globally [3].


Inhalation dose Profile in different types of houses

Radon Profile in different types of houses

Thoron Profile in different types of houses

Fig. 4 Types of houses Vs Rn/Tn concentrations and inhalation doses.

The twin chamber dosimeter has been designed specifically for inhalation dosimetry in field where both radon and thoron are present. These dosimeters were deployed in the monazite area of Chavara region in Kerala. Inhalation dose estimations were carried out by the methodology developed. Results of measurements in a few Panchayats are shown in Fig.4.

Conclusions

SSNTD based passive dosimeters are useful for long term monitoring of radon and its progeny concentrations. The twin cup dosimeters designed for the measurement of radon and thoron in the monazite areas of Kerala, give a meaningful evaluation of the dose in a mixed field where both radon and thoron are present.

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Energy Dispersive X-ray Fluorescence Analysis - An Excellent tool for Elemental Analysis of Environmental Matrices

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*Dr. **B.S. Negi** joined Bhabha Atomic Research Centre in 1969 after completing one year training course of Training Division. He obtained Ph.D. degree from Mumbai University in 1988. He has been associated with the development and use of nuclear and related techniques (EDXRF & INAA), systems for the measurement of toxic trace elements in environmental samples (air particulates, soil, flyash, coal etc.) and statistical analysis of the data to identify pollution sources. He is also involved in the R&D activities related to the natural and man made radionuclides in environmental samples like air filters, dry and wet deposition samples collected at various sampling stations spread all over the country and analysed at Low Level Radioactivity Measurement Laboratory of this Division. The laboratory is being upgraded under his supervision with advance system to handle new challenges in this field.*

Introduction

The energy dispersive x-ray fluorescence (EDXRF) technique is multi-elemental, non-destructive and relatively fast as compared to other analytical techniques. The sensitivity this instrumental technique offers is generally adequate for analysis of elements of importance in the environmental samples. Therefore, it has become almost the preferred one in environmental monitoring, where a large number of samples are required to be analysed. We have used this method extensively to analyse environmental matrices, such as, air particulates, flyash and sediment cores and several other sample types on a lesser scale over the past twenty years. The method of analysis is fairly well known now and procedures adopted by us are reported elsewhere [1,2]. In this article an attempt is made to briefly describe the various applications using EDXRF in our laboratory.

Methodology

The EDXRF system consists of an X-ray source (radioisotope source or an X-ray tube) to generate characteristic X-rays in the sample, high resolution low energy photon Si(Li) detector and a multichannel pulse height analyser. The elemental concentrations are quantified from the peak intensities of the sample X-ray fluorescence spectrum. This could be accomplished either by a comparative method or by semi-empirical method. In the comparative method a standard, with known concentrations of elements to be analysed and having approximately similar matrix as the sample, is used to avoid errors due to absorption and enhancement

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effects in the sample. Samples such as coal, fly ash, soil / sediment and vegetation which can be prepared in the form of pellets were analysed. Air particulate filters and other thin samples do not need any sample preparation and quantification is done using thin film standards of single or multiple elements with proper absorption corrections [3]. The overall QA / QC were ensured by analysing Standard Reference Materials available from Agencies such as IAEA and NIST. The accuracy of measurement for soil, fly ash and vegetation samples have been estimated to vary from 4 to 10 percent for various elements. In the case of air filter samples the accuracy is 15 % except for Al and Si (20%), K and Cl (10%) and Fe and Pb (5%).

Advances in EDXRF Technique

The EDXRF technique has undergone many changes in terms of improvement in lower energy limits, energy resolution, detection limits and required sample weight / volume. The usefulness of the conventional Si(Li) detectors in low energy range (up to 3 KeV) is limited due to absorption in the entrance Be window of the cryostat. Also, the accurate efficiency determination of a Si(Li) detector in this region presents serious problems due to a lack of low energy radioactive standards and the discontinuity of the efficiency response caused by the K absorption edge of Si at 1.84 KeV. In most environmental sample analyses, the ability to detect light elements below Al would be an added advantage for the complete material characterisation. By employing window-less or removable window detectors with electron excited systems, the low energy sensitivity of the EDXRF is considerably increased. An attractive alternative to a window-less detector is an ultra thin window detector, which usually consists of an aluminium coated mylar or formvar foil. Recently, a detector employing a 0.5 μm thick polymer window has become commercially available. The window is claimed to be transparent virtually to all x-rays but opaque in the visible range and strong enough to withstand high vacuum employed in the cryostat. This development offers great possibilities for the determination of light elements.

In the field of X-ray tubes, the recent advances include the development of micro focus and portable tube excitation systems. A compact micro focus x-ray tube, producing a 10 micrometer spot, suitable for high resolution magnified images has been introduced. As for excitation sources, synchrotron radiation are being used which provide enhanced counting rates [4].

In an XRF system the lower limits of detection are dictated by the background produced due to the sample backing material. A new system, Total Reflection X-ray Fluorescence (TXRF) spectrometer is now commercially available. In TXRF spectrometer the incident beam is highly collimated and strikes the sample at an angle where total reflection occurs and hence the scattered x-ray background is almost eliminated [4]. The system uses synchrotron radiation and gives absolute detection levels that are several orders of magnitude lower than the conventional EDXRF systems and more importantly very low weight (less than microgram) samples can be analysed.

Applications

The application of EDXRF to monitor the elemental concentrations in total suspended particulate matter (TSPM) at a national level was attempted way back in 1979-81 [2], when a large number of aerosol samples were collected from Bangalore, Mumbai, Chandigarh, Coimbatore, Gulmarg, Jaipur, Kanpur and Nagpur. The elemental concentrations were subjected to factor analysis to get information on the pollution sources at these sampling stations. Some of the aerosol sources that could be identified were wind blown soil dust, combustion source, oil refinery emissions at Mumbai, rock salt mining at Jaipur, alumino silicate (kyonite) and Mn mining at Nagpur and fuel oil burning at Kanpur. The weight percentage of all the elements measured was found to vary from 6.85 % at Kanpur to 32 % at Jaipur. The percentage weight accounted at other stations were - Bangalore: 21.5, Mumbai: 23.7, Chandigarh: 17.8, Coimbatore: 12.5, Gulmarg: 11.9 and Nagpur: 29.6. The weight percentage of various elements measured at Mumbai, Bangalore, Nagpur and Jaipur are presented in Fig. 1. The unaccounted weight should be due to C, N, O and a few elements like Na and Mg.

Lead is amongst the metals known to be toxic and whose levels in the environment have shown step-wise increase over the years. The last sharp

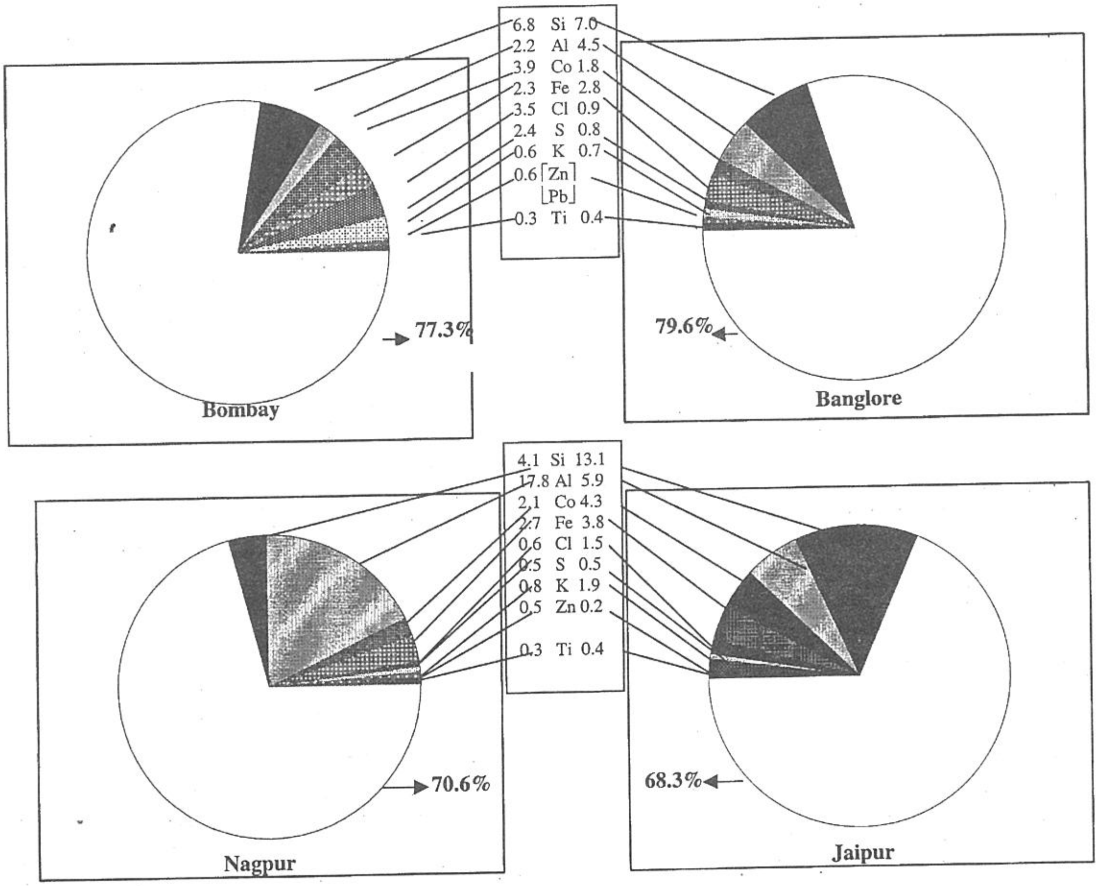

Fig. 1 Weight percentages of elements in air particulate samples.

increase in lead concentrations in air was due to automotive emissions. The lead injections into the atmosphere was estimated [5] to be around 440 to 470 kilo tons per year of which the contribution of auto emissions was approximately 90%. The atmospheric lead in seven cities in India are summarised in Table 1. The concentrations varied from 0.05 to 0.21 $\mu g/m^3$ at various sampling stations and followed a lognormal distribution at most of the places [6].

In India approximately 70 % of total energy is generated by Thermal Power Stations which use coal with a high ash content of 30 - 40%. The total coal used in our power plants is of the order of 300 million tones per year producing nearly 90 million tones of ash per year. Various toxic elements entry into the environment from the coal ash is mainly due to its reuse and dispersion. The elemental concentrations in coal ash samples collected from various thermal power plants all over the country were determined. The study showed that the elemental concentrations in fly ash vary widely, but within the ranges cited in the literature for various coal types used while the ash content varied from 4 % (for lignite) to 40 %. A total of 17 elements could be analysed by this method including toxic elements like S, Pb, Cr, As and Cu [7].

In a related study, possible groundwater contamination from a fly ash pond was evaluated [8]. In Table 2, the estimated leach water quality for various toxic elements are given. Based on these and the cation exchange capacity (CEC) of soil at the disposal site (15-30 meq/100 g) and other relevant parameters like groundwater hydrology, pond size

TABLE 1. Arithmatic and geometic mean concentration of Pb in air at a few cities in India

City	Pb conc. in air ($\mu g/m^3$)			
	A. Mean ± S.D.	G. Mean ± G.S.D.	Minimum	Maximum
Mumbai (88)	0.21 ± 0.20	0.12 ± 3.41	0.02	0.83
Bangalore (55)	0.08 ± 0.05	0.07 ± 1.65	0.02	0.15
Nagpur (60)	0.15 ± 0.01	0.11 ± 2.09	0.04	0.68
Jaipur (62)	0.09 ± 0.01	0.08 ± 1.81	0.02	0.26
Chandigarh (33)	0.09 ± 0.01	0.07 ± 1.95	0.02	0.22
Kanpur (15)	0.31 ± 0.10	0.20 ± 2.44	0.10	1.41
Coimbatore (8)	0.06 ± 0.02	0.05 ± 2.00	0.02	0.15

Samples cover an year's period (1980) except for Kanpur and Coimbatore where the samples were collected during only three months. Number of samples are given in parenthesis in the first column.

TABLE 2. Results of leaching tests on Manuguru fly ash

Element permissible	Concentration[a]	Total leach %	Leach water quality ($\mu g/mL$)	Discharge limit surface water[b] ($\mu g/mL$)	Drinking water[c]	
					Desirable ($\mu g/mL$)	($\mu g/mL$)
Cr	98	0.665	0.00037	2.0	0.05	0.05
Fe	29300	0.15	1.10	-	0.3	1.0
Co	8.6	2.12	0.01	-	-	-
Cu	77	0.47	0.02	3.0	0.05	1.5
Zn	93	3.52	0.186	5.0	5.0	15.0
As	4.1	BDL[d]	-	0.2	0.05	0.05
Cd	0.10	-	-	2.0	0.01	0.01
Hg (ppb)	8.21	8.64	0.00004	0.01	0.001	0.001
Pb	12.8	2.04	0.015	0.1	0.05	0.05

[a]Concentration is in ppm unless otherwise specified. L/S ratio = 100, [b]ISI- 2490, [c]ISI - 10500, [d]BDL - Below Detection Limit

and geology of the site, it was concluded that there is no possibility of groundwater contamination due to the ash pond.

At Mount Abu, Rajasthan the aerosol load and its composition were studied for qualifying the site for installation of a gamma ray telescope. The dust particles were also examined for their size and geometry using a scanning electron microscope. Correlation coefficients among various elements in the dust showed that it is made up of mainly two components- wind blown ground dust and particulates arising out of wood /coal burning and apart from high dust loads. Just before the monsoon the site was acceptable [9].

The elemental composition and mass distribution in fine particulate aerosols (<2.0 µm), is gaining importance due to their association with respiratory and cardiovascular diseases. The fine size particles have a long residence time in the atmosphere and are hence easily transported over long distances. The EDXRF along with INAA technique were used to study elemental composition of two size fractions – fine (<2.0 µm) and coarse (2-10 µm) aerosols collected on filters at two sampling locations – Chembur and Borivli of Greater Mumbai, under an IAEA contract. The results of analysis of these aerosol samples showed that the concentrations of crustal elements, namely Ca, Fe, K, Na, Sc, Si and Ti at Chembur in the coarse fraction are two to three times higher as compared with Borivli. In the fine fraction, the concentration levels of Fe, Sc and Ti are smaller at both the sites. At Borivli the concentration of K is more by a factor of two as compared to Chembur. The concentrations of anthropogenic elements are similar at both sites in fine aerosol fraction, whereas the same is not observed for coarse fractions. The correlation coefficients and factor analysis in both size fractions at these locations suggest four sources of pollutants, namely wind blown soil dust, sea salt, refuse and wood/coal burning. At Chembur, contribution from wear and tear of vehicle tyres (high factor loading of Cr and Zn), though less prominent, was also observed. The mean concentrations of elements are given in Table 3 [10].

In another application, though not directly connected to environmental science, geochemical studies were carried out on core samples (shale and limestone) from the shelf off the coast of Mumbai [11]. The analysis was by INAA and EDXRF and for U, Th and K by direct gamma ray spectrometry as well. Our investigations showed that the trace element abundances of the shales off the west coast

TABLE 3. Mean concentrations (ng/m^3) of elements in size fractionated aerosols

	Chembur (80 samples)		Borivili (20 samples)	
	2-10 μm	<2 μm	2-10 μm	<2 μm
As	13.89 ± 58.18	3.86 ± 7.41	10.5 ± 0.30	5.07 ± 7.80
Br	22.48 ± 31.60	18.30 ± 12.20	21.98 ± 7.78	0.98 ± 0.55
Ca[a]	5.56 ± 3.06	0.53 ± 0.93	2.48 ± 2.44	0.34 ± 0.23
Cl[a]	1.70 ± 1.64	0.32 ± 0.28	1.98 ± 2.27	0.10 ± 0.25
Co	4.04 ± 2.58	0.96 ± 0.72	1.76 ± 1.68	0.96 ± 1.21
Cr	70.58 ± 81.66	36.4 ± 39.3	35.0 ± 19.0	52.6 ± 30.2
Fe[a]	6.07 ± 3.57	0.78 ± 0.45	2.41 ± 1.36	0.74 ± 0.40
Hg	4.70 ± 4.60	3.94 ± 3.16	2.18 ± 1.52	2.10 ± 1.87
K[a]	0.48 ± 0.40	0.22 ± 0.14	0.24 ± 0.20	0.44 ± 0.44
La	2.29 ± 1.82	0.53 ± 0.38	0.12 ± 0.06	0.05 ± 0.03
Pb[a]	0.34 ± 0.38	0.17 ± 0.17	0.17 ± 0.05	0.17 ± 0.06
S[a]	0.95 ± 0.50	0.94 ± 0.69	0.24 ± 0.37	0.81 ± 0.69
Sb	6.51 ± 7.91	3.06 ± 3.28	4.13 ± 7.08	2.20 ± 2.64
Sc	1.51 ± 0.96	0.18 ± 0.17	0.54 ± 0.32	0.13 ± 0.06
Si[a]	8.77 ± 4.93	2.00 ± 1.56	3.91 ± 2.65	0.93 ± 1.13
Ti[a]	0.57 ± 0.33	0.10 ± 0.12	0.20 ± 0.09	0.14 ± 0.17
Zn[a]	0.72 ± 0.42	0.18 ± 0.18	0.07 ± 0.04	0.09 ± 0.08

[a] Concentrations in g/m^3, elements were measured by EDXRF.

of India are generally similar to marine shales elsewhere. The depositional setting was predominantly an argillaceous one and the sediments were derived from weathering and transportation of the Deccan Trap flows. Clay and detrital components governed the element abundances in these sediments. A break in the chemistry was observed at a depth of about 1600m, corresponding to a palaeontological age of 22.5 million years, and was attributed to a change in the depositional environment and/or the provenance due to some tectonic event.

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Environmental Issues in the Front End of Nuclear Fuel Cycle and their Quality Management

Shri A.H. Khan *graduated from St. Columba's College, Hazaribagh and joined the Health Phsycis Division of BARC in 1965. He obtained his M.Sc. degree from the University of Bombay. Shri Khan has served the uranium mining and milling industry as health physicist for 35 years. He is now Head, Radiation Protection Section (Nuclear Fuels) in the Environmental Assessment Division. Shri Khan's areas of interest includes uranium mine ventilation, radiation protection and environmental surveillance in the mining and processing of uranium and thorium ores. He has about 50 publications in this field. For over 10 years Shri Khan has been Member-Secretary of Safety Committee for UCIL and Projects of AMD, appointed by SARCOP/AERB. Shri Khan has attended several Technical Committee and Advisory Group Meetings of the IAEA in Vienna and participated in the IAEA expert mission in Slovenia to evaluate the effectiveness of the decommissioning of uranium mining, milling and tailings management facilities.*

Introduction

The front end of nuclear fuel cycle comprises of mining and processing of uranium and thorium ores, and fabrication of fuel assemblies for the nuclear power plants. The three underground mines at Jaduguda, Bhatin and Narwapahar operated by the Uranium Corporation of India Ltd (UCIL) in Bihar produce uranium ore which is processed in the mill at Jaduguda to produce magnesium diuranate commonly known as yellow cake.

The beach mineral sands containing monazite occurring at several locations along the south west and east coast of peninsular India are mined and processed by the Indian Rare Earths Ltd (IREL) at the mineral separation plants at Chavara (Kerala), Manavalakurichi (Tamilnadu) and Orissa Sands Complex (OSCOM) at Chatrapur in Orissa to recover heavy minerals and monazite. The monazite, a mineral containing thorium and rare earth phosphates, is chemically processed at the Rare Earths Division at Udyogamandal to produce thorium concentrates and rare earths. This thorium concentrate is further processed at OSCOM to produce thorium nitrate. Pilot plants to recover the small quantity of uranium present in monazite are also installed at both sites.

The Nuclear Fuel Complex (NFC), Hyderabad, fabricates fuel assemblies for our nuclear power plants.

The waste management practices during mining and processing of uranium and thorium minerals with a view to minimize the environmental impact are briefly discussed in this article. The environmental surveillance and recent monitoring data obtained during operation of these units are also reviewed.

Mining and Processing of Uranium Ore at UCIL

Underground Mining

The Jaduguda mine developed to a depth of 900 metres, in three stages over the years, has a horizontal strike length of about 800 metres and design production capacity of 1000 tonnes of ore per day. The central shaft serves as entry for men and material and as main ventilation intake route. Using latest mining machinery the ore excavated from different locations is brought to a central location and hoisted to surface in a skip and discharged on to a conveyor system leading to the mill. The Bhatin mine with a production capacity of 250 tonnes per day is a relatively small mine developed up to a depth of about 135 metres. It has entry through an adit which also serves as intake route for ventilation air and

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transport of the excavated ore to the surface. The Narwapahar mine designed to produce 1000 tonnes of ore per day is one of the most modern mines in the country. Trackless mining with decline is used as one of the entries to excavate the ore up to a depth of about 140 metres. A vertical shaft has also been sunk to a depth of 355 metres for mining of deeper deposits [1].

Ore Processing

The ore produced in the three mines is processed in the mill at Jaduguda to extract uranium. The nearby copper concentrator plants' waste tailings containing about 0.005 - 0.009% of U_3O_8 are upgraded by tabling at the respective sites and brought to Jaduguda for processing in the mill to recover uranium. The initial ore processing briefly comprises of crushing, screening, wet grinding to the required size of -200 mesh and dewatering to control pulp density. This is followed by leaching with sulphuric acid in the presence of an oxidising agent (MnO_2) in air agitated vessels. Temperature of 40 - 50°C is maintained by passing steam. The leachate is filtered and purified using ion exchange process. Uranium is precipitated as magnesium diuranate (yellow cake) by addition of magnesia slurry to the pure liquor [2].

Waste Management (UCIL)

Mine Wastes

(i) *Solid waste*: Rocks with U_3O_8 content below 0.03% are considered waste. During ore winning operations care is taken to excavate minimum quantity of waste. The very low radioactive contents of the solid wastes from mines do not pose any significant problem. This waste rock is partly used as mine backfill material and the rest is used for land fill within the premises and for strengthening the tailings pond embankment.

(ii) *Liquid waste*: Large quantities of water are encountered in mines. As it contains dissolved uranium and radium the mine water is collected, clarified and reused at appropriate stage in the mill process. Mine water from Bhatin and Narwapahar mines are brought through pipe lines to the effluent treatment plant (ETP) at Jaduguda.

(iii) *Gaseous waste:* The mine air from different operating levels, carrying radon and blasting gases, is let out through two return air exhaust adits located about 30 m above the ground in isolated and unoccupied areas . Similar exhaust air outlets are provided at the other two mines.

Mill Wastes

(i) *Mill tailings*: The bulk of the ore processed in mill in combination with the reagents used emerges as waste or 'tailings'. It comprises of the barren cake from filters containing all the undissolved radionuclides and the barren liquor from ion exchange columns having some dissolved activity. The tailings contain all the decay products of uranium originally present in the ore except for the parent uranium which has been extracted. Only about 15% of the activity present in the ore goes with the "yellow cake". After decay of the shorter lived component (^{234}Th) about 70% of the original activity of the ore remains with the tailings [3]. ^{226}Ra and ^{230}Th present in the tailings require long term management. Besides these, the tailings also contain the bulk of the chemical additives used during processing. Safe disposal of tailings is, therefore, an important aspect of the uranium ore processing.

(ii) *Run off water and other effluents*: The runoff water from ore yard is used in the process. Overflow from the magnetite (a byproduct) settling pits is sent to the ETP for treatment. Effluents from storm water drains are treated for use as industrial water.

(iii) *Airborne pollutants:* Air borne dust during ore handling, crushing and grinding operations are controlled at source by water spray, dry fog spray and dust extractor with water scrubbing system provided at appropriate stages. The slurry carrying the dust so extracted is utilised in the process. A series of prefilters and HEPA filters are provided in the final product area to retain the radioactive dust, only clean air is let out.

Tailings Treatment, Containment and Consolidation

The barren liquor from the ion exchange columns is neutralised with lime stone slurry initially to a pH of 4.2 - 4.3 followed by addition of lime slurry to a pH of 10 - 10.5 and mixed with the barren cake slurry to a final pH of 9.5 - 10. At this pH the residual uranium, radium, other radionuclides and chemical pollutants including Mn get precipitated. The treated slurry is classified into coarse and fine fractions using a hydrocyclone. The coarse material forming nearly 50% of the tailings is sent to mines as backfill. The fine tailings or 'slimes' are sent for permanent containment into an engineered tailings pond. The slimes along with the precipitates settle down and clear liquid is decanted. A series of decantation wells and side channels are provided to lead the decanted liquid to the effluent treatment plant (ETP) .

At Jaduguda two tailings containment ponds with engineered embankments on downstream side of natural drainage are now nearly filled up. The third stage of the tailings pond which is currently in use, is also located nearby in a similar setting [4]. The underlying soil and the bedrock of these tailings ponds have very low permeability. The tailings ponds are fenced to prevent unauthorised access. A vegetation cover of non-edible grass and plant such as ***Saccharum spontaneum*** (kansh), ***Typha latifolia*** (cat-tail) and ***Ipomoea carnia*** (Amari) has been provided over the used-up portion of the first two tailings ponds [5]. This vegetation cover helps in suppressing generation and dispersal of dust and consolidates the tailings, besides merging it with the local landscape.

Water Reclamation and Effluent Treatment

Though lime neutralization of tailings largely takes care of the dissolved pollutants in the process effluents, subsequent reduction of pH in the tailings pond over a period of time increases concentrations of some radionuclides and chemical constituents in the decanted effluents. Hence, these are further treated to meet regulatory discharge limits. In the ETP the tailings pond effluents are clarified, a part of which is sent for reuse in the milling process. The rest is treated first with $BaCl_2$ and then with lime to precipitate the radioactive and chemical pollutants. It is clarified and the settled sludge carrying the precipitates is sent to the tailings pond and clear effluent is discharged to environment after pH adjustment [2].

Mining and Processing of Thorium Mineral

The Indian Rare Earths Ltd (IREL) has been engaged in mining and processing of beach mineral sands from coastal Kerala, Tamil Nadu and Orissa. These sands contain monazite, the main thorium mineral, along with other minerals of economic importance such as ilmenite, zircon, rutile, garnet and sillimenite [6]. The beach sands contain 0.1 to 5% monazite which in turn contains about 8 to 9 % of thorium oxide, 0.25% uranium oxide besides 55 - 60 % rare earths and 29 - 30% P_2O_5 [7].

Surface mining and dredging with wet concentrator is employed to recover heavy minerals from the placer areas. After initial concentration in hydrocyclones the heavy sand is dried and fed to the mineral separation plants (MSP) located close to the sea shore near monazite deposits. Variations in the electromagnetic properties and densities are utilized for separation of minerals. Hydrocyclones, froth floatation and air tabling techniques are employed for gravity separation. High tension and magnetic separators are used to separate the minerals on the basis of their electrical conductivity and magnetic susceptibility. The sand is either recycled or used for back-filling the mined out areas. These operations are not of much environmental concern [8].

The monazite is treated with caustic soda lye, leached and passed through filters. From the filtrate trisodium phosphate is recovered as byproduct. The sludge is treated with dilute hydrochloric acid to dissolve the rare earths and filtered. The filtered cake at this stage contains all the thorium and over 90% of uranium locked up in it as hydroxide.

The hydrochloric acid extract contains rare earths, traces of lead and ^{226,228}Ra.The solution is treated with barium chloride, sodium sulphide and dilute sulphuric acid and filtered to obtain mixed cake, which is a solid waste containing barium sulphate carrying radium and lead sulphide. Rare earths remain in solution which is processed for production of rare earths compounds, mainly rare earths chlorides. Small quantities of rare earth fuorides and oxides (especially cerium) and compounds of heavy rare earths are also prepared.

Mineral sand mining using dredge and mineral separation operations similar to those in Kerala and

Tamilnadu are carried out at OSCOM. A thorium plant is also located here. The thorium concentrate in the form of hydroxide and oxalate obtained from Udyogamandal is first washed with dilute caustic soda solution to remove chlorides and then digested with commercial 55% nitric acid to dissolve uranium, thorium and residual rare earths. Repeated selective solvent extraction is followed to separate and purify uranium, thorium and rare earths. Purified uranium is converted to ammonium diuranate and thorium nitrate is crystallised from back extracted nitrate solution. Rare earths are precipitated as hydroxide with caustic soda. About 250-350 tonnes of concentrate are processed annually to produce nearly 120-150 tonnes of thorium nitrate [8].

Waste Management (IREL)

Solid Waste

The solid waste from the mineral sand separation operations being free from monazite is backfilled in mined out areas. The solid waste from thorium concentrate plant at Udyogamandal comprises of the ETP sludge, undissolved monazite and mixed cake carrying $PbS-Ba(Ra)SO_4$ with the average ^{228}Ra content varying from about 130 to 3000 $Bq.g^{-1}$. These are stored in retrievable containers kept in underground RCC trenches. The solid waste from the ETP operations having low activity are presently disposed in a controlled area.

At OSCOM solid waste are generated in the form of acidic cake during feed preparation for recovery of thorium nitrate and alkaline cake during rare earth recovery and sludge from neutralisation of liquid waste. The acidic and alkaline wastes are repulped, mixed and neutralized with sodium carbonate and filtered. The ^{228} Ra content of this waste is about 100 - 150 $Bq.g^{-1}$ and ^{226}Ra content is about 5 - 10 $Bq.g^{-1}$. Small amounts of thorium and uranium are also present. The filtered solid waste cake is filled in polythene bags and buried in specially engineered RCC trenches in a controlled area.

Liquid Waste

Liquid effluents from the monazite digestion plant are alkaline and those from the rare earths processing plant are acidic in nature. They contain mainly ^{228}Ra, relatively lower activity of ^{226}Ra and conventional pollutants like phosphates and fluorides. The two streams of the effluent are mixed, neutralised and further treated with lime and calcium chloride. The calcium phosphate preciptate carries more than 95 % of the radionuclides, phosphates and fluorides. The treated effluent are allowed to settle in post treatment tanks, filtered, diluted and discharged in to the Periyar river.

Liquid effluents at OSCOM are categorised into nitrate bearing, non-nitrate bearing and peripheral drain effluents. After retention in a settling pond the drain effluents are monitored and recycled or released to the coastal environment. The non-nitrate and nitrate bearing effluents are treated separately. The active effluents contain unrecovered thorium and uranium as well as ^{228}Ra. These are treated with lime and $FeSO_4$ to precipitate radioactive and chemical pollutants. After settling of the precipitates the liquid effluents is sent to the tailings pond. Most of the effluent is recycled, a small portion is finally released to the coastal environment in diluted form.

Airborne effluents

Airborne effluents such as acidic vapours are scrubbed with water/dilute caustic soda so as to keep the releases minimum and are monitored regularly to check compliance with limits specified.

Fuel Fabrication at NFC

The NFC has a number of facilities for production of natural and enriched uranium oxides, ceramic fuel fabrication and those for zirconium oxide and zirconium sponge. The magnesium diuranate received from UCIL and the imported UF_6 are first converted to ammonium diuranate (ADU) in separate plants. The ADU is then calcined and reduced to UO_2. The UO_2 powder is precompacted, granulated and finally pelletised and sintered. The sintered pellets are machined, cleaned and loaded into zircaloy tubes and sealed for use as fuel assemblies in nuclear reactors.

Waste Management

Comprehensive waste management and control systems are in place at the plants.

TABLE 1. U (nat) and ^{226}Ra Concentrations in Surface Waters at Jaduguda

Location	$U_{(nat)}$, mg.m^{-3}		^{226}Ra, Bq.m^{-3}	
	Range	Mean	Range	Mean
Gara River (NRW), U/S	0.3 - 4.4	1.5	1 - 18	9
Gara River (NRW), D/S	0.6 - 13.1	3.7	5 - 75	18
Gara River (JAD), U/S	0.5 - 34.4	3.5	3 - 61	12
Gara River (JAD), D/S	0.5 - 54.9	14.8	5 - 282	44
Subarnarekha River U/S	0.5 - 5.4	1.4	4 - 48	18
Subarnarekha River D/S	0.5 - 11.9	5.0	7 - 55	20
DWC		100		300

NRW: Narwapahar, JAD : Jaduguda

Solid waste: The uranyl nitrate raffinate cake contains small residual values of uranium in the range of 0.1 to 0.8%.These are packed and returned to UCIL for processing along with the ore to recover the residual uranium and disposal of waste along with the mill tailings at Jaduguda.

Liquid waste: Liquid waste originating from the natual uranium plants comprise mainly of NH_4NO_3 and $NaNO_3$ [9]. These are treated to reduce the uranium levels to below 50 mgl^{-1} before selling them to glass and explosive industries. The NH_4F from enriched uranium plant is treated with lime to immobilize the fluoride and the slurry is sent to Solar Evaporation Pond for concentration and storage.

Gaseous waste: The air containing uranium dust is filtered before discharge to the environment. Wet rotoclone, electrostatic precipitator and HEPA filters as appropriate are provided in the exhaust system of different plants to trap the uranium particles.

Environmental Surveillance

A comprehensive environmental surveillance programme is essential to evaluate the effectiveness of control measures, assessment of environmental impact and ensure regulatory compliance. Regular monitoring of different environmental matrices such as air, water, sediments, soil and vegetation is carried out at all sites for the relevant radioactive and conventional pollutants.

Uranium tailings are low specific activity material. The gamma radiation levels of 1.4 to 2.0 Gy.h^{-1} observed at the centre of the tailings ponds at Jaduguda reduce to 0.50 Gy.h^{-1} at the boundary and gradually reduce to the local background of 0.10 to 0.15 Gy.h^{-1} within a short distance. Similarly, due to large atmospheric dilution the radon levels of about 30.0 Bq.m^{-3} observed above the tailings surface reduce to the local background value of about 10.0 Bq.m^{-3} at about 0.5 km from the tailings pond. The $U_{(nat)}$ and ^{226}Ra content of the inlet and outlet effluents is an indicator of the effectiveness of the ETP in controlling release of radioactivity in the aquatic environment at UCIL. Decontamination efficiency of the ETP is generally about 90-95%.

$U_{(nat)}$ and ^{226}Ra concentrations observed in the surface waters in Gara and Subarnarekha rivers, downstream of UCIL operations, are presented in Table 1. These are comparable to the respective background levels and are within the prescribed limits. The uranium and radium concentrations of 0.5 - 2.0 mg.m^{-3} and about 7 - 15 Bq.m^{-3}, respectively, reported for areas near UCIL are also of the order of the local background levels [10].

At IREL, Udyogamandal, the environmental radiation of 0.07 to 0.5 μGy.h^{-1} and the thoron progeny concentration of about 1 mWL are typically similar to those obtained in the region. Periyar river is the recipient of the treated effluent from the monazite and rare earths processing plant. The ^{228}Ra in the river water is in the range of 0.061 to 0.016 Bq l^{-1} depending on the distance from the plant. The radioactive and chemical pollutants in river water are well within the respective limits.

At OSCOM the environmental radiation levels are typically of the order of the local background of 0.05 to 0.25 Gy.h^{-1}. At a few far away locations, even higher values of 0.3 to 0.8 Gy.h^{-1} are observed due to the presence of monazite. These parameters are within the regulatory limits. The uranium monitoring data for ground water near NFC are similar to the natural background in the area.

Conclusions

The state of the art technologies are used for the safe management of waste from the industries at the front end of the nuclear fuel cycle. The in built controls, treatment and surveillance have been effective in controlling the environmental releases of radioactive and chemical pollutants. The impact of these operations on the local environment is only marginal and meets the regulatory requirements.

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Chemical Composition of Aerosols and their Source Apportionment in the Ambient Environment

__Dr. T.N. Mahadevan__ received his Ph.D., from the Mumbai University for his Thesis on the Aerosol Size Distribution and its Chemical Composition in Urban, Rural and Marine Environments. He has been actively associated with the Environmental Quality Monitoring programmes of the Environmental Assessment Division, BARC over the last three decades and has a number of publications in both national and international journals. He has been a visiting faculty in various academic courses dealing with Environmental Sciences. As an active ombudsman of SOCLEEN, the lead NGO group with good technical expertise his contribution towards environmetalism in public domain is creditable.

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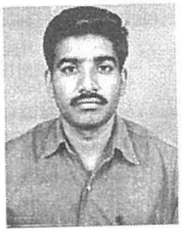

Introduction

The particle size of interest in atmospheric sciences varies from molecular clusters of 0.001 µm to dust particles as large as 100 µm, distinguished as nuclear mode [<0.2 µm], accumulation mode [0.2-2.0 µm] and coarse mode [>2.0 µm]. In air quality management [AQM] however, the rationale behind the measurement of aerosols or suspended particulate matter [SPM] though intrinsically connected with its implication for regulatory compliance for total mass, $PM_{10\mu m}$ and $PM_{2.5\mu m}$, encompasses within it a wider perspective of scientific interest.

The principal function of compliance monitoring however is for the attainment or non-attainment of National Air Quality Standards [NAQS]. The reference method for SPM should be a mass based gravimetric standard that is defined primarily by design certification and shall be concurrent with the emerging continuous measurement technologies, involving instrumental and classical methods. Filter handling and storage, and laboratory analysis are just as important variables as the sampler design. In the Indian context the high volume air sampler with and without the PM_{10} cut-off is considered as the reference method and is consistent with NAQS goals which are considered reasonable and easy to implement.

Studies on the size distribution and elemental/ionic composition of the air particulate has been part of the research and development program of the Environmental Assessment Division, BARC to understand the source characteristics based on specific elements of signature using various receptor models [1-4]. In addition, the data have been used to understand the radiative forcing, actinic flux and NO_2 photolytic constant [5,6]. Both conventional chemical methods [ASVM, AAS, ICP-AES] and nuclear analytical methods like

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TABLE 1. Concentration levels of trace elements and ionic composition in aerosols, their Mass Median Aerodynamic Diameters (MMAD) and crustal enrichment factors from Chembur-Trombay region

Element / Ion	Mass concentration ng [$\mu g/m^3$]		MMAD mm	Enrichment factor (Crust)
	Size ≤ 2.1 μm	Size > 2.1 μm		
[Al]	0.246 ± 0.150	1.813 ± 0.78	5.94 ± 0.57	0.6
As	10.17 ± 9.16	8.4 ± 9.1	1.53 ± 0.53	40
Br	19.93 ± 12.0	9.82 ± 5.97	1.15 ± 0.08	60
[Ca][a]	1.19 ± 0.56	7.02 ± 3.63	5.82 ± 0.44	-
Cd	1.83 ± 1.35	0.77 ± 0.60	1.35 ± 0.62	100
Co	1.14 ± 0.75	0.99 ± 0.70	5.12 ± 0.16	3
Cr	13.37 ± 9.47	55.61 ± 29.37	4.83 ± 0.2	4
Cu	14.22 ± 12.47	19.18 ± 8.38	3.47 ± 0.42	7
Eu	0.025 ± 0.032	7.79 ± 0.08	5.6 ± 0.12	0.7
[Fe]	0.246 ± 0.89	3.11 ± 1.41	5.67 ± 0.11	1 (ref.)
Hf	0.10 ± 0.096	1.01 ± 1.72	5.27 ± 0.83	0.8
Hg	2.15 ± 3.22	1.17 ± 2.37	1.24 ± 0.06	600
[K]	0.8 ± 0.72	0.8 ± 0.97	2.29 ± 0.77	1
La	0.83 ± 0.62	2.79 ± 1.87	4.91 ± 0.36	0.9
[Mg]	0.44 ± 0.33	1.09 ± 0.73	4.13 ± 0.98	3
Mn	52.8 ± 32.66	142.4 ± 64.13	3.97 ± 0.49	3
[Na]	0.50 ± 0.56	1.49 ± 1.43	3.9 ± 0.2	4
Pb	285.3 ± 226.6	216.2 ± 207.4	1.58 ± 0.26	200
Sb	12.19 ± 8.64	5.35 ± 4.16	1.25 ± 0.24	80
Sc	0.122 ± 0.151	1.013 ± 0.603	6.27 ± 0.31	1
Se	1.91 ± 1.243	0.653 ± 0.482	1.26 ± 0.33	20000
Sm	0.135 ± 0.095	0.92 ± 0.353	5.31 ± 0.23	3
Th	0.159 ± 0.153	0.606 ± 0.34	5.15 ± 0.58	1
Zn	201.9 ± 164.5	1176 ± 100.7	1.54 ± 0.24	60
[Cl]	2.88 ± 2.11	3.5 ± 3.71	2.07 ± 0.86	-
F	15.6 ± 10.96	79.9 ± 42.0	3.85 ± 0.35	-
[NO_3]	4.18 ± 1.93	1.67 ± 1.23	1.42 ± 0.4	-
[SO_4]	7.86 ± 3.99	2.39 ± 1.85	0.71 ± 0.37	-
[NH_4]	3.55 ± 1.47	0.36 ± 0.33	0.57 ± 0.09	-
[TSPM]	60.2 ± 29.4	92.7 ± 38.9	3.33 ± 0.8	-

NOTE : All values are based on the average concentrations from three sampling sites

[a] High calcium concentration is due to the influence of Ca emissions from the fertilizer industry at one of the sites

INAA and EDXRF with their multi-element capabilitiy have become powerful tools in the chemical assay of air particulates. This article attempts to descrive one of our specific case study on urban pollution.

Experimental

The sampling program for size separated aerosols using the 9 stage-1 CFM- Andersen sampler from three sites in the Chembur-Trombay Region [***Site 1 -Industrial***], SPM from the BARC Hospital, Anushaktinagar [***Site 2- Residential***] and Matunga [***Site 3 - arterial freeway with mobile source emissions***] have been considered for the case study. The sampling period at ***site 1*** varied from 5-10 days to obtain quantifiable matter in all the size ranges [polythene substrates and Whatman 41 filters], at ***site 2*** it was weekly samples [glass fiber filters; flowrate 600 lpm] and 24-48 h averaging period at ***site 3*** [millipore 0.8m filters, 18-20 lpm]. The sampling heights for ***sites 1 & 2*** were around 30 m and at ***site 3*** it was 6 m above the ground level. Nearly 15 elements in the samples from ***site 1*** have been analyzed by the INAA in two irradiation schedules using a thermal neutron flux of 10^{12} n/cm^2/sec^{-1}. After appropriate cooling period, the samples were wet digested and analyzed for 4 elements by DPASV. The samples from ***site 2*** were analyzed by flame AAS and at ***site 3*** by INAA, AAS and DPASV methods. Details of the analytical methods are described elsewhere [1,2]. Factor analysis method has been used for source apportionment of the database from ***sites 2 & 3***.

Data Analysis and Interpretations

The SPM load and their elemental concentration in 2 specific size ranges [≤2.1 μm and >2.1 μm] at *site 1* are presented in Table 1 along with their mass median aerodynamic diameters [MMAD]. The enrichment factor [EF] with reference to the crustal source is also given. As can be seen the anthropogenic source elements like As, Cd, Cu, Hg, Pb, Sb, Se, Zn and Br are in the fine size fraction [MMAD ≤ 1.5 μm] of the SPM and crustal

TABLE 2. Percentage deposition of trace metals in the human respiratory tract using the ICRP model: site Chembur–Trombay region

Element	Conc. [G.M.] (ng/m^3)	MMAD μm	Percent deposition[a]				
			ET1	ET2	BB	bb	AI
Al	2000	5.94	32.72	38.78	1.97	1.34	5.54
As	10.2	1.53	20.08	25.72	1.65	1.88	11.02
Cd	0.67	1.53	18.53	23.74	1.55	1.89	11.20
Cr	58.1	4.83	33.68	39.83	1.79	1.12	5.49
Cu	22.5	3.47	31.36	38.22	1.87	1.30	7.06
Fe	4720	5.68	34.39	40.05	1.70	1.02	4.71
Hg	2.9	1.24	19.28	24.72	1.41	1.58	10.33
La	2.62	4.90	33.75	39.87	1.79	1.12	5.42
Mn	148	3.97	32.44	39.07	1.86	1.23	6.43
Na	2430	3.90	32.31	38.97	1.83	1.24	6.52
Pb	164	1.58	22.45	28.69	1.59	1.52	9.85
Sb	5.3	1.45	21.33	27.31	1.53	1.55	10.03
Se	1.7	1.26	19.49	24.99	1.42	1.58	10.30
Th	0.69	5.15	33.99	39.96	1.76	1.09	5.18
Zn	365	1.52	21.94	28.07	1.56	1.54	9.93
NH_4	1940	0.57	10.13	12.49	0.86	2.05	11.74
NO_3	1920	1.62	21.05	26.97	1.51	1.55	10.08
SO_4	7830	0.71	12.44	15.63	0.99	1.85	11.22
Br	24.2	1.13	16.34	20.90	1.40	1.92	11.38
F	0.09	3.85	32.21	38.90	1.86	1.25	6.58

*ICRP Publication No. 66

[a] ET1 , ET2 - Extra Thoracic.; Bb - Bronchial; bb - Broncholar; AI - Alveolar Interstital.

sources like Fe, Co, Cr, Eu, La, S, Th and F have MMAD's in the range of 4-6 μm. The aerosols generated from gas to particle conversion reactions of SO_4, NO_3 originating from their precursors are also in the fine size fraction. The percent deposition of the elements in the upper respiratory tract using the ICRP 66 Human Respiratory Tract [HRT] model are given in Table 2. The heavy metals with lower MMAD's tend to deposit more in the alveolar region and only soluble particles in the lung fluid pass out and enter the blood stream. Since the volume of air inhaled by a normal individual in a day is 20 m^3, the dose exposure value by the inhalation pathway can be evaluated. The annual average standards for SPM, PM_{10} and Pb levels stipulated by the Central Pollution Control Board [7] are 360, 150 and 1.0 $\mu g/m^3$ for industrial areas and 140, 60 and 0.75 $\mu g/m^3$, for residential areas, respectively.

The elemental concentration data in air particulate from *site 3* are given in Table 3 along with the MMAD values. The lower MMAD values for SPM and the trace elements at this site as compared with *site 1* (Table 1) suggest the direct influence of the source emissions inspite of the possible re-entrainment of dust with their adsorbed chemicals. Effect of vehicular traffic is clearly seen by the high concentration of Pb, Cr, Cu, Fe etc.

The varimax rotated factor analysis using the SPSS software at *site 3* is depicted in Table 4. Four factors were selected based on the total % variance which has 70%. The Br values were corrected to the sea water concentration using Na as the indicator element. About 78% of the Br is contributed by annthropogenic sources. *Factor 1* with nearly 40% variance indicates crustal source as the major contributor to ambient aerosols at *site 3*, followed by anthropogenic elements As, Cr Sb, Cd, Pb, Cu and Zn in *Factor 2*. While Br is expected to be associated with automobile Pb (since the samples at this site have been collected before the introduction of unleaded gasoline), the weak correlation between Br and Pb could be due to the influence of data outliers. The sample averaging time also plays a crucial role in mobile source emission estimation. The distribution of Cr and Zn both in *Factors 1 and 2* could be from crustal and re-entrained deposited dust from automotive sources. The group of elements K and Eu in *Factor 4* could be due to re-entrainment of deposited dust. Br and Hg stand out as independent sources (*Factor 3*). While Br could be predominantly from automobile emissions, source of Hg is not clear.

TABLE 3. Ambient air concentrations at Matunga (Site 3)

Elements	Mean concentration	MMAD μm
Fe	9.16	5.4 ± 0.24
Zn	0.79	1.9 ± 0.24
Cr	156	4.6 ± 0.29
Cu	63.7	2.9 ± 0.68
Cd	2.44	1.3 ± 0.53
Pb	522	1.7 ± 0.49
Co	3.60	4.8 ± 0.21
K	2.31	2.5 ± 0.19
Na	3.04	3.2 ± 0.36
As	25.60	1.8 ± 0.62
Br	101	1.1 ± 0.11
La	0.50	5.2 ± 0.36
Sm	1.05	5.8 ± 0.28
Hg	4.02	1.4 ± 0.22
Eu	0.13	5.4 ± 0.16
Th	0.95	4.8 ± 0.37
Sb	20	1.2 ± 0.08
Sc	1.7	5.9 ± 0.39
BrC	82.9	-
TSPM	250	2.9 ± 0.6

As at *site 3* Factor 1 comprised crustal source elements (variance 46%). *Factor 2* represents combustion sources including automobiles and other industries, *Factor 3* shows refuse burning and Ni is identified as a separate group. Since there are several oil refineries and a fertilizer industry which may be using different metal catalysts in the manufacturing processes, located at a few kilometers south east of the *site 2*, appropriate source inventory for these along with additional marker elements of significance would be beneficial.

TABLE 4. Rotated factor matrix of air constituents at Matunga (Site 3)

Species	Factor 1	Factor 2	Factor 3	Factor 4
TSPM	0.71	0.40	-0.11	0.01
Sm	0.91	0.01	-0.09	0.01
La	0.83	-0.06	0.01	-0.02
As	0.18	0.71	0.18	-0.01
Na	0.02	-0.62	0.24	0.06
K	0.63	0.01	0.07	0.64
Eu	-0.13	0.25	-0.07	0.87
Hg	-0.11	0.01	0.53	-0.19
Th	0.83	0.24	0.09	0.01
Cr	0.55	0.56	0.01	0.14
Sb	0.38	0.79	0.18	0.15
Fe	0.86	0.18	-0.03	-0.01
Zn	0.58	0.52	0.21	0.03
Co	0.83	0.28	0.05	0.09
Cd	0.46	0.55	0.04	-0.23
Pb	0.19	0.72	0.13	0.41
Cu	0.01	0.63	0.03	0.23
BrC	0.07	0.17	0.92	0.09
Eigenvalue	7.3	2.6	2.06	1.32
Pct of Var	38.5	13.5	10.8	7
Cum Pct	38.5	52.0	62.8	69.8

Conclusions

The use of both nuclear and conventional analytical techniques were used to obtain extensive data on trace metal concentrations in aerosols. The objectives of the effort were on the data application in aerosol source apportionment studies. The determination of MMADs has helped in understanding their size specificity and inhalation in the human respiratory tract by deposition. Factor analysis as the main multivariate model approach for data analysis has enabled us to clearly understand the possible source contribution at Anushaktinagar and Matunga (*site 2 & 3*). While Pb, Cd, Cu, Zn, Hg, Sb, As, Ni and Br indicate the presence of anthropogenic source, Fe, Co, La, Sm, Ca and K are indicative of crustal source. K and Zn have an additional source in the combustion of plant matter. Ni and Hg as separate source vectors need to be investigated. More such studies are needed to understand the Mumbai SPM source profiles.

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Application of Radioactive ^{210}Pb Studies for Geochronology of Toxic Elements

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Introduction

River, fresh water lakes and coastal marine areas are historical sites of civilization. In modern times, due to increase in population, large scale industrialization and newer methods of farming, these water bodies are continuously being loaded with a large amount of elements, which were either absent earlier or present in small quantities. Lake and estuarine sediments provide a basis for reconstructing many aspects of impact of anthropogenic activity on the environment. In such studies, establishment of accurate geochronology of sedimentation is of vital importance not only for dating events, but also for establishing the rate of change [1,2]. The possible interaction of various anthropogenic pollutants, in the near shore environment assumed significance three decades ago with the release of conventional waste from various industries and domestic sewage in the coastal water of Mumbai. The Thane creek water is the ultimate recipient of liquid effluents from a number of industries. Significantly high concentrations of mercury in the surface sediment and biota have been reported [3]. The presence of anthropogenic lead in sediment near the location of industrial efluents is reported by Jha et al. [4]. This article discusses the application of sedimentation rate obtained through ^{210}Pb technique for understanding the time history of a heavy metal from the vertical concentration profile.

Study Area

The Thane creek, which is a part of Mumbai Harbour Bay is a land-locked mass connected with the Arabian Sea to the south. At the head is the Thane creek through which opens one arm of the Ulhas River after traversing the Thane-Kalyan main land belt. The Thane-Belapur stretch is about 20 km long and 2 km wide with an area of 2650 hectares. The bay is subjected to semidiurnal tides and asymmetry exists in both their periods and range. The water movement is mainly governed by the tidal actions. During the southwest monsoon period, there is also an influx of about 1.0 to 1.5 x 10^6 m^3 of fresh water from the river per tidal cycle, considerably affecting the circulation pattern. The Ulhas water flows into the Thane Creek only in high floods during southwest monsoon months (June–September, rainfall ~250 cm y^{-1}). During this period salinity drops down to 4‰. During the rest of the year the salinity is maintained in accordance with the ingress of seawater (maximum 38‰) [5]. Sampling was carried out at 3 locations where the surface water temperature varied between 22.5 and 32.4°C and the depth of water column varied from 8 to 15 meters.

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Approach for Geochronology

Because of the complicated nature of recent deposits, their geochronology requires not only careful selection of such deposits, but also accurate analyses of various chronological data. The radioisotope ^{210}Pb present in the environment (half life = 22.3 years) is ideal for dating lake and coastal sediment deposition during the last century, a period of time during which appreciable geochemical changes would have occurred both due to natural and anthropogenic activities.

Most of the ^{210}Pb in the atmosphere results from the decay of ^{222}Rn escaping from the earth crust [6]. The ^{222}Rn flux from the ocean is about 2 orders of magnitude lower compared to that from the land surface since ^{226}Ra concentration in sea water is significantly less than that in the earth crust. This ^{210}Pb is removed from the atmosphere to the surface by wet precipitation and dry fallout on time scales shorter than its half-life. The annual deposition rate of ^{210}Pb on the earth is of the order of 25 mBq/cm^2 and shows significant geographical variations. Concentration of the deposited ^{210}Pb in the sediment core can be traced for determining the sedimentation rates. The ^{210}Pb dating is based on the following assumptions: (i) The loss of ^{210}Pb from the sediment depth horizons is only by radioactive decay (i.e.; there is no mixing of various layers and there is no chemical mobility of ^{210}Pb after deposition), (ii) the radionisotope flux at the sediment-water interface has remained constant and (iii) the in-situ concentration of ^{210}Pb supported by ^{226}Ra in the sediment is constant. Under the above conditions, the sedimentation rate from vertical distribution of excess ^{210}Pb in the core is obtained from the relation:

$$A_{(Z)} = A_o \exp(-bZ) \qquad (1)$$

where $A_{(Z)}$ is the activity of excess ^{210}Pb in the sediment (Bq/kg) at any depth Z, from the sediment-water interface, A_o is the activity of excess ^{210}Pb(Bq/kg) in the freshly deposited sediment at depth Z=0 (the sediment water interface) and b is the slope of the line for the logarithmic excess of ^{210}Pb activity versus depth and is equal to λS^{-1} where S is sedimentation rate in cm/y and λ is the radioactive decay constant (0.0311 y^{-1} for ^{210}Pb). Thus, from the slope of semi-log plot of excess ^{210}Pb Vs. depth Z, the sedimentation rate is calculated.

Sample Collection and Processing

Core samples were collected at three locations (S1, S2, and S3) in the Thane Creek, during 1996 using a gravity corer, its inner and outer diameters being 5.2 and 6.0 cm respectively. The sampling strategy followed is the procedure by Carpenter et al. [7]. The length of the core, collected with the help of an adjustable piston rod with silicone packing ranged from 25 to 60 cm. The gravity coring unit was lowered as slowly as possible into the sediment to prevent lateral motion of the pressure wave created by the descent of the corer. The collected cores were extruded vertically and sliced at 2 cm intervals. Care was taken during coring to ensure minimum disturbance of the sediment water interface. The textural composition of the core sample was mainly clay and silt. The total clay material was 48 to 65% having a mean grain size of 2 to 9 µm. Mineralogical and major elemental analyses of sediments from the Trans Thane creek [8] indicate domination of montmorillonite, degraded chlorite, illite and to some extent silica.

Experimental

^{210}Pb Determination

The determination of ^{210}Pb content is based upon the measurement of its grand daughter ^{210}Po, which is assumed to be in secular equilibrium with its parent. Carpenter et al. [9] and Saravan Kumar et al. [10] have carried out analysis of ^{210}Pb and ^{210}Po in lakes and marine sediments and established secular equilibrium between the isotopes. The basic radiochemical procedure involves successive leaching of the sediment samples with aqua regia, the residual solids were filtered off and solution was dried and converted to chloride with concentrated HCl. The final solution was taken in 0.5M HCl and Po was deposited spontaneously on the silver disc. ^{208}Po was added to each sample prior to acid digestion for yield determination. Activities of ^{210}Po along with the ^{208}Po tracer were measured by alpha spectrometry using a silicon surface barrier detector connected to a multi channel analyser.

Determination of Elements Hg and Pb

All the core sections were freeze dried and after grinding and homogenization, stored in polythene

TABLE 1. Analysis of Hg and Pb in standard reference materials

Sl.No.	Element	Reference material	Observed value	Reference value
1.	Pb^a (ppm)	IAEA-356 Marine sediment	347.2 ± 31	347
2.	Hg^b (ppm)	IAEA-356 Marine sediment	7.5 ± 0.6	7.62
3.	Pb^c (Bq/kg)	IAEA-135 Marine sediment	44.8 ± 3.5	48.0

[a]Analysis by EDXRF, [b]Analysis by CVAAS, [c]Alpha spectrometry of ^{210}Po,
Standard deviation values are obtained from eight replicates.

bottles. Adequate precautions were taken during sampling and handling to prevent contamination of the sediment. Energy Dispersive X-Ray Fluorescence (EDXRF) was used to analyse sample pellets made of 500 mg of freeze dried samples mixed with 500 mg of cellulose powder. The concentration of Pb in the sample was estimated by comparison method using a Standard Reference Material. The analysis of Hg was carried out by cold vapor AAS [11]. The concentration of metals in the sediment was calculated on dry weight basis. The quality of the measurements was assured by analysis of Standard Reference Material IAEA-356 Marine Sediment for Hg, Pb and certified reference material IAEA-135 Marine sediment for ^{210}Pb (Table 1). The precision of the measurements was within ±10%.

Results and Discussion

Figs. 1a, 1b and 1c depict the vertical profiles of excess ^{210}Pb in different sections of the core collected from the three locations. The linear sedimentation rates for the cores collected from these sites were found to be 0.77, 0.92 and 0.17cm/y respectively. Figs. 2a, 2b and 2c represent the year wise depth profile of Hg concentration in the

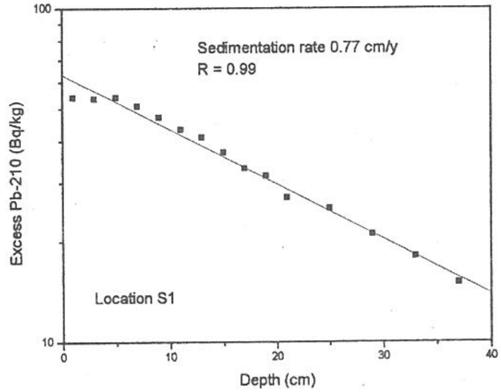

Fig. 1a Depth concentration profile of excess ^{210}Pb in sediment cores collected at Airoli in Thane Creek

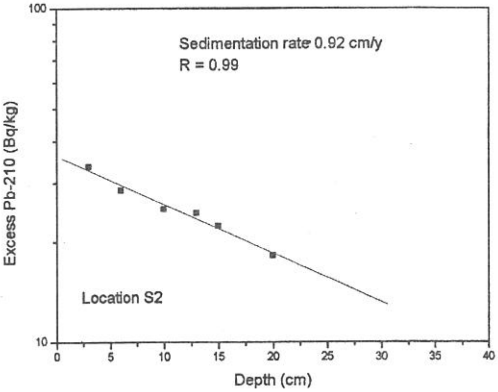

Fig. 1b Depth concentration profile of excess ^{210}Pb in sediment cores collected at Ghansoli in Thane Creek

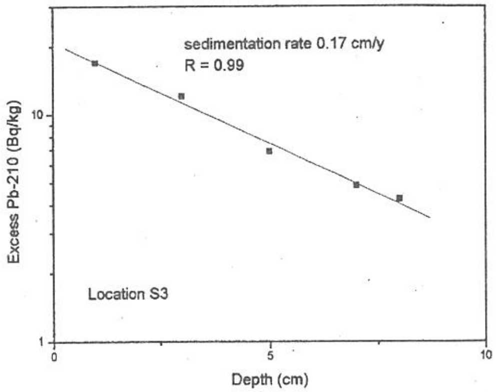

Fig. 1c Depth concentration profile of excess ^{210}Pb in sediment cores collected at Koparkhairne in Thane Creek

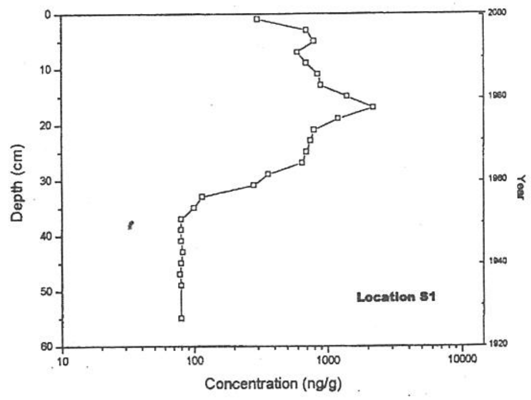

Fig. 2a The vertical concentration profile of Hg (ng/g) is sediment cores collected at Airoli of Thane Creek)

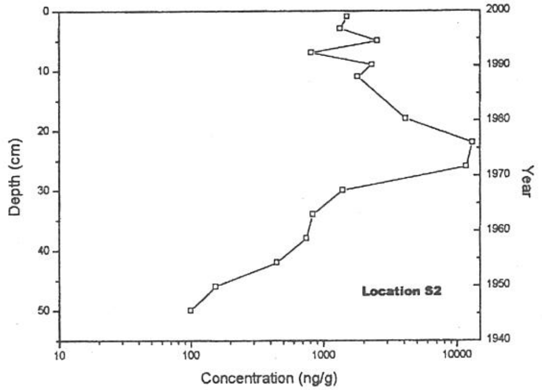

Fig. 2b The vertical concentration profile of Hg (ng/g) is sediment cores collected at Ghansoli of Thane Creek)

sediment core collected at these three sampling locations. The surface concentrations of Hg at S1 and S2 were similar. The concentration of Hg in S1 remained constant between 35-60 cm depth. The increase in Hg concentration was observed from 1960 onwards at both S1 and S2 locations, and it reached peak concentration around 1975. The concentration distribution with depth in the upper 10 cm strongly suggested fresh inputs of Hg at S3 compared to S1 and S2. There is an indication that S1 and S2 sites might have received a higher input of Hg about two decades earlier based on the ^{210}Pb chronology. Depth profiles of Pb concentration in the sediments collected at the three sampling locations are shown in Figs. 3a, 3b and 3c respectively. The vertical profiles of Pb revealed higher concentrations of 35-74 μg/g in the initial 1-25 cm layers in S1 and S2, compared to bottom section concentration of 20-37 μg/g, reflecting contributions from industrial effluents. In addition, the magnitude of the concentrations of Pb 22-30 μg/g, in the core collected from S3 remained more or less the same throughout the entire depth of the core (Fig 3c).

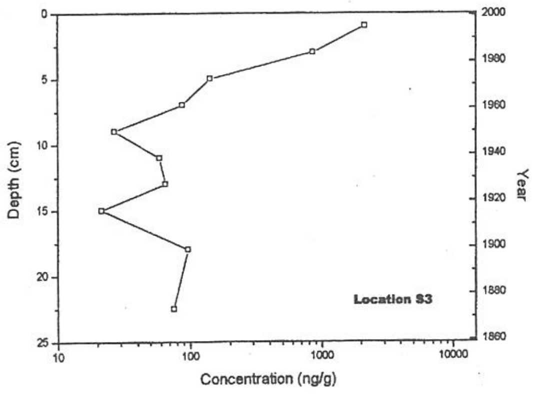

Fig. 2c The vertical concentration profile of Hg (ng/g) is sediment cores collected at Koparkhairne of Thane Creek)

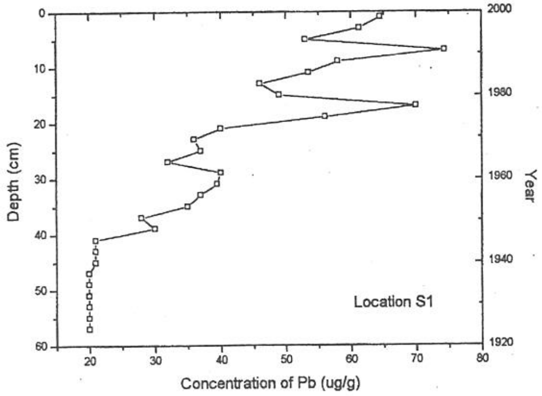

Fig. 3a The vertical concentration profile of Pb (μg/g) is sediment cores collected at Airoli of Thane Creek)

Conclusion

^{210}Pb dating technique was used successfully for obtaining sedimentation rates in Thane Creek. Depth profiles of Hg and Pb show the anthropogenic input over the years into the Trans Thane Creek coastal environment. The positive evidence of the

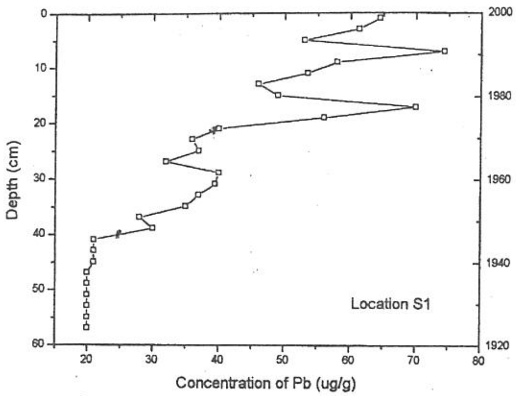

Fig. 3b The vertical concentration profile of Pb (µg/g) is sediment cores collected at Ghansoli of Thane Creek)

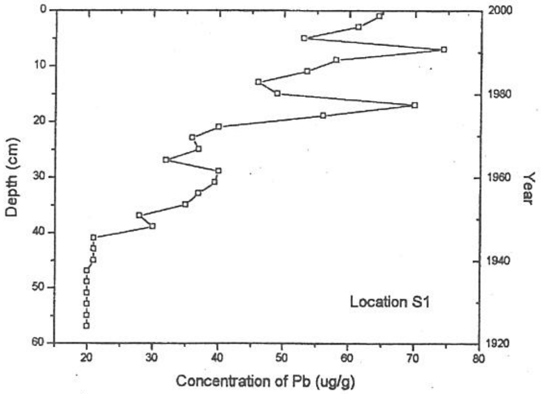

Fig. 3c The vertical concentration profile of Pb (µg/g) is sediment cores collected at Koparkhairne of Thane Creek)

continued inputs of Hg at third site and a decade or two earlier at S1 and S2 was established by this study. The vertical concentration profile of Pb in sediment core collected from first two sites revealed earlier input at S1 as compared to S2.

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Instrumentation for Nuclear Aerosol Studies

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Introduction

Understanding the characteristics and the behaviour of nuclear aerosols in the context of the nuclear fuel cycle is important both during their routine operations and during the extremely unlikely, yet highly significant, event of reactor accidents. In the former case, the principal concerns relate to occupational safety of nuclear workers and the assessment of long term incremental contributions to the environment, if any. In the case of the latter, these pertain to improving our ability to predict the ultimate aerosol releases to the environment from reactors under a postulated sequence of accidental conditions. Identification of the accident scenarios and development and validation of aerosol behaviour codes under each of these scenarios constitute the thrust areas in nuclear safety research.

As part of the defense-in-depth philosophy followed in the design of Nuclear Power Plants (NPPs), various system failures and consequent accident scenarios are postulated and engineered safety features (ESFs) are provided to ensure that the consequences of the Design Basis Accidents (DBAs) in the public domain are minimal. However, the occurrence of the accidents at Three Mile Island (TMI), USA and Chernobyl (erstwhile Soviet Union) has brought out the necessity for giving due consideration to the Beyond Design Basis Accidents (BDBAs), which have extremely low probability of occurrence. An assessment of the consequences of the BDBAs calls for a good understanding of the behaviour of the released radioactive fission products and other aerosols within and outside the containment facility.

Several theoretical and experimental studies have been carried out the world over to understand the complex mechanisms of particle dynamics and thermal hydraulics which govern aerosol behaviour. The theoretical studies comprise of formulation of several codes for estimation of the releases, the build-up, decay and transport of the aerosols, chemical interaction studies specially relating to iodine and hydrogen in steam environments etc. under varying accident conditions. These codes are validated by experimental studies, which further give inputs for modification of the codes for a better accuracy of prediction. Such studies also give an idea about the adequacy of the various ESFs such as suppression pool, aerosol filters, containment spray systems and air coolers associated with these nuclear installations.

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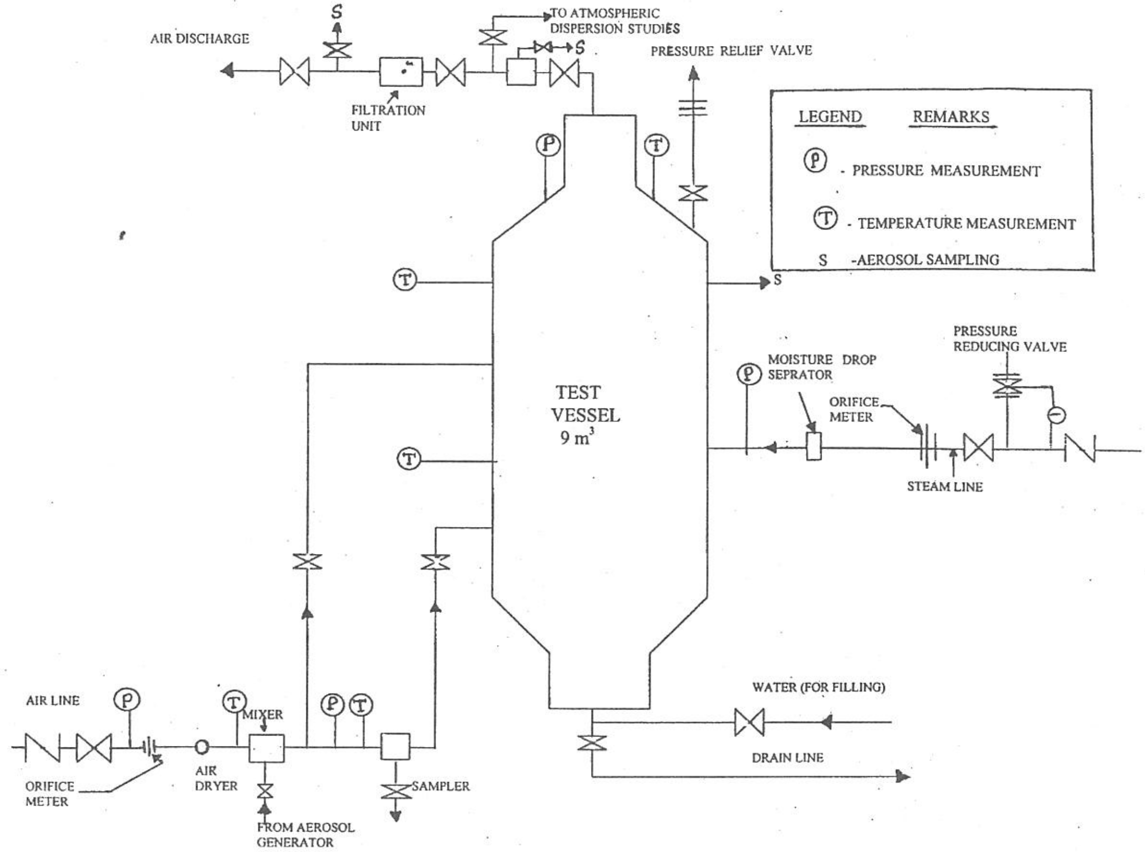

Fig. 1 Nuclear aerosol test facility at BARC.

Some of the important experimental studies related to the behaviour of aerosols in the context of nuclear reactor safety are the NAUA experiments, Marviken tests, DEVAP program, NSPP tests, DEMONA tests, LACE tests and the more recent FALCON and the PHEBUS tests [1]. Each of these tests were aimed at studying different accident sequences and the associated interaction and depletion processes in varying environmental conditions prevalent in the test facility. The data generated from these facilities were used for validation of the relevant computer codes.

As a first step towards taking up such studies in the Indian context, a programme was initiated in the BARC to carry out aerosol behaviour simulation experiments in a test facility with a view to validating the existing containment aerosol behaviour codes. The facility consists of a 9 m^3 stainless steel test vessel having various provisions for aerosol loading, injecting steam, inserting aerosol sampling tubes and control instrumentation (Fig. 1). It is housed in a building along with aerosol generator and data acquisition systems. The experiments being planned are (i) initial mass balancing, (ii) aerosol homogeneity tests in air space, (iii) temporal mass and number concentration decay and evolution of distribution, (iv) wall deposition measurements and (v) aerosol mass leak fraction under a prescribed vent rate. It is proposed to carry out these studies both under dry and wet conditions, the latter being achieved by injecting steam into the aerosol environment. The results will be compared with the predictions of the available aerosol transport and behaviour codes.

The experiments mentioned above require aerosol generators which yield high concentration of

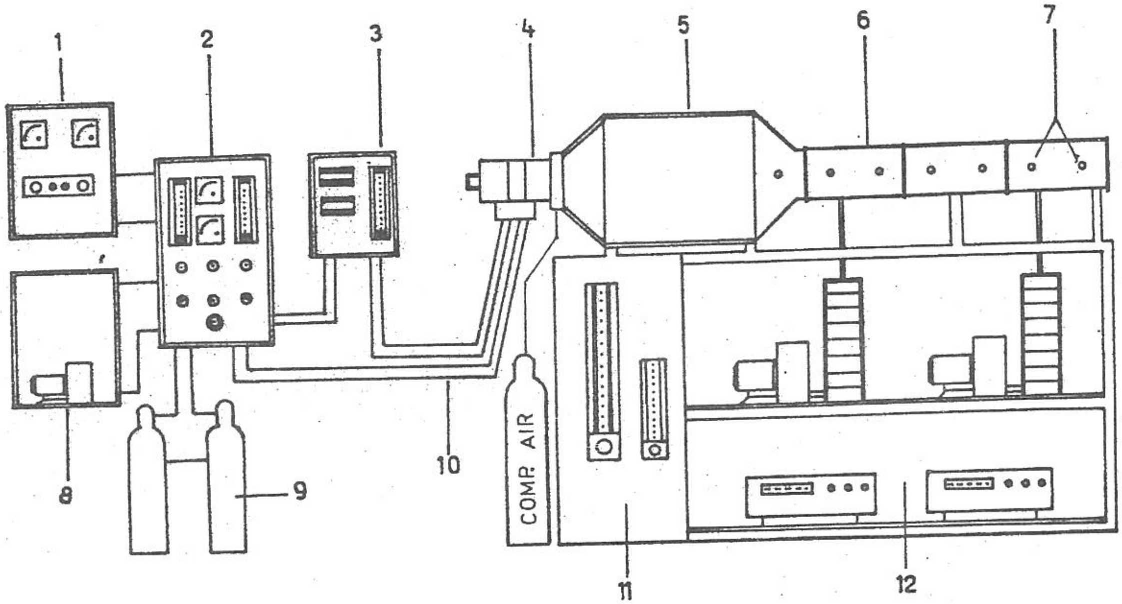

Fig. 2 Schematic of the Plasma Torch Aerosol Generating System developed at BARC.

aerosols (~ 1-10 g/m^3) of materials which conform to the molten fuel and core structural materials expected in reactor accidents. The measurements need to be carried out with robust and well calibrated systems that cover wide concentration and particle size ranges. This article discusses these instruments and provides a brief account of some of the aerosol experiments conducted in small-scale laboratory chambers.

Aerosol Generation System

While nebulizers, based on atomization principle, serve as aerosol generators for nonmetallic particles and droplets in inhalation studies and other laboratory experiments, for nuclear aerosol simulation applications, aerosol generators capable of producing intense source of solid materials including metals, ceramics and composites, are required. The Plasma Torch Aerosol Generator (PTAG) which serves as a continuous source of particles at high concentrations is used for this purpose. The processes involved in aerosol generation using a plasma torch are: (a) Liquifaction and vaporization of metals/ceramics to be aerosolized in the plasma core having temperature of about 15,000°C, (b) Gas phase exothermic oxidation forming highly volatile oxide at a given temperature in the reaction chamber and (c) Rapid quenching of gaseous oxide vapour to form airborne particles.

Fig. 2 gives the schematic view of the PTAG developed in BARC [2]. The concentration, quality and the size distribution of the generated aerosols depend on various process variables such as torch power, flow rate, composition and physical properties of the material to be aerosolized, the material feeding mechanism, rate of feed and type and rate of carrier gas. The torch has a minimum power level of 3 KW and maximum of 20 KW. Optimisation of these variables has been carried out to obtain the desired characteristics of the output aerosols. A summary of the results obtained from several experiments is presented in Table 1.

TABLE 1. Summary of the results obtained with torch power level of 12 KW

Sl. No.	Powder material	Conc. (g/m^3)	Generation rate (g/min)	MMAD (μm)	GSD
1.	Copper	2.51	0.163	1.09	3.56
2.	Tin	3.0	0.195	4.55	2.19
3.	Nichrome	2.1	0.136	2.45	2.74

Instrumentation for Aerosol Measurements

Mass-size Distribution

Aerosol behaviour studies in vessels require the estimation of the mass and composition of the material deposited on the walls as well as those remaining air borne at a given time. Wall deposition estimates are made by collecting the deposit on metal foils or on test coupons positioned at various locations on the walls of the vessel. These are subjected to gravimetry using micro balance to obtain deposited masses. The size distribution may be ascertained through optical and electron microscopy and the chemical/elemental constituents are identified using analytical instrumentation and spectrometric techniques.

Instruments based on inertial impaction are widely used [3] for the measurement of the mass-size distribution of the aerosols in the air space. These consist of a nozzle through which the aerosol to be size separated is passed. The output stream is directed against a flat impaction plate, which deflects the flow to form an abrupt 90° bend in the streamlines. Particles with sufficient inertia are unable to follow the streamlines and impact on the flat plate, while the smaller particles follow the streamlines, escape impaction and flow out of the impactor. The parameter that governs the collection efficiency is the Stoke's number (stk) given by

$$\mathrm{stk} = \frac{\rho_p d_p^2 U C_c}{9 \eta d_j} \qquad (1)$$

Where, ρ_p and d_p are particle density and diameter respectively, U is the mean flow velocity in the nozzle, C_c is the Millikan-Cunningham correction factor used for particle sizes below 1.0 µm, η is the viscosity of the gas and d_j is the nozzle diameter. The collection efficiency for a given stage rises sharply from zero around stk value of about 0.25.

Practical limitations on the nozzle diameter and the exit velocities limit the smallest cut-off sizes that can be measured with impactors to 0.2-0.3 µm. However, by operating the impactor at a very low downstream absolute pressure, this limit can be extended to 0.05 m. The mass-size distribution in several intervals can be obtained using a cascaded impactor which is a series of several impactors arranged in order of cut-off size with the largest cut-off size first. The collected mass is analysed using gravimetry to obtain the characteristics of the size distribution such as the Mass Median Aerodynamic Diameter (MMAD) and the Geometric Standard Deviation (GSD). Some of the commonly used cascade impactors based on gravimetric analysis are the Andersen 8-stage and 14-stage low pressure impactor, and the Berner impactor.

Since gravimetric analysis is to be carried out externally and not in real time, various techniques have been evolved to measure the deposited mass online thereby achieving automatic real time operation. Some of the impactors based on these modified techniques are described below:

Quartz Crystal Microbalance (QCM) Cascade Impactor

This is a near real-time mass concentration measurement system from California Instruments Inc. operating at a flow rate of 0.24 lpm, which segregates the aerosol sample into 10 size classes ranging from 0.05 to 25 µm. The deposited masses on the stages are detected by using piezoelectric quartz crystals as mass monitors [4]. The change in the signal frequency of the crystal configuration is directly related to the aerosol mass deposited on the sensor crystal. The QCM cascade impactor has a mass sensitivity of 1.4 ng/Hz and can be used for detecting particle concentrations as low as 10 $\mu g/m^3$. The instantaneous results of a measurement are printed with an in-built printer in the form of mass concentrations recorded on each stage as well as a histogram plot of the size distribution.

Electrical Low Pressure Impactor (ELPI)

This instrument combines electrical detection with impactor size classification for the measurement of particle size distribution, a

TABLE 2. Summary characteristics of some commercial impactors

Type of impactor	Andersen 8-stage impactor	Andersen low pressure 14-stage impactor	Quartz crystal micro-balance cascade impactor	Electrical low pressure impactor	Online α impactor (for radon progeny)
Operating flow rate	28.0 Lpm	2.8 Lpm	0.24 Lpm	25.0 Lpm	85.0 Lpm
Stage No.	Stage Cut-off sizes (in μm)				
1.	9.0	35.0	25.0	2.0 (LP)	15.5
2.	5.8	21.7	12.5	1.0 (LP)	7.5
3.	4.7	15.7	6.4	0.52 (LP)	3.7
4.	3.3	10.5	3.2	0.28 (LP)	1.8
5.	2.1	6.6	1.6	0.16 (LP)	0.9
6.	1.1	3.3	0.8	0.083 (LP)	0.495
7.	0.7	2.0	0.4	0.056 (LP)	0.27
8.	0.4	1.4	0.2	0.029 (LP)	0.1
9.	<0.4 (BF)	0.9 (LP)	0.1		0.05
10.		0.52 (LP)	0.05		
11.		0.23 (LP)			
12.		0.11 (LP)			
13.		0.08 (LP)			
14.		<0.08 (BF)			

LP: Low pressure stages, BF: Back-up Filter

technique first used by Tropp and co-workers [5]. The principle used in this technique is to charge the particles using a unipolar charger and then measure the current using electrometer from electrically isolated collection stages in the impactor. The particle collection onto the different impactor stages is dependent on the aerodynamic size of the particles. The measured current signals are converted to size distribution using particle size dependent relations describing the properties of the charger and the impactor stages. A system built by Keskinen et al. [6] reported mass detection limits lower than the Quartz crystal method in the sub-micron size range. Also, the parallel current measurement results in a fast response, making it suitable for measuring a rapidly changing size distribution. This impactor was effectively used in quantitative aerosol measurements at the VICTORIA facility simulating the LWR containment during a hypothetical core melt accident [7].

Alpha Impactor for Radon Progeny

This instrument is based on the principle of simultaneous α- measurement of the activity of short-lived radon progeny deposited on the different stages of a low pressure impactor [8]. This impactor operates at a high flow rate of 85 lpm and has nine low pressure stages with cut-off diameters ranging from 0.05 to 15.5 μm. Each stage has an aluminium foil as the substrate and a passivated implanted planar silicon (PIPS) detector which monitors α decay isotopes ^{218}Po (RaA) and ^{214}Po (RaC') online during air sampling. The signals of each detector are amplified and stored in a multichannel analyzer to obtain the spectra from which the Activity Median Aerodynamic Diameter (AMAD) can be obtained.

Measurement of Number Concentrations

The governing equations used in computer codes to describe aerosol behaviour are generally formulated in terms of the number concentrations in space and size classes. Although it is possible, in principle, to extract this information from the mass-size distribution data through inversion algorithms, it is restricted to particles of homogeneous and known composition and for slowly varying distributions. In view of this, it is more prudent to obtain direct information on number concentrations for validating the codes. The measurement of gross number concentrations is

TABLE 3. Instruments for number concentration measurements

System	Principle	Type of measurement	Concentration range	Size range covered
CNCs(manual, pulsed flow, continuous flow)	Condensation growth, light transmission / scattering	Total number concentration	50-10^7/cc	>0.003 μm
Single particle OPCs	Particle light scattering in laser beam	Number size distribution in 5-8 classes	0.01- 10^5/cc	0.1 - 5 μm
Electrical Mobility Analysers	Particle charge neutralisation and mobility classification	Number size distribution in about 140 size channels	2-10^8/cc	0.005-1.0 μm

carried out with condensation nucleus counters and photometers while the size distributions are ascertained using the more sophisticated optical counters and electrical aerosol analysers. When aerosols are highly dense as is possible in test facility studies, appropriate dilutions of the samples drawn from the experimental vessel may be required to bring the concentrations within the prescribed detection ranges of the instruments. A brief description of some of these instruments and their techniques is given in the following section.

Condensation Nucleus Counters

The ability of particles to grow, regardless of their initial size, to large micrometer sized droplets is exploited in the development of Condensation Nucleus Counters (CNCs) used for measuring the total number concentration of particles. A simple system (Pollak counter) consists of a 60 cm long vertical tube with water saturated ceramic lining, a light source at the top and a photo-detector at the bottom. The sample is drawn into the tube which is sealed and pressurised with nuclei free air. A time delay is provided for the air to get saturated with water vapor at that pressure. Then a valve is opened to allow adiabatic expansion down to normal atmospheric pressure, leading to super saturation condition of the vapor and condensation on the particles. This gives rise to the formation of haze which attenuates the light transmission, which is detected by a photo detector. Using this instrument, particles above 0.004 μm can be detected.

Optical Particle Counters

Unlike the CNCs, optical particle counters (OPCs) are designed to size classify and detect particles by the principle of light scattered from a high intensity coherent source such as the laser diode or a laser beam. A typical OPC consists of a laser source (e.g. He-Ne laser at 632.8 nm) giving rise to a continuous laser beam, which is focussed onto a narrow view area (1 mm dia) using focussing optics. The air containing the aerosol flows through the view volume as a thin stream such that only one particle is present in the volume at a given time. The light scattered by this is detected by a photodiode placed at an angle with respect to the beam direction. Depending upon the amplitude of the signal, the particles are classed into different size groups using Pulse Height Analysers. Many commercial systems are available which can detect particles over a size range above 0.1 μm. The concentration range is adjustable by controlling the flow rate and sampling times. Concentrations in the range of 10^{-2}-10^5 particles per cc may be measured with these systems.

Electrical Aerosol Mobility Analyser

When an aerosol passes through a bipolar ionic environment, it undergoes neutralization and attains a steady-state charge distribution, regardless of its initial shape, composition and charge. The fraction of particles carrying different units of charge is a function only of its diameter. This principle is exploited to obtain mobility classification of particles in an externally applied electric field. The instrument consists of a radioactive neutralizer, cylindrical electrical separation unit into which aerosol is sampled at a low flow rate, sweeping high voltage power supply, a CNC for counting the segregated particles exiting at the outlet and software system for inverting the out put count data to obtain original size distribution. A system known as the Scanning Mobility Particle Sizer (SMPS) is marketed by TSI Inc., USA, to detect and classify particles in the range of 0.005-1 μm

Aerosol Behaviour Measurements

Studies on the aerosol decay and deposition rates were carried out in the laboratory using nebulizer generated aerosols, for the purpose of gaining experience with the proposed large scale experiments in the test facility. First of the studies [9] was carried out in a glass enclosure having a volume of 324 L and a surface to volume ratio of 0.089 cm^{-1}. Flourescein dissolved in liquor ammonia was nebulized using BARC nebulizer, which generated dry flourescein aerosols of MMD of 0.85 μm and σg of 2.1. The chamber, whose sides were covered with aluminium foils to measure surface deposition patterns, was filled with this aerosol for 10 minutes. The air space was monitored for a period of about 2 hours through intermittent sampling with QCMCI for mass decay and Automatic CNC for number decay. At the end of the experiments, the aluminium foils were removed and subjected to spectro-photometric analysis to estimate the mass fractions deposited on various surfaces.

The mass and the number concentration decay data obtained by the sampling instruments were subjected to exponential fit to extract aerosol decay rates. ACNC introduces a mean flow rate of 2 lpm, and the contribution from this was subtracted in evaluating the effective aerosol decay rates. Data were also fitted with theoretical estimates based on the diffusional deposition and gravitational sedimentation models (Fig.3). While the mass decay rate of 0.03/min could be fitted with theory, there was considerable departure between theory and experiment for number decay rate (0.078/min). Similarly, the observed deposition ratios on surfaces (roof, floor and the 4 sides) could also not be explained satisfactorily from theory. It was suspected that the electrostatic charge present on the nebulized aerosols could have affected the deposition mechanisms, besides the possibility of an altered gas medium density due to ammonia that filled the chamber along with the aerosol. In order to incorporate these effects into the theory, specific information on the charge content, charge on the glass surface and the effective density of the gas would be required.

In the second set of experiments [10] decay characteristics were examined using cigarette smoke aerosols in a metallic chamber of volume 500 L with a surface to volume ratio of 0.075 cm^{-1}. The QCMCI measurements yielded a MMAD of 0.42 μm and σ_g of 2.0 for these aerosols. Three types of experiments were carried out. (i) Normal decay, (ii) decay upon neutraizing the possible charge on the smoke aerosols with a 5 mCi Sr-90 beta source and (iii) decay upon charging the particles with a unipolar ionizer. The peak number concentration was found to be about $3x10^5$/cc. The subsequent number decay was monitored with automatic CNC.

The observed and theoretically modelled decay characteristics in all the three cases are shown in Fig. 3. Neutralization caused a small increase in the decay rate, from a normal rate of 0.02/min to 0.025 /min. As this change was rather nominal, a mean decay rate of 0.022/min was attributed to the uncharged system. The unipolar ionizer had a dramatic influence in enhancing the decay rate by a factor of 6, i.e. to a value of 0.12/min. This was explainable by applying the electro-dispersion theory of charged aerosols.

Conclusions

The BARC test facility is intended to cater to the requirement of simulating aerosol behaviour in vessels with a view to validating the computer codes describing their behaviour in the containment. While cascade impactors, condensation nucleus counters and optical counters serve as the basic requirements of carrying out an integral validation of the codes, more sophisticated instruments, such as the Electrical Mobility Analyser, are of immense value in obtaining fundamental information on size dependent effects, especially at lower (sub-micron) sizes. Experiments carried out with small scale laboratory chambers have provided a preliminary experience in the use of these instruments for

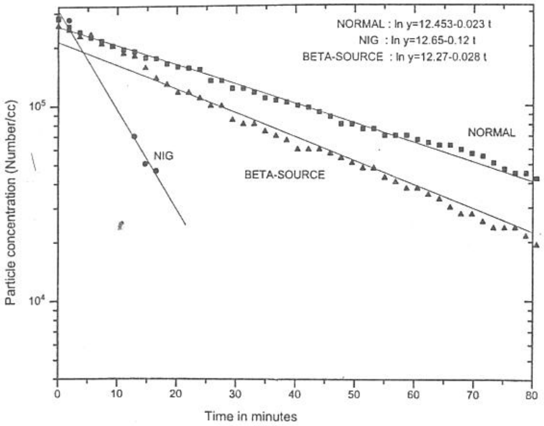

Fig. 3 Theoretical and experimental fits to the decay of the number concentrations of cigarette smoke aerosols in a 500 L enclosure.

carrying out aerosol decay studies as well as on the theoretical interpretation of the data. This experience provides us with useful inputs for planning and executing the measurement strategies to be adapted in the studies on the decay and deposition of aerosols in the large-scale test facility system.

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Assessment of Heavy Metals in Biological Materials

Dr. R. M. Tripathi obtained his Masters of Science (Chemistry) from Lucknow University and Ph. D. from Bombay University. After successful completion of one year training course during 1981-82 in chemistry discipline, he joined Air Monitoring Section of Bhabha Atomic Research Centre, Bombay. He has worked on development of analytical techniques for study of toxic heavy metals in environmental and biological materials using spectroscopic and electroanalytical techniques. His main areas of interest are heavy metals in environment, atmospheric removal processes for heavy metals, precipitation chemistry, speciation of organo metallic compounds, intake and biokinetic studies of heavy metals. He has participated in many advanced training programmes/ workshops organized by IAEA under RCA programmes. He was deputed to institute of physical and chemical analysis, GKSS Research Centre, Germany for the speciation study of mercury in environment. He is a recognized guide of Mumbai University for M.Sc. and Ph.D. students in Analytical Chemistry. He has 65 scientific papers in international/ national journals and conferences to his credit.

Introduction

It has been known for several decades that trace quantities of certain elements exert a positive or negative influence on plants, animals and human life. However, more recently greater interest has been taken with regard to the specific role of these trace elements. Pollution due to toxic trace metals is considered to be of great importance for population at large due to their non biodegradable nature and long biological half lives. They get accumulated in different compartments of environment as well as in human body. They are toxic at very low concentrations and can cause profound biochemical changes in the body even at ultra trace levels. Exposure to very low concentrations of metals like lead and cadmium may produce adverse effects on health and behaviour of population. Although metals such as copper (Cu) and zinc (Zn) are essential for human beings, chronic metabolic disturbances may result from excess or deficiency of these metals. Heavy metals are present in trace or in ultra trace quantities in biological matrices. Both toxicity and necessity vary from element to element and from species to species. Thus, information on levels of heavy metals in biological system is important in assessing the risk to human health. Differential Pulse Stripping Voltammetry (Anodic and Cathodic) and Electro Thermal-AAS (ET-AAS) are highly sensitive techniques for estimation of trace metals. These have been used for the estimation of trace metals in biological matrices like blood, urine and tissues of Mumbai population and some results are discussed here.

Sample Collection and Analysis

Sample Collection and Processing

Blood samples (~ 2 ml) were collected from 542 children with special care by vein puncture using cleaned syringes and needles, into heparinized pretreated clean polypropylene tubes. The samples were then wet digested in duplicate with electronic grade nitric acid and perchloric acid. Digested samples were made up to 5 ml using 0.25% nitric acid. Extreme care was taken to avoid any contamination. Reagents with low background impurities were only used. Maternal blood (~2 ml) was collected by vein puncture while cord blood was collected immediately after delivery. Liver biopsy samples were collected from suspected liver disease patients from different hospitals in Mumbai and Pune, on filter papers after removing blood. Dried liver biopsy samples were digested (~ 2 mg) with 1 ml conc. HNO_3 and 0.5 ml $HClO_4$ and evaporated nearly to dryness. The residue was taken in 5 ml of

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0.25 % HNO3. Filter paper blank samples were also digested using same procedure simultaneously.

Precautions

Problems of contamination and loss of elements are prevalent at every stage of trace metal analysis. This problem is especially relevant for lower concentration of analyte and smaller the sample being analysed. There is a tendency for metals to get adsorbed on the walls of the containers, if they are not pretreated. On the other hand, the acid treated samples may leach some of the metals from the container itself. Quartz, teflon and high purity polyethylene containers have been used for collection, decomposition and storage of samples prior to analysis. The details of precautions taken during trace analysis are given else where [1]. In the present study, all laboratory wares used in sample collection, ashing, analysis and storage were soaked in 10 % HNO_3 for several days and then rinsed thoroughly with distilled and double distilled water, respectively before use.

Analytical Technique

Levels of Pb, Cd, Cu, Zn and Se in the processed samples were estimated by Differential Pulse Stripping Voltammetric technique (DPASV) with hanging mercury drop electrode. These metals were estimated in ammonium acetate nitric acid medium and blank correction were made. Blank samples always showed extremely low levels of trace metals. The analysis of Fe and Mg was carried out using flame atomic absorption spectrometry while for the estimation of Cr, As and Mn, ET-AAS has been used. Details of the measurement procedures are mentioned elsewhere [2, 3].

The reliability of the procedure of estimation of Pb, Cd, Cu, Zn, Fe and Mg in biological samples by DPASV technique has been checked by analysing various standard reference materials. Standard reference materials like Animal blood (A-2 and A-13) and Fish tissue (MA-B-3/TM) obtained from International Atomic Energy Agency (IAEA), were analysed for Pb, Cd, Cu, Zn, Fe and Mg. The results agreed within ±7% of certified values. The validity of the method was further ascertained by cross method checks, spike recovery and replicate analysis

Results and Discussion

Metals in Whole Blood of Children

The concentrations of Pb, Cd, Cu and Zn in blood of 6-10y old children residing in different suburbs of Mumbai and Thane are presented in Table 1. The blood lead levels were found to vary from 8.6 to 14.4 $\mu g\ dL^{-1}$. Different scales of toxicity have been evolved for children and adults in terms of their lead levels in blood. Most of the developed western countries have adopted 15 $\mu g\ dL^{-1}$ as the safe limit for the blood lead level in children. In view

TABLE 1. Concentration of Lead in children's blood at different locations in Mumbai during 1984-1996.

Location	No. of samples	Lead		Cadmium		Copper		Zinc	
		GM	GSD	GM	GSD	GM	GSD	GM	GSD
Borivili	12	10.4	10.4	0.18	3.36	76.3	1.25	449.8	1.28
Byculla	117	11.0	1.99	0.09	3.46	89.8	1.44	443.4	1.50
Deonar	46	9.5	2.29	0.08	3.11	74.6	1.34	443.1	1.38
Goregaon	21	9.1	1.30	0.04	1.51	74.6	1.16	388.9	1.43
Govandi	20	8.9	1.42	0.11	2.84	76.2	1.28	409.7	1.33
Jogeshwari	20	8.6	1.32	0.04	1.17	71.8	1.15	383.6	1.44
Khar	17	9.0	1.53	0.06	1.86	72.2	1.18	340.5	1.50
Vile Parle	19	9.1	1.46	0.06	1.75	74.9	1.22	376.6	1.42
Parel	168	10.4	1.91	0.10	2.77	87.4	1.40	431.6	1.40
Sion	34	9.6	1.49	0.16	2.53	84.0	1.31	339.0	1.23
Thane-1	10	10.7	1.49	0.07	2.20	62.9	1.17	322.9	1.30
Thane-2	37	12.0	1.86	0.14	3.65	82.5	1.30	302.9	1.41
Vakola	21	14.4	1.64	0.11	2.18	88.2	1.40	456.9	1.34

Thane-1 : Near Thane college (3000 m from smelter); Thane-2 : Shrirang Society (1000 m from smelter) of expected toxicity at all levels, opinions have been expressed to adopt 10 μg dL^{-1} as the blood lead limit for children [4]. In general, the average blood lead of Mumbai children is close to the blood lead limit of 10 μg dL^{-1}. The levels of Cd, Cu and Zn in children's blood were found to vary from 0.04-0.18, 62.9-89.8 and 302.9-456.9 μg dL^{-1}, respectively.

The blood Pb concentration of children generally correlate with air Pb concentration and is used as an index of air Pb pollution in atmosphere. In the present study, 6-10 y old children are considered as a single age group and atmospheric concentration of Pb from different locations are correlated with blood lead of children residing in those locations. A good correlation between air lead and blood lead is observed for locations having normal atmospheric concentrations and is given by the equation PbB = 3.6 PbA + 8.48 (correlation coefficient of 0.88). Where PbB is the blood lead level (μg dL^{-1}) and PbA is the air lead concentration (μg m^{-3}). The observations of total blood lead levels suggest that for every μg m^{-3} increase in atmospheric lead, the blood lead of children can increase by 3.6 μg dL^{-1} [5] . Many investigators have observed an increase of 3-5 μg dL^{-1} in blood Pb of children for every μg m^{-3} increase of atmospheric lead [6]. The variation in the children's blood lead levels in Mumbai during the study period (1984-1998) reveals a decreasing trend (Fig. 1).

TABLE 2. Heavy metal concentration (μg/L) in urine samples from MUMBAI

Sl. No.	Element	GM	Minimum	Maximum
1.	Pb	6.9	0.41	424.4
2.	Cd	0.34	0.07	1.76
3.	Cu	175.3	2.4	1097
4.	Zn	374.7	30	1227
5.	As	1.78	0.75	2.54
6.	Mn	0.3	0.15	1.9
7.	Se	5.2	2.9	8.3

Metals in Urine Samples

The heavy metal concentrations in urine samples from Mumbai are summarized in Table 2. The geometric mean concentrations of Pb, Cd, Cu, Zn, As, Mn and Se in urine sample for Mumbai children were found to be 6.9, 0.34, 175.3, 374.7, 1.78, 0.3 and 5.2 μg/L, respectively. The correlation coefficients between urinary Cu and Zn levels observed for Mumbai children was 0.65 .

Metals in Cord blood

The concentrations of heavy metals in maternal and cord blood samples collected from different locations in Mumbai were determined [7]. The levels of Pb, Cd, Cu and Zn in maternal and cord blood samples were found to be 6.4, 0.07, 108.5, 633.5 and

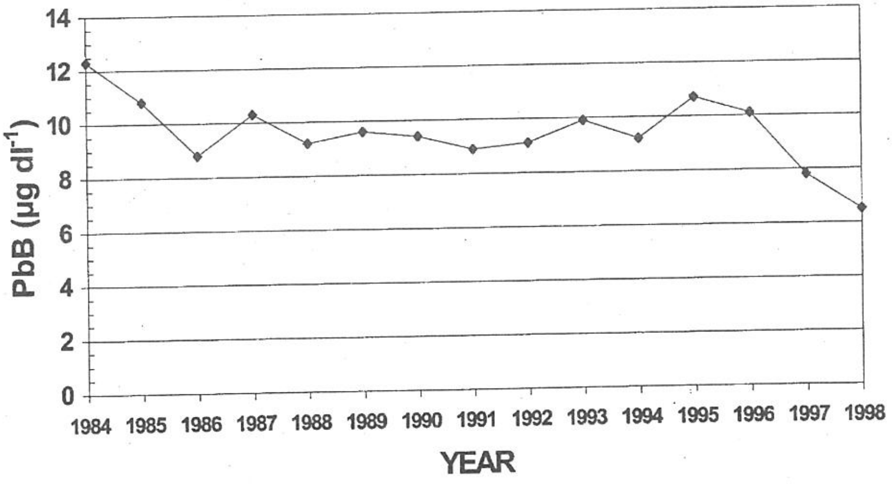

Fig. 1 Variation in Children's Blood Lead during 1984-1998 at Mumbai

5.1, 0.06, 51.1, 252.7 μg/dL, respectively. The concentrations of these elements were found to be high in mother's blood as compared to the cord blood. The levels of Fe and Mg in maternal and cord blood samples were found to be 35.4, 2.0 and 54.0, 2.3 mg/dL, respectively. The concentrations of Fe and Mg in the mother's blood were found to be lower than those in cord blood.

Cu in Liver Biopsy

Estimation of Cu content in liver, blood and urine is very useful to understand Indian Childhood Cirrhosis (ICC), Wilson's disease (WD) and other pediatric liver disorders. Heavy metals in liver biopsy samples of suspected liver disease patients from Mumbai and Pune have been analysed. The geometric mean concentrations of Pb, Cd, Cu and Zn in liver samples along with geometric standard deviation and range have been given in Table 3. A large variation in the concentrations of Pb (0.14-153.0), Cd (0.10- 16.9), Cu (1-2141) and Zn (7.7-176.1) μg/g (dw) liver was observed at Mumbai. The variation in the levels of metals can be attributed to the nature of subjects (control, suspected and under treatment cases of liver disease). Out of 85 suspected liver disease cases from Mumbai, 36 cases (42 %) were found to have Cu levels greater than 60 (64.7 - 2141) μg/g. The mean concentrations of Pb, Cd, Cu and Zn in suspected cases from Pune were found to be 0.80, 0.26, 153.9 and 121.1 μg/g, respectively.

TABLE 3. Heavy metal concentration (μg/g, d.w.) in liver biopsy samples of children suspected for liver disease from MUMBAI and PUNE during 1994-2000

Place	Element	GM	GSD	Min.	Max.
Mumbai (n=85)	Pb	1.75	7.04	0.14	153.0
	Cd	0.44	4.25	0.10	16.9
	Cu	48.0	4.17	1.00	2141
	Zn	40.4	2.78	7.7	176.1
Pune (n=62)	Pb	0.80	3.21	0.18	8.80
	Cd	0.26	2.91	0.08	2.20
	Cu	153.9	6.74	2.0	3000
	Zn	121.1	4.21	37.5	982.1

An attempt was made to find out for the possible correlation between liver copper concentrations and the age of the Mumbai children (Sastry et al, 2000). Total subjects were divided into five different age groups of , 1-5, 5-10, 10-15 and 15. The geometric mean concentrations of liver Cu in the aforementioned groups were found to be 94.9, 31.3, 57.4, 36.5 and 35.7 (μg/g) d.w., respectively. The percentage distribution of Cu concentrations in liver biopsy samples from Mumbai has shown that around 37% of subjects have the liver copper levels in concentration range of 20-50 (μg/g).

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Applications of Chromatographic Technique for Estimation of Organic Pollutants

Dr. (Smt.) G.G. Pandit has joined Environmental Assessment Division (EAD) of Bhabha Atomic Research Centre, in 1981 after graduating from 24th batch of Training School. She obtained M.Sc. (Organic Chemistry) from University of Mumbai, in 1980 and Ph.D. (Sciences) from University of Mumbai in 1990 for her thesis entitled "Source Reconciliation of Atmospheric Hydrocarbon". Her specialisation includes development and standardisation of methodologies for monitoring of various organic pollutants such as Volatile Organic Compounds (VOCs), Polycyclic Aromatic Hydrocarbons (PAHs) and Organochlorine Pesticides in the different environmental matrices. At present, she is working on characterisation and risk assessment of Persistent Organic Pollutants (POPs) in indoor and outdoor aerosols and in coastal marine environment. Her field of interest also includes speciation of mercury in marine environment.

Introduction

The development of gas chromatography and high performance liquid chromatography has contributed significantly to the determination of toxic organic contaminants in the environment and in foods. In addition, conventional column and thin layer chromatography (TLC) methods are powerful techniques for clean-up processes of environmental samples. Chromatography, thus, has the advantage of accommodating both the clean-up and the separation of pollutant of interest. Chromatographic techniques can be applied to isolate diverse kinds of toxic organic pollutants ranging from extremely volatile organic compounds to non volatile pollutants such as polycyclic aromatic hydrocarbons. Organic pollutants are emitted into the environment from a variety of natural and anthropogenic sources. With the rapid advancement of industrial and agricultural technology, the problem of environmental pollution by chemical carcinogens has escalated, many of them organic in nature. Some of the organic pollutants are highly resistant to photolytic, chemical and biological degradation and remain in the environment for prolonged periods. These pollutants are termed as Persistent Organic Pollutants (POPs) and they can be found in measurable amounts in air, water and food. This article discusses the applications of chromatographic technique for determination of volatile and persistent organic pollutants in the environment.

Organic pollutants in the atmosphere, depending upon their vapour pressure, can be divided in three categories: (1) Volatile Organic Compounds (VOCs) such as ethylene, propylene, benzene, toluene and xylenes, (2) Semi-Volatile Organic Compounds (SVOCs) such as organochlorine pesticides like Hexachlorocylcohexane (HCH) and Dichlorodiphenyl- trichloroethane (DDT), Polycyclic aromatic hydrocarbons upto 3 and 4 ring compounds such as naphthalene, anthracene and pyrene, and (3) Non Volatile Organic Compounds (NVOCs) such as 4 and 5 ring polycyclic aromatic hydrocarbons like benzo (a) pyrene, perylene and dibenzo (a, h) anthracene.

Estimation of Volatile Organic Compounds (VOCs) in Air

Major sources of VOCs are releases from chemical industries, refinery operations, solvent evaporation and vehicular exhaust. Some of these VOCs are deleterious to human health while some are precursors to more toxic air pollutants such as aldehydes and oxidants including ozone. Monitoring of VOCs in the air is important to evaluate the risk of exposure to the carcinogenic compounds.

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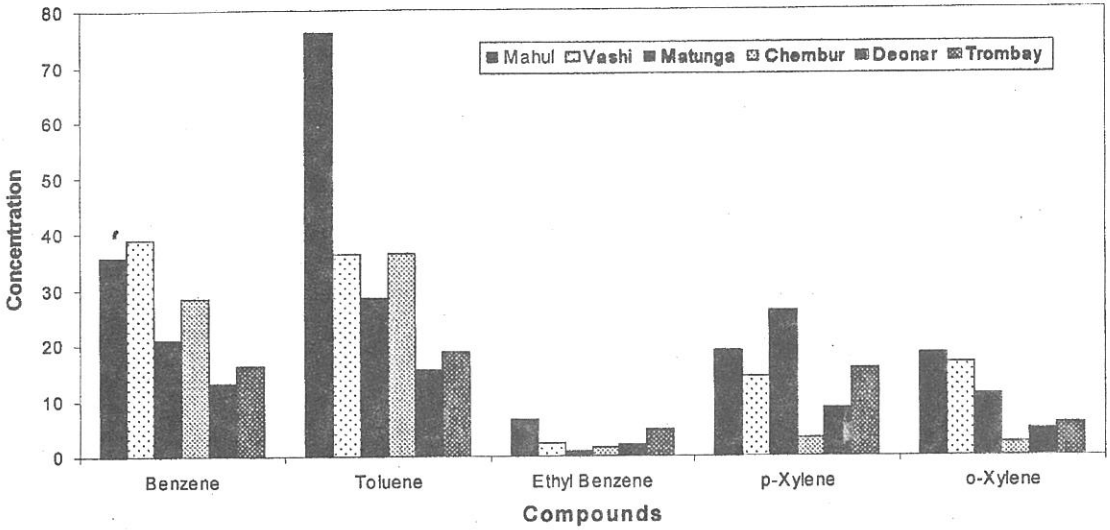

Fig. 1 *Concentration of volatile organic compouns at different locations in Mumbai (μg/m^3)*

Extensive studies have been conducted on measurements of VOCs in different regions of Mumbai in indoor and outdoor air samples using cryogenic preconcentration method and gas chromatography with flame ionization detector [1-3]. Contribution of automobiles and industrial emissions to atmospheric levels of the VOCs is evaluated by comparing the ratios of selected hydrocarbons such as ethylene/ acetylene and benzene/ toluene in ambient air samples [4]. Concentration of VOCs at different locations in Mumbai are shown in Fig. 1.

Estimation of Polycyclic Aromatic Hydrocarbons in Aerosols Using High Pressure Liquid Chromatography

Polycyclic Aromatic Hydrocarbons (PAH) are released into the atmospheric air through incomplete combustion of fossil fuels. Major sources are coal fired power plants, organic flares in petrochemical industries and automobile exhausts. Organic refuse incineration is also a potential source. Releases from domestic cooking stoves and cigarette smoke are the two indoor sources of these compounds. Study on the concentrations of the PAHs in atmospheric air is important since many of the PAHs and their nitro derivatives are found to be carcinogenic and mutagenic. PAHs in atmospheric air are associated with small size particles (0.08 - 0.2 μm). These aerosols penetrate into the pulmonary region of the lung where the clearance mechanisms are slower and hence there is a greater risk due to prolonged exposure. Reversed phase high performance liquid chromatography (HPLC) with ultra violet detection was optimised for separation and quantification of PAHs in air particulate matter [5]. Studies on monitoring of total suspended particulate matter (TSPM), benzene soluble organics and the PAHs in air samples collected in indoor environment of some tenements at Trombay where kerosene is used as cooking fuel have been carried out compared with the concentration of the same in outdoor environment in near vicinity of the tenements [6]. Concentration of PAHs in indoor and outdoor environment at Trombay is shown in Fig. 2.

Estimation of Organochlorine Pesticide Residues Using Gas Chromatography (GC) with Electron Capture Detector (ECD)

Organochlorine pesticides are potentially hazardous to living systems because of their bioaccumulation capacity in lipid and their resistance to degradation. Organochlorine insecticides, an important component of the Persistent Organic pollutants (POPs), are found in all parts of the environment and have been shown to be

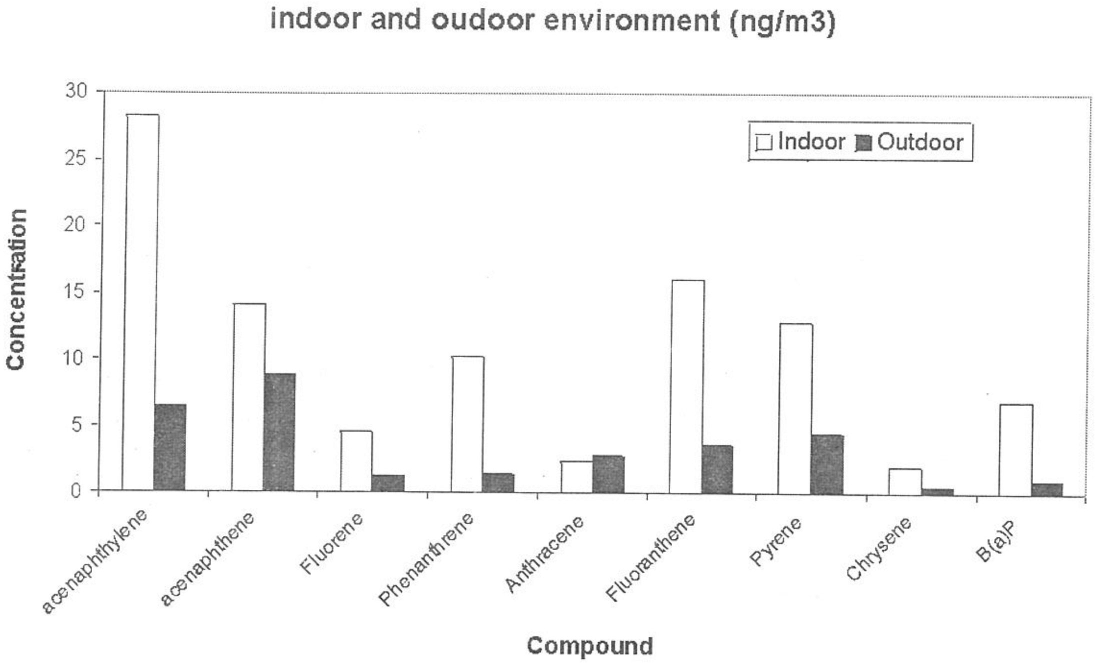

Fig. 2 Concentration of polycyclic aromatic hydrocarbons in indoor and outdoor environment (ng/m^3)

present in almost every compartment of the global ecosystem, especially in most human and animal adipose samples, milk and in all aquatic ecosystems.

Estimation of Organochlorine Pesticide Residues in Coastal Marine Ecosystem

Ocean acts as the ultimate sink of synthetic chemicals. It is known that a large portion of pesticide residues reaches the oceans through agricultural runoff, atmospheric transport and sewerage discharge. There is a need to elucidate the distribution, behavior and fate of these compounds in various environmental compartments in the tropical areas. The determination of organochlorine pesticides concentrations in fish samples may indicate the extent of aquatic contamination and the accumulation characteristics of these compounds in tropical aquatic biota.

Sediment and fish samples were collected from the East and West Coast of India and analyzed for organochlorine pesticide residues using Gas Chromatography with Electron Capture Detector (GC-ECD) system. HCH isomers and DDT and its metabolites are the predominantly identified compounds in most of the samples. Despite the higher quantity of consumption, HCH and DDT levels in fish in India were lower than those in temperate countries suggesting a lower accumulation in tropical fish, which could be due to rapid volatilization and degradation of these insecticides in the tropical environment. The predominance of and HCH reflects the use of technical grade HCH in India [7]. The high temperature in the tropics also enhances the elimination rate of chemicals in fish, as the biological half lives of semi-volatile compounds such as DDT are short at high temperature.

Estimation of Organochlorine Pesticide Residues in Aerosol

Dispersal of pesticides through the atmosphere is responsible for environmental contamination on a regional and global scale [8]. Being an agrarian country, organochlorine pesticides are widely used in India. Earlier studies, [9,10] reporting high levels of DDT and HCH in Indian troposphere, were carried out in the environs where large scale agricultural activities take place. Study has been carried out at Trombay, Mumbai to determine the levels of

TABLE 1. Range and mean concentrations of Organochlorine pesticide residues in milk and milk products

Compounds	Milk (ng/mL) N = 22	Curd (ng/g) N = 18	Milk powder (ng/g) N = 8	Butter (ng/g) N = 6	Cheese (ng/g) N = 6
α-HCH	0.18 - 1.28 (0.49)	0.03 - 0.6 (0.65)	0.4 - 6.0 (3.6)	3.1 - 3.4 (3.2)	0.16 - 8.6 (5.69)
β-HCH	0.08 - 3.64 (0.62)	0.06 - 1.15 (0.45)	0.15 - 14.9 (6.76)	< 0.5 - 10.8 (6.17)	0.02 - 13.2 (5.72)
γ-HCH	0.1 - 1.84 (0.47)	0.04 - 0.54 (0.27)	0.49 - 3.9 (1.97)	2.5 - 5.1 (3.77)	0.12 - 6.12 (3.37)
δ-HCH	< 0.03 - 0.19 (0.1)	< 0.03 - 0.25 (0.06)	0.03 - 1.7 (0.68)	< 0.03 - 2.7 (0.9)	< 0.03 - 3.23 (1.35)
Σ HCH	0.35 - 6.76 (2.07)	0.27 - 2.42 (1.98)	1.07 - 22.7 (13.01)	9.5 - 19.0 (14.03)	3.54 - 25.9 (16.11)
DDD	< 0.07 - 9.9 (2.33)	< 0.07 - 6.9 (1.13)	0.73 - 11.4 (5.51)	12.3 - 63.2 (36.63)	< 0.07 - 22.9 (8.27)
DDE	0.22 - 5.5 (1.33)	0.06 - 0.7 (0.48)	< 0.02 - 7.4 (2.52)	0.3 - 31.9 (13.43)	0.15 - 5.2 (3.12)
DDT	< 0.25 - 2.9 (1.05)	< 0.25 - 5.5 (1.2)	8.6 - 18.6 (12.6)	8 - 25.1 (20.97)	< 0.25 - 26.7 (9.53)
Σ DDT	0.64 - 13.5 (4.69)	0.06 - 10.9 (2.76)	13.9 - 27.4 (20.62)	42.4 - 122.2 (71.03)	2.05 - 53.6 (20.91)

% Mean is given in the paranthesis

airborne organochlorine pesticides in aerosols. Samples are collected on filter papers using high volume sampler at Trombay, Mumbai which is largely an urban-industrial area with no agricultural activities. The filter papers were extracted using hexane and analyzed by GC-ECD system. Results showed the detectable presence of these residues in Trombay aerosols; the source of which may not be local [11].

Estimation of Organochlorine Pesticide Residues in Milk and Milk Products

Organochlorine pesticides have been extensively used in tropical countries in malaria control programs and against livestock ectoparasites and agricultural pests resulting in contamination of air, water and soil with their residues. The residues of these pesticides get accumulated in milk producing animals such as cows and buffaloes through contaminated feed, grass/hay and inhaled air. Being highly lipophillic, organochlorine pesticides are primary stored in fat-rich tissues in these animals and they are subsequently translocated and excreted through milk fat. Study has been carried out to assess the intake of these residues through milk and milk products. Samples of various brands from Mumbai region were collected and analyzed to determine the contamination levels of organochlorine pesticide residues using GC-ECD and the results are given in Table 1. Total HCH levels in milk and milk product samples were found to be lower than total DDT levels which can be attributed to extensive use of DDT in antimalaria sanitary activities. Total DDT levels in butter were found to be higher than total DDT levels in milk samples. The intakes of these residues through milk and milk products by Mumbai population have been found to be lower than the acceptable daily intake (ADI) levels [12].

Estimation of Methyl Mercury in Marine Samples Using High Pressure Liquid Chromatography

Mercury exists in the environment, both in inorganic and organic forms. Environmental studies have shown that the elemental and ionic mercury released into the environment are converted into highly toxic organo mercury compounds [13]. The contamination of methyl mercury in fish samples is potential hazard to human health. Reversed phase high performance liquid chromatography (HPLC) with ultra violet detection was optimised for separation and quantification of organomercury compounds, at sub nanogram level in coastal sediment and fish samples. The advantages of the HPLC method of separation and estimation are (i) the separation is done at room temperature, thus avoiding any thermal degradation of these compounds and (ii) the high sensitivity of the UV detection making the determination of parts per billion (ppb) levels of these compounds in environmental samples easy.

The concentrations of methyl mercury with respect to total mercury 5.9-65.5 ng/g (3-8%) were in sediment distinctly lower compared to fish samples (20.4-344.5 ng/g (33-97%)). The daily intake of methyl mercury through marine food is about 0.5 g and forms 62% of the intake of total mercury [14].

Quality Assurance

The procedures used for the estimation of organic pollutants were verified using synthetic standard mixtures. The efficacy of the methodology was assessed through the analysis of standard reference material obtained from IAEA (IAEA 140 plant homogenate, IAEA 142 mussel homogenate, IAEA 350 Tuna fish and IAEA 383 sediment). The results were in good agreement with the certified values.

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Environment

In this article an attempt is made to describe environment and some of the well known effects like deforestation, greenhouse effect, acid rain and smog with a view to provide information to the beginners in Environmental sciences. A few air pollution events are included. A mention is made on the radon levels in the environment. Water pollution and other issues are not dealt with in this article.

The dictionary defines the word ***Environment*** as surroundings. There are quite a few definitions of the environment, one of which is "Environment is the sum of all social, economical, biological, physical and chemical factors which constitute the surrounding of man, who is both creator and moulder of his environment". Thus it is the total set of surrounding components such as air, water, land and biota. Environment is not static. Changes in the environmental affect human beings and other living organisms. Modern technology certainly has affected the environment, some changes being adverse and others not so. It is generally felt that the modern man equipped with superior skills and technology, has interfered with natural environment probably without understanding the repercursions that resulted in ecological imbalances, environmental degradation and global warming to name a few changes. Any undesirable change in physical, chemical and biological characteristics of air, land and water resulting in harmful effects constitute environmental contaminants. Certain health problems like Minamata disease in Japan during 1953-60, itai itai due to cadmium poisoning, detection of hematological disorders due to lead poisoning were consequences of environmental pollution with toxic elements. Modern man was forcefully awakened to these undesirous changes and ***Environment Movement*** took its birth in mid sixties. The surge of public interest in environmental matters that developed in sixties has been a welcome development as it gave an impetus to learn about the changes in the surroundings that are occurring although often unfound concerns do surface.

The concern about environmental degradation is, however, not a new phenomenon. For instance, in the 4th century BC the Greek philosopher Plato worried about the effects of deforestation and soil erosion. The roots of modern environmental concern may be found in Victorian Britain when natural history became a popular pastime. As the effects of rapid and often uncontrolled industrialisation became evident, the emphasis shifted from the study of nature to a desire to protect it.

Three areas are of major concern to understand the environment and to maintain its quality. They are (a) pollution, (b) population and (c) resource conservation. It is often mentioned that there are a few undesirable by-products of technology that are inter- related which cause complexities and produce deleterious effects. Important among them are modern war, exponential growth of population, wastage of raw materials, inadequate urban design and organisation, poverty and population. The subject is so diversified that it is impossible to include all the important issues. Some aspects of environmental concern are described in what follows.

Deforestation and population growth

Soil erosion and land conservation have been concerns since Biblical times. Deforestation has been associated with the evolution of living styles, population growth and agricultural needs. Modern technologies made it possible for people to live longer in more comfort with great leisure. Longevity resulted in uncontrolled growth of population which in turn forced to have more agricultural land leading to a large scale deforestation. It took about 1650 years to double the population from 250 millions in the first century to 500 millions in 1650 AD where as later the doubling period has been amazingly and alarmingly shorter. The population became 10^9, $2. 10^9$ and $4. 10^9$ by the years 1800, 1900 and 1975 AD

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respectively. From this trend, it is expected that it would be 10^{10} by 2025 AD. The consequences of uncontrolled population growth was recognized as early as in 1798AD.

Greenhouse Effect

The atmosphere of the earth acts in a very similar way to a greenhouse. Sunlight penetrates through the transparent air and causes the ground to warm. The atmosphere then acts as a blanket, keeping the warmth of the earth from escaping back into space. This effect is due to certain gases like carbon dioxide, water vapor, ozone, methane, nitrous oxide, and the chlorofluorocarbons (CFCs) which are very good at absorbing the heat energy before it is lost to space. These gases are called "greenhouse gases", some of them are present in the atmosphere and some are added to it due to human activities. Without the greenhouse effect, the entire planet would be much colder, by 35°C than it presently is. Swedish chemist, Svante Arrhenius, in 1896 took note of the industrial revolution then getting underway and realized that the amount of carbon dioxide being released into the atmosphere was increasing due to increase in the world's consumption of fossil fuels, particularly coal. His understanding of the role of carbon dioxide in heating Earth, even at that early date, led him to predict that if atmospheric carbon dioxide doubled, Earth would become several degrees warmer. Such a global warming would probably bring other, sometimes deleterious, changes in climate; for example, changes in precipitation, storm patterns, and the level of the oceans. Now it is well established that the levels of greenhouse gases are increasing continuously due to industrial and other emissions. For the last 15 to 20 years, we have been seeing a fairly steady rise in temperatures inferring that we are now in a global warming phase. The world-wide rise in temperature, is estimated to be 2^o to 6^oC over the next 100 years. Warming of this magnitude would alter climates throughout the world, affect crop production, and cause sea levels to rise significantly. If this happened, millions of people would be adversely affected by major floodings.

Acid Rain

Acidic deposition, or acid rain as it is commonly known, occurs when emissions of sulfur dioxide (SO_2) and oxides of nitrogen (NO_x) react in the atmosphere with water, oxygen, and oxidants to form various acidic compounds. This mixture forms a mild solution of sulfuric acid and nitric acid. Sunlight increases the rate of most of these reactions. Air pollution from the burning of fossil fuels is the major cause of acid rain. These compounds then reach the earth in either wet form (such as rain, snow and fog or dry form (such as gas and particles). The wind blows these acidic particles and gases onto buildings, cars, homes, and trees. Dry deposited gases and particles are sometimes washed from trees and other surfaces by rainstorms, the runoff water adds those acids to the acid rain, making the combination more acidic than the rain alone. The combination of acid rain plus dry deposited acid is called acid deposition. Prevailing winds transport the compounds, sometimes hundreds of miles, across state and national borders. Electric utility plants account for about 70 percent of annual SO_2 emissions and 30 percent of NO_x emissions in the United States. Mobile sources (transportation) also contribute significantly to NO_x emissions. Overall, more than 20 million tons of SO_2 and NO_x are emitted into the atmosphere each year.

Acid rain causes acidification of lakes and streams and damages trees at high elevations. e.g. red spruce trees above 2,000 feet in elevation. In addition, acid rain accelerates the decay of building materials and paints, including irreplaceable buildings and cultural heritage statues and sculptures. SO_2 and NO_x gases and their particulate matter derivatives, sulfates and nitrates, contribute to visibility degradation and impact public health.

Smog

Smog is a mixture of solid and liquid fog and smoke particles formed when humidity is high. Smog is a form of air pollution which arises from the interaction of sun light with various constituents of the atmosphere. Smog is characterized chemically by high level of oxidants, which irritate the eyes and throat, damage plants and cause rubber like product to crack. Decreased visibility is one of the consequences of smog. The first recognition of adverse effects of smog were felt during the early years of World War II by the Los Angeles residents as eye irritation, severe reduction in visibility, crop damage and the rapid deterioration of rubber products

The number of undesirable components in smog, however, is considerable, and the proportions highly variable. They include ozone, sulphur dioxide, hydrogen cyanide, and hydrocarbons and their products formed by partial oxidation. Ozone, an invisible gas, is not emitted directly into the air, but forms when nitrogen oxides from fuel combustion and volatile organic gases from evaporated petroleum products react in the presence of sun light. Ozone levels are highest during the warm months when there are strong sun light and high temperatures. Nitrogen oxides are produced when fossil fuels are burned in motor vehicles, power plants, furnaces and turbines. Carbon monoxide is a by-product of combustion that comes almost entirely from motor vehicles. Fine particulates are emitted directly as smoke and diesel soot, and form in the air out of nitrogen oxides and sulfur oxides can reach deep into the lungs.

Smog prevention requires control of smoke from furnaces; reduction of fumes from metal-working and other industrial plants; and control of noxious emissions from motor vehicles and incinerators. Internal- combustion engines are regarded as one of the main contributors to the smog problem, emitting large amounts of contaminants, including unburned hydrocarbons and oxides of nitrogen.

Some Air Pollution Episodes

There have been several episodes in history which illustrate the harmful effects of acute short-term exposure to air pollution. Among those and three such episodes are described here.

Belgium's Meuse Valley : December 1930

During a five-day fog 63 people died, most of the deaths occurring on the fourth and fifth days. Older persons with previously known diseases of the heart or lungs accounted for the majority of fatalities. The signs and symptoms were primarily those caused by a respiratory irritant. They include chest pain, cough, shortness of breath and irritation of the eyes. Sulfur dioxide gas is suspected as the cause of the disaster.

Donora, Pennsylvania : Oct. 25, 1948

Twenty people died and approximately 7,000 or 50% of the population, experienced acute illness when temperature inversion and air stagnation occurred. Persons of all ages became ill, but those over 55 were more severely affected. Those with previous heart or respiratory disease, particularly bronchial asthma, suffered most. Symptoms were primarily respiratory and secondarily gastrointestinal, and included cough, sore throat, chest constriction, shortness of breath, eye irritation, nausea and vomiting. The onset of the illness for most persons occurred on the evening of the third day. Of the 20 who died, 14 had some known heart or lung disease.

London, England : 1948, 1952 and 1956

Three episodes during which heavy fogs and air pollution were associated resulted in the death of nearly 5,000 people. The episode in December of 1952 alone, resulted in at least 3,000 deaths. More than 80% of these deaths occurred among individuals with known heart and respiratory disease. During each of these incidents, comparable conditions were present: limited air supplies as a result of low-lying temperature inversions and faint winds, and a continuing heavy output of air pollution from multiple sources. Also, in none of the incidents was technology sophisticated enough to properly monitor the air and diagnosis of the specific causes of the illness and deaths were based on limited evidence gathered after the disasters.

Global Warming: Times of India News on 16-09-2000

More evidence that earth is warmer than at any time in the past 1000 years, particularly in the last 50 years and the nineties being warmest, has come from investigations on ice cores from Himalayan glacier. This was obtained by an international team led by Prof. L. Thompson, Ohio State University. According to them it was the highest climatic record ever received and it clearly confirmed global warming, one that was caused by human activity. Isotopes of hydrogen and oxygen were used to estimate the temperatures while dust concentrations corresponded to dryness. The ice cores showed the time when the monsoon rains failed such as the 6 years beginning from 1790 when the resulting drought killed more than 600,000 people in one Indian territory alone. The amount of dust trapped in ice cores quadrupled in the twentieth century, with concentration of chloride doubling for the same period suggesting an increase in the dryness of air.

Radon Levels [from Radiochim Acta 70/71 (1995) 345]

Radon-222 and its daughter products are important atmospheric radio nuclides because they are responsible for a sizable fraction of the total public exposure to ionising radiations. Typical exhalation rates of ^{222}Rn from the soil are of the order of 1 atom/cm^2.s or 2 x10^{-4} Bq/cm^2.s. Radon-222 can highly accumulate in houses with poor ventilation rates. According to estimates, indoor ^{222}Rn may be responsible for more than 10% of the US incidence of lung cancer. Indoor activity is typically between 10 to 100 Bq/m^3, e.g. Swiss houses on the average have 60 Bq/m^3.

Efforts towards Environmental Protection [from Encarta 99]

By the mid-1990s, the need to properly integrate environmental protection with social and economic policies has led environmental activists to form strategic partnerships. For instance, Greenpeace, a group of insurance companies, and the G-77 group of developing countries worked together to influence the first review of the Convention on Climate Change agreed at the United Nations Conference on Environment and Development (commonly known as the Earth Summit, held in Rio de Janeiro in June, 1992). In April 1996, Real World was founded in the United Kingdom—a coalition of over 30 pressure groups covering issues of the environment, development, social justice, and democratic renewal, and united by what members see as the root cause of their individual areas of concern - the inherent unsustainability of current world trends in economic and social policy. Sustainable development is increasingly seen as a central concept in evolving new strategies for future growth. These issues have been discussed in a few conventions organised by UN. Continuous efforts are being focussed by many groups all over world towards environmental protection.

Literature Update

There is a large number of publications on Environmental issues, environmental monitoring and assessment, and other related topics. In view of this, a list of selected publications from 1997 and two review articles published in 1995 on environmental radioactivity related just to give an idea of various types of R&D work that is being pursued currently. Also a few web sites addresses are provided with.

Some Useful Web Sites

http://www.epa.gov/epahome/standards.html

http://www.wpi.org/wpi/prodserchemmethods/chemmeth.asp

http://www.samplepre.duq.edu

http://vis.nist.gov/SRMcatalog/

http://www.pas.aus.net/products/ref_mat.html

http:/ www.jrc.org/irmm/index.asp

http://pwl.netcom.com/~qaa/links.html

http://www.fasor.com/~iso25/

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Some selected list of recent publications

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