BIOMONITORING OF AIR POLLUTION THROUGH TRACE ELEMENT ANALYSIS

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Abstract

Studies are being carried out to determine the potential and reliability in the use of local lichen species for biomonitoring air pollution in Ghana. The location of most of the gold mines in forest areas of the country presents the gold mining industry as a suitable setting for such investigations. The nuclear-related techniques being used in the multielement analysis of lichen samples and air filter samples are instrumental neutron activation analysis (Miniature Neutron Source Reactor) and energy dispersive x-ray fluorescence analysis (tube-excitation). Validation of the quantitative methods of the INAA through analysis of standard and certified reference materials of orchard leaves NBS SRM 1571 and BCR-CRM No. 279 gave very good results for most elements analyzed. Elemental analysis of identified lichen samples will be done bearing in mind microclimatic factors, specie type and nature of soil.

1. BACKGROUND AND SCOPE OF PROJECT

1.1. Background

Gold has become the largest single source of export earnings in Ghana, and the gold ore deposits occur predominantly as arsenopyrites and within sulphide compounds. The gold-mining process of this type of ore requires high temperature roasting, resulting in the release of pollutants into the atmosphere.

Earlier work carried out [1] on "Use of nuclear analytical techniques in the study of environmental pollution associated with solid wastes", an IAEA CRP GHA 4903/RB (1998-1992), identified some heavy metal pollutants in gold tailing samples using EDXRF analysis. Recent analysis of different types of gold ore samples using reactor neutron activation analysis (INAA) identified additional heavy metals. Therefore, high temperature roasting of gold ore releases oxides of sulphur, arsenic, antimony, and other heavy metal pollutants into the atmosphere. Nevertheless, among the associated environmental matrices investigated so far, ambient air is the least studied. This situation can be attributed to the lack of adequate logistics and trained manpower, as well as the expensive, laborious and time-consuming nature of direct sampling of aerosols for trace element analysis.

The location of most of the gold-mining activities in the Moist Evergreen and Semi-Deciduous Forests in Ghana, consequently makes biomonitoring of air pollution a worthwhile venture.

Very little work has been done in the country on biomonitoring of pollution. There is, however, an on-going study being carried out in the Institute (NNRI) on "Seaweed as

bioindicators for monitoring toxic element pollutants in the marine ecosystem" [2]. IAEA project GHA/9486. Twelve seaweed species were sampled along the cost of southern Ghana in a bid to screen them for use as bioindicators. Instrumental neutron activation analysis was used to measure the concentration of twenty-six chemical elements ranging from 1-87,668 $\mu g.g^{-1}$ DW. The elements Al, As, Ca, Cl, K, Mg, Mn, Na and V were found in most of the seaweed species in relatively high concentration. The high values of these elements in the macroalgae suggest that they may serve as suitable bioindicators for studying coastal pollution. Further studies are being carried out.

1.2. Scope of Project

The primary objective of the present project is to contribute towards the development of an alternate, reliable and less expensive method of environmental monitoring, for the sustainable development and reduction of environmental pollution attending exploitation of the mineral resources of Ghana through:

1. Investigating the potential and reliability of indirect monitoring of heavy metal pollutants in ambient air of gold-mining industries using local lichens, and nuclear-related analytical techniques (EDXRF and INAA).

2. Studying the quantitative linkage between elemental concentration in the lichen samples (indirect sampling) and in the ambient air (direct sampling onto filters)

3. Establishing a protocol and procedures for the use of local lichens for biomonitoring air pollution in Ghana.

1.3. Other Collaborative Works

The NNRI have been collaborating with both national and international institutions in environment-related studies.

1.3.1. NNRI carried out a baseline environmental studies (atmospheric environment) for the Ghana National Petroleum Corporation in the southwestern corner of Ghana. The study was in fulfillment of part of the requirement of Environmental Impact Assessment for the Tano Field Development and Gas Power Project [3].

1.3.2. Joint environmental study between NNRI and Tema Oil Refinery (TOR) on "Ambient air quality monitoring in relation to activities of TOR", including plume modelling.

1.3.3. Under the framework of a Memorandum of Understanding between NNRI and Laboratoire National de la Santé Publique (LNSP) of Cote d'Ivoire, a joint project has been initiated to study environmental pollution associated with the AFEMA gold mines in la Cote d'Ivoire.

2. METHODS

Subject to the adoption of a common protocol at the RCM, the strategies/plans in use or to be used are as indicated below:

2.1. Sampling and Sample Preparation

2.1.1. Lichen Mapping/Sampling

Location, identification, and mapping out of lichen species in the gold-mining areas of Prestea is yet to be done. The distribution of the population of identified species will be mapped out into zones:

Zone 0	=	lichen desert
Zones 1-4	=	struggle zone
Zone 5	=	outer area of struggle zone
Zone 6	=	normal zone

Sampling for lichens and air will be done within and outside mapped zones. To take into consideration the influence of microclimatic factors (refer Figure 1) sampling will be done twice in the year, December – February and July – August. The lichen, together with its substratum, shall be removed with plastic tools from trunks and branches of trees at about 2.0m above ground, and bagged in labelled, transparent polythene bags.

2.1.2. Sample Preparation

Lichen samples will be presented for analysis by separation of the lichen from substratum, washing with distilled water to remove sand and dust, drying, grinding, homogenization and, (in the case of EDXRF analysis) pelletization [4-6]

2.2. Analytical Methods/Quality Assurance

2.2.1. Neutron Activation Analysis

The NAA facility is a Miniature Neutron Source Reactor (GHARR-1) operating between 3-15 kW at a thermal neutron flux of 1-5 x 10″ $ns^{-1}cm^{-2}$. The irradiation scheme used is as shown in Table I.

The gamma-ray spectroscopy system comprises an N-type High Purity Germanium detector model GR 2518, HV Supply Model 3105, Spectroscopy Amplifier Model 2020 (all manufactured by Canberra), and a PC-based multichannel analyzer SILENA EMCAPLUS. The detector operates at – 3000 V, and has a resolution of 0.85 KeV and 1.8 KeV for Co-60 gamma ray energies respectively. Spectrum evaluation and quantitative analysis was carried out using the gamma analysis software SPAN 5.0. Quality Assurance was implemented through the analysis of standard reference materials including orchard leaves (NBS SRM 1571) and BCR-CRM No. 279. (Refer Tables II and III).

2.2.2. Energy Dispersive X-ray Fluorescence Analysis

The EDXRF spectrometer consist of a tube-excited x-ray system (Molybdenum target) with a secondary target arrangement, a Canberra Si (Li) detector with FWHM of 175 eV at 5.9 KeV, a Canberra HV bias supply, Spectroscopy Amplifier 2025, and an ACCUSPEC MCA card. The XRF laboratory participated, this year 1998, in an IAEA Intercomparison survey of XRF Laboratories. The exercise aimed at assessing all steps of the analytical work [7] and identifying major sources of deficiencies included:

- test of detector characteristics
- test of the PUR circuitry
- test of count rate performance of x-ray tube based spectrometer
- test of sensitivity calibration of the XRF spectrometer
- test of spectrum background and spectrometer blank
- evaluation of spectrum analysis
- intercomparison samples (aluminium foil, artificial water, geological and biological materials).

Evaluation of results from participating laboratories by the IAEA are on-going.

3. RESULTS

The meteorological condition prevailing in the project area has been summarised in Figure 1. These results were derived from the data of measurements taken by the Meteorological Services Department from 1988 – 1997. The weather pattern is typical of conditions in the southern half of the country.

Tables II and III show the results of INAA analysis of only those SRM/CRM standards with biological (botanical) matrices. There were good agreement in the values obtained for most of the elements analysed.

4. PLANS FOR FUTURE WORKS

	ACTIVITIES	**PERIOD (1999)**
4.1.	Analysis of SRM/CRM samples using EDXRF	January
4.2.	Administrative contacts with Ghana Chamber of Mines	January
4.3.	Field trip to Prestea mines for mapping and sampling	January/February
4.4.	Species identification and sample preparation	March
4.5.	Laboratory analysis of lichens and air filters with XRF and NAA	April - July
4.6.	Field trip for sampling	July/August
4.7.	Laboratory analysis	September-October
4.8.	Evaluation and interpretation of results	November
4.9.	Production of Report	November/December

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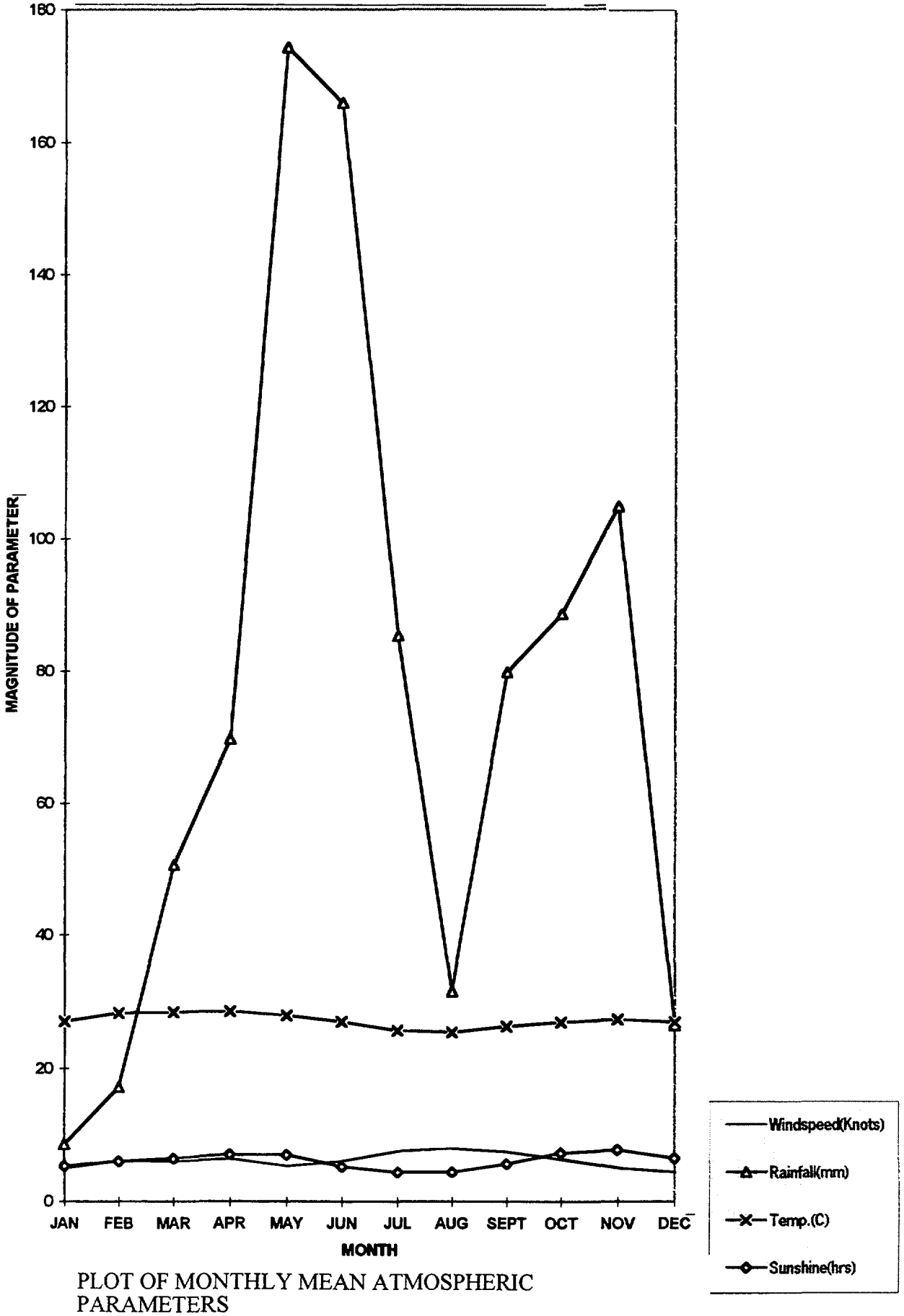

PLOT OF MONTHLY MEAN ATMOSPHERIC PARAMETERS

TABLE I: The irradiation scheme adopted and the corresponding (n, γ) products.

TYPE & HALF-LIFE OF (n, γ) PRODUCT RADIONUCLIDE	NEUTRON FLUX x 10^{11} $ns^{-1}cm^{-2}$	IRRADIATION TIME T (M)	DECAY TIME t_d (M)	COUNTING TIME t_c (S)	(n, γ) PRODUCT RADIONUCLIDE
SHORT-LIVED 20S $\leq T_{1/2} <$ 20M	1 - 5	0.5 - 2	2 - 10	600	Al-28,Br-80,Ca-49, Mg-27,V-52,Cu-66, Ti-51,Ag-108,Sb-122M
MEDIUM-LIVED 20M$\leq T_{1/2} <$ 5H	5	10	20-60	600	Ba-139,Cl-38,Dy-165, I-128,Mn-56,In-116M, Sr-87M,Si-37,Zn-71M, Ni-65,Ru-105,Eu-152M
MEDIUM-LIVED 5H$\leq T_{1/2} <$ 5D	5	60	1-3 D	1000-3000	As-76,Br-82,Au-198, Cd-115,Cu-64,Ca-47, Ce-143,La-140,Na-24, W-187,U-239,Sb-122, Sm-153,Zn-69M,Zr-97, Hg-199M,Pd-109,K-42, Ho-166,Yb-175,Mo-99
LONG-LIVED $T_{1/2} >$ 5D	5	6 H	3-14	3000-5000	Ag-110M,Cr-51,Fe-59, Ce-141,Hg-203, Hf181,Nd-149,Yb-177, Rb-86

TABLE II

NEUTRON ACTIVATION ANALYSIS SRM RESULTS SHEET

SRM Material: Orcahrd Leaves

Identification Code: SRM 1571

Type of Standard: National Sureau of Standards

Date of Certificate of Analysis:

Date Analyzed:

Analyzed By:

IDENTIFIED ELEMENT	CONCENTRATION (ppm)		IDENTIFIED ELEMENT	CONCENTRATION (ppm)	
	SRM VALUE	THIS WORK		SRM VALUE	THIS WORK
Ca (%)	2.09 ± 0.03	1.52 ± 0.19	Cr	2.6 ± 0.3	
K (%)	1.47 ± 0.03	1.40 ± 0.11	Ni	1.3 ± 0.2	
Mg (%)	0.62 ± 0.02	0.57 ± 0.01	Mo	0.3 ± 0.1	
P (%)	0.21 ± 0.01		Hg	0.155 ± 0.01	
Fe	300 ± 20		Cd	5	
Mn	91 ± 4	80.0 ± 5.8	Se	0.11 ± 0.01	
Na	82 ± 6	86.3 ± 3.7	Th	0.08 ± 0.01	
Pb	45 ± 3		U	0.064 ± 0.00	
Sr	37 ± 1	37.0 ± 6.9		6	
Zn	25 ± 3			0.029 ± 0.00	
Cu	12 ± 1	9.36 ± 0.70		5	
Rb	12 ± 1				
As	10 ± 2	10.02 ± 1.34			
Sb	2.9 ± 0.3	2.98 ± 0.40			

Table III: Results of Standard Reference Material BCR-CRM No 279 showing Certified/Indicative values and Local Laboratory values

Elements	Certified/indicative values	This Work	Units
* As	3.09±0.20	4.39±1.5	µg/g
Al	1.9±0.05	1.67±0.03	mg/g
Br	322.0±4.0	364.9±5.8	µg/g
Ca	27.0±0.8	25.4±1.7	mg/g
Cl	26.9±1.0	27.8±0.4	mg/g
Fe	2.43±0.03	2.53±0.04	mg/g
I	158.0±4.0	188.8±7.2	µg/g
K	13.9±0.9	14.0±0.3	mg/g
Mg	13.1±0.6	13.6±1.2	mg/g
Mn	2.15±0.07	2.54±0.03	mg/g
Sc	0.53±0.02	0.59±0.3	µg/g

* *Certified value*