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CO-ORDINATED RESEARCH PROJECT

ON

USE OF NUCLEAR AND RELATED ANALYTICAL TECHNIQUES IN STUDYING HUMAN HEALTH IMPACTS OF TOXIC ELEMENTS CONSUMED THROUGH FOODSTUFFS CONTAMINATED BY INDUSTRIAL ACTIVITIES

Report on the First Research Co-ordination Meeting

Vienna, Austria, 18-22 March 2002

INTERNATIONAL ATOMIC ENERGY AGENCY

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USE OF NUCLEAR AND RELATED ANALYTICAL TECHNIQUES IN STUDYING HUMAN HEALTH IMPACTS OF TOXIC ELEMENTS CONSUMED THROUGH FOODSTUFFS CONTAMINATED BY INDUSTRIAL ACTIVITIES

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Vienna, Austria, 18-22 March 2002

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DISCUSSION NOTES

1. OVERALL OBJECTIVE

To provide a scientific basis for better assessment of selected pollutants in the food chain with a view to elucidating their impacts on human health and nutrition. Results of this study will enhance the existing body of knowledge and can be used to develop preventive strategies.

2. SPECIFIC OBJECTIVE

To determine the extent to which toxic element levels in food are affected by surrounding industrial activities and to assess potential human exposure from the consumption of such foodstuffs.

3. EXPECTED RESEARCH OUTPUTS (RESULTS)

- Harmonized protocols and procedures for sampling and analyses;
- Compiled results for toxic element levels and their average daily dietary intake (ADDI) / dietary intake;
- Evaluated toxic element exposure levels based on biological indicators (where applicable);
- Publications of the study results in an IAEA TECDOC, and in peer-reviewed journals by participants.

4. ACTION PLAN (ACTIVITIES)

4a. Core research activities:

1 Identification of the study areas and population groups (see Table 1).
2 Collection of information on food consumption patterns of the population groups under study (e.g. through questionnaires).
3 Development of harmonized protocols and validation of analytical methodologies in compliance with ISO/IEC 17025 (see Table 1)
4 Collection and analysis of food samples, and estimation of the dietary intake.
5 Collection and analysis of biological indicators (where applicable: see Table 1).
6 Evaluation of possible relationships between human exposures and biological indicators for the pollutants studied.

4b. Supplementary activities:

- Speciation studies of pollutants.
- Comparison of present and previous data on relevant parameters.
- Possible production and distribution of laboratory intercomparison samples.
- Potential distribution of RM's for analytical method validation

TECHNICAL ASPECTS
5. SELECTION OF STUDY AREAS

- Most of the participants have selected their sites based on all or any of the following criteria:
- History and/or present status of pollution
- Pilot studies
- Identification of highly polluted sites

- Medical indications
- Food grown/produced/processed in the area concerned

5.1. Criteria for the selection of an appropriate sampling site

- Sampling sites will be selected to allow sampling of appropriate amount of foods so that significant results can be obtained.
- Land-owner agreement and/or participation (where applicable)

5.2. Questionnaire for selecting population groups

- A sample questionnaire will be provided by IAEA. This document may be adapted by the participants according to their specific requirements.

5.3. Food survey of the population groups

- A sample questionnaire will be provided by IAEA. This document may be adapted by the participants according to their specific requirements.

5.4. Types of samples to be collected

Table 1 provides relevant information.

5.5. Number of samples to be collected, sample size and sampling frequency

Samples selected for testing should be both representative and of sufficient size and frequency so that meaningful results can be obtained. CODEX (CX-MA 013) may provide relevant general information. Where applicable normal harvest times should be taken into consideration depending on the type of foods concerned. Other sample types may be collected more frequently. In general it is recommended that participants use their own integrity to sort out the best sampling strategies to solve their specific research survey.

6. SAMPLING TECHNIQUES AND EQUIPMENT

- Processes such as pre-sampling, sampling, packaging, transport, storage, handling, treatment, etc. should be carried out, according to recommended guidelines (India will provide relevant information from CODEX, the Czech Republic will provide sampling guidelines for biological materials as well as some QAQC documents on good laboratory practices, Canada will provide their in-house sampling questionnaires and the IAEA will distribute relevant information from the IAEA publication TRS 197)
- Appropriate precautions should be taken to avoid external contamination
- Sample integrity with respect to chemical components should be preserved
- A standard operating procedure (SOP) for each type of sample should be developed according to the specific needs of the individual research programmes. These should be distributed among all participants for discussion, amended and adopted. This procedure should be finalised prior to the collection of samples and accordingly, in the early stage of the Coordinated Research Programme. The end of September 2002 is the deadline for all participants to provide their protocols to the list-server. To smoothen the collection of appropriate information and preparation of the protocols;
- A list-server network will be set up by India and information about the participation will be provided

7. ANALYSIS

7.1. Sample preparation

- Sample preparation guidelines are available from various sources as discussed in paragraph 7
- Transport and short-term storage of biological samples should not compromise the integrity of the samples (e.g. temperature, acidity, moisture)
- For long-term storage, drying, deep-freezing, freeze-drying and evaporation may be used, where appropriate
- Non-contaminating devices (e.g. Ti, Teflon, quartz knives, etc.) should be used for sample disintegration and homogenisation
- Laboratory samples should be prepared in sufficient quantities for possible repetition of analysis
- Samples should be clearly and uniquely marked/labeled

7.2. Analytes to be determined in relation to specific sources of pollution

Information is provided in Table 1

7.3. Recommendations for nuclear analytical techniques

- Nuclear analytical technique (NAT) such as INAA, PIXE, PIGE, XRF should be the primary technique of analysis.
- Instrumental neutron activation analysis (INAA) should be used first, where available. If the desired element, detection limit, precision, and/or accuracy cannot be achieved then preconcentration NAA (PNAA) and/or radiochemical NAA(RNAA) should be used depending on the facilities available.
- Although each NAT should be optimised for the elements of interest, a slight adjustment of irradiation, decay and counting time may provide data for additional elements (e.g. co-contaminants) that could be useful for the purpose of interpretation of data.
- Comparator and/or k0 methods in NAA can be used for standardization.
  XRF: EDXRF - Care should be taken in matching the matrices of the RMs to be used with those of the sample to be analysed. TRXRF – Ensure that the sample holder is cleaned for every sample.

7.4. Recommendations for other analytical techniques

Other techniques such as AAS, AFS, ICP-AES, ICP-MS, ASV, HPLC and GC may be used as necessary.

AAS: The choice of graphite furnace, flame, hydride generation and cold vapour, should be based on the concentration of the analyte and interferences encountered. The instrument should have a functioning background correction system. Calibration should be based on calibration curve or, in the case of interference, on the method of standard addition.

ICP-MS: Care must be taken to avoid, or correct for mass overlaps and matrix effects.

ASV: Standard methods are available for a number of elements. A prerequisite for interference free analyses is that the sample solution is completely free from organic residues.

7.5. Reference analytical laboratories

IAEA's Seibersdorf laboratories and/or participating laboratories may be requested to provide guidance regarding the specific needs of the participants
.

7.5.1. As sources of specialised advice
7.5.2. To assist other participants regarding specific samples and/or analytes
7.5.3. For cross-checking purposes

8. DATABASE MANAGEMENT AND DOCUMENTATION

The sampling, analysis and calibration data as well as standards used for the purposes of the experiments must be evaluated for their reliability. A database should be established in each participating laboratory. Software used must be authenticated and preferably be compatible within the overall framework. Multivariate statistics (e.g. cluster analysis) may be used to sort the data to identify similarities/generalities. The database (original/raw and derived data) has to be maintained, to be confidential and only accessible to authorised personnel.

Any other database that the evaluator uses may be referenced. If required it should be authenticated or permission for use obtained. This is the responsibility of the individual project coordinator.

9. QUALITY ASSURANCE AND CONTROL

9.1. Existing written protocols for (1) sampling, (2) sample preparation, (3) analysis

The wide diversity of research interests amongst all participants will most likely require a large variety of protocols. Participants may request protocols from other laboratories and make their own available through the list-server. Reference is also made to paragraph 7 (this number must be adapted in the final version) in this regard.

9.2. In-house QA/QC standards

The wide diversity of research interests amongst all participants will most likely require a large variety of in-house standards. Participants should provide information on their relevant standards and where possible make them available for distribution to interested participants through the IAEA.

9.3. Recommended QA/QC procedures for the analysis

- Each participant should follow available guidelines for analytical quality assurance and analytical quality control during the whole analytical process.
- Certified Reference Materials (CRMs), having the same or similar matrix composition and analyte levels, should be analysed in parallel to the samples and/or for linking them to in-house reference materials.

- Analytical quality control measures should be pursued. This can be done through in-house reference materials linked to CRMs, or intercomparison of two or more independent analytical methods, self-verification principle in NAA (The Czech Republic will distribute a paper on this topic) or other possible approaches.
- External QA/QC procedures, e.g. interlaboratory comparisons will be carried out; materials for such exercises will be provided by Sweden. Participation in suitable proficiency testing (PT) programmes is strongly recommended (e.g. by ISO/IEC 17025). Several different PT programmes are available. It is also possible that the IAEA will organize suitable PT-programmes in the near future.

9.4. QA for data reporting and evaluation

- Results should be accompanied by an uncertainty evaluation according to the EURACHEM/CITAC and/or ISO guidelines (references to be provided).
- In-house software for data treatment should be validated (see ISO/IEC 17025).
- Appropriate statistical evaluation should be carried out following the examination of the distribution of data.

ORGANISATIONAL ASPECTS

1. Co-operation within the group
The participants are requested to communicate with one another using the list-server that will be set up soon.

As described above, the participants are requested to circulate their draft protocols for comments and possible amendments prior to the beginning of actual sampling.

Participants are encouraged to co-operate on a bilateral and/or multilateral basis, especially if their research interests are closely related. The co-operation may take any form including exchange of sampling and analytical methodologies, expertise, data, and samples for comparative and/or complementary analyses (e.g. to increase the number of analytes).

Participants who may experience difficulties in any project-related area should feel free to contact other participants who may have more experience.

Participants are requested to share relevant publications and reports from their own countries which may not otherwise be available in the open literature.

Participants are requested to acknowledge the contribution of the IAEA quoting the CRP in their publications and circulate these amongst the participants.

2. Co-operation with other institutions
Participants are strongly encouraged to interact with local, regional, national and/or international institutes/organizations/ministries, for example of environment, health and nutrition, with a view to obtain reports, information, guidelines and regulations from them. The data collected in the participant's own country and/or in the framework of this CRP could be communicated to the appropriate authorities.

3. Next RCM
The next RCM will be planned in the second half of 2003 (possible nominations: China, Brazil, Peru)

TABLE I: PRESENT STATUS IN INDIVIDUAL COUNTRIES

Country	**General Target Industries**	**Specific Target Industries**	**Target Elements (specific) [possibly]**	**Target Samples**	**Main Food Groups**	**Target Bio-indicators**	**Target Population Gropus**	**Analytical Techniques**
Brazil	Mining, Smelting, Processing	Au mines	Multi-element (As)	Food & Environmental	Vegetables, Fruits	Hair	Adults	NAA, HPLC, ICP-AES
Canada	Water Pollution	Organic Pollutants	EOX	Fish	Fish (+N)	None	None	NAA, HPLC, NMR, MS, GC
China	Pesticide, Herbicide	Pesticide	EOX	Food	Milk, Meat, Fish, Edible Oil (+N)	Hair	Children	NAA, GC-MS, HPLC
Czech Republic	Phosphate fertilizers	Phosphate fertilizer production	REE, U, Th [F]	Food	Wheat, Vegetables, Fruits	Hair	Adults	NAA, PAA, PIXE, PIGE
Ghana	Multiple Industries	Cement/Batteries/Petroleum Refining/Al Smelting/Steel Industries	Multi-element	Food & Environmental	Vegetables	None	None	NAA, XRF
India	Pesticides, Petrochemical	Pesticide and Petrochem ical	Al, Pb, Cd, Hg	Food	Vegetables, Milk, Eggs (+R)	None	None	NAA, HPLC, ICP-MS
Nigeria	Multiple Industries & Mining	Sn mining / Lead smelting	Multi-element (Pb, As, Zn, Sn)	Food	Tubers, Fruits, Vegetables, Cereals, Dairy	Hair, (Blood)	Children, Adults	TR-XRF, (AAS)
Peru	Multiple Industries & Mining	Cu, Fe, Pb, Zn, Hg mines	Multi-element	Food & Environmental	Vegetables, (Fruits)	(Hair)	(Children)	NAA, XRF, TR-XRF, ASV, AAS
Russian Federation	Multiple Industries	Pb-Zn, Pb-As glass plant, phosphate fertilizer	Multi-element (As, Pb, F, REE)	Food & Environmental	Vegetables, Fruits	Blood, Teeth, Nails, Hair	Adults, (Children)	NAA, AAS, XRF
South Africa	Gold mining	Au (U), Cu (P), Coal, Heavy minerals	TE-NORM	Food	All food-groups (+N)	None	None	INAA, gamma-spec
Slovenia	Past mines and present smelters	Pb, Zn, Hg mines	Hg, Pb, Cd, As, Zn, Se	Food & Environmental	Vegetables, Fruits, Poultry	None	None	NAA, AAS, AFS, HPLC, GC
Sweden	Water Pollution	Inorganic Pollutants	Pb, Cd, As, Hg	Fish	Fish muscle (+N)	None	None	ICP-MS, AES, AAS
Uzbekistan	Multiple Industries	Zn, Cu, Au, In, Ga, Os, etc. refineries and phosphate fertilizer production	Multi-element (Hg, Cd, U)	Food & Environmental	All local food-groups	Hair	Adults, (Children)	NAA, (+)
Vietnam	Metal Refineries	Au, Sn mines	As, Hg, Sn, Zn, Se, Cd, Pb	Food	Vegetables, Meat, Fish	None	None	NAA, ASV, AAS, XRF

Annex: Logical Framework for CRP on the Use of Nuclear And Related Analytical Techniques in Studying Human Health Impacts of Toxic Elements Consumed Through Foodstuffs Contaminated by Industrial Activities (Project E4.02, Task 9)

Narrative Summary	Objective Verifiable Indicators	Means of Verification	Important Assumptions
***Overall Objective*:** To provide a scientific basis for better assessment of inorganic environmental pollutants in the food chain in view of elucidating their impacts on human health.	N/A	N/A	N/A
***Specific Objective*:** To determine the extent to which toxic element levels in foods are affected by surrounding industrial activities and assess the human exposure to such contaminated foodstuffs.	Amounts of toxic elements in foods from polluted areas have been determined, measurements of biological indicators carried out, and assessments of human exposure made.	Final report of the study findings available to appropriate persons.	• National support is provided to institutions. • Constant co-ordination occurs between stakeholders. • Appropriate technical support is provided to CRP by PO.
***Outputs*:** 1. Harmonized protocols for sample collection, handling, and storage, and analytical processes. 2. Compiled results of analytical measurements. 3. Evaluated exposures and estimated body loads. 4. Published results of the studies carried out.	1. Number of participants using harmonised protocols. 2. Number of measurements performed. 3. Number of measured, documented and evaluated assessments. 4. Number of publications.	Published protocols, progress reports, RCM reports, TECDOC, and publications in journals.	• Protocols are appropriate, workable and validated. • Participants follow established protocols and participate in PT. • Sufficient resources available in institutions. • Quantity and quality of data appropriate for publication.

***Activities*:** 1. Call for CRP applications. 2. Form network of participants. 3. Maintain co-ordinated research. 4. Develop and issue harmonised protocols. 5. Carry out sampling campaigns. 6. Evaluate human exposure and evaluate possible relationships. 7. Collate reports and synthesise results.	1. Number of applications received. 2. Number of Research Contracts and Agreements awarded. 3. Number of RCMs organised; collaborations are active. 4. Number of issued protocols; reported results of PT. 5. Number of collected and analysed samples. 6. Number of evaluated data and interpreted results. 7. Number of individual reports received by the Agency.	1. Applications submitted. 2. Approvals by PCC sub-committee. 3. RCM reports. • Progress reports, publications	• Suitable proposals are submitted. • Participants have the required expertise and facilities. • National support is provided. • Participants have access to or ability to obtain relevant health information. • Reports are timely submitted to Agency.

PART II:
HIGHLIGHTS
AND
ACHIEVEMENTS

TITLE: IRON QUADRANGLE, BRAZIL: ASSESSMENT OF THE HEALTH IMPACT CAUSED BY MINING POLLUTANTS THROUGH THE CHAIN FOOD APPLYING NUCLEAR AND RELATED TECHNIQUES

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SCIENTIFIC BACKGROUND

Minas Gerais, a Brazilian state, is rich in mineral occurrences, mainly in the Iron Quadrangle considered one of the richest mineral-bearing regions in the world. Apart from extensive Fe ores, hydrothermal Au mineralization can be found in Archean greenstone belt formations, occurring with other minerals in varying proportions. Active Au mining has been going on in the Nova Lima area since early 1700`s at the famous Morro Velho Mine. Other major Au deposits can be discerned within the volcanic sedimentary sequence of the Nova Lima group in Raposos. These deposits lie within the district of Nova Lima, 15 km from Belo Horizonte, the capital of Minas Gerais State, and drain into the Das Velhas River, the main source of water supply to Belo Horizonte and other cities. Many studies have been carried out pointing out that the mineral exploration and correlated activities, including the 'garimpo'- small scale mining - are the main sources of metal contamination in water courses, river sediment and fish. According to the studies, there is strong evidence of contamination exactly in this area: high concentrations of arsenic in surface water, sediment, soil and children's urine were confirmed. The gold mineralization is supposed to be the main source of elevated total As contents in surface water. Concerning children's urine, the source of contamination has not been determined. Most of investigations are interested in determining only As and Hg in water, sediment and fish. No study to determine other important elements has been carried out so far. It is highly important to investigate contamination by other mining pollutants in different matrixes – mainly foodstuff – to determine how much human health is affected by a long-term exposure to such elements. The importance of this study consists in not only providing a scientific basis for better understanding of the element transported from the polluted source to the chain food, but also in revealing the health impact on the population. The people who live around the mining areas consume local water and grow vegetables, fruits, medicinal plants for their own use. It is relevant to state that there is not any data about the contamination level in such foodstuffs. Biological samples as hair and nail will be also collected from people who live in this region.

SCIENTIFIC SCOPE

This Project will focus on the assessment of health impact caused by contaminated food supply. The samples will be collected during the dry and wet seasons. The project will cover, among other subjects, correlation studies between the food elemental results of exposure and health indices used to assess effects aiming at epidemiological purposes; study of bioavailability of some pollutants to be chosen after elemental results and identify the species using tracer methods involving stable and radioactive isotopes. The achievements during the first year will define the specific and strategic sampling sites; water, soil, plants and food will

be collected from regions nearby and far from the mining area; the samples will be prepared to be analyzed mainly by means of k0-Instrumental Neutron Activation Analysis. This Project is inserted in the Monitoring Program of Das Velhas River Basin, already conducted by FEAM-Fundação Estadual do Meio Ambiente (State Foundation for Environment), a governmental institution responsible for all subjects related to environment in Minas Gerais State. It will also be inserted in another project involving CDTN/CNEN, UFOP (Federal University of Ouro Preto), UFZ (Umweltforschungszentrum Leipzig Halle – Germany) and FEAM. Concerning health, the investigation will be conducted with the physicians of the Secretaria Municipal de Saúde (Municipal Department of Health) and it is also inserted in a Public Health Awareness Program. This Project will be the first assessment to be carried out using nuclear technique, involving environment and health impact concerning mining element pollutant and foodstuff in the Iron Quadrangle, one of richest regions in Brazil of mineral occurrence and severely contaminated due to diversified mineral exploration. Surely the data emerged from this Project will guide the actions of the Monitoring Programs conducted by FEAM.

OUTPUT ALREADY AVAILABLE

Sediment's samples from Ecological Region of Tripuí, geologically inserted in the Iron Quadrangle, were analysed. This ecological reserve is close to Ouro Preto City and does not present any mineral occurrence of economical interest. Some sediment samples were collected from small rivers that cross the Tripuí area in order to assess the metal elemental concentration in this Iron Quadrangle. This park was chosen to be sampled because it is located in the same geological area of Nova Lima region, where this project is intended to be developed. On the other hand it is far enough from the areas where there is gold mining activities and is not supposed to be affected by such activity. Some results for As and Sb in sediment samples obtained by k0-Instrumental Neutron Activation Analysis are showed. The same samples were analysed by Radiochemical Laboratory at CDTN, RL/CDTN, and by Laboratory for Radiochemistry at Jožef Stefan Institute, Ljubljana, LR/JSI. The results show that all Sb concentrations are higher than the Reference Certified Material IAEA/Soil 7. For As, some concentrations are also higher.

PROGRAMME OF WORK FOR 2002

To choose specific and representative sites to collect soil, plant, lichen, sediment samples, during the dry and wet seasons; to harmonize protocols for collecting foods; to collect food that is grown in this area and consumed by the local population; to collect soil and plant far from this area in order to compare the concentrations of pollutants; to collect food that is grown far from this area; to prepare the samples to be analyzed and to begin the elemental concentration determinations in the samples.

EXPECTED RESULTS FOR 2002

The elemental concentration determinations in the samples will guide the main actions for next year.

PROGRAMME OF WORK FOR 2003

1. Depending on the metal concentration results, biological material such as hair and nail from the people who live around the mining areas will be collected in order to assess the level of exposure to the pollutants, as well as will be collected biomonitor samples from a comparative group formed by individuals not exposed to the same environment and that do not consume the same foodstuff;
2. To begin the elemental concentration determinations in the biological samples,
3. To carry out correlation studies between the food elemental results of exposure and health indices and
4. To select toxic elements to study the bioavailability.

TITLE: STUDIES OF ORGANOHALOGEN CONTAMINATION OF FISH USING NEUTRON ACTIVATION, LIQUID CHROMATOGRAPHY, NUCLEAR MAGNETIC RESONANCE, AND MASS SPECTROMETRIC TECHNIQUES

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SCIENTIFIC BACKGROUND

The marine environment has long been a dumping ground for a variety of wastes of both an organic (e.g. sewage) and an industrial (e.g. pulp mill effluent) nature. In addition to these direct means of input, there is a strong evidence to support the theory proposed in the early 1970's that significant amounts of persistent organopollutants (POP) are being deposited into low-temperature regions from terrestrial sources by a variety of short- and long-range atmospheric and oceanic transport mechanisms. A major component of POP is the group of compounds known as extractable organohalogens (EOX), which is primarily made up of extractable organochlorines (EOCl) and to a smaller degree also includes extractable organobromine (EOBr) and extractable organoiodine (EOI) compounds. The EOCl compounds include chlorinated pesticides such as dichlorodiphenyltrichloroethane and its metabolites (SDDTs), hexachloro-cyclohexanes (SHCHs), and chlordane compounds (SCHLs), as well as polychlorinated biphenyls (PCBs), polychlorinated dibenzo-p-dioxins (PCDDs), and polychlorinated dibenzofurans (PCDFs).

In 1975, researchers used neutron activation analysis (NAA) to measure total EOCl content of some marine fish oils and found that their levels were 1.5 to 5 times higher than that of PCBs or DDTs determined by gas chromatography (GC). It has also been reported in a Canadian project by Chatt and coworkers that between 74% and 99% of EOCl in several species of fish cannot be accounted for by PCBs and chlorinated pesticides.

We have been doing research on EOX over the last 10 years or so. We first evaluated the potential of NAA for the simultaneous and quantitative measurements of EOCl, EOBr and EOI, and then assessed the extent of contamination of shrimp and cod fish from the Great Lakes and of marine mammals by EOX. The highest concentrations of EOCl were found in the brain, testes, and ovaries of cod. We have developed gel permeation chromatography (GPC), reversed-phase chromatography (RPC), NMR, and various types of mass spectrometry methods for the separation and identification of at least a couple of new EOCl compounds in cod ovaries.

SCIENTIFIC SCOPE OF THE PROJECT

The long-range objective of this project is to characterize the extractable organohalogen species in cod lipids. We will also carry out a survey of EOX in various fish samples purchased from markets across Canada and estimate the average daily dietary intakes (ADDI) of EOX. The specific objectives are as follows. We propose to systematically evaluate the relative extraction efficiencies of single and mixture of solvents for the bulk extraction of EOCl, EOBr, and EOI compounds. We will develop NAA methods using short-lived nuclides for the determination of chlorine and bromine. We will design a quality assurance program for the reliable determination of chlorine, bromine, and iodine at ppb to ppm levels. We will comprehensively characterize the cod brain, testesticular and ovarian extracts by fractionation using semipermeable membrane dialysis in organic solvents followed by the quantitative determination of the halogens by NAA. We will characterize the EOX compounds using High-resolution gel permeation chromatography (HPLC), ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectroscopy, Fourier transform infra-red (FTIR) spectroscopy, various mass spectrometric (MS) techniques, and NAA.

OUTPUTS ALREADY AVAILABLE

Work done so far has been published in the following papers.

W.H. Newsome, P. Andrews, B.S. Conacher, R.R. Rao and A. Chatt, “Total organochlorine content of fish from the great lakes”, J. Assoc. Off. Anal. Chem. 76, 703-706(1993).
J.W. Kiceniuk, A. Chatt, J. Holzbecher, and B. Zwicker, “Toxicological implications of extractable organohalogens in tissues of aquatic animals from the Canadian Arctic and northwest Atlantic. DFOGPTCP Wrap-up Conference”, 19-20. 1997.
J.W. Kiceniuk, B. Zwicker and A. Chatt, “Determination of extractable organic bromine and chlorine in biological compartments of Atlantic cod (Gadus morhua) by neutron activation analysis”, J. Radioanal. Nucl. Chem. 235 , pp. 291-294 (1998).
J.W. Kiceniuk, J. Holzbecher and A. Chatt, “Extractable organohalogens in tissues of beluga whales from the Canadian Arctic and the St. Lawrence River”, Environ. Pollut. 97, pp. 205-211 (1997).

PROGRAM OF WORK FOR 2002

We will carry out a systematic study on the extraction efficiency of EOX in a range of solvents with different polarities and develop a simple and efficient method for the extraction of EOX from cod. A complete removal of any residual halide ions from the organic phase of the solvent extraction system is essential for the accurate measurement of total EOX by most analytical methods. We will develop washing methods for obtaining the maximum removal of the residual halide ions.

The halogen levels in the extracts will be determined by neutron activation analysis (NAA), using the ^{38}Cl, ^{80}Br, ^{128}I nuclides of chlorine, bromine and iodine, respectively. We will optimize the irradiation-decay-counting times to obtain the maximum sensitivity for the simultaneous determination of three elements. It may be possible to use the short-lived nuclides of bromine and chlorine (^{79}mBr and ^{38}mCl) which will allow for higher throughput of samples. We will use the Dalhousie University SLOWPOKE-2 reactor and both conventional and Compton suppression gamma-ray spectrometry for NAA.
To effectively manage analysis, a total quality management plan (TQMP) will be employed. This plan will cover protocols for all critical steps from pre-sampling factors to the total

uncertainty budget of the results reported, e.g. site selection, sample selection and collection, transport, preservation, receiving, analysis, data processing, proficiency testing, etc. Once the TQMP has been established then the task of quality control (QC) at each of the steps will be undertaken. Both internal and external quality assessments will be carried out using elemental comparator standards and certified reference materials, respectively. We will initiate this program in 2002 and may continue it to 2003, if needed.

EXPECTED OUTPUTS/RESULTS FOR 2002

We will complete the development of EOX extraction methods and of the NAA methods. We hope to either complete or nearly complete the total quality management plan (TQMP). We plan to either publish about two papers or have them accepted for publication by the end of 2002.

PROGRAM OF WORK FOR 2003

First we will complete any work, such as the TQMP, left over from 2002.

We will collect fish samples according to our protocols and analyze them for EOX levels.

At present, no reference material or certified reference material is available for EOX. It might well be possible to prepare a small amount of such a material, if funding becomes available.

We will start developing HPLC, GC, NMR, FTIR, and MS methods for the characterization of EOCl compounds.

TITLE: EVALUATION OF HALOGEN ELEMENT LEVEL IN FOODSTUFFS CONTAMINATED BY PESTICIDES AND HERBICIDES IN BEIJING AND ITS HEALTH IMPACT ON CHILDREN BY NUCLEAR ANALYTICAL AND RELATED TECHNIQUES

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CHINA

SCIENTIFIC BACKGROUND OF THE PROJECT

The halogen elements (F, Cl, Br and I), when they exist as organohalide compounds (e.g. chlorinated pesticides, polychlorinated biphenyls and dibenzo-p-dioxins/dibenzofurans, etc.), have long been known as persistent environmental pollutants. Although human exposure to this type of pollutant comes from air, water and diet, many studies have shown that about 95 % of organochlorine compounds intake are estimated to come from food.

It is reported that about 4.9 million tons of HCHs and 0.4 millions DDTs had been used from 1960 to 1983 in China. Although the use of these pesticides and herbicides in agriculture has been officially banned since 1983, their persistent metabolites and residues still exist in the environment. These pesticides and herbicides in the environment can be finally accumulated and concentrated in milk and other foodstuffs through the food chain. A preliminary result obtained by nuclear analytical technique in our laboratory indicated that the concentration of organohalide compounds in the dairy products in Beijing was quite high with the maximum of 615.5 ng/ml. However, up to now little information about the pollution status of organohalide compounds in various foods and their impact on human health, especially on children - a sensitive population, is available.

The traditional analytical techniques, like gas chromatography (GC), GC-mass spectroscopy (GC-MS) and high performance liquid chromatography (HPLC), etc. cannot reflect the overall pollution status of organohalide compounds. Many reports have indicated that the contents of organochlorine compounds given by GC only amounted to about 10 - 20 % of the actual contents. Due to the advantageous nuclear properties of Cl, Br and I, neutron activation analysis is able to easily evaluate the whole pollution status of the halogen elements and their organic species, when it combines the organic extraction techniques.

SCIENTIFIC SCOPE OF THE PROJECT

In the framework of this CRP organized by IAEA the emphasis of our project lies in 3 aspects: (1) Establishment, improvement and validation of the neutron activation method to analyze the organohalide compounds in foodstuffs and human hair in combination with organic extraction; (2) Monitoring, evaluation and identification of the contamination levels by halogen element, especially organohalogens, in foodstuffs taken from the Beijing supermarkets by NAA, GC-MS and HPLC; and (3) Evaluation of the health impact of organohalide compounds on children.

OUTPUT FOR 2001

- Over 100 milk samples have been collected monthly during the period between February and October of 2001. The milk was not restricted to local sources, also from other provinces.
- Working chemical standards for Cl, Br, I and organohalide compounds--α,β,γ and δ-HCH, heptachlor, aldrin, heptachlor epoxide, chlordan, 4.4'-DDE, 4.4'-DDD, ,4.4'-DDT- were prepared.
- Preliminary experimental condition for NAA of halogens via Cl-37 (n,γ) Cl-38, Br-79 (n,γ) Br-80 and I-127(n,γ) I-128 at the Miniature Neutron Source Reactor was set. The detection limits for Cl, Br and I in milk sample are 55 ng, 8 ng and 4 ng, respectively.
- The organic extraction procedure for organochlorine pesticides in milk was established and its recovery was determined to be quantitative.
- Gas chromatographic analyses were carried out by a Varian 3800 gas chromatograph equipped with a ^{63}Ni electron capture detector. α,β,γ and δ-HCH, heptachlor, aldrin, heptachlor epoxide, chlordan, 4.4'-DDE, 4.4'-DDD, ,4.4'-DDT were spiked into milk to determine the chemical recovery and to check the reliability and reproducibility of the procedure, which were satisfactory.
- The concentrations of organohalide compounds in 33 milk samples from 7 different regions of China determined by NAA combined with the organic extraction were determined. Their regional difference is evident, from 615.5 μg/L to below the detection limits. Generally, the levels of the organohalide compounds in milk are increasing from north to south, which is likely attributed to many factors, e.g. climate, soil composition, biomass and, more importantly, industrialized level.
- Three papers have been submitted, in which 2 have been accepted.

PROGRAMME OF WORK FOR 2002

- More food samples will be collected, including, fish, meat, egg and others from Beijing supermarkets.
- An elaborated neutron activation analysis scheme will be developed to improve the detection limits for Cl, Br and I. Meanwhile, the analytical methods for halogens and their organic compounds will be validated.
- More food samples will be analyzed for halogens and organohalide compounds by the hyphenated NAA.
- Collecting the relevant information on typical food consumption, and production and use of pesticides and herbicides in the studied area.

EXPECTED OUTPUT FOR 2002

All the programmes listed in section 4 will be completed and more two papers will be prepared and submitted.

PROGRAMME OF WORK FOR 2003

- Human hair, urine and blood (if possible) will be collected from about 50 preschool children, 4 to 7 ages, from 2 nurseries located at the urban and rural regions, respectively.
- The analytical method for determination of halogens and their organohalide compounds in the above biological samples will be established.
- Intake amount of organohalogen compounds via food consumption and their impact on children' health will be preliminary evaluated.

TITLE: USE OF NAA, PAA, PIXE AND PIGE IN STUDYING HUMAN EXPOSURE TO TOXIC AND OTHER ELEMENTS CONSUMED THROUGH FOODSTUFFS CONTAMINATED BY INDUSTRIAL ACTIVITIES

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SCIENTIFIC BACKGROUND AND SCOPE OF THE PROJECT

Pollution of the environment by industrial activities presents a significant health risk to man. One of the possible pathways of pollutants from the environment to human organisms is the consumption of foodstuffs polluted by industrial activities. It is well known that many industries discharge gaseous, liquid, and solid wastes containing toxic elements into various compartments of the environment, including agricultural land. Thus, toxic elements may enter the food chain, depending on their bioavailabilty. A great deal of data exists on the response to incident acute exposure, but there is little or no information on the effects of chronic exposure to low amounts of many toxic elements. This makes our understanding of the specific fate of some elements in humans incomplete. Since the toxic elements may be present in crops and foodstuffs in a wide range of concentrations from minor to ultra-trace levels, very sensitive analytical techniques with a wide dynamic range should be used for their determination. Nuclear and related techniques, such as neutron activation analysis (NAA), particle induced X-ray emission (PIXE), etc. are uniquely suited for the determination of most of the toxic elements due to many favourable features of these techniques, and namely NAA may be used to verify the accuracy of other analytical techniques.

There are various industries in the Czech Republic that are potential sources of environmental pollution. Several years ago, the Czech Republic joined an European programme of environmental monitoring (part of the programme UN/ECE ICP Vegetation – Heavy Metals) that is based on analysis of mosses, mostly Pleurozium Schreberi, as recognized biomonitors of atmospheric pollution. Moss samples are collected in about 200 localities all around the country employing a grid of approximately 20 x 20 km. Collection of the samples and their analysis using inductively coupled plasma mass spectrometry (ICP-MS) is performed by the Laboratory of Trace Elements of the Research Institute of Ornamental Gardening in Průhonice. The elements followed include Ag, Al, As, Ba, Be, Bi, Cd, Ce, Co, Cr, Cs, Cu, Fe, Ga, In, La, Li, Mn, Mo, Ni, Pb, Pr, Rb, S, Sb, Sc, Se, Sr, Th, Tl, U, V, Y and Zn. In addition, Hg is assayed using a single purpose atomic absorption spectrometer AMA-256 (Altec, Czech Republic) with built-in preconcetration of Hg by amalgamation.

Four main polluted regions have been identified in the Czech Republic from the results of the above monitoring. One is in north Bohemia where elevated concentrations of the elements Al, As, Cr, Cu, Hg, Mn, Ni, S, Se, Sr, Zn are found. The well-known sources of this pollution are: (i) burning of lignite in several power plants; (ii) discharges from several types of chemical industry that are located in this region. The second polluted region is in South-West Bohemia, rather localized around a non-ferrous metallurgical plant. This region is polluted mainly with

the elements Bi, In, Pb, Sb, Sn. The major ferrous-metallurgy plants situated in north Moravia cause pollution with the elements Ag, Cd, Fe, Mo in this region. The level of pollution in north Bohemia and Moravia has significantly decreased due after the installation of desulphatation units at most lignite-fired power plants and other pollution abatement strategies employed in the last 5-10 years. However, formerly unidentified pollution has been discovered in south Moravia, where elevated contents of the elements Ba, Be, Co, Ga, U, Th, Y and several rare earth elements, such as Ce, La, Pr, were found. The most probable reason of pollution is due to discharges from a phosphate-fertilizer production plant. Since south Moravia is one of the most important agricultural regions of the Czech Republic, it has been decided to carry out the study of pollution of agricultural crops and the transfer of the pollutants in the food chain, namely into locally produced foodstuffs, in this region.

SAMPLING

The following crops and/or vegetables will be collected in 3-4 localities in the polluted region: wheat and fodder for cattle due to their significant position in the food chain, vegetables, such as kale, cauliflower, spinach, parsley and cucumber, fruits, such as apple, apricot and wine grapes. Soil from the collection sites will also be analyzed to be able to study bioavailability of the pollutants.

Biological samples will be transported to laboratory at 4^{o}C, surface contamination with soil will be removed mechanically, the samples will be washed with distilled water, desintegrated and mixed in a blender with a Ti knife. The resulting material will be freeze dried and further homogenized in the dry state. Soils will be sieved, air dried and homogenized in an agate mortar.

ANALYTES AND ANALYTICAL TECHNIQUES

A number of elements will be determined by INAA and PIXE with the main emphasis on the rare earth elements (REE), U and Th. If determination of REE, U and Th in biological materials by INAA will not be feasible, RNAA methods will be developed. Since it is expected that the region studied may also be polluted with F (due to its high content in phosphate rocks), at attempt will be done to determine fluorine contents in the above biological materials and soils. For this purpose, INAA employing the reactions $^{19}F(n,\gamma)\ ^{20}F$ and $^{19}F(n,p)^{19}O$ with thermal and fast neutrons, respectively, and PAA with radiochemical separation (RPAA) using the reaction $^{19}F(\gamma,n)^{18}F$ that is free from nuclear interferences for irradiation with up to 20-MeV bremsstrahlung will be tested. The most promising technique for fluorine determination is Proton Induced Gamma Emission (PIGE) in which measurement of the 110 keV and 190 keV γ-lines produced in the $^{19}F(p,p',\gamma)^{19}F$ reaction by bombardment with a 2.7 MeV proton beam may yield a fluorine detection limit in the range of several μg g^{-1} for biological materials and around hundred μg g^{-1} for soils. Experimental facilities for these techniques are available at the Nuclear Physics Institute, Řež near Prague.

WORK PLAN FOR 2002

a) Pilot sampling of agricultural crops and soils will be performed in the above region and their preliminary analyses will be carried out.
b) Based on the results of preliminary analyses, the analytical techniques will be tuned and/or improved for the given purpose and validated.

TITLE: INDUSTRIAL RELATED CONTAMINATION OF PERI-URBAN FRESH VEGETABLES

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SCIENTIFIC BACKGROUND AND SCOPE OF PROJECT

Tema is the industrial nerve centre of Ghana.

Major industries include:

- Aluminium smelting and processing
- Petroleum refining and processing
- Steel works
- Manufacturing of dry cell batteries
- Cement

Vegetables produced are:

- Cabbage (Brassica oleraceae var. capitata)
- Carrot (Duacus carota)
- Lettuce (Lactucca sativa)
- Onion (Allium cepa)
- Sweet pepper (Capcicum annuum)

Areas used for cultivation are:

- Backyard gardens
- Along drains
- Walkways
- Streets
- Undeveloped parcels of land

Channels of distribution are:

- Under sheds
- Along streets
- Urban markets

Vegetables are liable to contamination from pollutants emitted into the environment.

MAIN OBJECTIVES

- Determine the extent to which toxic element levels in foods are affected by surrounding industrial activities
- Assess the human exposure to such contaminated foodstuffs.

SPECIFIC OBJECTIVES

- Monitor As, Cd, Cr, Hg, Ni, Pb, Co, Mn, Se, Sn and Mo in vegetables grown in the Tema Municipal District, due to pollution from industrial activity
- Assess human exposure to such contaminated foods through monitoring of the distribution and marketing channels.

METHODS

- Identify sampling areas within the Tema municipality including
  (a) Identification of the growers and their marketing outlets and
  (b) Identifying the sources of water used for cultivation by means of a questionnaire;

- Quantify the level of toxic elements in the soil and water bodies used for the cultivation of vegetables, using nuclear and related analytical techniques;
- Analyse foods from the farms at the selected sampling areas using neutron activation analysis and X-ray fluorescence analysis.

PLANS FOR FUTURE WORK

- Year Two:
  (a) Follow the distribution outlets to identify the of produce into the food chain.
  (b) Carry out field survey to classify the cultivated areas as low, medium and high levels of contamination.
  (c) Monitor the level of contaminations in the produce.
  (d) Dialogue with Environmental Protection Agency (EPA), Standard Boards (SB) and Industrial establishments.

- Year Three:
  Institute, in collaboration with EPA, SB and Industrial establishments, pollution control measures.

- Year Four:
  Monitor the level of contamination in the produce both in the field and on the market outlets.

TITLE: ALUMINIUM, CADMIUM, LEAD & MERCURY LEVELS IN HUMAN FOOD CHAIN (IN KARNATAKA, INDIA) AND THEIR INTERACTION WITH MICRONUTRIENTS – COPPER, IRON, ZINC AND VITAMIN A

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SUMMARY

The toxic metals like cadmium, lead and mercury get into the food chain due to environmental contamination. The intake of toxic metals like lead, cadmium, mercury and aluminium by the people in the developing countries is comparatively more than their counterparts in the developed countries. This may be due to prevalence of higher amounts of these metals in the minerals or due to inadequate measures and enforcement regulation to control the entry of toxic metals into food chain. This is of great concern from the point of protecting the health of people in developing countries. It is also reported that these toxic metals also affect the nutritional status of essential micronutrients like Cu, Fe, Zn and Vitamin A in the human system. These micronutrients are required for good health and longevity and their availability is influenced by several dietary inhibitors including heavy metals. Therefore, the present study was taken up to study the prevalence of these metals in the most viable source of food commodities which contributes to this contamination.

The study is extended to investigate the toxic metals levels (Al, Cd, Pb & Hg) in vegetables, eggs and milk in four regions of Karnataka. These are the high-risk commodities selected for the study. The vegetables including root and leafy vegetables are more prone for contamination due to soil and water contamination. The high contaminant level in egg may be due to feeding the poultry birds with contaminated feeds and water. Similarly high Pb, Cd and Hg levels in milk are due to feeding the animals with contaminated feeds and water.

The future plan includes survey of Al, Cd, Pb & Hg, As in contaminated vegetables, eggs and milk samples from four regions of Karnataka state, determination of Al leaching from anodized and unanodized Al utensils, selection of high risk foods with respect to heavy metal contamination and metal-metal interactions with reference to above toxic metals with micronutrients (Cu, Fe, Zn and Vitamin A).

The levels of different metals (Al, Cd, Hg and Pb) were as described below:

In the studies conducted on the toxic metals in vegetables, eggs and milk Al content in cauliflower, spinach, milk and carrot puree was 20, 1.9, 4.5 and 1.0 ppm respectively. The Hg was analysed by NAA and the content in cauliflower, spinach, milk and carrot puree was 0.18, 0.05, 0.09 and 0.05 ppb respectively. The Pb content in root vegetables (carrot, radish, onion and potato) ranged from <0.1 to 7.88 ppm on dry wt. basis. In the leafy vegetables (spinach, cabbage & coriander) the Pb content ranged from <0.1 to 10.59 ppm. Milk and egg samples contained Pb levels at < 0.5 to 4.2 ppm. The Cd content in leafy vegetables were < 0.1 to 1.58 ppm. The root vegetables also had the Cd content almost in the same range of <0.1 to 1.61 ppm. The levels of Cd in milk and eggs varied from < 0.1 to 1.9 ppm.

Interaction of Retinyl Palmitate with Zn++, Pb++ and Fe++ Salts in Vitro indicated that $ZnSO_4$, $Pb(NO_3)_2$ and $FeSO_4$ seemed to affect the fluorescence spectra by changes in the fluorescence intensity (FI) and increase in emission maxima.
The emission maxima for retinyl palmitate at Ex 325 is 470 nm. In the presence of these divalent metal ions it is increased to around 480 nm. Simultaneously the RFI is not linear with concentration, erratic and hence given as a range. There has been no consistency in the results.

Aluminium leaching from anodized and unanodized utensils in the presence of tartaric and citric acid and also during Rasam, Yogurt and Tea infusion will be computed. 5% citric and tartaric acid solutions were stored in anodized and commonly used utensils at room temperature for 24 hrs in MQ water. Yogurt was prepared in Al utensils and Tea infusion and Rasam were prepared in Al utensils. All the studies were carried in MQ water. Sample preparation for Al estimation was done under laminar flow hood to avoid dust contamination. Al was estimated using ICP-AES. Bovine liver was used as reference material. MQ water blank was run as blank. Al leaching is more in commonly used utensil compared to anodized utensils. Leaching is more in citric acid compared to tartaric acid. Al leaching is high in yogurt, tea insusion and rasam preparation. The studies indicate commonly used Al utensils cannot be used for acidic food preparation. The availability of Al from Al citrate at pH 3.0 is 70%, while at pH 8.0 it is 20%. But in tartaric acid complex, Al availability is 40% at pH 3.0, while at pH, it is 8% only. This data clearly indicates that citrate favour more Al availability at 3.0 compared to pH 8.0. The data also indicates that citrate favour more free Al compared to tartarate.

TITLE: DIETARY INTAKES OF ESSENTIAL AND TOXIC ELEMENTS IN SEVERAL GROUPS OF NIGERIANS CONSUMING FOOD EXPOSED TO SPECIFIC INDUSTRIAL POLLUTION SOURCES

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SUMMARY

The importance of industries to national development is well recognized. However, for sustainable national development, the environmental impacts (particularly as it affects human health) of these industries must also be well monitored. Ingestion through food and water is one of the two major routes for these toxic pollutants to accumulate in man and thereby impact his health. The other major route being inhalation from the air.

Chemical elements can be categorized under three headings depending on their biological functions in the human body. Thus we have essential, non-essential, and toxic elements. The manifestation of both essentiality and toxicity is dependent on the quantities ingested into the system and for this purpose there are Recommended Dietary Allowances and Provisional Tolerable Intakes (PTI) for both essential and toxic elements respectively, as recommended by the FAO/WHO. The feeding pattern of the individual (type and frequency of diet) is crucial in determining the amount of each element that is eventually ingested.

The impact of ingested toxic elements could be different for various groups of subjects. Children, for instance, are known to be more susceptible to the deleterious effects of lead than adults (1). Apart from age, other factors such as social economic status (affecting general nutritional quality), stress, physiological conditions such as pregnancy could also greatly modify the impact of the same amount of ingested toxic element in various individuals. (2,3). Another important modifier of the impact of toxic elements in man is the presence of other elements leading to synergistic effects or competitive inhibition in absorption. Yet another factor that can affect the impact of elements in man is the bioavailability. This depends on both the chemical form in which the particular element is found in the food as well as the matrix of the food. For instance phytates seriously inhibit the absorption of zinc in food (4).

In this project food samples originating from industrially-polluted areas will be surveyed, sampled and analysed for trace elements. The industries to be selected will be ones with clear marker pollutants which have been in operation long enough for the possible impacts to be measurable. The marker pollutants must also be ones that are known to have significant health impact in man. The dietary intakes of these elements by various groups in the population will be assessed. In the course of this CRP, sampling will take place in communities situated in the vicinities of the following Industrial activities:

- The Tin/Lead Smelter factory in Jos, Plateau State of Nigeria (North East)
- The three Oil Refineries at Kaduna, Kaduna State, Portharcourt, Rivers State and Warri, Delta State)
- The National Fertilizer Plant in Cross River State; and
- Three Cement factories each from South West, North East and Middle Belt of Nigeria

For the first year of the CRP, our attention will be directed at the tin and lead smelting factory at Jos, Plateau state of Nigeria. In this factory, liquid effluents are discharged into a nearby stream, which eventually ends up in a fish pond. The stream also partly serves to irrigate a vegetable farm whose products are sold commercially. Solid wastes (mainly slag from the smelting process) are dumped nearby on land separated from the factory by a fence. Part of the solid wastes are routinely incorporated into the soils probably as 'manure'. Within this area, fruit items such as tomato, and root crops (cassava) are grown.

We have previously measured the levels of some toxic elements associated with tin mining and tin/lead smelting in Jos. At various sites on the Jos plateau, we found that toxic heavy metals like Sn, Pb, As, Bi and Ni were highly enriched in the soils, in air particulates and in mine wastes. We have also reported the Pb content of the edible vegetables grown on farms located in the vicinity of the Smelter. The Pb contents range from 600 – 1200 ug/g which is outrageously high.

In the first year of this CRP we shall conduct more detailed assessment of the environmental contamination of food both in the metropolis of Jos and around this Smelter in particular. Furthermore, we shall assess the dietary burden of these toxic contaminants in various groups of the population.

In 2003, we plan to carry out an identical study at another type of industry, most likely the oil refineries located in the Delta region of Nigeria.

TITLE: DETERMINATION OF TRACE ELEMENTS AND HEAVY METALS IN AGRICULTURAL PRODUCTS CULTIVATED AT THE RIVER RIMAC IN THE CITY OF LIMA

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SCIENTIFIC BACKGROUND

The main river of the City of Lima is the Rimac River the water of which is used to irrigate the agricultural land of the Rimac River valley. There are many manufacturing and mining industries along the Rimac river valley. The river is a receptor of a significant load of metals the origin of which is the tailings and waste of mining activities in the high valley and industrial activities downstream, respectively.

One of the uses of the river water is to irrigate the agricultural production areas of the nearer valleys. Although there is no reported local data of the degree of contamination of agricultural products and its effects on human health, there is a strong suspicion that the agricultural products cultivated in this valley and distributed in markets of Lima could be contaminated with heavy metals and an excess of trace elements by means of the superficial and subsurface waters of infiltration from the contaminated superficial waters, with the consequent potential risk to health of the population consuming the agricultural products irrigated with contaminated waters.

There is very limited and insufficient information about the chemical and element contamination of food in Lima and of the agricultural products cultivated in the valleys. Most of the existing studies have focused on microbiological contamination.

The environmental impact of this contamination affect not only the cultivated areas but also the ecosystem, flora and fauna, and of course, the health humans through the food chain.

The essential trace elements have an important role in the human nutrition because they perform a number of vital functions in the body as constituents of enzymes, hormones, vitamins and other biological molecules, and for this, the optimum concentration of trace elements is the basis for the health of living beings, including humans.

SCOPE OF THE PROJECT

The Determination of Trace Elements and Heavy Metals in Agricultural Products Cultivated at the River Rimac in the City of Lima project has the following objectives:

- Determine the degree of contamination by trace and heavy metals in agricultural products consumed by the population and cultivated along the river Rimac valley in Lima.

- Establishing baseline values and assessment of time trends of the contamination by pollutants in order to relate their effects to the nutritional status and human health.
- Determine the quality and safety of food that populations are consuming and provide information on the element composition of the diet for a large sector of the population to improve the quality of foodstuffs.
- Create a list of the concentration of trace and heavy metals in the agricultural cultivated products from the identified area.
- Provide information to the national authority for health and environmental monitoring, DIGESA, so as to allow the implementation and/or improvement of policies and programs to control the contamination and its effects on the human health.
- Disseminate the benefits of the use of nuclear energy and nuclear analytical techniques.

OUTPUTS

The first information obtained from wholesale market was a statistic about the kind of food that these markets receive and its origin. But most of them are not about vegetables.

The first inspection along the valley permit the identification of sampling sites and of four sampling products such as beetroot, turnip, radish and cabbage. In the medium valley the main product cultivated are fruits such as peach, apples and avocado.

PROGRAMME OF WORK FOR 2002

- Identifying the critical agricultural areas potentially affected by contamination from industrial activities, in the vicinity of Lima, Peru.
- Selection of food to be studied according to the production and consumption importance.
- Establishment of appropriate sampling plan to obtain representative samples.
- Collecting and analysing the collected samples, using neutron activation analysis, X-ray fluorescence spectrometry, and complementary non-nuclear techniques.
- Evaluating of obtained results

EXPECTED OUTPUTS FOR 2002

To obtain data and information about the content of trace elements and heavy metals in selected agricultural products.
To disseminate information in order to generated the establishment and/or improvement of environmental sanitary vigilance in health programs.

PROGRAMME OF WORK FOR 2003

Other valleys providing agricultural products to Lima required surveillance of the degree of contamination by heavy metals and trace elements. These are the Lurin and Chillon valleys. We consider of utmost importance to extend the project to the agricultural products of the said valleys.

TITLE: USE OF INAA, AAS AND XRF IN STUDYING HEALTH IMPACTS OF TOXIC ELEMENTS CONSUMED THROUGH FOODSTUFFS CONTAMINATED BY INDUSTRIAL ACTIVITIES IN RUSSIA

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SHORT SUMMARY

The current economic situation in Russia results in that vegetables and plants grown in private small-holdings account for over 50% of the population's diet. In some regions of Russia (Ural, Altai) mining and metallurgical works remain the sole economic factor of existence and development despite the obvious damage to the environment through contamination with heavy and toxic metals. Crop rotation is actively being extended to the land immediately bordering on the zones of industrial enterprises within the range of 1–5 km. This land has been affected by waste discharged from the enterprises for many years. The cultivated soil may contain high gross concentrations of toxic elements. The local residents generally consume food products mostly grown in the immediate vicinity of the sources of pollution. These foods are: vegetables (potato, cabbage, etc.), fruits and berries (apples, black berry, etc.) The vegetation is an intermediate step in the trophic chain of soil and man for nutritionally as well as toxicologically important elements. The harmful effects of lead and its compounds on human health have been studied around the world. Problems of contamination of these materials with other toxic elements (for example, As, Cd, Cr, Cu, Hg, Ni, Zn, etc.) have not yet been systematically studied in Russia, although their harmful effects on human health appear to be as important as that for lead.

The authors of the project are involved in realization of the following national programs:

- Federal program of the RF government «Protection of the Environment from Lead contamination and diminishing its impact on population health» (1997-2003)
- Cooperative program of the Ministry of Public Health of RF «Prophylactic measures on diminishing lead and other toxic elements impact on neuro-psychic development of children» (1999-2003)
- Program of the Ministry of Science and Technology of RF «Investigation of regularities of element-toxicants distribution in natural media (air, water, soil), biota and man's biosubstrates in the regions of intense technogenic impact» (2000-2004).

The basic objectives of this project are to evaluate the potential adverse health effects that could arise to the local residents including children from the consumption of foods grown in areas which are highly polluted by intense industrial activities.

The specific objectives of the project are:

- To study the transfer of potentially toxic levels of elements such as Al, Ag, As, Au, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Sb, Se, Sn, Th, U, V, Zn, and rare-earth elements (REE) from soils, surface and drinking waters, and air exposed to high levels of industrtial pollution (in particular mining, metallurgy, and glass works) and other anthropogenic sources. The areas of interest are: Belovo lead-zinc enterprise in Kemerovo Region of West Siberia; Pb-As crystal production in Gus Khrustalny in Vladimir Region and phosphate fertilizer plant in Voskresensk in Moscow Region of Central Russia;
- To measure the levels of the above elements in soils, surface and drinking water, air, in various types of vegetable and fruit such as potatoes, carrots, raddishes, tomatoes, cucumber, cabbage, lettuce, apples, different berries;
- To develop various types of neutron activations analysis (NAA) and atomic absorption spectrometry (AAS), X-ray fluorescence (XRF) methods for the reliable measurement of the above elements;
- To design a comprehensive quality assurance programme; and
- To estimate the exposure of man (children) to toxic elements using indicators such as the average daily dietary intakes and the element levels in biosubstrates namely blood, urine, teeth, and hair.

For the purpose of the proposed project we have selected the following areas: Belovo lead-zinc enterprise in Kemerovo Region of West Siberia, Karabash copper smelter in Chelyabinsk Region of the South Urals, and Gus Khrustalny in Vladimirskaya Region and Voskresensk in Moscow Region of Central Russia. Control sites will also be selected from the same regions.

Samples to be collected from these areas include soils, water, air, vegetables and fruits (potatoes, carrots, raddishes, tomatoes, cucumber, cabbage, luttece, apples, and different berries), milk and milk products, meat and meat products. Preliminary studies indicated that these products generally have higher than normal concentrations in industrially contaminated areas. The list of elements includes As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Sb, Se, Sn, Th, U, V, Zn, and REE. Some of these elements are either known to be toxic or potentially toxic at higher concentrations, and rest could be useful for source aportionment. The average daily dietary intake of the above elements can serve as a useful indicator. The biosubstrates namely blood, urine, teeth, and hair can reflect the body-burden of certain elements thereby the health status.

The principal analytical technique which will be used in this project is neutron activation analysis (NAA). The atomic absorption spectrometry (AAS) and X-ray fluorescence analysis (XRF) will be used as a complementary technique.

In the framework of this CRP the working plan for the first year is the following:

Months 1-6:

- Collection and assessment of current information on toxic element emissions from the industrial enterprises in the South Urals (copper smelter in Karabash, Chelaybinsk Region), Altai, Siberia (zinc smelter in Belovo) and Central Russia (Pb-As crystal production in Gus-Cruystalny and phosphate fertilizer plant in Voskresensk)
- Collection of literature data about contamination of soils by toxic element emissions

and about the accumulation of toxic elements in cultivated agriculture plants, especially in edible vegetables, in polluted areas

- Planning of the study (selection of areas exposed to emissions of the examined industrial enterprises, reference areas, selection of local cultivated agriculture plants for the study)
- Development of harmonized protocols concerning the sampling of soils and selected agriculture plants, and storage of samples

Months 7-12:

- Sampling of soil samples at selected sampling sites, determination of pH and humus.
- Sampling of vegetable samples in selected contaminated and reference areas.
- Development of analytical methods (INAA, AAS, and XRF)
- Design of a quality assurance program
- Preliminary analysis of samples
- Preparation of the interim report

TITLE: ANALYSIS OF FOOD BY NUCLEAR AND RELATED ANALYTICAL TECHNIQUES

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SHORT SUMMARY

The work on the project started in 2000 with the selection of foods consumed in the Witwatersrand area of South Africa which is recognised to be the economic heartbeat of the country. A dietician was consulted in identifying the most important food groups for human nutritional health, as well as typical examples of foodstuffs belonging to a specific food group. From this information a suite of 14 foodstuffs were chosen. The primary investigation was aimed at natural occurring radioactive materials (NORM) to explore the capability of our laboratories in analysing the nuclides involved through low- and high-energy gamma-ray spectrometry. The main objective being to investigate our capability and capacity to prepare and analyse these foodstuffs and estimate the committed effective dose to consumers. Information gained served to define future strategies for food analysis for NORM. From this survey it appeared that for certain radionuclides radiochemical separations will be required to arrive at the sensitivities needed to perform adequate dose estimations. For some of the foodstuffs positive values for a suite of radionuclides has been obtained, urging further investigation in the total NORM-nuclide content. Future work will focus on INAA and radiochemical separations to determine all relevant nuclides of the uranium, thorium and actinium decay series. Uranium and thorium content of the foodstuffs under survey will be determined by neutron activation analysis and in the same time the capability of INAA for the determination of toxic and essential elements will be surveyed. This report provides information on the work performed so far and the work envisaged for the year 2002. All actions are defined according to our QAQC procedures applicable at our ISO/IEC 17025 accredited laboratories.

TITLE: POTENTIAL HUMAN EXPOSURE TO Pb, Cd, Zn, As and Hg TROUGH CONSUMPTION OF FOODSTUFFS GROWN OR BRED NEAR MINING AREAS IN SLOVENIA

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SLOVENIA

SHORT SUMMARY

The environmental conditions of the general population in the Meža valley and the town of Idrija are site specific and unique because of their long-term (chronic) exposure to toxic metals (especially lead and mercury, respectively) through different sources. Nowadays when both mines, namely the lead/zinc and mercury mines, have been closed since 1995 and 1994, the main source is through consumption of foodstuffs grown or bred near their homes. Many of people consume their own food because of their low social status. A second factor is the low mobility of the population which is the specific for the country in general. So food contamination cannot be neglected, especially since according to literature data, lead and mercury can be harmful (neurotoxicity) even in very low levels for children, who are the most critical and vulnerable group. This is because children have higher rates of respiration and metabolism than adults.

In present study (project) the review of the previous data regarding food contaminants (Zn, Cd, Pb, Hg As) and essential elements (Se) will be done in areas of interest:

a) Area around lead mine and smelter in Mežica valley (Zn, Cd, Pb, As)
b) The area near Idrija mercury mine (Hg, Se,Cd)

Thereafter for selected 'food' samples the present situation will be checqued and supplemented. In Mežica valley the total concentrations of Zn, Cd and Pb (FAAS/ETAAS) together with As and Se (RNAA/HG AFS) will be determined in crops grown in contaminated soils and compared to available data for the same crops from non-contaminated area.

In the area near Idrija mercury mine the Hg and Se (RNAA, CV AAS, HG AFS) concentrations will be followed in similar way. Determinations of Se will be included regarding its detoxication role as an essential part of antioxidative enzymes and by forming the insoluble complexes with some metals either in food or after digestion in humans.

Further the partitioning of Zn, Cd and Pb in sediments and soils from mining area in the Mežica valley and area around lead smelter "operational speciation" by the use of sequential extraction procedure (BCR scheme) will be applied. On the basis of the data on distribution of these elements between easily and sparingly soluble sample fractions estimation on the extent of metal pollution will be made and data compared to non-contaminated area. Speciation of Zn in aqueous soil extracts will be also performed in selected soil samples by applying anion-exchange convective interaction media (CIM) DEAE fast monolithic chromatography with

FAAS and ES-MS-MS detection. The obtained results will be compared with total concentrations in crop samples from the same locations.

Since individual chemical forms of elements defenitlly determine bioavailability and toxicity some speciation studies will also be performed on foodstuffs, from contaminated areas, with exceeding maxiumum permissible trace element levels. The speciation studies will include:

1. Arsenic speciation since it is already known that inorganic forms are much more toxic than organic species;
2. Mercury speciation (MeHg, Hg)
3. Biological speciation – cellular distribution of metals between water soluble and unsoluble parts (supernatant and pellet)

For speciation studies IE/GC HPLC techniques will be combined with above mentioned methods.

During this and next year (2002/2003) the review of the previous data will be done and metal determinations in samples obtained in Idrija and other above mentioned activities will be started.

TITLE: TRACE ELEMENTS IN FISH FOR CONSUMPTION

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SHORT SUMMARY

Fish is a major food in many countries. Certain population groups may have specific consumption patterns due to geographical conditions or may be at risk at specific times, e.g. during pregnancy. It is thus of major importance that fish and fish products are safe for consumption.

Contamination of fish by toxic elements may be caused by effluent from populated areas, or industrial activities from which waste water may contaminate local waters. Mining activities are also known to contaminate local waters with an array of elements, including Pb, Cd and Zn. Another problem is the acidification of freshwater lakes making e.g. Al and Hg more mobile. The level of As is invariably higher in marine fish, than in the same species from fresh or brackish waters. Large predatory species from marine waters, e.g. sharks and tuna, may have high levels of Cd and Hg in the muscle tissue.

Several international bodies, e.g. the European Union (EU) and Codex Alimentarius have an interest in setting maximum residue limits (MRL) for Pb, Cd, Hg and As in certain foods, in order to protect the population from overexposure to these toxic metals. Much of the background data for these MRLs are old and have not been produced using today's analytical quality assurance (AQA) demands.

The scope of this project is:

1. To produce data for Pb, Cd and Hg using modern analytical techniques and following modern AQA procedures.
2. To analyse total As and inorganic As in certain fish species to elucidate if the ratio total/inorganic As is different for different species of fish.
3. To produce data for Co, Cr, Cu, Mn, Ni and Zn, using modern analytical techniques and following the AQA procedures required today.
4. These data will be used part of the material necessary for up to date risk assessment procedures carried out nationally as well as internationally.

Samples of fish is collected from the different fishing districts with the help of state and local organisations.

Pb, Cd, Co, Cr, Cu, Mn, Ni and Zn is determined by atomic absorption spectrometry (AAS)
Total Hg is determined by hydride generation-ICP-atomic emission spectroscopy (HG-ICP-AES)
Total As will be determined by ICP-MS
Inorganic As is determined by HPLC-ICP-MS after an extraction-process.

Data available so far indicate that:

- Tuna is very low in Pb, but may be fairly high in Cd.
- Fish from freshwater lakes tend to have higher Hg-levels that fish from the brackish Baltic Sea.
- The level of inorganic As in salmon is below the detection limit, whereas the total level is in the order of 1 mg/kg or higher.

For 2002 the work will focus on establishing further data for Pb, Cd and Hg in many different species and continue speciation-analysis of As in mackerel and plaice.

For 2003 focus may shift to other types of foods for which relevant data are lacking, e.g. inorganic/total As in rice.

TITLE: USE OF NUCLEAR AND RELATED ANALYTICAL TECHNIQUES IN STUDYING HUMAN EXPOSURE TO TOXIC ELEMENTS CONSUMED THROUGH FOODSTUFFS CONTAMINATED BY INDUSTRIAL ACTIVITIES

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SHORT SUMMARY

Contamination of the environment is one of the most important problems of the present century. Monitoring of the environment having the aim to determine the present situation, to detect sources of contamination, and to elaborate measures for reduction of the environment contamination, and, finally, to reduce harmful impact on human health deals with surface (including drinking) water, atmosphere (regional, occupational, etc.), soil. Less widely is monitored biota (plants, human and animal samples, etc.). Role of intake of toxic elements with foodstuffs is rather still unstudied. Project is especially important for Uzbekistan because of some peculiarities of the typical local diet and limited import of foodstuffs. The quality of food in Uzbekistan is monitored very randomly for very limited number of toxicants like nitrates, pesticides, and mercury. The quality of food provided and sold on small markets (bazaars) by private producers is out of toxic elements monitoring.

There are several heavily contaminated areas in Uzbekistan. For the proposed CRP should be chosen the following two – Amalyk and Samarkand. As a reference area Tashkent (the capital) should be chosen. The main analytical method will be Instrumental Activation Analysis together with other related nuclear and non-nuclear methods.

Programme of work for 2002 will include selection of studied and reference area, collection and systematisation of information on environmental situation and health status on the selected areas of the study, designing experimental protocol and sampling programme, determination of the typical local diet composition and determination of the most important components of local diet, determination of the priorities of elements to be determined to obtain comparable data, validating analytical methods and procedures to be used within the project (neutron activation analysis, XRF-analysis, and other available methods), collecting and analysing pilot samples to evaluate the appropriateness of the study design, choice and preparing appropriate software for data processing and evaluation to estimate the frequency distribution pattern and choice the linear or geometrical approximation, to detect possible correlations, to estimate acceptability (or fruitfulness) of multifactor statistical treatment procedures (principal components, Fisher discriminant analysis, trees, etc.).

Expected outputs/results for 2002 are selection of the study area (areas) and reference area. Systemisation of available information on environmental situation and health status on the selected areas of the study. Determination of the typical local diet composition and determination of the most important components of local diet. Determination of priorities of

elements to be determined to obtain comparable data. Preparation of written analytical procedures and AQAS/AQAC. Collection and analysis of most typical samples of foodstuffs. Estimation of the homogeneity of the diet components elemental composition to determine number of samples to be collected in the 2003 year and to determine significantly elevated elements to estimate of elements priority. Choice and preparing appropriate software for data processing and evaluation. Preparation of the 2003 Programme.

Programme of work for 2003 should include collection and analysis of samples.

TITLE: USE OF NUCLEAR AND RELATED TECHNIQUES IN STUDYING HEALTH IMPACTS OF TOXIC ELEMENTS (As, Hg, Cu, Pb, Zn, Se and Cd) CONSUMED THROUGH FOODSTUFFS CONTAMINATED BY INDUSTRIAL ACTIVITIES

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SCIENTIFIC BACKGROUND OF THE PROJECT

A) Science:

- DNRI having a good policy for scientific and technical analytical development in present and also in the futrue, such as: adding some new analytical equipment, carrying out QA/QC for NAA...
- DNRI having 21 persons whose have been working in CATER science 1984,
- Carried out 14 national scientific research projects, 4 IAEA reseach contracts and many technical contracts, among some projects have relating with this research contract.

The main projects have been carrying out:

1. UNDP-IAEA Research Contract No. 8549/RO on air pollution monitoring studies in Vietnam using nuclear- related analytical techniques. (12 /1995 - 12/1997)
2. FAO/IAEA Research Contract No. 7477/R1/RB on Factors of Radionuclide Transfer from Air, Soil and Fresh water to the Foodchain of Man in Monsoon-tropical conditions of Vietnam (1994 – 1996).
3. UNDP-IAEA Research Contract No. 8923/RO on “Reference Asian Man” (1997-2000).
4. Study and development of analytical techniques to estimate the quality of fresh water with impact of ores – mining, National Project (1999).
5. Analysing of heavy metals in see- water and weeds; National Project (2000).
6. Separating and enriching of heavy – toxic metals in aerosol samples have colleced at Dalat and HoChiMinh Cities for environmental monitoring (since 1996 to now).
7. The concentration of toxic elements and radionuclides in environmental objects in different areas of Vietnam.
8. Supporting the sustainable development of agriculture and improving the quality of human life;
9. Investigation of environmental pollution by heavy metals and other toxic elements coming from industrial manufacturing and development. The samples of soil, water, plant, aerosol have been collected in different areas of Vietnam for determination of toxic elements and radionuclides.
10. IAEA - RCA Project RAS/2/010 “ QA/QC for nuclear – related analytical methods”
11. Study and development of radiochemistry Nuclear Activation Analysis (RNAA) to determine trace elements in some purity materials (2002 – 2003).

B) Technology:

- Dalat Nuclear Reactor with thermal power 500 kW, it is a kind of research reactor, former TRIGA Mark II reactor. Contruction of this reactor is cluding:
  +) Two dry channels (7-1, 13-2) and a thermal column with pneumatic transfer systems for determination of elements which have the short lived isotopes (from 3 seconds to 30 minutes),
  +) One wet channel (1-4), a neutron trap and a rotary specimen rack in the graphite reflector consisting of 40 irradiation positions to irradiate for long lived isotopes (above 30 minuts).
- 8 multichannel analysers: MCA (Canbera) with AccuSpect program to accept spectrum and Gannas program to data process.
- 2 X-ray Fluorescenes and some physico-chemical analysers such as: Polarography, UV-VIS, AAS.

C) Analytical methods have been using at DNRI:

- Neutron Activation Analysis (INAA, RNAA, DNAA, PGNAA).
- X-Ray fluorescene.
- Related analytical methods: Polarography, Stripping Voltammetry, UV-VIS, AAS.

The sensitivity of these methods is very good to determine the content and composition of the elements in kinds of different samples such as: food, footstuffs, environmental... samples.

D) The typical specialities of sampling stations of this project are:

- HoChiMinh City is a biggest city of Vietnam with population of about five millions, Dongnai and Baria-Vungtau are also large cities and besides Ho Chi Minh City.
- HoChiMinh City, Dongnai and Baria-Vungtau are the biggest industrial cities of Vietnam where having many factories, processing zones that can made pollution of the living environment. Those are: refine of Iron, Tin, Petroleum; Production of battery; textile industry; make shoes; process food... These activities have been made contamination of air, water and in particular for foodstuffs such as: Vegetable (Salat, Celery, Tomato, Waterconvolvulus...); fresh-water fish (Carp, Snacke-head, Tench...); meat (Chicken, Duck, Pork, beef.).

The evaluation of concentration of toxic heavy metals (As, Hg, Se, Cu, Pb, Zn and Cd) in foodstuffs is very necessary because of the health impacts of these metals.

SCIENTIFIC SCOPE OF THE PROJECT

- Complete study for analytical procedures for As, Hg, Se, Cu, Pb, Zn and Cd content in foodstuffs.
- Estimating for contamination of heavy- toxic metals through foodstuffs at three collected cities.
- To exchange the experience in the applications of used analytical methods for studying of environmental pollution.

PROGRAMME OF WORK FOR 2002

- Collection of information related to selected Cities: HoChiMinh City, Dongnai and Baria-Vungtau.
- Selecting study and reference sampling sites within the study areas: air, water, soil (March-April).
- Designing experimental protocols, sampling program and anlytical procedures (April - May 2002).
- Sampling foodstuffs: Vegetable (Salat, Celery, Tomato, Waterconvolvulus...); fresh-water fish (Carp, Snacke-head, Tench...); meat (Chicken, Duck, Pork, beef...) about 60 samples (June-July, 2002).
- Analysis the collected samples for As, Hg, Se, Cu, Pb, Zn and Cd content (August-October, 2002).
- Evaluation of getting experimental results (November- December, 2002).

EXPECTED RESULTS FOR 2002

- Analytical procedures for As, Hg, Se, Cu, Pb, Zn and Cd content in foodstuffs.
- Preliminary Estimating for contamination of foodstuffs by heavy- toxic metals at collected cities.
- Collection of special sampling sites for next year work at three collected industrial Cities.

PROGRAMME OF WORK FOR 2003

- Sampling foodstuffs at special sites within the study areas: Vegetable (Salat, Celery, Tomato, Waterconvolvulus...); fresh-water fish (Carp, Snacke-head, Tench...); meat (Chicken, Duck, Pork, beef...).
- Analysis the collected samples for As, Hg, Se, Cu, Pb, Zn and Cd content.
- Examination and evaluation of getting experimental results.
- Total Estimating for contamination of foodstuffs by heavy- toxic metals at three collected industrial cities.

PART III:
COUNTRY REPORTS

IRON QUADRANGLE, BRAZIL: ASSESSMENT OF THE HEALTH IMPACT CAUSED BY MINING POLLUTANTS THROUGH THE CHAIN FOOD APPLYING NUCLEAR AND RELATED TECHNIQUES

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Abstract

Minas Gerais, a Brazilian state, is rich in mineral occurrences, mainly in the so-called Iron Quadrangle considered one of the richest mineral-bearing regions in the world. Many studies have been carried out indicating that mineral exploitation and correlated activities, including the 'garimpo' - small scale mining - are the main sources of metal contamination in water courses, river sediment and fish. According to these studies, there is strong evidence of contamination exactly in this area because of high concentrations of arsenic determined in surface water, sediment, soil and children's urine. Most investigations were concerned with determining only As and Hg in water, sediment and fish. No study to determine other important elements has been carried out so far. It is highly important to investigate contamination by other mining pollutants in different matrixes – mainly foodstuff – to determine how much human health could be affected by long-term exposure to such elements. The importance of this study consists in not only providing a scientific basis for better understanding of element transported from the pollutant source to the chain food, but also in revealing the health impact on the population. The people who live around the mining areas consume local water and grow vegetables, fruits and medicinal plants for their own use. It is relevant to state that there are no data about the contamination levels in such foodstuffs. The work plan during the first year will define the specific and strategic sampling sites. Water, soil, plants, food and airborne particulate matter will be collected in the regions both close to and far from the mining area. The samples will be prepared for analysis mainly by means of k_0-Instrumental Neutron Activation Analysis (k0-INAA).

1. SCIENTIFIC BACKGROUND AND SCOPE OF THE PROJECT

Minas Gerais, a Brazilian state, is rich in mineral occurrences, mainly in the Quadrilátero Ferrífero (Iron Quadrangle), considered one of the richest mineral-bearing regions in the world [1, 2, 3]. It is well known for the occurrence of iron and gold ores. Apart from extensive Fe ores, hydrothermal Au mineralization can be found in Archean Greenstone Belt formations occurring with other minerals in varying proportions.

Au metallogeny in the Iron Quadrangle has a complex history. In the Archean an interplay of volcanic exhalative sedimentary processes in Greenstone Belts produced and hosted sulfide-

rich Au deposits, like the Nova Lima Group. This group comprises Morro Velho, Raposos, Cuiabá, and other mining regions. Recycling processes caused Au permanency in the Iron Quadrangle from the Archean to Upper Proterozoic when deposits were formed through hydrothermal remobilization from the first-formed concentrations. The main gold mineralizations of the Iron Quadrangle are associated with the Nova Lima Group, which characterizes the Rio das Velhas (Das Velhas River) Supergroup as a Greenstone Belt.

Active Au mining has been going on in the Nova Lima area since the early 1700's at the famous Morro Velho Mine. The hydrothermal deposits contain several sulfides as major accompanying minerals in the form of pyrite, FeS_2, pyrrhotite, FeS, and arsenopyrite, FeAsS, in varying proportions. Other major Au deposits can be discerned within the volcanic sedimentary sequence of the Nova Lima group in Raposos. These deposits lie within the district of Nova Lima, 10 km from Belo Horizonte, the capital of Minas Gerais State, and drain into the Das Velhas River, the main source of water supply for Belo Horizonte and other cities. Associated with the exploitation and processing of the ores, several metals are released to the environment.

Many studies have been carried out showing that mineral exploitation and correlated activities, including 'garimpo' – small scale mining - are the main sources of metal contamination in water courses, river sediment and fish. According to these studies, there is strong evidence of contamination exactly in this area: high concentrations of arsenic in surface water, sediment, soil and children's urine were confirmed [2 – 11]. The gold mineralization is supposed to be the main source of elevated total As contents in surface water. Concerning children's urine, the source of contamination has not been determined. There are no available official studies by the health authorities to assess the impact of local As or other metal – enrichment on adults or children's health.

Most investigations were concerned with determining only As and Hg in water, sediment and fish. No study to determine other important elements has been carried out so far. It is highly important to investigate contamination by other mining pollutants in different matrixes – mainly foodstuff – to determine how much human health could be affected by long-term exposure to such elements.

The importance of this study consists in not only providing a scientific basis for better understanding of element transported from the polluted source to the chain food, but also in revealing the health impact on the population. The people who live around the mining areas consume local water and grow vegetables, fruits and medicinal plants for their own use. It is relevant to state that there are no data about the contamination levels in such foodstuffs.

Within specific scope of this Project, relevant research studies developed at CDTN include:

- "Workplace and occupational health: the first metal evaluation using nuclear and analytical techniques in the State of Minas Gerais – Brazil", Chief Scientific Investigator Maria Ângela de B. C. Menezes, in Regional Co-ordinated Research Programme on "Assessment of levels and health-effects of airborne particulate matter in mining, metal refining and metal working industries using nuclear and related analytical techniques", supported by IAEA, (BRA9473) - conclusion in March/2001 – carried out by CDTN/Radiochemical Laboratory [13 – 16];
- "Determination of methylmercury in fish tissue by gas chromatography" – performed by CDTN/Chemical Laboratory [5];
- "Hg speciation in water" – carried out by CDTN/Chemical Laboratory;

- "Study of the effectiveness of home-made teas in treatment of child dehydration and diarrhoea", project conducted together by CDTN/Radiochemical Laboratory and UFMG (Federal University of Minas Gerais);
- "Study of the composition of diabetic mother's milk" - CDTN/Radiochemical Laboratory and Escola de Medicina/UFMG (Medicine Faculty);
- "Study of the composition of the food produced and consumed in the State of Minas Gerais", CDTN/Radiochemical Laboratory;
- "Study of total Hg presence in gold mining fields in the State of Minas Gerais" – carried out by CDTN/Chemical Laboratory and FEAM-Fundação Estadual do Meio Ambiente (Environmental State Foundation);
- IAEA's CRP "The use of 99mTc as an absorbable tracer for studying the dynamics of fine sediments in suspension", BRA-10891 - carried out by Radiochemical Laboratory;
- "Ethnobotanic, morphoanatomic and chemical study of medicinal plants popularly used as diuretics", project conducted together by CDTN and Pontifícia Universidade Católica (Catholic University) - carried out by Radiochemical Laboratory;
- "Study of interactions involving water, sediment, soil, root and grass located in the Das Velhas River basin flooded areas" – carried out by CDTN/Radiochemical Laboratory and Department of Nuclear Engineering/UFMG;
- "Hg contamination in "garimpos" in Minas Gerais State: environment and health impacts" - carried out by CDTN/Chemical Laboratory and FEAM [5].

Other projects involving international partners are:

- Distribution, speciation and transport of Hg, As and Sb in sediment, water and biota released to the environment by means of natural and anthropogenic processes" (Doctorate Thesis) – part of an international project number 910018/00-6 CNPq/DLR. It is being developed together by CDTN/Chemical and Radiochemical Laboratories, the Geochemical Research Group at the Department of Geology/UFOP, Brazil, and the UFZ - Department for Inland Water Research in Magdeburg, Germany.

The present project - Iron Quadrangle, Brazil: assessment of the health impact caused by mining pollutants through the chain food applying nuclear and related techniques - will be developed by CDTN and main partners: Departamento de Geologia (Geological Department) - Federal University of Ouro Preto, FEAM - Fundação Estadual do Meio Ambiente (Environmental State Foundation) and Secretaria Municipal de Saúde (Municipal Health Secretary).

The Fundação Estadual do Meio Ambiente (Environment State Foundation) is responsible for environment policies in Minas Gerais State inclusive of industrial and mining activities. This Foundation is involved not only with improvement and prevention strategies, but also research related to pollution and the quality of soil, water and air. One of its important tasks is to give support to cities on the establishment and development of management systems in order to prevent and correct environmental pollution and degradation.

2. METHODS

One of the tasks throughout this first year is to choose specific and representative sites to collect soil, plant, sediment and other samples, during the dry and wet seasons, besides biological human samples such as nail and hair. The usual sampling, preparation and storage methods for each matrix will be applied.

The main technique to determine the elemental concentration will be the neutron activation analysis involving the k_0-INAA and conventional analysis with or without radiochemical procedures. Irradiations will be performed in the TRIGA MARK I IPR-R1 reactor. Other techniques available at CDTN will be also applied if needed including ICP-AES, AAS and XRF.

CDTN has some experience in the specific topic of speciation of elements including Hg to determine its species in water. Some methods are being developed aiming at the same Hg speciation in sediment as well as speciation of As and Sb in water. All these experiments are being carried out using non-nuclear methods, even though nuclear techniques are available at CDTN. This project is an excellent opportunity to encourage the application of nuclear techniques in such studies. Depending on the element, methods using radiotracers will be applied.

Several certified reference materials will be analysed together with the samples in order to verify the accuracy of the analytical methods. For instance, IAEA/Soil-7 (International Atomic Energy Agency), GBW 08303-Polluted Farmland Soil (Beijing Municipal Environmental Monitoring Centre), BCR-176-Trace Element in a City Waste Incineration Ash (Community Bureau of Reference, Commission of the European Communities), GXR-3, GXR-6 (United States Geological Survey) and GBW 09101-Human Hair (Shanghai Institute of Nuclear Research). To analyse samples in replicate will be another method to verify the reproducibility of the results. To participate in intercomparison programmes will be a useful way to check the methods applied. The software SYSTAT® 7.0 for Windows® will be used in the determination of elemental and matrices correlations and other statistical calculations.

3. RESULTS AND DISCUSSION

The Ecological Area of Tripuí is geologically inserted in the Iron Quadrangle. This ecological reserve is close to Ouro Preto City and does not present any mineral occurrence of economic interest. Some sediment samples were collected from small rivers that cross the Tripuí in order to assess the elemental concentrations in this region. This park was chosen for sampling because it is located in the same geological area as the Nova Lima region, where this project is intended to be developed. On the other hand, it is far enough from the areas where there are gold mining activities and is not supposed to be affected by such activity.

Some results for As and Sb in sediment samples obtained by the k0-method are presented in Table I. The same samples were analysed by the Radiochemical Laboratory at CDTN, RL/CDTN, and by Laboratory for Radiochemistry and Radioecology of the Jožef Stefan Institute, Ljubljana, LRR/JSI [17, 18]. The accuracy of the results was checked by the use of the Certified Reference Material IAEA/SOIL-7 (Table 1). Good agreement between the two laboratories for the investigated elements was obtained. The results show that all Sb concentrations are higher than the Reference Certified Material IAEA/Soil 7. For As, some concentrations are also higher.

TABLE I: COMPARISON OF RESULTS FOR AS AND SB OBTAINED BY K0-METHOD IN TWO LABORATORIES FOR SOME SEDIMENT SAMPLES FROM TRIPUÍ ECOLOGICAL AREA AND FOR IAEA SOIL-7:

Sample		As ($\mu g.g^{-1}$)	Sb ($\mu g.g^{-1}$)
IAEA/SOIL-7			
	Certified	13.4 ± 0.9	1.7 ± 0.2
RL/CDTN	Experimental	12 ± 1	1.8 ± 0.4
LRR/JSI	Experimental	14.2 ± 0.6	1.81 ± 0.08
S-1			
RL/CDTN		25 ± 1	4.8 ± 0.2
LRR/JSI		24.0 ± 1.0	4.48 ± 0.18
S-2			
RL/CDTN		25 ± 3	11.5 ± 0.3
LRR/JSI		24.1 ± 1.0	8.95 ± 0.36
S-3			
RL/CDTN		10 ± 2	205 ± 5
LRR/JSI		8.62 ± 0.35	215 ± 10
S-4			
RL/CDTN		12 ± 1	22 ± 1
LRR/JSI		12.6 ± 0.6	20.2 ± 0.9

4. PLANS FOR FUTURE WORK

1. To choose specific and representative sites to collect soil, plant, lichen and sediment samples, during the dry and wet seasons,
2. To harmonize protocols for collection of foods,
3. To collect food that is grown in this area and consumed by the local population,
4. To collect soil and plants far from this area (background levels) in order to compare the concentrations of pollutants,
5. To collect food that is grown far from this area,
6. To prepare the samples to be analyzed,
7. To begin elemental concentration determinations in the samples,
8. Depending on the metal concentration results in the samples analysed, to collect biological indicators such as hair and nails from that population in order to assess the level of exposure to pollutants, as well as to collect biomonitor samples from a comparative group formed of individuals not exposed to the same environment and that do not consume the same foodstuffs,
9. To begin elemental concentration determinations in the biological samples,
10. To carry out correlation studies between the food concentrations indices of exposure and health,

11. To select toxic elements for study of bioavailability and
12. To perform speciation studies using tracer methods involving stable and radioactive isotopes.

In the first year of the project, the first 7 items should be accomplished.

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STUDIES OF ORGANOHALOGEN CONTAMINATION OF FISH USING NEUTRON ACTIVATION, LIQUID CHROMATOGRAPHY, NUCLEAR MAGNETIC RESONANCE, AND MASS SPECTROMETRIC TECHNIQUES

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Abstract

Extractable organohalogens (EOX) are organic compounds that contain chlorine, bromine, and/or iodine, which can be obtained by liquid/liquid or liquid/solid extraction. These are generally referred to as extractable organochlorine (EOCl), extractable organobromine (EOBr), and extractable organoiodine (EOI) compounds. A brief literature survey is given here describing the problem. Appropriate extraction methods will be developed in this study for EOX from fish samples. Neutron activation analysis methods will be developed for the quantitative determination of the halides in the extracted fractions. A total quality management plan will be designed in this project to obtain reliable results. Attempts will be made to prepare a reference material for EOX.

1. SCIENTIFIC BACKGROUND AND SCOPE OF THE PROJECT

1.1. Scientific Background

The marine environment has long been a dumping ground for a variety of wastes of both an organic (e.g. sewage) and an industrial (e.g. pulp mill effluent) nature. In addition to these direct means of input, there is a strong evidence to support the theory proposed in the early 1970's that significant amounts of persistent organopollutants (POP) are being deposited into low-temperature regions from terrestrial sources by a variety of short- and long-range atmospheric (1-3) and oceanic transport mechanisms (4). It has also been suggested that the oceanic bodies are themselves a sink because of a tendency for POP to partition from air to water and to suspended particulate found in the water (2,4). The polar regions are even more susceptible to this mechanism of input; in addition to the high ratio of ocean to land in the polar regions, the lower temperatures make the deposition of POP even more favourable (as the rate of evaporation is lower than that of condensation) and the rate of decomposition slower (5-7). The levels of the compounds deposited in this way may be high because they become concentrated in the polar regions which are small in area relative to the temperate and tropical regions. Wania and Mackay (8) have suggested that global fractionation of volatile compounds is also occurring during the atmospheric transport. In this process, different POP migrate at different rates as they move from the lower latitudes to the poles. As a result, a gradient develops in which one finds the more volatile compounds at higher latitudes than less volatile compounds.

A major component of POP is the group of compounds known as extractable organohalogens (EOX), which is primarily made up of extractable organochlorines (EOCl) and to a smaller degree also includes extractable organobromine (EOBr) and extractable organoiodine (EOI) compounds. In studies relating levels of known compounds to the total EOCl, known compounds comprised only 0.1 to 16% of the total amount of EOCl in fish tissues on a weight

basis (9). Many of the identified compounds that comprise EOCl are well known anthropogenics of which a significant number have been targeted by regulatory agencies throughout the world. Constituent compounds include, but are not limited to chlorinated pesticides such as dichlorodiphenyltrichloroethane and its metabolites (ΣDDTs), hexachloro-cyclohexanes (ΣHCHs), and chlordane compounds (ΣCHLs), as well as polychlorinated biphenyls (PCBs), polychlorinated dibenzo-p-dioxins (PCDDs), and polychlorinated dibenzofurans (PCDFs). In addition to the thousands of known anthropogenic compounds that may be present in a given extract there are also more than 2,000 halogenated natural products that may also be present (10). There are also certain brominated compounds that are of interest such as polybrominated biphenyls, PBBs (11,12). Many of the remaining organically bound halogens have yet to be identified. The fact that they have not been identified does not make them irrelevant, the levels are not trivial and so they may very well have important health implications. It has been observed that these unknown components tend to be found in the higher molecular weight fractions usually associated with biological molecules such as lipids (9,13).

In 1975, Lunde and coworkers (14,15) used neutron activation analysis (NAA) to measure total EOCl content of some marine fish oils and found that their levels were 1.5 to 5 times higher than that of PCBs or DDTs determined by gas chromatography (GC) and that 5 to 50% of the chlorine remained after treatment with concentrated sulphuric acid (15). Clean-up of samples with sulphuric acid prior to analysis by GC is a common practice and is known to provide good recoveries of PCBs, DDT, HCH, lindane, heptachlor and toxaphene (16) and therefore provides a good means of isolating these chemically persistent compounds as a group. It has also been reported in a Canadian project by Newsome, Chatt and their coworkers (13) that between 74% and 99% of EOCl in several species of fish cannot be accounted for by PCBs and chlorinated pesticides. In a literature review, Boyd (17) concluded that about 85% of chlorine in fish and 95% of chlorine in the sediments cannot be accounted for by known organo-chlorine compounds.

1.2. Our Previous Studies

We have been doing research on EOX over the last 10 years or so. Our first study on this subject (13) was supported by Health Canada research contracts (1990-93), followed by the Research Contracts (1994-95) and Research Agreements (1995-98) from the North Atlantic Fisheries Centre (NAFC, DFO) of the Department of Fisheries and Oceans (DFO), and lately by a Strategic Grant (1998-01) and by a Research Grant (1998-02, 2002-06) from the Natural Sciences and Engineering Research Council (NSERC) of Canada. The overall objectives of the first two projects were to evaluate the potential of NAA for the simultaneous and quantitative measurements of EOCl, EOBr and EOI, and to assess the extent of contamination of fish from the Great Lakes (Health Canada project) and of marine mammals (DFO project). In the DFO project, we also investigated the distribution of EOX within the tissues of individual beluga whales from the Gulf of St. Lawrence and the Arctic Ocean, and compared the distribution in tissues of belugas from these two very different environments (18-20).

Having established the applicability of NAA for the determination of EOX, we initiated a joint project with DFO to determine the tissue distribution of EOCl and EOBr in shrimp and then cod fish. Groundfish accounted for 1/3 of the $1.12 billion landed value of fish on Canada's Atlantic coast in 1994 (21). Cod were the most important of the groundfish species fished. Cod fish, when available, is consumed extensively by both North American and European population groups. The demise of the cod stocks was a contentious and unresolved issue between Canada and EU, but whatever the major factors were it is prudent to consider

the possibility of the role of EOX. There are large variations in egg viability of cod and the determinants of egg viability are presently unknown (22). Tissues, eggs and bile of adult Atlantic cod raised in captivity and fed natural food with no additional halogenated compounds of any kind were analyzed by NAA. There was a large difference in the tissue distributions of EOCl and EOBr. The highest concentrations of EOCl were found in the brain, testes, and ovaries of cod. In the NSERC Strategic Grant (1998-01), we concentrated our research on the characterization of EOCl in cod ovaries. We have developed gel permeation chromatography (GPC), reversed-phase chromatography (RPC), NMR, and various types of mass spectrometry methods for the separation and identification of at least a couple of new EOCl compounds in cod ovaries.

1.3. Overall Scope of the Project

The long-range objective of this project is to characterize the extractable organohalogen species in cod lipids. We will also carry out a survey of EOX in various fish samples purchased from markets across Canada and estimate the average daily dietary intakes (ADDI) of EOX.

The specific objectives are as follows. We propose to systematically evaluate the relative extraction efficiencies of single and mixture of solvents for the bulk extraction of EOCl, EOBr, and EOI compounds. We will then extract a large amount of cod brain, testes, and ovaries using the most efficient solvent system to provide pools of lipid for the fractionation of EOX compounds. We will develop NAA methods using short-lived nuclides for the determination of chlorine and bromine. We will design a quality assurance program for the reliable determination of chlorine, bromine, and iodine at ppb to ppm levels. We will comprehensively characterize the cod brain, testesticular and ovarian extracts by fractionation using semipermeable membrane dialysis in organic solvents followed by the quantitative determination of the halogens by NAA. We will characterize the EOX compounds using High-resolution gel permeation chromatography (HPLC), ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectroscopy, Fourier transform infra-red (FTIR) spectroscopy, various mass spectrometric (MS) techniques, and NAA.

2. WORK PLAN FOR 2002-03

Since both parties have signed the Research Agreement for the CRP very recently, there are no experimental details on the project that can be reported here. Hence, the work plan for 2002-03 is described below.

2.1. Extraction Efficiencies of Solvents

There was not much information available in the literature comparing the relative extraction efficiencies of various solvents for EOX when we started our original work in this field several years ago. Our experience shows that a single solvent system for the extraction of total lipids is not particularly successful because no suitable polarity can be achieved with any single solvent. In our past studies, we have used a mixture of acetone and cyclohexane for the extraction of EOX from shrimp. Other investigators also used this mixture or an isopropanol-acetone mixture. No systematic study on the extraction efficiency of EOX in a range of solvents with different polarities has yet been reported. We will carry out such a study and develop a simple and efficient method for the extraction of EOX from cod in this project during the coming year. We plan to measure EOX levels in other fish species in future years.

It may very well be necessary to examine the extraction procedure with each species and modify as required.

A complete removal of any residual halide ions from the organic phase of the solvent extraction system is essential for the accurate measurement of total EOX by most analytical methods. The washing process must be effective in removing all inorganic halides, but at the same time it should not cause any loss of organohalogens from the organic phase. In the past, we have used ammonium phosphate, sodium nitrate, and sulfuric acid in shrimp. We concluded that three washings with ammonium phosphate and sodium nitrate were the efficient way to remove residual halide ions. From another set of experiments, we selected anhydrous sodium sulfate to remove water from the organic extracts. We will use similar experiments to obtain the maximum removal of the residual halide ions from the cod and other fish species.

2.2. Neutron Activation Analysis Methods

The halogen levels in the extracts will be determined by neutron activation analysis (NAA), using the ^{38}Cl, ^{80}Br, ^{128}I nuclides of chlorine, bromine and iodine, respectively. We will optimize the irradiation-decay-counting times to obtain the maximum sensitivity for the simultaneous determination of three elements. It may be possible to use the short-lived nuclides of bromine and chlorine (^{79}mBr and ^{38}mCl) which will allow for higher throughput of samples. Otherwise, we will use the medium-lived (with half-lives from minutes to hours) nuclides. We will use both conventional and Compton suppression gamma-ray spectrometry to achieve no interference and low detection limits. We will use the Dalhousie University SLOWPOKE-2 reactor and its associated facilities for NAA.

2.3. Total Quality Management Plan

The term quality assurance (QA) should figure prominently in all analytical measurements. All activities involving sample material can affect the final result. To effectively manage analysis, a total quality management plan (TQMP) will be employed. This plan will cover protocols for all critical steps from pre-sampling factors to the total uncertainty budget of the results reported, e.g. site selection, sample selection and collection, transport, preservation, receiving, analysis, data processing, proficiency testing, etc. Once the TQMP has been established then the task of quality control (QC) at each of the steps will be undertaken. Both internal and external quality assessments will be carried out using elemental comparator standards and certified reference materials, respectively. We will initiate this program in the first year of the project and may continue to the second year, if needed.

2.4. Possible Preparation of a Reference Material

At present, no reference material or certified reference material is available for EOX. It might well be possible to prepare a small amount of such a material. If funding becomes available, serious consideration will be given to this objective.

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EVALUATION OF HALOGEN ELEMENT LEVEL IN FOODSTUFFS CONTAMINATED BY PESTICIDES AND HERBICIDES IN BEIJING AND ITS HEALTH IMPACT ON CHILDREN BY NUCLEAR ANALYTICAL AND RELATED TECHNIQUES

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Abstract

Several monitoring programmes for chlorinated pesticides and their metabolites and residues have been conducted on a large scale to evaluate actual food contamination in China. A more recent programme (1996-2000), i.e. Food Pollution and Its Control in Beijing indicated that the chlorinated pesticides contamination in food is a serious problem, because of their extensive use from 50s to late 60s. In the framework of this CRP organized by IAEA, we are focused on evaluation the level of halogen elements and their organic species in foodstuffs contaminated by pesticides and herbicides using neutron activation analysis combined with organic extraction technique. The preliminary results show that the extractable organahalide concentrations in Chinese milk samples are quite high. The highest reaches 615.5 ng/ml. Their health effects on children will be evaluated via the analysis of the contents of organohalide compounds in hair samples and clinical diagnostics. The activities completed or being implemented related to this project at present and the working plan for next two years are outlined in this report. Other related information will be provided as well.

1. SCIENTIFIC BACKGROUND AND SCOPE OF THE PROJECT

The halogen elements (F, Cl, Br and I), when they exist as organohalide compounds (e.g. chlorinated pesticides, polychlorinated biphenyls and dibenzo-p-dioxins/dibenzofurans, etc.), have long been known as persistent environmental pollutants [1,2]. Their toxic effects are generally undisputed. Although human exposure to this type of pollutant comes from air, water and diet, many studies have shown that about 95 % of organochlorine compounds intake are estimated to come from food and that their intake by the general population depends greatly on the geographical area and food structure.

It is reported that about 4.9 million tons of HCHs and 0.4 millions DDTs had been used from 1960 to 1983 in China [3]. Although the use of these pesticides and herbicides in agriculture has been officially banned since 1983, their persistent metabolites and residues still exist in the environment. Furthermore, it is estimated that about 1000 tons lindane and 5000 tons DDTs are manufactured annually for export and sanitary purposes in China [4]. Part of them is still being used in forestry and the control of ectoparasites of livestock. More seriously, in some regions of China the phenomenon of the illegal production and use of DDTs and HCHs in agriculture is not rare at present. All the above factors result in the pollution of air, water, soil, plant, animal and finally foodstuffs by organohalide compounds. The recent survey reports that HCHs and DDTs and their metabolites are at the levels of 0.1 to 1.1 ng/ml in river water [5] and their contents in soil can reach as high as 455 ng/g [6]. These pesticides and

herbicides in the environment can be finally accumulated and concentrated in milk and other foodstuffs through the food chain.

Several monitoring programs for chlorinated pesticides residues have been conducted on a large scale to evaluate actual food contamination level in China. A more recent monitoring program (a Major Project organized by State Science and Technology Ministry of China in the Ninth Five-Year Program (1996-2000) -- Food Pollution and Its Control in Beijing) indicated that the chlorinated pesticide contamination in food is a serious problem, mainly attributed to their extensive use from 50s to late 80s. A preliminary result obtained by nuclear analytical technique in our laboratory indicated that the concentration of organohalide compounds in the dairy products in Beijing was quite high with the maximum of 615.5 ng/ml [7]. However, up to now little information about the pollution status of organohalide compounds in various foods and their impact on human health, especially on children – a sensitive population, is available.

It should be emphasized that the traditional analytical techniques, like gas chromatography (GC), GC-mass spectroscopy (GC-MS) and high performance liquid chromatography (HPLC), etc., can not reflect the overall pollution status of organohalide compounds. Many reports have indicated that the contents of organochlorine compounds given by GC only amounted to about 10 - 20 % of the actual contents [8-14]. Due to its advantageous nuclear properties of Cl, Br and I, neutron activation analysis is able to easily evaluate the whole pollution status of the halogen elements and their organic species via the following nuclear activation reactions Cl-37 (n,γ)Cl-38 ($t_{1/2}$=37.24 min, Eγ=1642 keV), Br-79 (n,γ) Br-80 (17.6 min, 617 keV) and I-127 (n,γ) I-128 (25.0 min, 443 keV), when it combines the organic extraction techniques. Lunde et al. measured the contents of extractable organochlorines in some sea fish oils by NAA and found that their levels were 1.5 to 5 times higher than those of PCBs and DDTs determined by gas chromatography [14]. Chatt and his coworkers evaluated the potentials of NAA for the simultaneous and quantitative measurements of extractable organohalides and assessed the extent of contamination of marine mammals by these pollutants [8,13]. They pointed that about 74% to 99% of extractable organochlorines in several species of fish were not able to be accounted for by PCBs and chlorinated pesticides. In a literature review, Boyd concluded that about 85% of chlorine in fish and 95% of chlorine in the sediments could not be attributed to known organochlorines [10]. The combination of NAA with organic separation and identification techniques makes it possible to solve the above problems. A systematic literature survey states that little work have been done on study the organohalides in foodstuffs and human tissues by the hybrid NAA technique.

In the framework of this CRP organized by IAEA, the emphasis of our project lies in 3 aspects: (1) Establishment, improvement and validation of the neutron activation method to analyze the organohalide compounds in foodstuffs and human hair in combination with organic extraction; (2) Monitoring, evaluation and identification of the contamination levels by halogen element, especially organohalogens, in foodstuffs taken from the Beijing supermarkets by NAA, GC-MS and HPLC; and (3) Evaluation of the health impact of organohalide compounds on children.

2. METHODS

2.1. Sampling

2.1.1. Food samples

The main food samples consumed daily by local people in Beijing, including milk, dairy products, meat, fish, edible oils and others, in which the concentrations of organohalogens compounds are likely high, will be collected from Beijing supermarkets. Over 100 milk samples have been collected monthly during the period between February and October of 2001. The milk was not restricted to local sources, also from other provinces. The milk samples were immediately analyzed after collection without storing in laboratory.

2.1.2. Biological samples

Human hair will be collected from about 50 preschool children aged from 4 to 6 from two nurseries, one in the urban and another in the suburb district of Beijing.

2.2. Standards

2.2.1. Chemical standards for Cl, Br and I

KCl (purity ≥ 99.95 %, Beijing Chemical Company), KBr (purity ≥ 99.95 %, Beijing Chemical Reagent Company) and KI (purity ≥ 99.99 %, North China Special Reagent Development Centre) were dissolved in bidistilled water and then their standard solutions with the concentrations of 0.946, 0.6132 and 0.464 μg/ml for Cl, Br and I, respectively, were prepared for use.

2.2.2. Chemical standards for organohalide compounds

Pesticide standards--α,β,γ and δ-HCH, heptachlor, aldrin, heptachlor epoxide, chlordan, 4.4'-DDE, 4.4'-DDD, ,4.4'-DDT were purchased from Sulpelco, USA. Working standard solutions were prepared by dissolving the appropriate amount of organochlorine pesticide with distilled isooctane.

2.3. Analysis

2.3.1. Neutron activation analysis

It will be applied to analyze the collected samples for the determination of organohalogens compounds via Cl-37 (n,γ) Cl-38, Br-79 (n,γ) Br-80 and I-127(n,γ) I-128, which are the short-lived nuclides and are easily determined. NAA will be performed at the Miniature Neutron Source Reactor equipped by pneumatic system. The preliminary experimental condition for NAA was 15 min, 2 min and 15 min for irradiation, decay and counting, respectively. An elaborated NAA scheme is being developed to improve the detection limits for Cl, Br and I.

2.3.2. Organic extraction procedure

The extraction procedure for organochlorine pesticides in milk used in this work is similar to that described by Wong and Lee [15]. 100 ml milk was put into a 500 ml separatory funnel. 200 ml acetone-cyclohexane mixture (1:1, v/v) was added in the funnel, shaken for 5 min and

then centrifuged at 3000 rpm for 10 min. The aqueous phase was repeatedly extracted twice. 3 portions of the organic phase were incorporated together, which was first cleaned up with 10 ml concentrated sulfuric acid, then washed 3 times with 1 % KNO_3, and finally washed by 2 % sodium sulfate solution. The purified organic extract was transferred to a flask and concentrated to about 2 ml by a rotary evaporator. 1 ml was analyzed by NAA and another 1 ml for gas chromatography. The extraction procedures for other samples are being established.

2.3.3. Gas chromatography

The GC analyses were carried out by a Varian 3800 gas chromatograph equipped with a ^{63}Ni electron capture detector, using a fused silica capillary column (CP-Sil 8 CB 50 m×0.25 mm i.d., with 0.12 μm film thickness). Operation conditions: injection temperature 250º; column (temperature programming) 130º for 5 min, then change to 220º with 20º/min, finally change to 270º with 4º/min and hold at 270º for 10 min; detector temperature 300º; oxygen-free nitrogen (99.999%) as carrier and make up gas.

2.4. Validation of analytical method

The hybrid technique of NAA combined with organic extraction for determination of total organohalide compounds in foodstuffs and biological samples has been or will be validated by the following 4 methods.

2.4.1. Spiked standard samples

α,β,γ and δ-HCH, heptachlor, aldrin, heptachlor epoxide, chlordan, 4.4'-DDE, 4.4'-DDD, ,4.4'-DDT are spiked into milk and other food samples to determine the chemical recovery and to check the reliability and reproducibility of the procedure.

2.4.2. Certified reference materials or standard reference materials

In our laboratory the available environmental and biological reference materials for the determination of total Cl, Br and I are GBW 08059 non-fat milk powder, GBW 08551 pork liver, GBW 09101 and 07601 human hair, etc. However, it is still lack of their organic species reference materials suitable for this study.

2.4.3. Intercomparison of two independent methods

Two or more independent analytical techniques are used for cross check of the analytical quality, which are NAA, GC-MS and HPLC.

2.4.4. External analytical quality assurance

An effort to perform the interlaboratory comparison will be made, e.g. with A. Chatt.

2.5. Evaluation of intake amount of organohalogen compounds and their impact on children' health

The intake amount of organohalide compounds will be evaluated by total diet survey for 50 preschool children in two Beijing nurseries. The health impact of organohalide compounds on children will be studied by analysis of their contents in hairs, which will be statistically

processed and compared with the intake amount, and clinical diagnostics of children' health status.

3. RESULTS AND DISCUSSION

3.1. Organic extraction recovery

One mililitre HCHs and DDTs mixture standard solution with two different concentrations was added in 100 ml milk samples to examine the recovery of the organic extraction procedure. The experimental method is described in Section 2.2.2. The determination method is gas chromatography. The recovery results for 8 isomers of HCHs and DDTs are listed in Table 1.

From the data in Table 1 it can be seen that the recovery of the organic extraction is between 83 % and 105 %, which is satisfactory and also falls in the range of 100 + 40 % set by Environmental Protection Agency, USA, for organochlorine pesticides. The variation coefficients are generally below 10 %, which is also acceptable.

3.2. Detection limits for analysis of halogen elements by NAA

According to the experimental conditions of NAA described in Section 2.2.1, the detection limits for Cl, Br and I in milk sample are 55 ng, 8 ng and 4 ng, respectively. It is possible to improve the detection limits if the irradiation time and counting time are extended. Further more, if using the more short –lived radioactive nuclides of Br-79m (4.86 s) and Cl-36m (715 ms), the detection limits could be further improved. For this purpose, the pseudo-cyclic NAA is needed.

TABLE I: THE RECOVERY OF THE ORGANIC EXTRACTION FOR ORGANOHALIDE COMPOUNDS DETERMINED BY GC OF SPIKED MILK

Pesticide	Added concentration mg/L	Y %	S %	Added concentration mg/L	Y %	S %
α-666	0.96	87	4.4	0.096	93	5.3
β-666	1.32	101	5.2	0.132	85	4.0
ν-666	0.84	88	2.3	0.084	92	2.9
δ-666	1.06	87	6.1	0.106	86	8.0
pp'-DDE	0.36	105	11.5	0.036	86	6.0
pp'-DDD	0.56	104	10.5	0.056	105	4.0
op'-DDT	0.48	94	10.6	0.048	87	3.5
pp'-DDT	0.64	99	10.0	0.064	83	2.9

Notes: 1.The analytical number is 10; 2. Y means the recovery; 3. S means the variation coefficient.

3.3. Preliminary results for organohalide compounds in milk

The concentrations of the extractable organohalide compounds in 33 milk samples from 7 different regions of China determined by NAA combined with the organic extraction method are listed in Table 2. It can be seen from the concentrations of organohalide compounds in Table 2 that the regional difference is evident, from 615.5 μg/L to below the detection limits. Generally, the levels of the organohalide compounds in milk are increasing from north to south. This evident geographical feature is likely attributed to many factors, e.g. climate, soil composition, biomass and, more importantly, industrialized level. The middle China is a developed region in comparison with north China. The use of pesticides and herbicides is also more popular than north China. The residues and metabolites of such persistent compounds may exist for long time in the environment, which contaminate the milk and other foodstuffs. Such a high level of these compounds implies a potential risk to human health, especially to sensitive population, because of their lipophilic property that results in the accumulation in human tissues.

3.4. Publication

One paper about the evaluation of concentrations of halogen element levels in milk samples by NAA has been accepted and another one on organochlorine compounds in milk submitted.

TABLE II: THE CONCENTRATIONS OF THE ORGANOHALIDE COMPOUNDS IN 33 MILK SAMPLES FROM 7 DIFFERENT REGIONS OF CHINA DETERMINED BY NAA AND ORGANIC EXTRACTION (MG/L)

No.	Production region	Organo-chlorine	Organo-bromine	Organo-iodine
1	Northeast China 1	-	-	-
2	Northeast China 2	33.4	-	0.81
3	North China 1	27.9	0.36	2.1
4	North China 2	70.9	-	0.19
5	Middle China 1	72.7	-	0.51
6	Middle China 2	239.8	0.71	0.46
7	Middle China 3	615.5	2.8	2.7

Notes : 1. The sample number for all regions is 4, except 9 for Middle China 3; 2. The concentrations of organohalide compounds are expressed as Cl, Br and I

4. PLANS FOR FUTURE WORK

In the framework of this CRP the working plan for next year is following:

- Establishing and validating a hyphenated method of neutron activation analysis with organic extraction to determine organohalide compounds in foodstuffs;
- Collecting representative food samples in Beijing area, including milk, dairy products, meat, fish and egg, etc.
- Collecting the relevant information on typical food consumption, and production and use of pesticides and herbicides in the studied area.

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USE OF NAA, PAA, PIXE AND PIGE IN STUDYING HUMAN EXPOSURE TO TOXIC AND OTHER ELEMENTS CONSUMED THROUGH FOODSTUFFS CONTAMINATED BY INDUSTRIAL ACTIVITIES

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Abstract

Soils, agricultural crops, vegetables and fruits grown in a region polluted mainly with the rare earth elements, Th, U, probably F and other elements will be assayed using neutron activation analysis (NAA), photon activation analysis (PAA), proton induced X-ray emission and proton induced gamma-emission (PIGE) to get a deeper insight into the transfer of the pollutants into the food chain.

1. SCIENTIFIC BACKGROUND AND SCOPE OF THE PROJECT

Pollution of the environment by industrial activities presents a significant health risk to man. One of the possible pathways of pollutants from the environment to human organisms is the consumption of foodstuffs polluted by industrial activities. It is well known that many industries discharge gaseous, liquid, and solid wastes containing toxic elements into various compartments of the environment, including agricultural land. Thus, toxic elements may enter the food chain, depending on their bioavailabilty. A great deal of data exists on the response to incident acute exposure, but there is little or no information on the effects of chronic exposure to low amounts of many toxic elements. This makes our understanding of the specific fate of some elements in humans incomplete. Since the toxic elements may be present in crops and foodstuffs in a wide range of concentrations from minor to ultra-trace levels, very sensitive analytical techniques with a wide dynamic range should be used for their determination. Nuclear and related techniques, such as neutron activation analysis (NAA), particle induced X-ray emission (PIXE), etc. are uniquely suited for the determination of most of the toxic elements due to many favourable features of these techniques, and namely NAA may be used to verify the accuracy of other analytical techniques.

There are various industries in the Czech Republic that are potential sources of environmental pollution. Several years ago, the Czech Republic joined an European programme of environmental monitoring (part of the programme UN/ECE ICP Vegetation – Heavy Metals) that is based on analysis of mosses, mostly Pleurozium Schreberi, as recognized biomonitors of atmospheric pollution. The methodology of the European bryomonitoring programme has been published [1], as well as the first results obtained in the Czech Republic [2,3].

Moss samples are collected in about 200 localities all around the country employing a grid of approximately 20 x 20 km. Collection of the samples and their analysis using inductively coupled plasma mass spectrometry (ICP-MS) is performed by the Laboratory of Trace Elements of the Research Institute of Ornamental Gardening in Průhonice. The elements followed include Ag, Al, As, Ba, Be, Bi, Cd, Ce, Co, Cr, Cs, Cu, Fe, Ga, In, La, Li, Mn, Mo, Ni, Pb, Pr, Rb, S, Sb, Sc, Se, Sr, Th, Tl, U, V, Y and Zn. In addition, Hg is assayed using a

single purpose atomic absorption spectrometer AMA-256 (Altec, Czech Republic) with built-in preconcetration of Hg by amalgamation. Results of analyses are graphically presented in the form of maps with colour-scaled presented element contents. The density of sampling location makes it possible to follow not only long-range transport of pollutants within Europe, but also to discover local pollution sources and their impacts.

Four main polluted regions have been identified in the Czech Republic from the results of the above monitoring. One is in north Bohemia where elevated concentrations of the elements Al, As, Cr, Cu, Hg, Mn, Ni, S, Se, Sr, Zn (and to a lesser extent Be, Ce, Co, Fe, Ga, La, and Li) are found. The well-known sources of this pollution are: (i) burning of lignite in several power plants; (ii) discharges from several types of chemical industry that are located in this region. The second polluted region is in South-West Bohemia, rather localized around a non-ferrous metallurgical plant. This region is polluted mainly with the elements Bi, In, Pb, Sb, Sn (and to a lesser extent also with Ag, Cd, Mo and Zn). The major ferrous-metallurgy plants situated in north Moravia cause pollution with the elements Ag, Cd, Fe, Mo (and to a lesser extent with In and Pb) in this region. The level of pollution in north Bohemia and Moravia has significantly decreased due after the installation of desulphatation units at most lignite-fired power plants and other pollution abatement strategies employed in the last 5-10 years. However, formerly unidentified pollution has been discovered in south Moravia, where elevated contents of the elements Ba, Be, Co, Ga, U, Th, Y and several rare earth elements, such as Ce, La, Pr, were found. The most probable reason of pollution is due to discharges from a phosphate-fertilizer production plant where imported phosphates and/or apatites are treated. Figs. 1-5 show examples of element pollution maps with “hot spots” for selected elements in the above regions. Since south Moravia is one of the most important agricultural regions of the Czech Republic, it has been decided to carry out the study of pollution of agricultural crops and the transfer of the pollutants into the food chain, namely into locally produced foodstuffs, in this region.

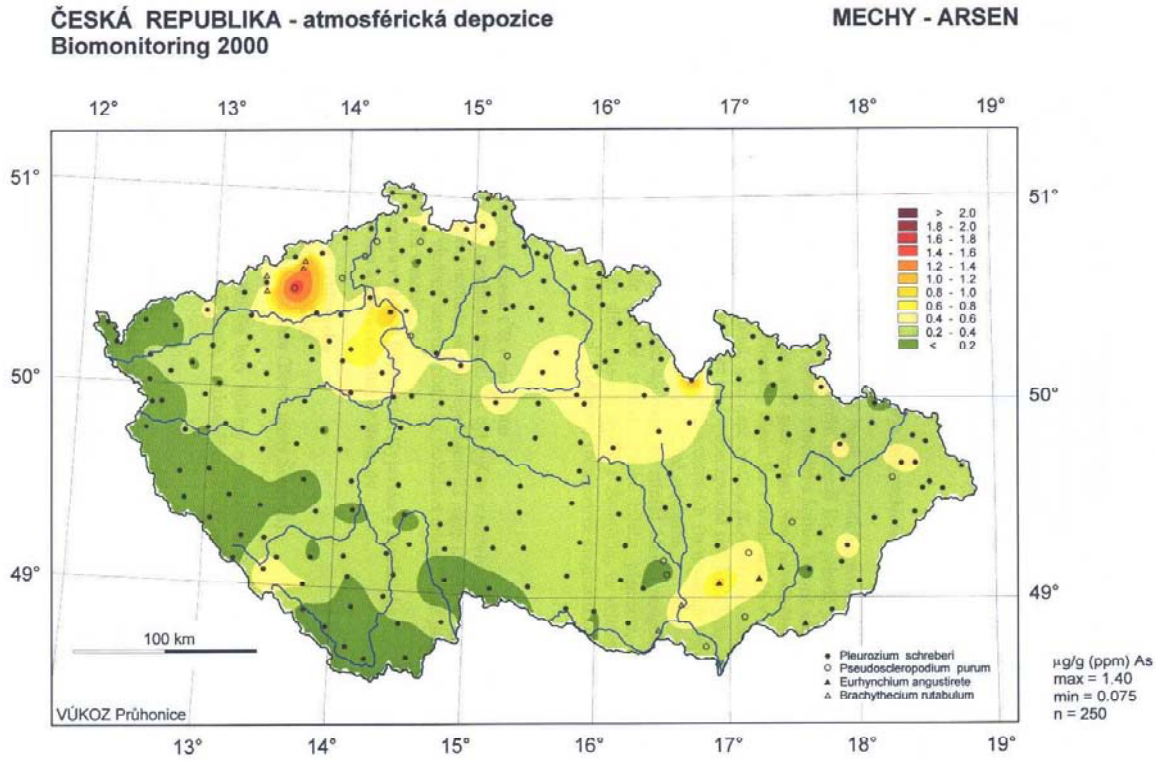

FIG. 1: Concentration of As in mosses in the Czech Republic

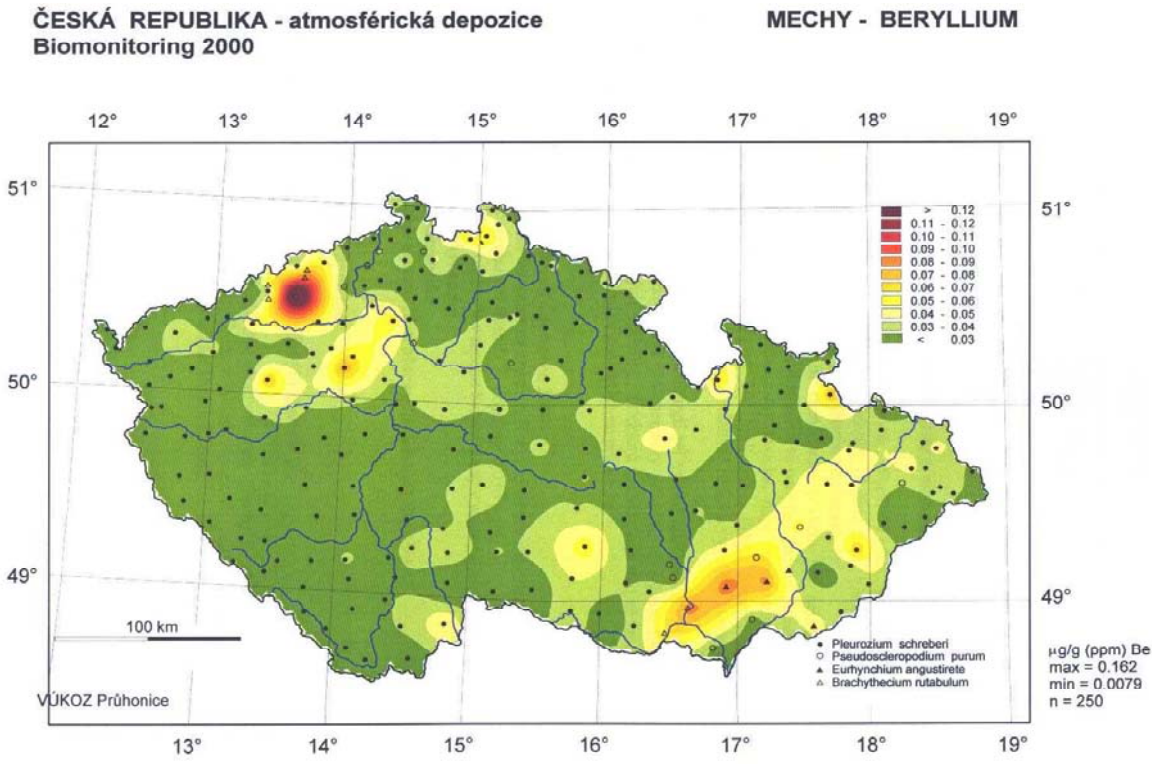

FIG. 2: Concentration of Be in mosses in the Czech Republic

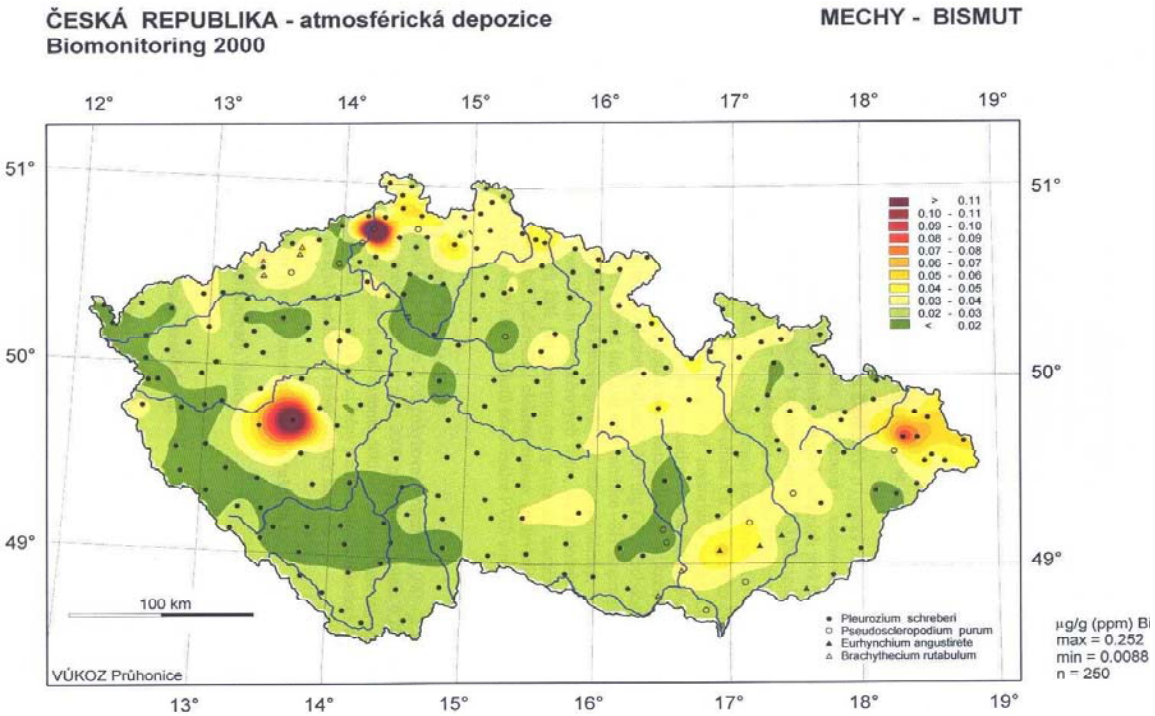

FIG. 3: Concentration of Bi in mosses in the Czech Republic

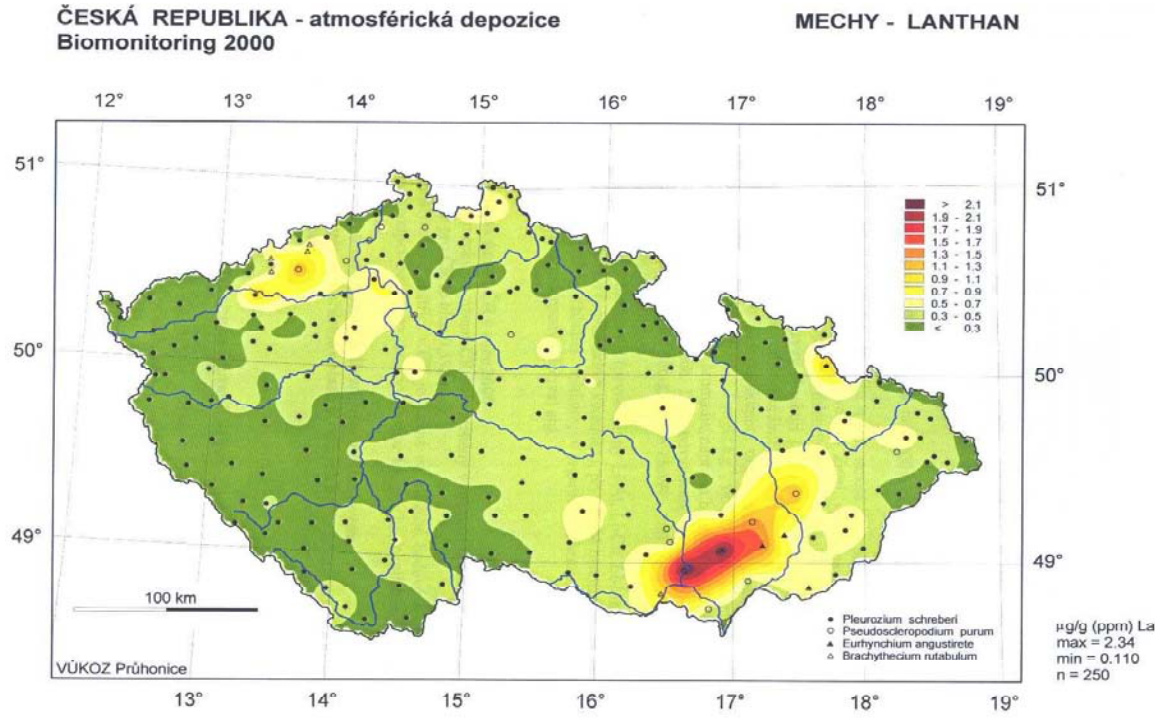

FIG. 4: Concentration of La in mosses in the Czech Republic

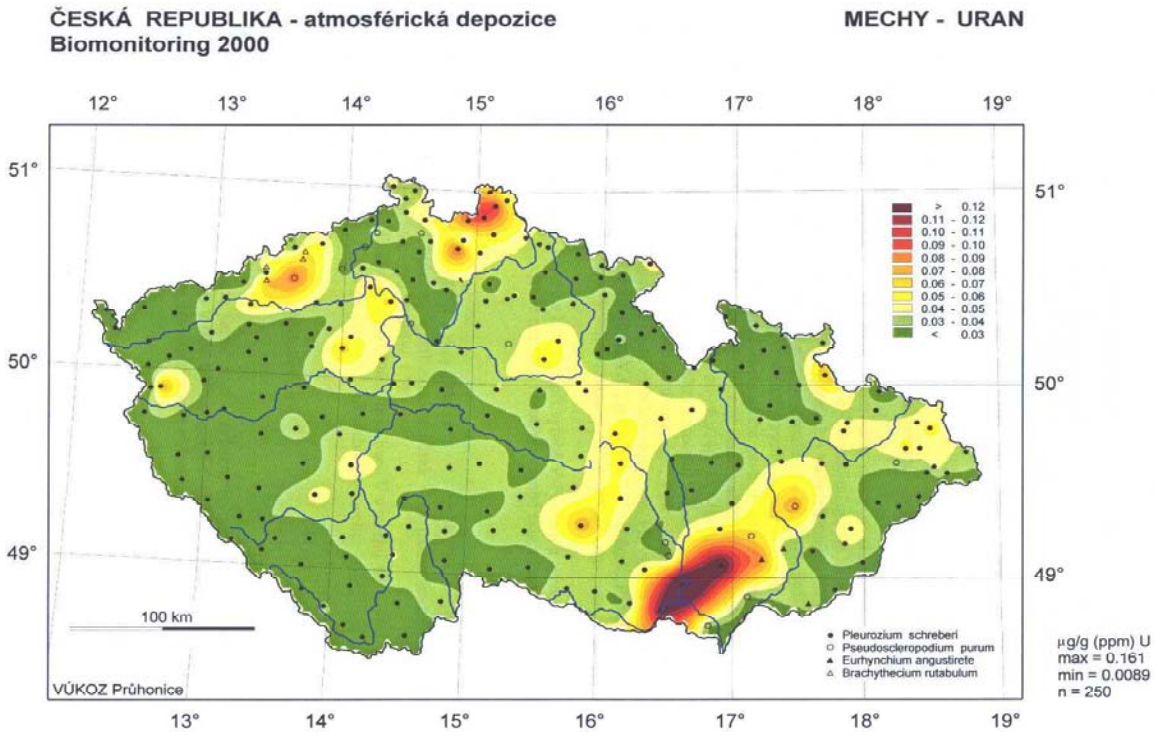

FIG. 5: Concentration of U in mosses in the Czech Republic

2. SAMPLING

The following crops and/or vegetables will be collected in 3-4 localities in the polluted region: wheat and fodder for cattle due to their significant position in the food chain, vegetables, such as kale, cauliflower, spinach, parsley and cucumber, fruits, such as apple, apricot and wine grapes. Soil from the collection sites will also be analyzed to be able to study bioavailability of the pollutants.

Sampling protocols will be used that are shown in Appendix I. Biological samples will be transported to laboratory at 4°C, surface contamination with soil will be removed mechanically, the samples will be washed with distilled water, desintegrated and mixed in a blender with a Ti knife. The resulting material will be freeze dried and further homogenized in the dry state. Soils will be sieved, air dried and homogenized in an agate mortar.

3. ANALYTES AND ANALYTICAL TECHNIQUES

A number of elements will be determined by INAA and PIXE with the main emphasis on the rare earth elements (REE), U and Th. If determination of REE, U and Th in biological materials by INAA will not be feasible, RNAA methods will be developed. Since it is expected that the region studied may also be polluted with F (due to its high content in phosphate rocks), at attempt will be done to determine fluorine contents in the above biological materials and soils. For this purpose, INAA employing the reactions $^{19}F(n,\gamma)^{20}F$ ($T_{1/2}$=11.0 s, Eγ=1633.6 keV) and $^{19}F(n,p)^{19}O$ ($T_{1/2}$=26.9 s, Eγ=197.1 keV) with thermal and fast neutrons, respectively, and PAA with radiochemical separation (RPAA) using the reaction $^{19}F(\gamma,n)^{18}F$ ($T_{1/2}$=1.83 h, Eγ=511.0 keV) that is free from nuclear interferences for irradiation with up to 20-MeV bremsstrahlung will be tested. The most promising technique for fluorine determination is Proton Induced Gamma Emission (PIGE) in which measurement of the 110 keV and 190 keV γ-lines produced in the $^{19}F(p,p',\gamma)^{19}F$ reaction by bombardment with a 2.7 MeV proton beam may yield a fluorine detection limit in the range of several μg g^{-1} for biological materials and around hundred μg g^{-1} for soils (a range of 3-19 μg g^{-1} in herbaceous vegetables has been reported, whereas in soils a median and a range of F contents are 200 μg g^{-1} and 20-700 μg g^{-1}, respectively [3]). Experimental facilities for these techniques are available at the Nuclear Physics Institute, Řež near Prague.

Analysis of the samples may also be complemented by determination of selected organic pollutants, such as polyaromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) using chromatographic techniques that are available at the Institute of Chemical Technology, Department of Food Safety and Analysis, Prague.

Quality control of elemental analysis will be pursued by co-analyzing suitable certified reference materials and/or by employing an independent analytical technique, such as ICP/MS.

4. WORK PLAN FOR 2002

a) Pilot sampling of agricultural crops and soils will be performed in the above region and their preliminary analyses will be carried out.
b) Based on the results of preliminary analyses, the analytical techniques will be tuned and/or improved for the given purpose and validated.

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Appendix I. **S A M P L I N G P R O T O C O L**

Protocol No.:

Sample: Code:

Tissue/part: Code:

Sampler: Sampler code:

Date: __ / __ / **0 1** **Time:** __ **h**

Area (code): **Coordinate: N** ___ . ___

Coordinate: E 0 __ __ . ___

Locality/land area/settlement:

Sampling description:

Sampled by (name):

Conditions:

Altitude (m): Temperature (°C):

Wind (m/s): Wind direction (deg):

Sky (x/8): Deposition: Significant weather:

Sampling site description; potential source of contamination:

Number of primary samples: weight of primary sample: g Total weight: g

Container labeled: Type:

Related blank sample: Protocol No.:

Deviation from SOPs:

Notice:

Transportation:

Conservant/cooling box:		Delivered by (name):	
Temperature (transport):	°C		

Sampled by - Signature

Delivered by - Signature

Laboratory identification:

Request to analyst:

trace metals	PCB/OCI	PAH	Pesticides		Other

State of sample at delivery to laboratory:

Container:	
Sample:	
Amount:	

Date of delivery to the laboratory: ☐☐ / ☐☐ / **0 0** at **:** h

Laboratory representative **(name):**

Laboratory representative - Signature

Laboratory records:

Laboratory registration No.:

Symbols used in the description of conditions

Beaufort

Grade	Windspeed					
	km/h		m/s		knots	
	min	*max*	*min*	*max*	*min*	*max*
0	0	1	0,0	0,2	0,0	0,4
1	1	5	0,3	1,5	0,5	3
2	6	11	2	3	3	6
3	12	19	3	5	6	10
4	20	28	6	8	11	15
5	29	38	8	11	16	21
6	39	49	11	14	21	26
7	50	61	14	17	27	33
8	62	74	17	21	33	40
9	75	88	21	24	40	48
10	89	102	25	28	48	55
11	103	117	29	33	56	63
12	**118**	more	**33**	more	**64**	more

SK:	Sky:	Coverage:
CLR	Clear	0/8
FEW	Few	1/8 - 2/8
SCT	Scattered	3/8 - 4/8
BKN	Broken	5/8 - 7/8
OVC	Overcast	8/8

Precipitation			
DZ	Drizzle	SN	Snow
RA	Rain	SG	Snow grains
SH	Showers	PL	Ice pellets
GR	Hail	IC	Ice crystals
GS	Hail/Snow		

Obscuration			
HZ	Haze	TS	Thunderstorm
BR	Mist	DS	Duststorm
FG	Fog	+FC	Tornado/waterspout

INDUSTRIAL RELATED CONTAMINATION OF PERI-URBAN FRESH VEGETABLES

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1. SCIENTIFIC BACKGROUND AND SCOPE OF PROJECT

Tema is an important municipal city in the coastal region of Ghana. It is the main seaport as well as industrial nerve centre of the country with a teeming population estimated at about a million people.

Major industries in Tema include aluminium smelting, petroleum refinery and processing, steel works, manufacture of dry cell battery as well as cement. Inappropriate disposal of industrial emissions and effluent from these industries causes environmental pollution in and around the city.

Peri-urban fresh vegetable production is a fast-growing activity in the municipality. It is carried out by low-income dwellers living in deprived quarters. Crops grown include cabbage (Brassica oleraceae var. capitata), carrot (Duacus carota), lettuce (Lactucca sativa), onion (Allium cepa) and sweet pepper (Capcicum annuum). They are cultivated as small holdings in backyard gardens or along drains, walkways, streets as well as on undeveloped parcels of land throughout the municipality.

The produce are hawked or sold under sheds along the streets, with sizeable quantities purchased by middle-women for retail in the urban markets. These fetch premium prices as produce quality appears perfect due to limited handling. The industry, therefore, provides supplementary income for many people and in some cases the only source of livelihood.

Fresh vegetables produced this way are liable to contamination from pollutants emitted into the environment. There is, therefore, the need to assess these produce for the presence or absence of these contaminants (heavy and toxic metals), using the techniques of Neutron Activation Analysis (NAA) and X-ray Fluorescence Analysis (XRFA

Main objectives:

- Determine the extent to which toxic element levels in foods are affected by surrounding industrial activities
- Assess the human exposure to such contaminated foodstuffs.

Specific objectives:

- Monitor As, Cd, Cr, Hg, Ni, Pb, Co, Mn, Se, Sn and Mo in vegetables grown in the Tema Municipal District, due to pollution from industrial activity.
- Assess human exposure to such contaminated foods through monitoring of the distribution and marketing channels.

The listed elements are toxic to humans when taken in large amounts and their toxicity increases with cumulative intake. The results of the study will provide us with baseline information to be used for the formulation of appropriate strategies for proper waste disposal and environmental monitoring and control of vegetables and other-stuffs production in the Tema Municipal District.

2. METHODS

- Identify sampling areas within the Tema municipality including
  (a) Identification of the growers and their marketing outlets and
  (b) Identifying the sources of water used for cultivation by means of a questionnaire.
- Quantify the level of toxic elements in the soil and water bodies used for the cultivation of vegetables, using nuclear and related analytical techniques;
- Analyse foods from the farms at the selected sampling areas using neutron activation analysis and X-ray fluorescence analysis.

3. PLANS FOR FUTURE WORK

(i) Year Two:

- Follow the distribution outlets to identify the of produce into the food chain.
- Carry out field survey to classify the cultivated areas as low, medium and high levels of contamination.
- Monitor the level of contaminations in the produce.
- Dialogue with Environmental Protection Agency (EPA), Standard Boards (SB) and Industrial establishments.

(ii) Year Three:

Institute, in collaboration with EPA, SB and Industrial establishments, pollution control measures.

(iii) Year Four:

Monitor the level of contamination in the produce both in the field and on the market outlets.

ALUMINIUM, LEAD, CADMIUM AND MERCURY LEVELS IN HUMAN FOOD CHAIN (IN KARNATAKA, INDIA) AND THEIR INTERACTION WITH MICRONUTRIENTS – COPPER, IRON, ZINC AND VITAMIN A

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1. INTRODUCTION

Micronutrient elements are indispensable for the survival of life. Nature and food habits govern the uptake, deposition, metabolic involvement and excretion of metals in human body. In this process, certain non-essential metals like Aluminium (Al), Lead (Pb), Cadmium (Cd) and Mercury (Hg) may accumulate in various organs during the life cycle. Essential trace elements like Copper (Cu), Iron (Fe) and Zinc (Zn), play dual role and they have beneficiary action at biologically optimum concentrations, whereas they affect biological function at very low or higher concentration. High concentration of lead (Pb) arising from automobile exhaust, pesticides, solders, water, dairy products; cadmium (Cd) arising from tanneries, nickel-cadmium batteries, stabilizers in plastic, glazed potteries, and mercury (Hg) arising from refineries, batteries, pesticides, amalgams, paints and industrial waste; are found in food. High concentration of Pb, Cd, Hg and Al are also reported in leafy vegetables grown on sewage run-off in urban areas. Main source of Al in our diet is from drinking water and through use of aluminium utensils for cooking of food.

There is a growing concern regarding the human health in developed and developing countries with respect to neurodegenerative disorders and carcinogenic potential caused by heavy metals when their levels exceed the Provisional Tolerable Weekly Intake (PTWI). The PTWI levels (mg/kg body weight) are 7 for Al, 0.025 for Pb, 0.007 for Cd and 0.005 for Hg.

Dietary exposure of humans to toxic trace elements leads to their accumulation in various tissues and consequently influence functional ability of essential elements. Studies show that Al, Pb and Cd alter or impair the optimal biological and physiological functions of Fe, Ca, Zn and Cu.

2. INDIAN AND INTERNATIONAL SCENARIO

2.1. Indian Scenario

Information on the levels of aluminium, lead, cadmium and mercury in staple, processed and semi-processed foods is scanty. Levels of Al, Pb and Cd in infant foods are 0.01, 3.92 and 1.71 µg/g respectively. Concentrations of 0.084 µg/g lead and 0.22 µg/g cadmium in cooked foods; 4.1-4.4 µg/g of lead in leafy vegetables; and 1.9- 2.2 µg/g in spices have been reported. Aluminium content (µg/g) ranged from 0.2 -1.9 in different processed and unprocessed foods such as vegetables; 0.1-0.81 in spices and herbs; 0.0-1.3 in packed fruit juices; and 0.3 in rice. It was also shown that Al leaching was more from un-anodized Al utensils into acid foods and also into water while Al leaching was low from anodized utensils.

A limited study has shown the interaction of Al and Pb with micronutrients such as Fe and Zn in serum. It was shown that children having high concentrations of Pb (>30 μg/dl) and Al (>50 μg/dl) have deficiency of Fe and Zn in serum samples.

2.2. International Scenario

In depth studies have been initiated in several countries around the world to determine the status of micro-nutrients, viz., Fe, Zn, iodine and Vitamin A. Investigations have also been carried out to study the effect of absorption promoters / inhibitors, such as ascorbic acid, polyphenols, phytates, dietary fiber, Ca and other heavy metals. Based on the data, several recommendations have also been made for optimizing and ensuring recommended Fe and Zn availability. Use of micro-chemical and trace analysis techniques for species-selective analysis of metals, viz., Pb, Cd, Fe, Zn has been reviewed recently. Analysis of metal – biomacromolecular complexes have been carried out using various hyphenated techniques (LC with AAS, ICP-AES, ICP-MS), wherein speciation of these metals in human milk has been specially addressed. Aluminium utensils are widely used in the world. There are limited studies on Al leaching from Al-pans and it was reported that Al leaches effectively into sauces, etc. Fluoride has been reported to have mild effect in leaching of Al from anodized Al utensils. However, high Al leaching from un-anodized Al utensils is reported. Al content from different American foods has been analyzed. High concentration of Al in tea leaves from Sri Lanka and South Africa has been documented. It was also reported that drinking water having more than 0.2 μg/g of Al reduces the availability of Ca and Zn in American population. The kinetics of binding ability of Al to Fe binding proteins like transferrin and ferritin has been studied to propose a model that Al reduces Fe binding in these proteins.

It is evident from the above data that there is a need for generation of in-depth database on the levels of these toxic metals in foods and water.

3. OBJECTIVES

1. Database generation of Al, Pb, Cd and Hg in staple foods like rice and wheat.
2. Assessment of Al leaching from anodized and non-anodized Al-utensils into stored water and acidic foods.
3. Selection of high risk foods based on the above database and assessment of their dietary intake by 24-hour recall method.
4. Study of selected (a) bio-markers like serum levels of Fe, Cu, Zn, Cr, Ca, Mg, Vitamin A and (b) bio-monitors like SGOT, SGPT, ceruloplasmin, in vitro and in vivo with rat as an experimental model in the presence of Al, Pb, Cd and Hg.

4. PLAN OF WORK

First Year

- Standardization of Al, Cd, Hg, Pb estimation using ICP-MS and NAA in processed and semi-processed foods and validation of methodology using standards, and certified reference materials (Bovine liver, Certified Reference Materials and NIST, USA are available in CFTRI, Mysore).
- Estimation of heavy metal levels using ICP-AES (CFTRI, Mysore) as a control point for comparison with ICP-MS and NAA.
- Quantification of Al in different processed foods.

Second Year

- Development of a model experiment for studying the kinetics of Al leaching from utensils (anodized and un-anodized) into different acidic foods as a function of pH, temperature and cooking practices.
- Establishing dietary levels of Al, Cd and Pb in foods based on their levels in different foods using the 24-hour dietary recall method.
- Studies on the heavy metal - micronutrient interactions using rat as animal model.

Third Year

- Estimation of the a) bio-markers like serum levels of Fe, Zn, Cr, Ca, Mg, Vitamin A and B) bio-monitors like Na+ K + ATPase, SGOT, SGPT, Cerulopasmin in rats fed with Al, Cd and Pb
- In vitro study of the mechanism of inhibition of target enzymes for heavy metals namely, Na+ K+ ATPase.

5. METHODOLOGY

The toxic elements may be present in food chain in a wide range of concentrations from ultra trace to trace levels and for their quantification only sophisticated methods such as ICP-AES, ICP-MS and NAA will be adopted.

5.1. Sampling method

Sampling of food products for the determination of heavy metals and micronutrients will be followed as per the procedure of Codex general method of sampling (CX-MA 013). Samples submitted for testing will be both representatives of the consignment under question and of sufficient size so that significant results can be obtained at the detection limits of the assay. This sampling plan will comply with international sampling methods.

Definitions used in the sampling as given will be used:

Lot: An identifiable quantity of food commodity delivered at one time and determined to have common characteristics, such as origin, variety, type of packing, packer, consignee or makings.

Sublot: Designated part of a large lot in order to apply the sampling methods on that designated part. Each subset must be physically separate and identifiable.

Incremental sample: A quantity of material taken from a sample place in the lot or sublot.

Aggregate sample: The combined total of all the incremental samples from the lot or sublot.

TABLE I: THE FOLLOWING ARE THE SUBDIVISION OF LOTS INTO SUBLOTS DEPENDING ON WEIGHTS

Lot weight (in tonnes)	Weight of sublot/No. of sublots	No. incremental sample	Aggregate sample weight (in Kg)
≥ 500	100 tonnes	100	30
>125 and <500	5 sublots	100	30
≥15 and ≤125	25 tonnes	100	30
<15	-	100	30

- On the condition that the sublot can be separated physically, each lot must be subdivided into sublots as indicated in the table.
- Each sublot must be sampled separately.
- The number of incremental samples for each sublot be as far as possible equal and total to 100.
- 30 g sample be drawn from each incremental sample to have aggregate sample of 30 Kg.
- 30 Kg aggregate samples are to be mixed thoroughly and required quantity be drawn for testing purposes.

5.2. Sample size

Quantity required for testing:

- Raw material: 3000 g of raw material ground to a fine powder.
- Liquid products or pastes: 500 mL of substance
- Finished products: 500 g of substance.

5.3. Sample preparation

As per the codex procedure of sampling, the required quantity of sample is taken for sample preparation. Solid samples are finely ground to pass through 40 mesh and semi-solids and liquid samples are blended properly for homogeneity.

5.4. Analysis

Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) and
Inductively Coupled Plasma - Atomic Emission Spectroscopy (ICP-AES):

5.5. Procedure

25 gms of sample will be acid digested (Ultra pure Nitric acid) in dust free environment. Special care will be taken for avoiding heavy metal contamination using the procedures of Savory and Will (1986). The chemicals (Nitric acid, EDTA etc) of high purity (>99%) and

MQ water with 18 Mega Ohms-cm-resistance will be used. All the samples preparations will be done in dust free environment and all-plastic vials will be used to avoid metal contamination.

Methodology for the estimation of Pb, Cd, Hg, and Al in food matrices using ICP-MS and ICP-AES will be standardized. Sample is fed to Nebuliser and optimal wavelength will be determined from standards scan charts. Validation of methodology will be done using metal standards traceable to Certified Reference Material (CRM) (Bovine liver) from National Institute for Science and Technology, USA.

5.6. Nuclear Activation Analysis (NAA)

Samples do not require any pre-treatment. Samples will be directly bombarded by nuclear radiation. After cooling time of 12-24 hrs the radiation specific to each metal will be analyzed using NAA. ICP-AES estimates at ppb level, while ICP-MS and NAA detect at pico gram levels.

The following Certified reference materials are available with CFTRI.

a) Bovine Liver from NIST, USA.
b) NIES CRM Rice Flour-unpolished (low, medium and high cadmium) from Japan.
c) NARA CRM material for Cd from Australia.

5.7. Heavy Metal and Micronutrient Interactions

Based on dietary content of these metals, rats will be administered with two different concentrations (low and high) of toxic metals (Al, Pb, Cd and Hg) through gastric intubations.

Blood samples will be collected after 6, 12 and 24 hrs from different groups and serum samples will be prepared. The essential metals namely Zn and Fe in serum will be estimated by ICP-MS/ICP-AES and Vitamin A by HPLC. The serum enzymes namely acetyl cholinesterase SGOT, SGPT, Ceruloplasmin and Na-K-ATPase activity will be assessed in the red blood cells. Parallely in vitro studies will also be done for specific interaction between the heavy metals and the availability of the micronutrients and Vit. A by monitoring the extent of interaction with protein such as Human serum albumin in the serum for their uptake and transport.

DIETARY INTAKES OF ESSENTIAL AND TOXIC ELEMENTS IN SEVERAL GROUPS OF NIGERIANS CONSUMING FOOD EXPOSED TO SPECIFIC INDUSTRIAL POLLUTION SOURCES

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Abstract

Dietary intakes of essential and toxic trace elements in various groups of the population consuming food exposed to specific industrial pollutants will be assessed. Industries with clear-cut marker elemental pollutants and which have been in operation for many years are selected. For the first year of study, the tin and lead smelting industry in Jos, Plateau state of Nigeria will be the focus. The common food products (and total diets) that are grown within the locality will be surveyed, sampled and analysed for the marker elemental pollutants. Other essential trace elements which could influence the absorption and metabolism of the marker pollutants will also be studied. Trace element analysis will be carried out mainly by the IAEA-donated TR-XRF system in our laboratory. Afterwards, food frequency questionnaires will be administered to 30 subjects each from 16 sub-groups of the population and their dietary intakes of the various elements of interest will be assessed. The sub-groups are chosen to take care of sociological differences in feeding habits as well as possible variation in the biological tolerance of toxic trace elements. For 5 subjects from each group, blood and headhair samples will be collected and analysed for the elements of interest. Previously obtained results from preliminary studies are presented.

1. SCIENTIFIC BACKGROUND AND SCOPE OF THE PROJECT

The importance of industries to national development is well recognized. However, for sustainable national development, the environmental impacts (particularly as it affects human health) of these industries must also be well monitored. Ingestion through food and water is one of the two major routes for these toxic pollutants to accumulate in man and thereby impact his health. The other major route being inhalation from the air.

Chemical elements can be categorized under three headings depending on their biological functions in the human body. Thus we have essential, non-essential, and toxic elements. The manifestation of both essentiality and toxicity is dependent on the quantities ingested into the system and for this purpose there are Recommended Dietary Allowances and Provisional Tolerable Intakes (PTI) for both essential and toxic elements respectively, as recommended by the FAO/WHO. The feeding pattern of the individual (type and frequency of diet) is crucial in determining the amount of each element that is eventually ingested.

The impact of ingested toxic elements could be different for various groups of subjects. Children, for instance, are known to be more susceptible to the deleterious effects of lead than adults (1). Apart from age, other factors such as social economic status (affecting general nutritional quality), stress, physiological conditions such as pregnancy could also greatly modify the impact of the same amount of ingested toxic element in various individuals. (2,3). Another important modifier of the impact of toxic elements in man is the presence of other elements leading to synergistic effects or competitive inhibition in absorption. Yet another factor that can affect the impact of elements in man is the bioavailability. This depends on both the chemical form in which the particular element is found in the food as well as the matrix of the food. For instance phytates seriously inhibit the absorption of zinc in food (4).

In this project food samples originating from industrially-polluted areas will be surveyed, sampled and analysed for trace elements. The industries to be selected will be ones with clear marker pollutants which have been in operation long enough for the possible impacts to be measurable. The marker pollutants must also be ones that are known to have significant health impact in man. The dietary intakes of these elements by various groups in the population will be assessed. In the course of this CRP, sampling will take place in communities situated in the vicinities of the following Industrial activities:

- The Tin/Lead Smelter factory in Jos, Plateau State of Nigeria (North East)
- The three Oil Refineries at Kaduna, Kaduna State, Portharcourt, Rivers State and Warri, Delta State)
- The National Fertilizer Plant in Cross River State; and
- Three Cement factories each from South West, North East and Middle Belt of Nigeria

For the first year of the CRP, our attention will be directed at the tin and lead smelting factory at Jos, Plateau state of Nigeria. A schematic map describing the location of the factory is presented Fig 1. It shows the relative location of the smelter with respect to other industries, mining areas, residential areas, farmlands, water resources and a major highway in the city. In this factory, liquid effluents are discharged into a nearby stream, which eventually ends up in a fish pond. The stream also partly serves to irrigate a vegetable farm whose products are sold commercially. Solid wastes (mainly slag from the smelting process) are dumped nearby on land separated from the factory by a fence. Part of the solid wastes are routinely incorporated into the soils probably as ‘manure’. Within this area, fruit items such as tomato, and root crops (cassava) are grown.

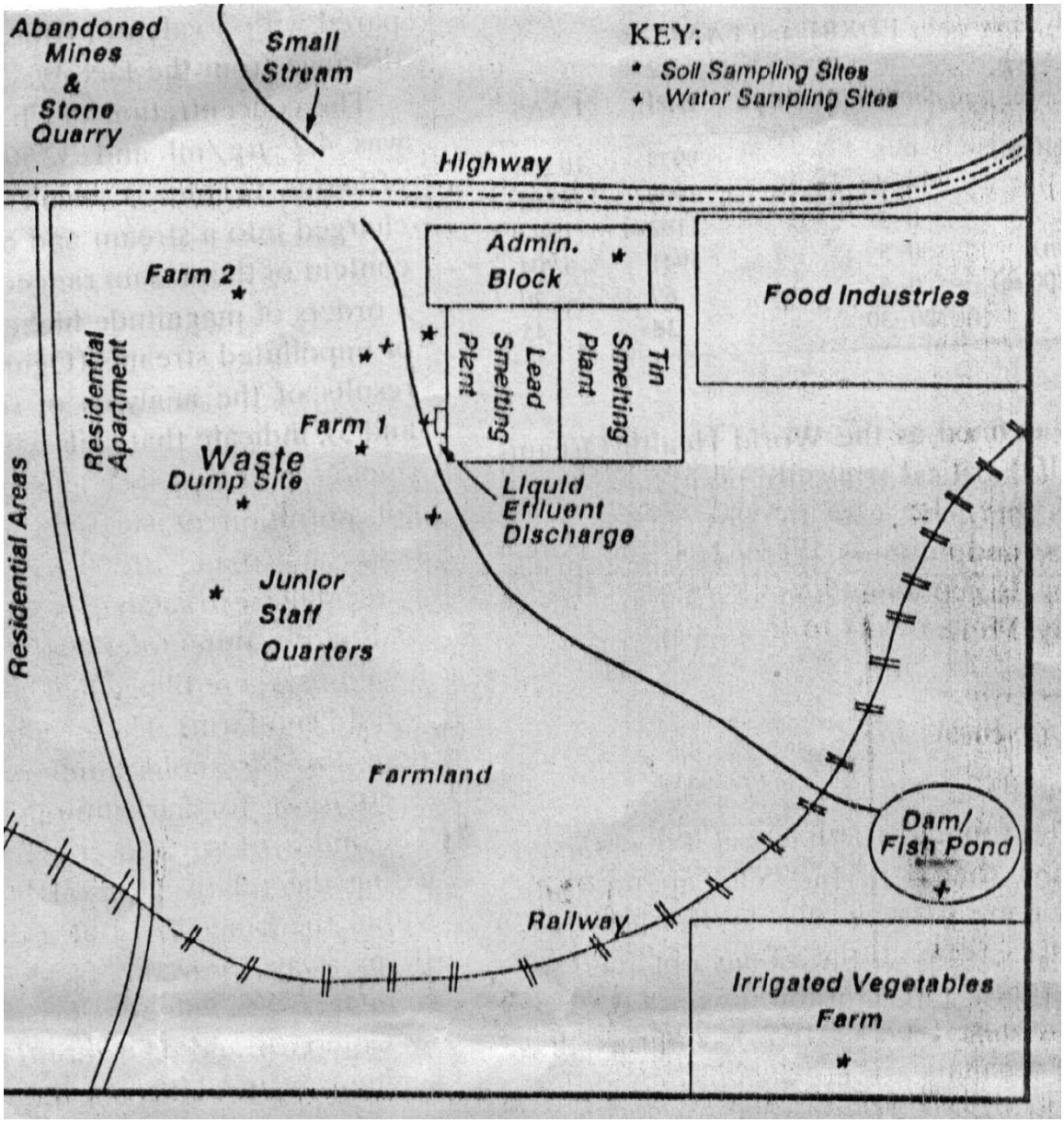

FIG. 1: Schematic Map of Sn/Pb Smelter and neighbourhood

2. METHODS

2.1. Sampling and sample sizes

Raw and semi-processed foodstuffs, diet samples, as well as hair and blood samples will be collected following guidelines contained in the IAEA Technical Reports Series 197 (1980) and similar publications. Double identities will be placed on samples at collection time. A standard form with all relevant information including Date, Location, Fresh weight, Collector, etc will be provided.

A food basket survey will be made to determine the main food items consumed in the locality, and the sources of these will be ascertained to be in the vicinity of the targeted industrial activity. Where, as in the situation for the Tin/Lead Smelter factory we intend to study in the first year, a main industrial activity is situated in the midst of a general several small scale activities, two studies will be carried out. One for the particular factory, and the other for the more wider-scale activities.

In general, at each site, roughly 55 basic food items covering the following groups will be procured: Meat (9 items), Drinks and Dairy Products (12 items), Legumes (2 items), Cereals (6 items), Vegetables (12 items), Fruits (6 items), Tubers (5 items), Derivatives/Semi-processed meals (3 items). Also 5 basic diets will be obtained from each Sampling Site. The food items (particularly the fruits and vegetables) will be made to cover the 2 main climatic seasons of the year. The materials will be bought from the market for the general studies, and for studies involving a particular industry, food items will be procured directly on location - from the farms/ponds etc.

Samples of individual food items will be cleaned, weighed and carefully labelled. At the laboratory, the edible portion of each foodstuff will be separated and either oven-dried (for tubers, legumes, and cereals), or freeze-dried (for meat, dairy products and drinks, vegetables and fruits). They will then be thoroughly homogenized either using a blender or an agate mortar. Possible contaminations by this procedure will be assessed beforehand by analyses of blanks. Homogenized powder will be stored in the refrigerator prior to analysis. Diet samples will be collected in polyethylene containers. These will then be freeze-dried and thereafter homogenised using polyethylene container and spatula. Water and soup samples will be analysed separate from diet samples. Wet and dry weights of all the samples will be noted.

For dietary intake and human impact assessment, the population normally consuming the food items collected will be divided into 16 sub-groups based on considerations previously mentioned. These are: Adult (age > 18 yrs) Male, Adult Female, Adolescent (12 yrs < age < 18 yrs) Male, Adolescent Female, Children (age <12 yrs) Male, Children Female, Pregnant Female (> 3 mo. pregnant), Lactating Female (> 3 mo. after childbirth and actively breast feeding). The eight Groups listed above will be repeated for Low and High Socio-Economic Status based on estimated annual total income of N120,000 to make 16 Groups in all.

A semi-quantitative food frequency questionnaire will be administered to 30 subjects from each sub-group (making 480 questionnaires in all). The questionnaire will be designed and administered by a team led by a qualified nutritionist. 24-hour recall interviews will be used in a number of cases to validate the questionnaires.

Of the 30 subjects chosen from each group for the dietary intake assessment study, blood and hair samples will be collected from 5 subjects from each sub-group for human impact

assessment study. Head hair will be collected consistently from the nape of each individual into pre-labelled polythene containers and stored in the refregerator before analysis. The samples will be cleaned by repeated washing and decantation for about 2 hours in an ultrasonic bath using only deionized water. About 10 ml venous blood will also be collected from each subject, by qualified medical personnel, using methods established in our laboratory over the past twelve years (5). About 2-3 ml of blood will be retained as wholeblood while the rest will be separated by high centrifugation into plasma and eythrocytes. The samples will be frozen in the deep-freezer till ready for lyophilization. They will afterwards be crushed and thoroughly homogenized in preparation for elemental analyses.

2.2. Analysis

The main technique for the analysis will be Total Reflection X-Ray Fluorescence (TX-XRF) based on our new facility recently donated by the IAEA. Graphite-Furnace Atomic Absorption Spectroscopy (GF-AAS) which is available at the nearby Centre for Energy Research and Development, could be used, where necessary, as a complementary technique.

Sample preparation will involve acid digestion of the powdered samples based on the methods of the Analytical Methods Committee of the Society for Analytical Chemistry, as described in literature. Our procedure for analysis by TR-XRF will be patterned according to Peter Wobrauscheck (6) and B. Holynska et al (7). Considerable efforts will be made first to ensure the accuracy and precision of our facility at acceptable levels by analyzing several certified reference materials (CRMs), by 'blind' analyses of composites of CRMs and by intercomparison with other laboratories both within and outside the current CRP.

3. RESULTS AND DISCUSSION

We have previously measured the levels of some toxic elements associated with tin mining and tin/lead smelting in Jos. At various sites on the Jos plateau, we found that toxic heavy metals like Sn, Pb, As, Bi and Ni were highly enriched in the soils, in air particulates and in mine wastes (8). The ranges of elemental concentrations of tailings and ores assoicated with tin exploration are shown in Table 1. In another report (9), we reported the Pb content of the edible vegetables grown on farms located in the vicinity of the Smelter. Pb contents range from 600 – 1200 ug/g. Kalac et al. (1990) also observed high concentrations of lead (11 – 194 ug/g) in musrooms close to a lead smelter in Bohemia, Czechoslovakia. The levels of lead in vegetables around the smelter are shown in Table 2.

TABLE I: RANGES OF ELEMENTAL CONCENTRATIONS OF TAILINGS AND ORES ASSOCIATED WITH TIN MINING IN JOS, NIGERIA

Sample	Al %	Si %	Ca %	K %	As ppm	Ni ppm	Zn ppm	Sn %	W %	Pb ppm	Bi ppm	Fe %
Field concentrates	1.57 – 8.36	20.77 – 25.73	0.20 – 0.41	0.31 – 2.06	<259 – 1000	<89 – 455	458 – 1282	0.35 – 0.37	<0.20 – 0.58	< 866	<664	2.43 – 18.85
Mine Tailings	1.26 – 8.83	23.06 – 26.82	0.22 – 0.38	0.62 – 4.14	<253 – 862	<95 – 1192	445 – 1105	<0.05 – 0.34	<0.20 –0.34	<767	<727 - 925	3.28 – 13.67
Mill Concentrates	1.11	26.43 – 24.68	0.32 – 0.62	<1.0 – 1.79	<231	<595	<411	0.58 – 9.61	<0.20 – 0.32	<700	<723 – 843	1.59 – 2.88
Monazites	1.15	7.63	0.98	ND	<410 – 700	754	580 – 1471	1.87 – 5.72	0.21 – 0.29	<656 – 1695	849	4.01

TABLE II: LEAD CONTMINATION OF VEGETABLES AROUND THE JOS TIN/LEAD SMELTER

Location	Pb in (ug/g dry weight)	Reference
Jos Pb Smelter:		Ref. 9
Farm 1: Tomato	918.63	Ref. 9
Farm 2: Tomato	612.43	Ref. 9
Dam Farm: Tomato	1224.82	Ref. 9
Carrots	979.85	Ref. 9
S/berries	1347.74	Ref. 9
Turnips	1194.23	Ref. 9
Nigeria		
Road side: Cassava tuber	28.4	Ref. 10
Maize grain	17.0	Ref. 10
Spain		
Industrial area: Carrots	0.081	
Agric. Area:	0.118	
Poland		
Industrial area: Carrots	9.4	Ref. 11

We had noted before that the very high levels of lead in food in the vicinity of the smelter was exarcebarted by the fact that in addition to the contamination of the soil, water from the polluted stream is being used for the sprinkler irrigation on the farms. In our previous studies, we did not sample the fish pond into which the polluted stream directly discharges; but this will be included in the study under this CRP.

We have previously determined the baseline levels of both essential and toxic elements in the blood and hair of Nigerians at various parts of the country, including at Jos (5,13). Pb was found in whole blood of unexposed healthy Nigerians in the range 0.017ppm – 0.325 ppm (with mean of 0.120 ± 0.060 ppm).

For this work, we expect to be able to determine and identify any contributions to the dietary intake of toxic elements arising from industrial activities. The risk to which various subgroups of the population could be exposed to will also be determined.

4. PLANS FOR FUTURE WORK

Upon a detailed determination of the contribution to the dietary intakes of various populations of toxic elements associated with tin mining and tin/lead smelting, we shall proceed to the other industries listed in the introduction above for similar studies.

We are interested in doing speciation studies also so as to determine the chemical forms of these toxic and essential elements. This will be result in better assessment of the risks to which the various population groups are exposed to by their dietary intakes of toxic elements arising from industrial pollutants.

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DETERMINATION OF TRACE ELEMENTS AND HEAVY METALS IN AGRICULTURAL PRODUCTS CULTIVATED AT THE RIVER RIMAC IN THE CITY OF LIMA

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Abstract

There are strong indications that the river Rimac valley is being contaminated with heavy metals and an excess of trace elements that come from some industrial and mining activities developed along the river Rimac valley. The agricultural products cultivated therein could be suffering the same effect. Nuclear and related analytical techniques will play an important role in the study of pollution by providing information concerning the degree of contamination in some agricultural products cultivated in the valley and consumed by the population of Lima.

1. SCIENTIFIC BACKGROUND AND SCOPE OF THE PROJECT

The Department of Lima, the capital of Peru, is situated in the central part of the Peruvian Coast and has a peculiar geography consisting of a narrow coastal strip and rising rapidly into the mountains. This confers to the city of Lima the characteristic of being within10 minutes of sandy beaches extending for100 kilometres, but also within 20 - 40 minutes it is possible to enjoy the sunny highland valleys [1]. These valleys are irrigated by some important rivers, the river Rimac and its basin is the principal one, situated in the above mentioned Department.

The highest part of the river valley reaches approximately 5000 meters above sea level and has a large number of lakes and mountain peaks that supply water to the rivers through thawing. At around 1000 meters above sea level the valley begins to widen allowing agricultural production. Due to the geographic of river Rimac valley, the river is most used for the generation of electricity, agricultural irrigation and the water supply [2]. Figure 1. shows a map of the basin.

The major production activities of the valley are: agriculture, mining, hydroelectric production and manufacturing industries. Fig 2. shows a map of the main manufacturing industries and mining activities along the valley.

Mining is the most important economic activity of Peru, it means mining is one of the most intense industries of the country. In the river Rimac valley there are many sites of mineral exploitation. The minerals are mostly mined as sulphurs including chalcopyrite (copper and iron sulphur), esfarelyte (zinc sulphur), galenite (lead sulphur), tetrahedrite (copper and antimonium sulphur), mercury sulphurs, etc. These have low solubility products, so that theoretically, in a first approximation, the processing plants do not unload dissolved minerals [2].

The Ministery of Health, through the General Direction of Environmental Health – DIGESA in the context of a National Program of Vigilance and Control of the Hydric Resources, is conducting the monitoring of the river Rimac along the valley from 25 monitoring stations and determining the physical, chemical and microbiological parameters at each station. The results of the analysis of the water samples show the presence of coliforms, arsenic, chromium and lead [5]. The river is a receptor of a significant load of metals, the origin of which is the waste and the tailings of mining activities in the high valley.

One of the uses of the river water is to irrigate the agricultural production areas of the nearer valleys. Although there is no local data reported of the degree of contamination and its effects on human health, there is a strong suspicion that the agricultural products cultivated in this valley and distributed in markets of Lima, could be contaminated with heavy metals and an excess of trace elements, by means of the superficial water that irrigates the soil, as well as, the contamination of underground water caused by the infiltration from the contaminated superficial waters with the consequent potential risk to health of the population consuming the agricultural products.

There is very limited and insufficient information about the chemical and element contamination of food in Lima and of the agricultural products cultivated in the valleys. Most of the existing studies have focused on microbiological contamination.

Some farmers claim that the soil is poor causing deterioration of the quality of the crops [6].

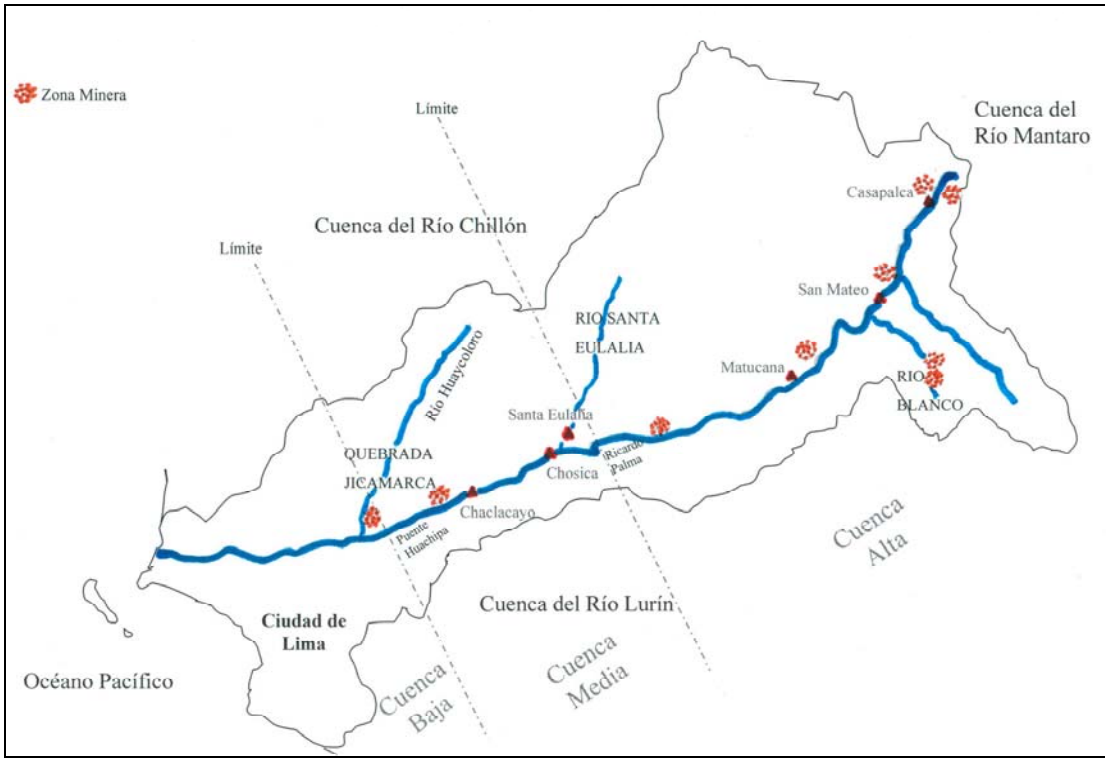

FIG. 1: Map of the River Basin [3].

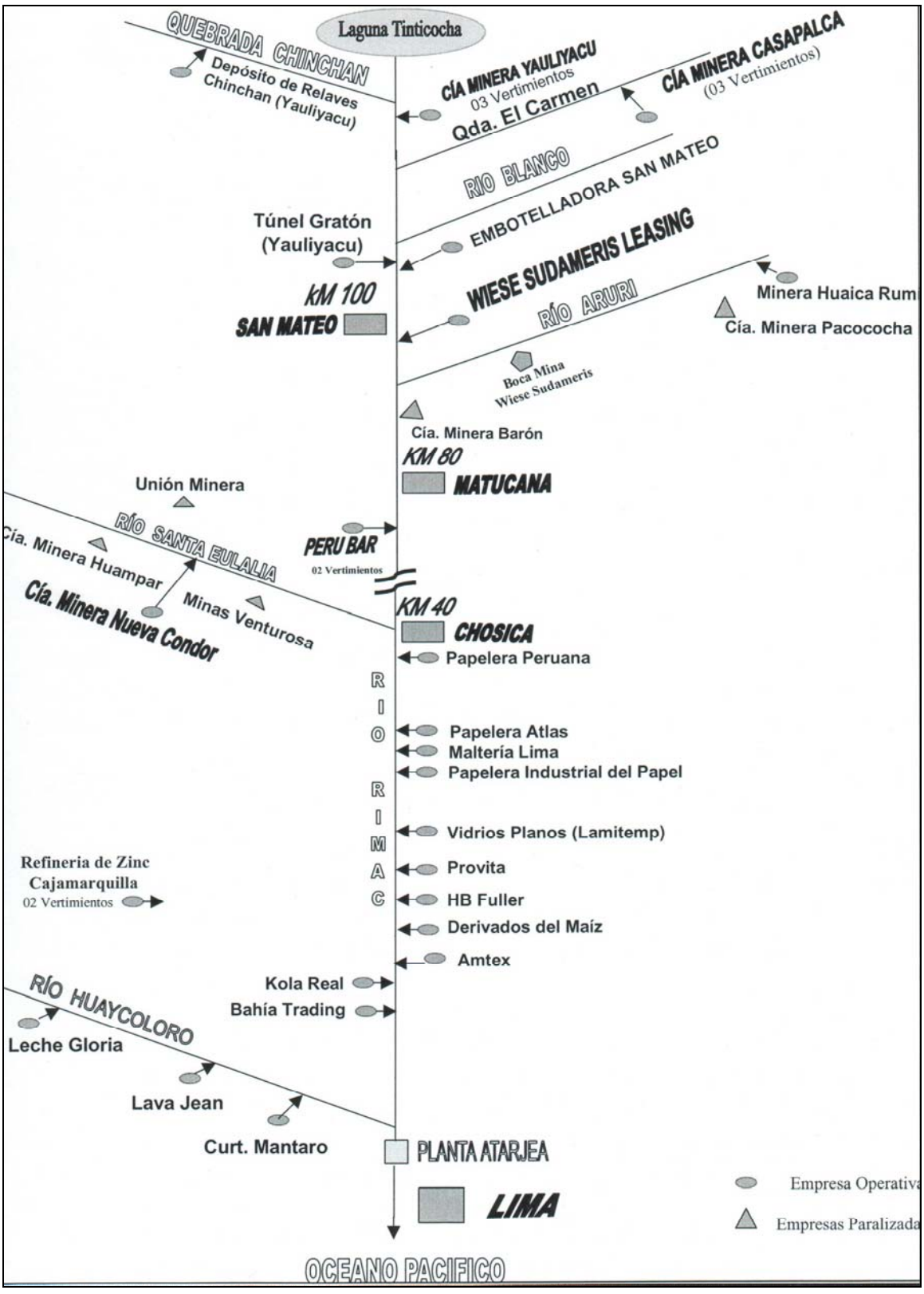

FIG. 2: Industries and other activities at the River Rimac Valley [4].

The environmental impact of the contamination affects not only the cultivated areas but also the ecosystem, flora and fauna, and of course, the health of humans through the food chain.

Others factors that can affect the content of trace element in agricultural products are [7]:

1. The trace element content of the soil, that determine the amount which the plant absorbs beyond the level necessary for growth. The availability of the trace element in the soil may depend upon its oxidation state and the pH of the soil.
2. The use of fertilizers and fungicides
3. The effect of processing and the manner in which the foods are handled and processed. It has been reported that with the use of stainless steel vessels, contamination with manganese can occur.

Associated with contamination is the risk to the health of inhabitants of cities and rural areas. The trace elements, particularly heavy metals such as lead, mercury, cadmium and arsenic are important because they can produce physiological and toxicological changes in humans when consumed.

Sixty five elements are called trace elements, which are classified into four main groups [8].

TABLE I: PHYSIOLOGICAL SIGNIFICANCE OF TRACE ELEMENTS.

1	2	3	4
Generally Essential	Partly Essential	Physiologically Beneficial	Physiological role hardly known
Mn, Fe, Co, Ni, Cu, Zn, B, Mo, I	Li, F, Si, V, Cr, As, Se, Sn, Pb	Sc, Ti, Ga, Ge,Be, Al, Br, Rb, Sr, Zr, Cs, W, Pt, Au, La, Pr, Sm	Y, Nb, Ru, Rh, Pd, Ag, Cd, In, Sb, Te, Ba, Hf, Ta, Re,Os, Ir, Hg, Tl, Bi, Ce,Nd, Eu, Gd, Tb, D y, Ho, Er, Tm, Yb, Lu

The essential trace elements have an important role in human nutrition because they perform a number of vital functions in the body as constituents of enzymes, hormones, vitamins and other biological molecules [9], and because of this, the optimum concentration of trace elements is the basis for the health of living beings, including humans [10].

The mining exploitation is a potential source of contamination, if metals, such as cobalt, copper, zinc, lead, mercury, cadmium, etc., are extracted and there is no effort to impede these metals joining the ecosystem. These will produce an overload that will cause disease and illness to living beings. Some reports [11], [12] give evidence of the toxic and harmful effects of heavy metals and their interaction with micronutrient deficiencies.

DIGESA and the Municipalities are conducting a program at the level of markets, called the suburb market. The objectives are to promote the hygiene, modernization and use of healthy technologies in order to give a better and safe service to the consumers; to establish a sanitary control of food in the markets; to diminish the risk associated with inadequate handling

practices through the training of vendors [13]. This program is helpful but needs to be complemented and extended because it only covers the vigilance of retail markets.

The Determination of Trace Elements and Heavy Metals in Agricultural Products Cultivated at the River Rimac in the City of Lima project has the following objectives:

1. Determine the degree of contamination by trace and heavy metals in agricultural products consumed by the population and cultivated along the river Rimac valley in Lima.
2. Establishing baseline values and assessment of time trends of the contamination by pollutants in order to relate their effects to the nutritional status and human health.
3. Determine the quality and safety of food that populations are consuming and provide information on the element composition of the diet for a large sector of the population to improve the quality of foodstuffs.
4. Create a list of the concentration of trace and heavy metals in the agricultural cultivated products from the identified area.
5. Provide information to the national authority for health and environmental monitoring, DIGESA, so as to allow the implementation and/or improvement of policies and programs to control the contamination and its effects on the human health.
6. Disseminate the benefits of the use of nuclear energy and nuclear analytical techniques.

Environmental studies cover a broad range of disciplines and include several tasks such as monitoring (routine analysis), research (studies of environmental pathways), modelling etc. [14] and therefore this project is being conducted in collaboration with the Instituto de Investigacion Nutricional (IIN) Nutrition Research Institute, a non profit institution working in areas related to nutrition and health, which has the responsibility for the sampling and sample preparation for the analysis. The IIN has been conducting studies about the types and quantity of food consumed by inhabitants in the city, specifically pregnant women and children. We have used this information as a reference to selected the agricultural products that will be sampled and analysed and are shown in Table II.

TABLE II: VEGETABLES MOST CONSUMED BY PREGNANT WOMEN AND CHILDREN.

Food description	No. pregnant Women (n = 100)	Food description	No. children 6-36 months (n = 188)
Onion	100	Onion	141
Carrot	97	Carrot	104
Tomato	89	Potato	93
Pea	84	Pumpkin	67
Pumpkin	79	Tomato	61
Celery	67	Celery	48
Coriander	59	Coriander	26
Lettuce	40	Pea	26
Corn	32	Spinach	10
Spinach	31	Corn	9
Sweet potato	29	Bean	9

Before sampling it is important to obtain background information through a pilot investigation in the wholesale markets of Lima where the agricultural products are transported before its distribution to the district markets. This exploration will give valuable information of the origin of the selected agricultural products.

Another action prior to sampling is an inspection to the area that will be selected for sampling. The sampling points could be those near the monitoring stations established by DIGESA.

Sampling will be conducted by sampling and storage procedures with the participation of at least one analyst to ensure that the samples are representative and that no significant changes in composition occur during sampling, transport and storage [15].

The Chemistry Department of the Nuclear Peruvian Energy Institute has the responsibility for the analysis of the samples.

2. METHODS

2.1. Sampling

The sample collection will be done based on the background information obtained in the preliminary investigation and inspection of the sampling sites, and will be as follows:

- Selection of foods based on table II.
- As a result of the inspection of sites, identify the sampling areas
- Establish a sampling plan, following a protocol design.
- Taking samples
- Transport samples to the laboratory
- Preparation of samples for the analysis: washing, rinsing, and preservation, either by cooling or by irradiation then grinding, homogenizing and storage.

2.2. Analysis

The role of analytical chemistry in this type of studies is of vital importance. The analytical techniques that will be used are: Instrumental Neutron Activation Analysis (INAA), Radiochemical Neutron Activation Analysis (RNAA), Energy Dispersive X-Ray Fluorescence (EDXRF), Total Reflexion X-Ray Fluorescence (TRXRF), Stripping Voltametry (SV) and Atomic Absorption Spectrometry (AAS). Table III shows the analytical techniques and the elements that will be analyzed by each.

To perform the analytical techniques mentioned above IPEN has a 10 Mw research reactor and six laboratory facilities implemented as followed: a laboratory for weighing samples and moisture determination including analytical balances, desiccators and a calibrated oven; a laboratory of NAA and XRF fitted with four gamma spectrometry equipments; a laboratory of instrumental techniques including SV equipment, AAS equipment, UV-V equipment, a fume hood and a microwave oven; a laboratory of biological samples preparation; including glove boxes and a fume hood; a radiochemical laboratory implemented with two hume hoods where samples are unpacked after irradiation and where radiochemical separation can take place; a laboratory for sample preparation including a small mill and homogeniser used for geological samples.

TABLE III: ANALYTICAL TECHNIQUES VS. ELEMENTS

Analytical Technique	Elements
INAA	Mn, Fe, Co, Cu, Zn, Mo, V, Cr, As, Se, Sc, Ti, Br, Rb, Sr, Cs, W, La, Al, Ba, Hf, Ce, Na, K
RNAA	Cd, (Hg in study)
EDXRF	Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Pb, Sr, Rb, Br
TRXRF	Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Pb
SV	Cu, Zn, Cd, Pb
AAS	Mg, Cu, Zn, Fe, Na, K

2.3. Analytical Quality Assurance and Quality Control

The laboratory has participated in a Quality Assurance Project to establish a Quality System that allowed us improve the laboratory practice. As a consequence we obtain greater accuracy so the laboratory will be nationally accredited.

The main goal is to ensure the accuracy of the data produced, and hence their comparability [16]. The laboratory applies the following means to achieve accuracy in the analytical results:

a) Existence of a quality assurance manual; where we have established the mission of the Chemistry Department and the quality policy besides the technical procedures.
b) Training personnel; who receive training through attending specialized courses or for studying and giving lectures about update publications to the entire chemistry group.
c) Good housekeeping of the laboratory; the control of indoor contamination in the lab is monitored constantly. A clean working area is available for handling the analytical samples.
d) The use of validated methods
e) The application of statistical control principles; the use of control charts, regression analysis, t- and F-tests, analysis of variance, etc.
f) External quality assurance control; participating in proficiency tests and intercomparison runs.
g) Comparison with results of other methods; results can be verified by other independent methods. All methods have their own particular source of error [14]. We search for good agreement in the results of the methods.
h) The use of reference materials (RMs) and certified reference materials (CRMs) in chemical analysis is the most important tool. All the analysis are carried out including these RMs and CRMs with their composition similar to the composition of the unknown sample.

3. WORKING PLAN AND OUTPUTS

3.1. Working plan for the first year

a) Identifying the critical agricultural areas potentially affected by contamination from industrial activities in the vicinity of Lima, Peru
b) Selecting the food to be studied according to the production and consumption importance.
c) Establishment of appropriate sampling plan to obtain representative samples.
d) Collecting and analysing the collected samples, using nuclear analytical techniques and complementary non-nuclear techniques.
e) Evaluating of obtained results.

3.2. Outputs: Results obtained (about sampling)

The first information obtained from wholesale market was a statistic about the kind of food that these markets receive and its origin. But most of them are not about vegetables.

The first inspection along the valley permit the identification of sampling sites and of four sampling products such as beetroot, turnip, radish and cabbage. In the medium valley the main product cultivated are fruits such as peach, apples and avocado.

3.3. Analytical results

The samples analysis stage has not begun, however the following tables shown the results obtained in the respective reference material analized by INAA: Table IV shows the results of some elements obtained in the Reference Material Lichen 336 from IAEA and its standard deviation of 6 replicates. There is a good agreement with the certified values. Table V shows the results of the Certified Reference Material Soil 7 from IAEA analized in a proficiency test of a Quality Assurance Project, ARCAL XXVI. The uncertainties are the overall estimated analytical uncertainty at 95% confidence level. These have quiet good agreement with the certified value.

TABLE IV: LICHEN 336 - IAEA (MG/KG)

Element	Certified Value	IPEN-CHEM (n=6)
Aluminium	680 (570-780)	751 ± 81
Arsenic	0.64 (0.56-0.72)	0.77 ± 0.02
Calcium	2600 (2400-3300)	2600 ± 100
Chloride	1900 (1650-2200)	2170 ± 85
Lanthanum	0.66 (0.55-0.76)	0.70 ± 0.02
Magnesium	610 (500-710)	700 ± 100
Manganese	64 (57-71)	70 ± 2
Potassium	1840 (1640-2040)	2300 ± 400
Sodium	320 (280-360)	342 ± 12
Scandium	0.17 (0.148-0.192)	0.21 ± 0.01
Vanadium	1.5 (1.2-1.7)	1.7 ± 0.2

TABLE V: CRM SOIL – 7 IAEA (MG/KG) 95%C.I

Element	IPEN-CHEM	Certified Value
Aluminium	45245 ± 799	47000 (44000 - 5100)
Antimony	1.6 ± 0.1	1.7 (1.4 -1.8)
Arsenic	13.1± 0.2	13.4 (12.5 -14.2)
Bromine	7.7± 0.17	7 (3 –10)
Calcium	155171 ± 792	163000 (157000 – 174000)
Cesium	5.4 ± 0.21	5.4 (4.9 – 6.4)
Cobalt	8.5 ± 0.36	8.9 (8.4 – 10.1)
Dysprosium	3.9 ± 0.14	3.9 (3.2 – 5.3)
Iron	25918 ± 106	25700 (25200 – 26300)
Hafnium	5.2 ± 0.17	5.1 (4.8 – 5.5)
Lanthanum	28 ± 0.0	28 (27 – 29)
Magnesium	12062 ± 2800	11300 (11000 – 11800)
Manganese	612 ± 7.8	631 (604 – 650)
Potassium	12334 ± 257	12100 (11300 – 12700)
Rubidium	51 ± 1.26	51 (47 – 56)
Samarium	5.4 ± 0.08	5.1 (4.8 –5.5)
Scandium	8.4 ± 0.13	8.3 (6.9 – 9.0)
Sodium	2291± 45	2400 (2300 – 2500)
Thorium	8.6 ± 0.15	8.2 (6.5 – 8.7)
Titanium	2946 ± 70	3000 (2600 – 3700)
Vanadium	65 ± 0.71	66 (59 – 73)
Uranium	3.4 ± 1.29	2.6 (2.2 – 3.3)
Ytterbium	2.6 ± 0.06	2.4 (1.9 – 2.6)

4. PLAN FOR FUTURE WORK.

Other valleys providing agricultural products to Lima required surveillance of the degree of contamination by heavy metals and trace elements. These are the Lurin and Chillon valleys. We consider of utmost importance to extend the project to the agricultural products of the said valleys.

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USE OF INAA, AAS AND XRF IN STUDYING HEALTH IMPACTS OF TOXIC ELEMENTS CONSUMED THROUGH FOODSTUFFS CONTAMINATED BY INDUSTRIAL ACTIVITIES IN RUSSIA

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Abstract

The current economic situation in Russia results in that vegetables and plants grown in private small-holdings account for over 50% of the population's diet. In some regions of Russia (Ural, Altai) mining and metallurgical works remain the sole economic factor of existence and development despite the obvious damage to the environment through contamination with heavy and toxic metals. Crop rotation is actively being extended to the land immediately bordering on the zones of industrial enterprises within the range of 1–5 km. This land has been affected by waste discharged from the enterprises for many years. The cultivated soil may contain high gross concentrations of toxic elements. Problems of contamination of natural media with toxic metals (As, Cd, Cr, Cu, Hg, Ni, Pb, Zn, etc) has not been systematized in Russia on the state level so far. The monitoring strategy for Belovo lead-zinc enterprise in Kemerovo Region of West Siberia, Gus Khrustalny in Vladimir Region, and Voskresensk in Moscow Region of Central Russia is discussed as well as analytical methods to be used (INAA, AAS and XRF). Examples from the previous experience of the authors are given.

1. INTRODUCTION

Preliminary investigations done by the authors [1-4] of the proposed project have revealed that the selected study areas are characterized by high levels of contamination of soil by toxic metals discharged as solid and liquid wastes as well as by aerosol from the factories. These agricultural soils have varying degrees of contamination, and different characteristics (for example, acid grey forest podzol in Central Russia and neutral black soil in Siberia).

The local residents generally consume food products mostly grown in the immediate vicinity of the sources of pollution. These foods are: vegetables (potato, cabbage, etc.), fruits and berries (apples, black berry, etc.) The vegetation is an intermediate step in the trophic chain of soil and man for nutritionally as well as toxicologically important elements. The harmful effects of lead and its compounds on human health have been studied around the world. In Russia, the "Report on lead contamination of the environment of the Russian Federation and its effect on human health" (Editor V.V. Shakin, 1997, in Russian language) was prepared. It systematically tabulated the data on urbanized territories where the lead concentration in various materials exceeded the maximum permissible levels. Problems of contamination of these materials with other toxic elements (for example, As, Cd, Cr, Cu, Hg, Ni, Zn, etc.) have not yet been systematically studied in Russia, although their harmful effects on human health appear to be as important as that for lead. Most of these elements are included in the Indicative List of Persistent Toxic Substances approved in Geneva (1999) [5].

Investigations by various authors have revealed relationship between the level of contamination of soils with toxic metals and their concentrations in edible vegetables grown on these soils. According to the assessment of the Institute of Nourishment of the Russian

Academy of Medical Sciences (1998), up to 85% of the total lead intake comes from food. There are similar intake assessments for a few other toxic metals. Yet, the problem of real intake of toxic metals through vegetables has not yet been completely solved because the actual amounts of locally-grown vegetables consumed from areas polluted with different metals have not been taken into consideration. Of much interest are cosmopolitan plants (potatoes, carrots, cabbage, tomatoes), which make up the bulk of the vegetable portion of the population's diet in all regions. The food safety problem is very important for Russia.

The economic situation in Russia dictates that vegetables and plants grown in private small holdings be consumed and these account for >50% of the population's diet. The cultivated soil may contain significantly high concentrations of As, Cd, Cr, Cu, Hg, Ni, Pb, Zn, etc. On the outskirts of large cities there are a lot of small unauthorized dumps containing used batteries, broken glass, paint remanants, tin cans, etc. These may also contribute to the soil metal burden. Vegetables and forage grown on these soils almost always contain high concentrations of these elements. Intake of these vegetables is potentially dangerous for man [6]. Their effect is particularly harmful for children.

The authors of the project are involved in realization of the following national programs:

- Federal program of the RF government «Protection of the Environment from Lead contamination and diminishing its impact on population health» (1997-2003)
- Cooperative program of the Ministry of Public Health of RF «Prophylactic measures on diminishing lead and other toxic elements impact on neuro-psychic development of children» (1999-2003)
- Program of the Ministry of Science and Technology of RF «Investigation of regularities of element-toxicants distribution in natural media (air, water, soil), biota and man's biosubstrates in the regions of intense technogenic impact» (2000-2004).

The basic objectives of this project are to evaluate the potential adverse health effects that could arise to the local residents including children from the consumption of foods grown in areas which are highly polluted by intense industrial activities.

The specific objectives of the project are:

- To study the transfer of potentially toxic levels of elements such as Al, Ag, As, Au, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Sb, Se, Sn, Th, U, V, Zn, and rare-earth elements (REE) from soils, surface and drinking waters, and air exposed to high levels of industrtial pollution (in particular mining, metallurgy, and glass works) and other anthropogenic sources. The areas of interest are: Belovo lead-zinc enterprise in Kemerovo Region of West Siberia; Pb-As crystal production in Gus Khrustalny in Vladimir Region and phosphate fertilizer plant in Voskresensk in Moscow Region of Central Russia;
- To measure the levels of the above elements in soils, surface and drinking water, air, in various types of vegetable and fruit such as potatoes, carrots, raddishes, tomatoes, cucumber, cabbage, lettuce, apples, different berries;
- To develop various types of neutron activations analysis (NAA) and atomic absorption spectrometry (AAS), X-ray fluorescence (XRF) methods for the reliable measurement of the above elements;
- To design a comprehensive quality assurance programme; and
- To estimate the exposure of man (children) to toxic elements using indicators such as the average daily dietary intakes and the element levels in biosubstrates namely blood, urine, teeth, and hair.

2. THE APPROACH AND METHOD

2.1. Approach

The following four sections comprise the overall project:

2.1.1. Site selection

For the purpose of the proposed project we have selected the following areas: Belovo lead-zinc enterprise in Kemerovo Region of West Siberia, Karabash copper smelter in Chelyabinsk Region of the South Urals, and Gus Khrustalny in Vladimirskaya Region and Voskresensk in Moscow Region of Central Russia. Control sites will also be selected from the same regions.

2.1.2. Sample types

Samples to be collected from these areas include soils, water, air, vegetables and fruits (potatoes, carrots, raddishes, tomatoes, cucumber, cabbage, luttece, apples, and different berries), milk and milk products, meat and meat products. Preliminary studies indicated that these products generally have higher than normal concentrations in industrially contaminated areas.

2.1.3. Elements of interest

The list of elements includes As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Sb, Se, Sn, Th, U, V, Zn, and REE. Some of these elements are either known to be toxic or potentially toxic at higher concentrations, and rest could be useful for source aportionment.

2.1.4. Indicies of health assessment

The average daily dietary intake of the above elements can serve as a useful indicator. The biosubstrates namely blood, urine, teeth, and hair can reflect the body-burden of certain elements thereby the health status.

The principle scheme of the interrelationship between eco-geochemical studies and medical-biological studies is given in Fig. 1.

2.2. Analytical techniques

The principal analytical technique which will be used in this project is neutron activation analysis (NAA). The atomic absorption spectrometry (AAS) and X-ray fluorescence analysis (XRF) will be used as a complementary technique.

2.2.1. NAA

Several of the above elements will be determined by various forms of NAA. Conventional instrumental NAA (INAA), cyclic INAA (CINAA), and epithermal NAA (ENAA) methods will be developed for the simultaneous determination of As, Co, Cr, Fe, Mn, Ni, Sb, Se, U, Th, V, Zn and REE in soils, water, air filters, vegetables, fruits, teeth, nail and hair. An internal as well as external quality assessment program will be designed to ensure the relaiblity of the results obtained.

INAA and ENAA will be done by Dr. M.V. Frontasyeva and her group at the Laboratory of Neutron Physics of the Joint Institute for Nuclear Research (JINR) in Dubna [7-8]. The conventional NAA will be used also by Dr. S. Lyapunov and his group at the Moscow Engineering and Physics Institute (MEPhI, Technical University), at the MEPhI reactor with a neutron flux of 10^{13} (cm^2 s), mostly for INAA at low concentrations.

INAA and ENAA of the samples will be carried out at the 2-MW pulsed fast reactor IBR-2 in Dubna: one site is cadmium-lined for activation with epithermal neutrons. The neutron flux density is 10^{12} n/(cm^2 s).

2.2.2. AAS

Concentrations of As, Cd, Cr, Cu, Hg, Ni, Pb in all types of sample will be determined by flame and graphite furnace AAS; and levels of As, Hg, Sb, and Se will be measured by hydride generation AAS (HGAAS). Dr. S.M. Lyapunov at the GIN RAS has a flame AAS (Quant-2A), the analogue of Perkin–Elmer model with the similar parameters which is currently being extensively used in geochemical studies.

2.2.3. XRF

The wave-length dispersed fluorescence analyzer ARF-6 (Russia) XRF-WD installation (the analogue of Philips system) will be used [9]. It is based of Ag and Rh tubes providing detection limits 1-2 ppm for elements from Fe up to Mo and 2 ppm for Co. Mostly powdered soil samples will be analyzed by this method. It provides high productivity along with low cost of the analysis.

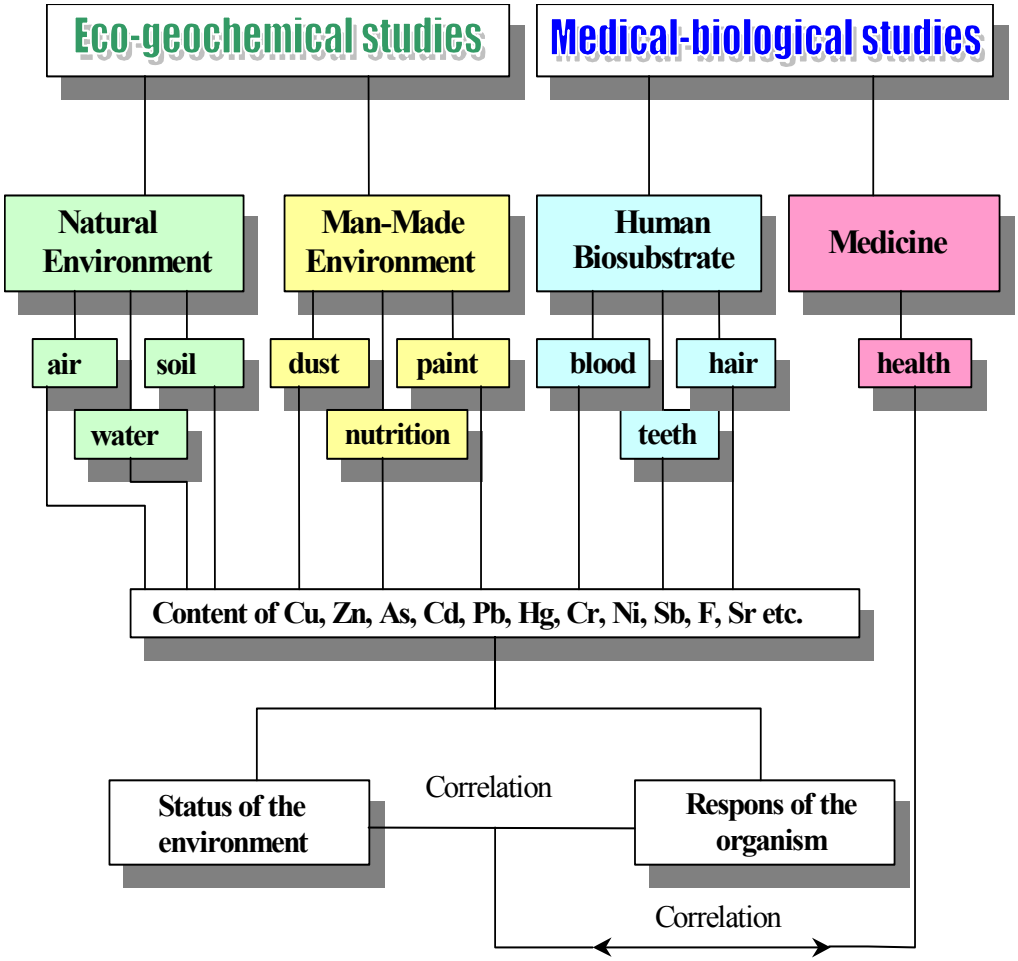

FIG. 1: The interrelationship between eco-geochemical and medical-biological studies

2.3. Validation of analytical methods

2.3.1. Certified reference materials or standard reference material

The analytical quality assurance was provided by using national and international standard reference materials (SRMs). Among them Human Hair (GBW 09101 and 07601), Pine needle, lichens, moss, soil, sediments, etc. As an example, the comparison of recommended and obtained by the authors results are given in Tables 1 and 2.

2.3.2. Intercomparison of independent methods

Two or more independent analytical techniques are used for quality control and quality assurance. Participation in IAEA intercomparisons while CRP is supposed.

TABLE I: INTERNATIONAL SRM OF HUMAN HAIR GBW 7601 (CHINA). CONCENTRATION IN PPM

Element	Na	Ca	Cr	Zn	Sb	Co	Cu	As
Recommend.	152±10	2900±200	0.37±0.05	190±5	0.095±0,012	0.071±0,008	10.6±0,7	0.28±0.04
Determined n=27	160±23	2600±410	0.42±0.08	185±8	0.11±0.01	0.08±0.01	9.0±0.9	0.29±0.09
Element	Fe	Se	Hg	Pb	Cd	La	Ce	Br
Recommend.	54±6	0.60±0.03	0.36±0.05	8.8±0,9	0.11±0.02	0.049	0.12	(0.36)
Determined n=27	59±5	0.47±0.05	0.38±0.03	8.0±0.6	0.13±0.03	0.07±0.02	0.17±0.05	0.37±0.09

TABLE II: RESULTS OF THE ANALYSIS OF IAEA SRM LICHEN-336. CONCENTRATION IN PPM

Element	Na	Fe	Cr	Co	Pb	Cu	Zn	Fe	Cd
Recommend.	320	426	1.03	0.287	5.0	3.55	31.6	426	0.117
Determined N=17	300± 30	400±20	1.10±0.09	0.33±0.04	4.5±0.3	3.1±0.2	26±2	420±10	0.12±0.02

2.4. Health impact

It has been reported that the industrial contamination of food supply in Russia has caused serious health effects including increased morbidity and mortality over the past few decades. The children are a particularly vulnerable population group for many reasons. It is therefore imperative to assess the health impact of this transfer of toxic elements to children. It could be done using indicators such as the average daily dietary intakes and the element levels in biosubstrates namely blood, urine, teeth, nails, and hair.

The Laboratory of Regional Problems of Health Institute of Forecasting at the Centre of Demography and Human Ecology in Moscow will evaluate the health status of the local residents, including children, in the study areas selected for this project [10-13].

According to the exsisting estimations, general tendency in the increase of children's morbidity (most sensitive to the environmental impact) is observed (B.Revich, technical report).

3. ASSESSMENT OF POSSIBILITY TO USE INDUSTRIAL WASTES IN AGRICULTURE

3.1. Introduction of compost from the sewage tanks of the plant to agriculture

Experiments with acidic (pH 4-6) soddy podzolic soils of the Moscow Region were carried out. The essence of the experiment was as follows: in the other equal conditions, to the squares where salad was growing, different amounts of compost were introduced. Doses introduced were 0.4; 0.8; 1.3; 1.9 kg/m^2. The experiment lasted for 1.5-2 months. The alive weight of vegetation and the accumulation of chemical elements in soils and vegetation were determined.

The results on the agricultural experiment with compost from sewage tanks are given in Table 3. One should note that the salad capacity increased by a factor of 1.4–1.6 at the maximal

introduction doses of compost. Data given in Table 3 show that the accumulation of practically all trace elements in soil takes place.

Thus, for example, concentration of Cr exceeds background values by 10 times; Fe, As, Sb – by 3-4 times. The concentration of bromine is an exclusion, it became lower that the background level.

TABLE III: CONTENT OF CHEMICAL ELEMENTS IN SOIL AND SALAD LEAVES RELATIVE TO THE INTRODUCED AMOUNT OF COMPOST, MG/KG

Object	Introduced Amount of Compost, kg/m^2	Na (%)	K (%)	Ca (%)	Sc	Cr	Fe (%)	Co	As	Br	Sb	La	Ce	Sm	Th	U
Soil (n=25)	Background	0.30	1.1	1.0	3.3	30	0.90	5.5	3.3	4.5	0.85	12	22	2.2	3.5	1.4
	0.4	0.27	1.1	0.95	3.0	36	0.80	5.9	5.1	6.0	1.1	12	21	2.2	3.2	1.4
	0.8	0.32	1.1	1.0	3.5	40	1.1	6.6	6.0	5.1	2.1	13	29	2.4	3.6	1.4
	1.3	0.9	1.6	1.4	6.6	160	3.0	11	8.4	3.4	2.3	26	43	5.1	5.6	2.0
	1.9	0.6	1.4	1.6	10.4	300	3.8	11	11	2.5	3.7	33	55	7.5	6.0	2.9
Salad (n=25)	Background	0.8	2.8	1.0	0.4	4.9	0.20	0.6	0.07	3.0	0.15	1.9	2.7	0.3	0.3	0.2
	0.4	0.8	2.9	1.0	0.4	5.6	0.17	0.7	0.08	2.8	0.15	2.3	3.0	0.3	0.4	0.2
	0.8	1.0	3.1	1.2	0.5	9.5	0.28	0.9	0.08	2.6	0.15	2.6	4.7	0.5	0.5	0.3
	1.3	1.6	2.1	2.4	0.9	20	0.31	1.0	0.25	3.1	0.27	3.4	5.8	0.6	0.7	0.3

Trace element accumulation takes place in vegetation also. First of all, one should note the increased concentrations of As and Sb which approach the maximum permissible levels (0.3 mg/kg) for food products (see Table 4). Besides, trace elements accumulation in soil differs from that in vegetation. To better understand the character of this accumulation, we calculated the coefficients of accumulation of trace elements in vegetation:

$$K_a = \frac{C_V}{C_S}$$, where

Ka is the coefficient of accumulation of a given element in vegetation;
CV is its concentration in vegetation;
CS is its concentration in soil.

The dependencies of coefficients of accumulation of the main trace elements in salad leaves on introduction doses of compost are demonstrated in Fig. 3. It is evidently seen that the maximum of accumulation of Na, K, Fe, and Cr and of some other important for the growth of the plant elements corresponds to the introduction dose of compost of 0.8 kg/m^2. The following increase of the dose leads to decrease of trace elements accumulation. It does not refer to As, unfortunately, so far its accumulation grows monotonously with the increase of the introduction dose.

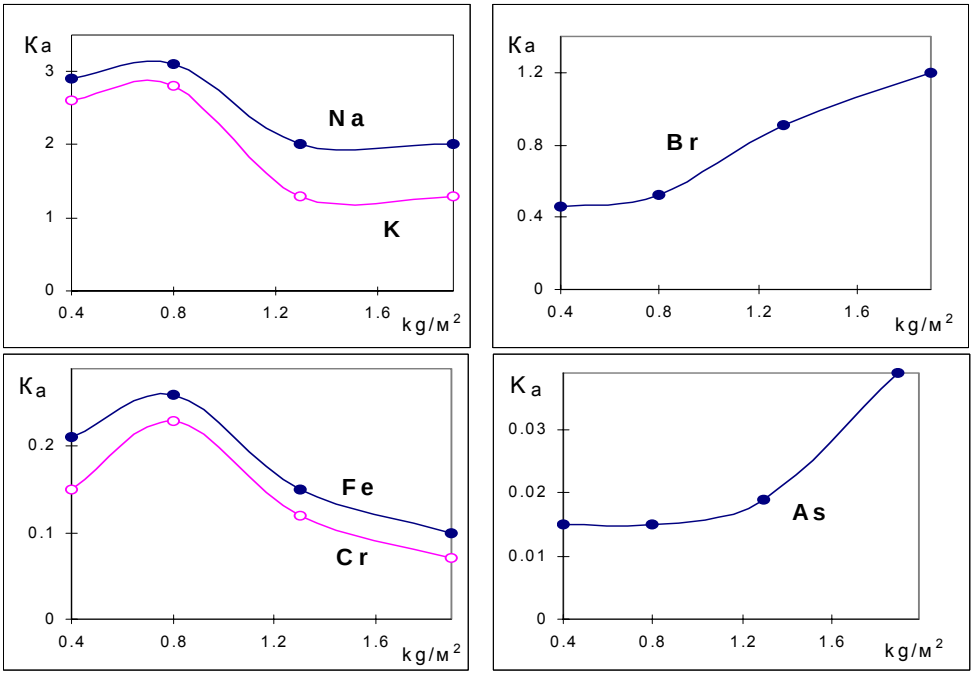

FIG. 2: The dynamics of trace element accumulation in salad leaves.

As follow from the given example:

- The accumulation of trace elements in soil takes place;
- The concentrations of As and Sb in salad leaves reach values close to the maximum permissible levels for these elements;
- The maximum crop capacity (alive mass of the vegetation) is achieved at introduction dose of compost of 1.9 kg/m^2, whereas the relative depletion in such trace elements as Na, K, Ca, Fe, and Cr takes place.

Table 4 contains data on trace element concentrations in some agricultural products grown in the vicinity of phosphate fertilizer plant in Moscow Region.

TABLE IV: MEAN VALUES OF TRACE ELEMENTS IN AGRICULTURAL PRODUCTS, PPM, DRY WEIGHT

Plant/Elem.	Cr	Fe	Co	Zn	As	Se	Sb	Br	Cs	Sr	La	Ce	Th
Potatoes n=48	0.7	95	0.13	21	<0.1	<0.1	0.05	0.3	<0.1	<10	<0.1	0.1	<0.01
Raddish leaves n=12	8.3	190	1.1	60	1.3	0.6	0.14	9.6	0.31	<10	2.2	3.7	0.59
Salad n=12	4.2	150	0.57	49	0.3	<0.1	0.21	4	0.24	<10	1.9	2.7	0.32
Cabbage n=9	0.3	110	0.07	19	0.1	0.1	0.03	1	<0.1	51	<0.1	0.1	<0.01
Dill n=9	0.3	220	0.1	52	<0.1	0.2	0.11	0.5	<0.1	20	0.5	0.9	0.02
Apples n=7	0.5	42	0.07	7,8	<0.1	<0.1	0.07	<0.1	<0.1	18	0.1	0.2	<0.01
MPL (wet weight)	0.2	-	-	10	0.2	0.5	0.3	-	-	-	-	-	-

To develop a strategy for a scientifically based monitoring system for agricultural areas affected by intense technogenic emissions in the selected regions of Russia and to assess this impact on food quality and finally on health of local residents, one should relay on the official maximum permissible levels of toxic element concentrations accepted in the Russian Federation for the main foodstuffs. Table 5 summarizes the available maximum permissible levels of toxic element concentrations in the Russian Federation for the main foodstuffs.

4. PLANS FOR FUTURE WORK

In the framework of this CRP the working plan for the first year is the following:

Months 1-6:

- Collection and assessment of current information on toxic element emissions from the industrial enterprises in the South Urals (copper smelter in Karabash, Chelaybinsk Region), Altai, Siberia (zinc smelter in Belovo) and Central Russia (Pb-As crystal production in Gus-Cruystalny and phosphate fertilizer plant in Voskresensk)
- Collection of literature data about contamination of soils by toxic element emissions and about the accumulation of toxic elements in cultivated agriculture plants, especially in edible vegetables, in polluted areas
- Planning of the study (selection of areas exposed to emissions of the examined industrial enterprises, reference areas, selection of local cultivated agriculture plants for the study)
- Development of harmonized protocols concerning the sampling of soils and selected agriculture plants, and storage of samples

Months 7-12:

- Sampling of soil samples at selected sampling sites, determination of pH and humus.
- Sampling of vegetable samples in selected contaminated and reference areas.
- Development of analytical methods (INAA, AAS, and XRF)
- Design of a quality assurance program
- Preliminary analysis of samples
- Preparation of the interim report

TABLE V: PERMISSIBLE LEVELS OF TOXIC ELEMENT CONCENTRATIONS IN FOODSTUFFS (MEDICAL AND BIOLOGICAL REQUIREMENTS AND HYGIENIC NORMS FOR THE QUALITY OF THE NUTRITION AND FOODS. №5061-89 MINISTRY OF HEALTH , USSR, 1990 Г., TEMPORAL HYGIENIC NORMS FOR SOME CHEMICAL ELEMENT CONTENT IN THE MAIN FOODS. № 2450-81 MINISTRY OF HEALTH, USSR, 1982 Г.), MG/KG

No	Food product	Pb	Cd	As	Hg	Cu	Zn	Sn	Fe	Sb	Ni	Se	Cr
1	Meat products (as well preserved in glass, aluminum and non-iron steel cans)	0,5	0,05	0,1	0,03	5,0	70	200	-	0,1	0,5	1,0	0,2
2	Fish, sea foods (as well preserved in glass, aluminum and non-iron steel cans)	1-2	0,2	1-5	0,3-0,7	10	40	200		0,5	0,5	1,0	0,3
3	Vegetable oil and butter	0,1	0,05	0,1	0,03-0,05	0,5-1	5-10	-	5	-	-	-	-
4	Milk products	0,1-0,3	0,03-0,1	0,02-0,2	0,005-0,02	1-4	5-50	200		0,05	0,1	0,5	0,1
5	Bread and corn	0,3-0,5	0,03-0,1	0,1-0,3	0,01-0,03	5-10	25-50			0,1	0,5	0,5	0,2
6	Sugar and sweets	0,5-1	0,05-0,5	0,3-1	0,01-0,05	1-50	3-100	-	-	-	-	-	-
7	Vegetables (as well preserved in glass, aluminum and non-iron steel cans)	0,5	0,03	0,2	0,02	0,2	5	200		0,3	0,5	0,5	0,2
8	Fruits (as well preserved in glass, aluminum and non-iron steel cans)	0,4	0,03	0,2	0,02	0,2	5	200		0,3	0,5	0,5	0,1
9	Juces, drinks	0,1-0,3	0,01-0,03	0,1-0,2	0,005	1-5	5-10	-	15	0,2	0,3	0,5	0,1

Children's nutrition

		Pb	Cd	As	Hg	Cu	Zn	Sn	Fe	Sb	Ni	Se	Cr
1	Canned meat	0,3	0,03	0,1	0,02	5	50	100					
2	Canned fish	0,5	0,1	0,5	0,15	10	30	100					
3	Fruit-and-berries cans	0,3	0,02	0,2	0,01	5	50						
4	Milk products	0,05	0,02	0,05	0,005	1	5						
5	Crop oriducts	0,1-0,3	0,02	0,1	0,01	5	10						
6	Special products for medical treatment	0,05-0,3	0,02-0,03	0,05	0,005-0,02								

Maximum permissible concentrations in drinking water, mg/dL 3

Elements	Pb	Cd	As	Hg	Cu	Zn	Sn	Fe	Sb	Ni	Se	Cr
Concentration	0,03	0,001	0,05	0,0005	1	1	-	0,3	0,05	0,1	0,01	0,05

Maximum permissible concentrations in soils, mg/kg

Elements	Pb	Cd	As	Hg	Cu	Zn	Sn	Fe	Sb	Ni	Se	Cr
Concentrations (gross)	32-130	0,5-2	2-10	2	30-132	55-220	-	-	4,5	20-80	-	-
Leaching forms	-	-	-	-	3	23	-	-	-	4	-	6

Maximum permissible concentrations in air, mg/m 3

Elements	Pb	Cd	As	Hg	Cu	Zn	Sn	Fe	Sb	Ni	Se	Cr
Concentration (aerosols)	0,0003	0,0003	0,003	0,0003	0,002	-	0,02	-	0,02	0,001	0,00005	0,0015

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ANALYSIS OF FOOD BY NUCLEAR AND RELATED ANALYTICAL TECHNIQUES

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Abstract

The work on the project started in 2000 with the selection of foods consumed in the Witwatersrand area of South Africa which is recognised to be the economic heartbeat of the country. A dietician was consulted in identifying the most important food groups for human nutritional health, as well as typical examples of foodstuffs belonging to a specific food group. From this information a suite of 14 foodstuffs were chosen. The primary investigation was aimed at natural occurring radioactive materials (NORM) to explore the capability of our laboratories in analysing the nuclides involved through low- and high-energy gamma-ray spectrometry. The main objective being to investigate our capability and capacity to prepare and analyse these foodstuffs and estimate the committed effective dose to consumers. Information gained served to define future strategies for food analysis for NORM. From this survey it appeared that for certain radionuclides radiochemical separations will be required to arrive at the sensitivities needed to perform adequate dose estimations. For some of the foodstuffs positive values for a suite of radionuclides has been obtained, urging further investigation in the total NORM-nuclide content. Future work will focus on INAA and radiochemical separations to determine all relevant nuclides of the uranium, thorium and actinium decay series. Uranium and thorium content of the foodstuffs under survey will be determined by neutron activation analysis and in the same time the capability of INAA for the determination of toxic and essential elements will be surveyed. This report provides information on the work performed so far and the work envisaged for the year 2002. All actions are defined according to our QAQC procedures applicable at our ISO/IEC 17025 accredited laboratories.

1. OBJECTIVE

The first phase of this Technology Action had the following objectives:

1. Identify a variety of common/typical foodstuffs produced and consumed in South Africa;
2. Determine the fresh/dry ratio and specific mass for each of these foodstuffs;
3. Determine the minimum detectable activities (MDA-values) for the suite of natural occurring radionuclide materials (NORM's) for each of the foodstuffs, making use of the present analytical capabilities of the Radioanalysis laboratory;
4. Set the objectives for the following phase of the Technology Action.

2. SAMPLES CHOSEN

A dietician was consulted in identifying the most important food groups for human nutritional health, as well as typical examples of foodstuffs belonging to a specific food group. The following was identified:

Main Food Group	Sub Food Group	Typical Examples	Sample Chosen	Detail	RA code
Fish	Fresh water *	Barbel	-	-	-
		Carp	King Carp	• Caught at Rooikoppies Dam, Rustenburg • General and plant eater • Edible parts only, bones, fins and head discarded	T072x001B
		Black Bass	-	-	-
Dairy	Butter	Salted	-	• Bought at general supermarket • No further sample preparation performed	T072x002A
	Milk	Full cream			
		Skimmed			
Meat	Beef	Stewing	Brisket	• Bought at Schoemansville Butcher, Hartbeespoort • All bones and visible fat were removed prior to sample preparation	T072x003A
		Steak			
		Oxtail			
	Pork	Leg of	Leg chops	• Bought at Schoemansville Butcher, Hartbeespoort • All bones and visible fat were removed prior to sample preparation	T072x003B
		Ribs	-	-	-
	Poultry	Chicken	Thighs	• Bought at Pretoria Market • Skin and bones were discarded • Meat was very fatty and could not be dried properly	T072x004A
			Livers		T072x004B
Eggs	Chicken	-	-	• Bought from Mooinooi Egg Farm (T Coetzee) • Mixed well (white & yellow) prior to sample preparation	T072x005A
Grains/Cereals	Wheat	-	-	-	-
	Mealies	-	-	-	-
Vegetables	Root	Carrots	-	-	-
		Beetroot	-	• From Brits area (T Coetzee) • Leaves removed prior to sample preparation	T072x007B
	Legumes	Peas	-	-	-
		Green Beans	-	• Bought at Pretoria Market • Very fresh and young. • Used whole vegetable	T072x008B
	Leafy	Spinach	-	-	-
		Cabbage	-	• Bought at Pretoria Market	T072x009B
	Tuberous	Potato	-	• Bought at Pretoria Market	T072x010A
		Sweet Potato	-	-	-
		Onion	-	• Bought at Pretoria Market • First layer of skin removed prior to sample preparation	T072x010C
	Yellow	Pumpkin	Hubart Squash	• Bought at Pretoria Market	T072x011A
Fruit	General	Tomato		• Bought at Pretoria Market	T072x012A

*: A client was approached and requested to catch a variety of freshwater fish for laboratory use. A freshwater fish expert was then invited to the laboratory to identify the fish received and explain the main eating habits of the particular specimen.

3. SAMPLE PREPARATION AND ANALYSES

3.1. Initial sample preparation

- RA-WIN-108/113: Since this study focuses on the primary pathways for human ingestion, it was decided to only study the edible parts of foodstuffs. Fish bones, eggshells, meat bones, etc. were therefore discarded prior to sample preparation. Samples were all dried at temperatures below 65^0C in order to prevent losses of volatile elements.

Performed on 27/06/2000

3.2. High-energy Gamma-spectrometry analysis

- RA-WIN-101: Dried and homogenised sample material was sealed in a calibrated geometry sample holder. Samples were then counted for 24 hours each on facility RA-FS-306, a high purity germanium detector system with a relative efficiency of 15%.

Performed on 8 September 2000 to 17 November 2000

- RA-WIN-158: Dried and homogenised sample material was sealed in a calibrated geometry sample holder. Samples were then counted for 24 hours each on the low-energy gamma-spectrometry facility RA-FS-305, a high-purity germanium detector system with an ultra-thin Be-window.

Performed on 24 February 2001 to 6 June 2001

4. ANALYTICAL RESULTS

1. The analytical results are presented as appendices to this report.
2. The reported uncertainty is a probable error calculated mainly from the counting statistics, and is not the normal standard deviation on replicate analyses.

5. REMARKS AND OBSERVATIONS

5.1. The moisture content of foodstuffs is relatively high, varying between 50 - 75% for meat and 80 - 95% for vegetables and fruit.

5.2. Accordingly, from the available data a preliminary attempt was made to calculate the committed effective dose in μSv/a for each radionuclide, for each sample matrix and for the population groups: Adults (> 17 a) and babies (< 1 a). Equilibrium with the respective mother/daughter nuclides are assumed for the direct short-lived progeny not analysed for.

Appendix 1 List the MDA-values obtained for the gamma-spectrometry measurements of the individual food stuffs.
Appendix 2 Lists the committed effective dose based on the MDA-value measured for each radionuclide (in Bq/kg), for each individual sample matrix.

5.3. The National Nuclear Regulator's Licensing Guide LG-1032, Rev 0 refers to a screening assessment criterion of 25 μSv for a specific pathway, taking all the NORM radionuclides into consideration. (The contribution from other pathways is also taken into consideration, so that an overall criterion of 250 μSv is followed.)

For a specific pathway criterion of 25 μSv/a, a committed dose of 5 μSv/a per individual radionuclide is regarded as acceptable. From Appendix 1 it is therefore clear that the detection limits for certain radionuclides are unacceptable (shaded areas). These are:

^{226}Ra: Unacceptable for most of the sample matrices, either because the moisture content is relatively high, and/or the assumed intake of the specific foodstuff per annum is low. For the worst case (fish, pork) the detection limit is too high by a factor of approximately 7. This factor can still be lowered by either (i) counting a larger sample (3 times larger), and (ii) making use of a more sensitive gamma-detector system. Counting for more than 24 hours per sample is not practical or affordable to the laboratory, taking the day-to-day work load into consideration.

^{210}Pb/^{210}Po: Unacceptable for all sample matrices. The detection limits for these radionuclides are so poor that gamma-spectrometry analysis should not be considered as an option. There is a restriction on the sample size for low energy gamma-spectrometry, and as stated before, it is not practical to count for more than 24 hours per sample. In general, the detection limits for these radionuclides are too high by a factor 7 to 900. These radionuclides should be analysed in foodstuff samples by radiochemical separation techniques.

^{228}Ra: Unacceptable for most of the sample matrices. The detection limit is too high by a factor of 2 to 39. This factor can still be lowered by either (i) counting a larger sample (3 times larger), and (ii) making use of a more sensitive gamma-detector system. Counting for more than 24 hours per sample is not practical or affordable to the laboratory, taking the day-to-day work load into consideration. It is recommended to investigate the gamma-spectrometry method further, due to the very lengthy radiochemical procedure for determination of ^{228}Ra (currently at our labs > 6 months).

^{228}Th/^{224}Ra Unacceptable only for the sample matrices with a relatively high moisture content and low intake per annum, i.e. fish and meat.

5.4. For some of the foodstuffs positive NORM-values have been obtained. These data and the corresponding dose to the two age groups are given in Appendix 3 and 4 respectively. From these data it can be observed that some foodstuffs are close to the 25 μSv/a level indicated by the South African National Nuclear Regulator and accordingly, the dietary habits of the population has to be surveyed to obtain better data on yearly consumption of the foodstuffs concerned (the first order estimation of the yearly dose is based on default intake values for foodstuffs adhered to by the National Nuclear Regulator).

6. FUTURE WORK

Work for the year 2002 has been planned. The technology action is provided in Annex 1. This phase of the project will deal with INAA of the foodstuffs under consideration to determine the uranium and thorium content to allow more detailed dose estimation and to perform multi-element analyses to allow evaluation of the nutritive value (essential and toxic elements) of the respective foodstuffs.

Appendix 1
Detection limits in Bq/kg wet mass

Food Category I:	Fish	Diary	Meat	Meat	Poultry	Poultry	Eggs
Food Category II:	Freshwater	Diary	Beef	Pork	Chicken	Chicken	Eggs
Description:	King Carp	Butter	Brisket	Leg chops	Thighs	Livers	Eggs (chicken)
Wet Mass [g]:	3806.8	1.0	4932.9	3768.9	3752.1	?	7191.7
Dry Mass [g]:	1979.5	1.0	1339.1	1090.4	1649.2	?	1781.6
% Moisture:	48.0	0.0	72.9	71.1	56.0		75.2
U-238 Series							
U-238							
Th-234							
Pa-234m							
U-234							
Th-230							
Ra-226	1.3	1.8	0.5	0.7	0.8	2.4	0.6
Rn-222	1.3	1.8	0.5	0.7	0.8	2.4	0.6
Po-218	1.3	1.8	0.5	0.7	0.8	2.4	0.6
Pb-214	1.3	1.8	0.5	0.7	0.8	2.4	0.6
Bi-214	1.3	1.8	0.5	0.7	0.8	2.4	0.6
Po-214	1.3	1.8	0.5	0.7	0.8	2.4	0.6
Pb-210	66.3	53.6	26.8	20.6	20.1	104.2	25.3
Bi-210	66.3	53.6	26.8	20.6	20.1	104.2	25.3
Po-210	66.3	53.6	26.8	20.6	20.1	104.2	25.3
U-235 Series							
U-235							
Th-231							
Pa-231							
Ac-227							
Th-227							
Ra-223							
Rn-219							
Po-215							
Pb-211							
Bi-211							
Tl-207							
Th-232 Series							
Th-232							
Ra-228	2.8	3.2	1.2	1.3	1.4	4.4	1.2
Ac-228	2.8	3.2	1.2	1.3	1.4	4.4	1.2
Th-228	0.9	1.4	0.5	0.5	0.6	1.8	0.5
Ra-224	0.9	1.4	0.5	0.5	0.6	1.8	0.5
Rn-220	0.9	1.4	0.5	0.5	0.6	1.8	0.5
Po-216	0.9	1.4	0.5	0.5	0.6	1.8	0.5
Pb-212	0.9	1.4	0.5	0.5	0.6	1.8	0.5
Bi-212	0.9	1.4	0.5	0.5	0.6	1.8	0.5
Po-212	0.5	0.9	0.3	0.3	0.4	1.2	0.3
Tl-208	0.3	0.5	0.2	0.2	0.2	0.7	0.2
K-40	11.8	11.6	5.0	5.3	5.9	18.9	5.1

Appendix 1 (Continued)
Detection limits in Bq/kg wet mass

Food Category I:	Vegetables	Vegetables	Vegetables	Vegetables	Vegetables	Vegetables	Fruit
Food Category II:	Root	Legumes	Leafy	Tuberous	Tuberous	Yellow	Fruit
Description:	Beetroot	Green beans	Cabbage	Potatoes	Onions	Pumpkin	Tomato
Wet Mass [g]:	5748.2	6019.0	8572.4	3990.9	10614.9	6906.6	6068.0
Dry Mass [g]:	1021.4	621.1	797.3	633.7	1191.1	717.0	297.1
% Moisture:	82.2	89.7	90.7	84.1	88.8	89.6	95.1
U-238 Series							
U-238							
Th-234							
Pa-234m							
U-234							
Th-230							
Ra-226	0.4	0.2	0.3	0.3	0.3	0.2	0.2
Rn-222	0.4	0.2	0.3	0.3	0.3	0.2	0.2
Po-218	0.4	0.2	0.3	0.3	0.3	0.2	0.2
Pb-214	0.4	0.2	0.3	0.3	0.3	0.2	0.2
Bi-214	0.4	0.2	0.3	0.3	0.3	0.2	0.2
Po-214	0.4	0.2	0.3	0.3	0.3	0.2	0.2
Pb-210	13.8	8.6	8.9	10.9	8.6	10.6	5.1
Bi-210	13.8	8.6	8.9	10.9	8.6	10.6	5.1
Po-210	13.8	8.6	8.9	10.9	8.6	10.6	5.1
U-235 Series							
U-235							
Th-231							
Pa-231							
Ac-227							
Th-227							
Ra-223							
Rn-219							
Po-215							
Pb-211							
Bi-211							
Tl-207							
Th-232 Series							
Th-232							
Ra-228	0.8	0.5	0.6	0.7	0.5	0.5	0.3
Ac-228	0.8	0.5	0.6	0.7	0.5	0.5	0.3
Th-228	0.3	0.1	0.2	0.2	0.2	0.2	0.1
Ra-224	0.3	0.1	0.2	0.2	0.2	0.2	0.1
Rn-220	0.3	0.1	0.2	0.2	0.2	0.2	0.1
Po-216	0.3	0.1	0.2	0.2	0.2	0.2	0.1
Pb-212	0.3	0.1	0.2	0.2	0.2	0.2	0.1
Bi-212	0.3	0.1	0.2	0.2	0.2	0.2	0.1
Po-212	0.2	0.1	0.1	0.2	0.1	0.1	0.1
Tl-208	0.1	0.0	0.1	0.1	0.1	0.1	0.0
K-40	3.1	1.7	2.2	2.5	2.0	1.9	1.1

Appendix 2
Radionuclides Dose Conversion Factor in Sv/Bq Committed Effective Dose in µSv/a per Unit Intake

			Fish	Diary	Meat	Meat	Poultry	Poultry	Eggs							
			Freshwater	Diary	Beef	Pork	Chicken	Chicken	Eggs							
			King Carp	Butter	Brisket	Leg chops	Thighs	Livers	Eggs (chicken)							
			Moisture:	48.00%	Moisture:	0.00%	Moisture:	72.85%	Moisture:	71.07%	Moisture:	56.05%	Moisture:	ERR	Moisture:	75.23%
			Intake in kg/a	Intake in kg/a	Intake in kg/a	Intake in kg/a	Intake in kg/a	Intake in kg/a	Intake in kg/a							
			100	30	6	2	200	40	200	40	75	15	3	0.5	30	6
	> 17 a	< 1 a	> 17 a	< 1 a	> 17 a	< 1 a	> 17 a	< 1 a	> 17 a	< 1 a	> 17 a	< 1 a	> 17 a	< 1 a	> 17 a	< 1 a
U-238 Series																
Ra-226	2.80E-07	4.70E-06	3.61E+01	1.08E+01	3.02E+00	1.01E+00	2.59E+01	5.19E+00	3.67E+01	7.34E+00	1.58E+01	3.16E+00	2.02E+00	3.37E-01	4.67E+00	9.34E-01
Rn-222	NA	NA														
Po-218	NA	NA														
Pb-214	1.40E-10	2.70E-09	1.81E-02	5.42E-03	1.51E-03	5.04E-04	1.30E-02	2.59E-03	1.83E-02	3.67E-03	7.91E-03	1.58E-03	1.01E-03	1.69E-04	2.34E-03	4.67E-04
Bi-214	1.10E-10	1.40E-09	1.42E-02	4.26E-03	1.19E-03	3.96E-04	1.02E-02	2.04E-03	1.44E-02	2.88E-03	6.21E-03	1.24E-03	7.95E-04	1.33E-04	1.83E-03	3.67E-04
Po-214	NA	NA														
Pb-210	6.90E-07	8.40E-06	4.57E+03	1.37E+03	2.22E+02	7.40E+01	3.70E+03	7.40E+02	2.84E+03	5.69E+02	1.04E+03	2.08E+02	2.16E+02	3.59E+01	5.24E+02	1.05E+02
Bi-210	1.30E-09	1.50E-08	8.62E+00	2.59E+00	4.18E-01	1.39E-01	6.97E+00	1.39E+00	5.36E+00	1.07E+00	1.96E+00	3.92E-01	4.06E-01	6.77E-02	9.87E-01	1.97E-01
Po-210	1.20E-06	2.60E-05	7.96E+03	2.39E+03	3.86E+02	1.29E+02	6.43E+03	1.29E+03	4.94E+03	9.89E+02	1.81E+03	3.62E+02	3.75E+02	6.25E+01	9.11E+02	1.82E+02
U-235 Series																
Th-232 Series																
Ra-228	6.90E-07	3E-05	1.93E+02	5.78E+01	1.31E+01	4.37E+00	1.71E+02	3.42E+01	1.73E+02	3.45E+01	7.30E+01	1.46E+01	9.09E+00	1.51E+00	2.42E+01	4.84E+00
Ac-228	4.30E-10	7.40E-09	1.20E-01	3.60E-02	8.18E-03	2.73E-03	1.07E-01	2.13E-02	1.08E-01	2.15E-02	4.55E-02	9.09E-03	5.66E-03	9.44E-04	1.51E-02	3.02E-03
Th-228	7.20E-08	3.70E-06	6.13E+00	1.84E+00	6.22E-01	2.07E-01	7.21E+00	1.44E+00	7.56E+00	1.51E+00	3.21E+00	6.43E-01	3.95E-01	6.59E-02	1.07E+00	2.15E-01
Ra-224	6.50E-08	2.70E-06	5.54E+00	1.66E+00	5.62E-01	1.87E-01	6.51E+00	1.30E+00	6.83E+00	1.37E+00	2.90E+00	5.80E-01	3.57E-01	5.95E-02	9.69E-01	1.94E-01
Rn-220	NA	NA														
Po-216	NA	NA														
Pb-212	6.00E-09	1.50E-07	5.11E-01	1.53E-01	5.18E-02	1.73E-02	6.01E-01	1.20E-01	6.30E-01	1.26E-01	2.68E-01	5.36E-02	3.29E-02	5.49E-03	8.95E-02	1.79E-02
Bi-212	2.60E-10	3.20E-09	2.22E-02	6.65E-03	2.25E-03	7.49E-04	2.61E-02	5.21E-03	2.73E-02	5.46E-03	1.16E-02	2.32E-03	1.43E-03	2.38E-04	3.88E-03	7.75E-04
Po-212	NA	NA														
Tl-208	NA	NA														
Total mev/a			1.28E+01	3.83E+00	6.26E-01	2.09E-01	1.03E+01	2.07E+00	8.02E+00	1.60E+00	2.95E+00	5.89E-01	6.03E-01	1.01E-01	1.47E+00	2.93E-01
Pb/Po excluded			2.41E-01	7.23E-02	1.74E-02	5.80E-03	2.12E-01	4.23E-02	2.24E-01	4.49E-02	9.52E-02	1.90E-02	1.19E-02	1.98E-03	3.10E-02	6.21E-03

Appendix 2 (Continued)
Radionuclides Dose Conversion Factor in Sv/Bq Committed Effective Dose in µSv/a per Unit Intake

		Vegetables	Vegetables	Vegetables	Vegetables	Vegetables	Vegetables	Fruit								
		Root	Legumes	Leafy	Tuberous	Tuberous	Yellow	Fruit								
		Beetroot	Green beans	Cabbage	Potatoes	Onions	Pumpkin	Tomato								
		Moisture:	82.23%	Moisture:	89.68%	Moisture:	90.70%	Moisture:	84.12%	Moisture:	88.78%	Moisture:	89.62%	Moisture:	95.10%	
		Intake in kg/a	Intake in kg/a	Intake in kg/a	Intake in kg/a	Intake in kg/a	Intake in kg/a	Intake in kg/a								
		170	68	130	52	130	52	130	52	130	52	130	52	130	52	
	> 17 a	< 1 a	> 17 a	< 1 a	> 17 a	< 1 a	> 17 a	< 1 a	> 17 a	< 1 a	> 17 a	< 1 a	> 17 a	< 1 a	> 17 a	< 1 a
U-238 Series																
Ra-226	2.80E-07	4.70E-06	1.85E+01	7.41E+00	8.44E+00	3.38E+00	1.10E+01	4.41E+00	1.19E+01	4.75E+00	9.46E+00	3.79E+00	7.64E+00	3.06E+00	5.75E+00	2.30E+00
Rn-222	NA	NA														
Po-218	NA	NA														
Pb-214	1.40E-10	2.70E-09	9.26E-03	3.70E-03	4.22E-03	1.69E-03	5.51E-03	2.21E-03	5.93E-03	2.37E-03	4.73E-03	1.89E-03	3.82E-03	1.53E-03	2.88E-03	1.15E-03
Bi-214	1.10E-10	1.40E-09	7.27E-03	2.91E-03	3.32E-03	1.33E-03	4.33E-03	1.73E-03	4.66E-03	1.86E-03	3.72E-03	1.49E-03	3.00E-03	1.20E-03	2.26E-03	9.04E-04
Po-214	NA	NA														
Pb-210	6.90E-07	8.40E-06	1.62E+03	6.47E+02	7.71E+02	3.09E+02	7.98E+02	3.19E+02	9.78E+02	3.91E+02	7.71E+02	3.09E+02	9.51E+02	3.80E+02	4.54E+02	1.82E+02
Bi-210	1.30E-09	1.50E-08	3.05E+00	1.22E+00	1.45E+00	5.81E-01	1.50E+00	6.02E-01	1.84E+00	7.37E-01	1.45E+00	5.81E-01	1.79E+00	7.17E-01	8.55E-01	3.42E-01
Po-210	1.20E-06	2.60E-05	2.82E+03	1.13E+03	1.34E+03	5.37E+02	1.39E+03	5.55E+02	1.70E+03	6.80E+02	1.34E+03	5.37E+02	1.65E+03	6.61E+02	7.89E+02	3.16E+02
U-235 Series																
Th-232 Series																
Ra-228	6.90E-07	3E-05	9.88E+01	3.95E+01	4.66E+01	1.87E+01	5.43E+01	2.17E+01	6.21E+01	2.48E+01	4.40E+01	1.76E+01	4.52E+01	1.81E+01	2.93E+01	1.17E+01
Ac-228	4.30E-10	7.40E-09	6.16E-02	2.46E-02	2.91E-02	1.16E-02	3.38E-02	1.35E-02	3.87E-02	1.55E-02	2.74E-02	1.10E-02	2.82E-02	1.13E-02	1.83E-02	7.31E-03
Th-228	7.20E-08	3.70E-06	3.64E+00	1.45E+00	9.64E-01	3.86E-01	1.76E+00	7.04E-01	2.33E+00	9.32E-01	1.81E+00	7.23E-01	1.81E+00	7.23E-01	1.10E+00	4.42E-01
Ra-224	6.50E-08	2.70E-06	3.28E+00	1.31E+00	8.70E-01	3.48E-01	1.59E+00	6.35E-01	2.10E+00	8.42E-01	1.63E+00	6.52E-01	1.63E+00	6.52E-01	9.97E-01	3.99E-01
Rn-220	NA	NA														
Po-216	NA	NA														
Pb-212	6.00E-09	1.50E-07	3.03E-01	1.21E-01	8.03E-02	3.21E-02	1.47E-01	5.87E-02	1.94E-01	7.77E-02	1.51E-01	6.02E-02	1.51E-01	6.02E-02	9.20E-02	3.68E-02
Bi-212	2.60E-10	3.20E-09	1.31E-02	5.25E-03	3.48E-03	1.39E-03	6.35E-03	2.54E-03	8.42E-03	3.37E-03	6.52E-03	2.61E-03	6.52E-03	2.61E-03	3.99E-03	1.60E-03
Po-212	NA	NA														
Tl-208	NA	NA														
Total mev/a		4.56E+00	1.82E+00	2.17E+00	8.69E-01	2.26E+00	9.03E-01	2.76E+00	1.10E+00	2.17E+00	8.69E-01	2.66E+00	1.07E+00	1.28E+00	5.13E-01	
Pb/Po excluded		1.25E-01	4.98E-02	5.70E-02	2.28E-02	6.88E-02	2.75E-02	7.86E-02	3.15E-02	5.70E-02	2.28E-02	5.65E-02	2.26E-02	3.73E-02	1.49E-02	

Appendix 3
Positive values in Bq/kg wet mass

Food Category I:	Fish	Meat	Eggs	Vegetables
Food Category II:	Freshwater	Beef	Eggs	Yellow
Description:	King Carp	Brisket	Eggs (chicken)	Pumpkin
Wet Mass [g]:	3806.8	4932.9	7191.7	6906.6
Dry Mass [g]:	1979.5	1339.1	1781.6	717
% Moisture:	48.0	72.9	75.2	89.6
U-238 Series				
U-238				
Th-234				
Pa-234m				
U-234				
Th-230				
Ra-226	0.87	0.35	0.25	0.13
Rn-222	0.87	0.35	0.25	0.13
Po-218	0.87	0.35	0.25	0.13
Pb-214	0.87	0.35	0.25	0.13
Bi-214	0.87	0.35	0.25	0.13
Po-214	0.87	0.35	0.25	0.13
Pb-210				
Bi-210				
Po-210				
U-235 Series				
U-235				
Th-231				
Pa-231				
Ac-227				
Th-227				
Ra-223				
Rn-219				
Po-215				
Pb-211				
Bi-211				
Tl-207				
Th-232 Series				
Th-232				
Ra-228				
Ac-228				
Th-228	0.74		0.28	
Ra-224	0.74		0.28	
Rn-220	0.74		0.28	
Po-216	0.74		0.28	
Pb-212	0.74		0.28	
Bi-212	0.74		0.28	
Po-212	0.47		0.18	
Tl-208	0.27		0.10	
K-40	180.90	73.62	36.91	64.08

Appendix 4

Radionuclides	**Dose Conversion Factor in Sv/Bq**		**Committed Effective Dose in µSv/a per Unit Intake**							
			Fish	Meat	Eggs	Vegetables				
			Freshwater	Beef	Eggs	Yellow				
			King Carp	Brisket	Eggs (chicken)	Pumpkin				
			Moisture:	48.00%	Moisture:	72.85%	Moisture:	75.23%	Moisture:	89.62%
			Intake in kg/a	Intake in kg/a	Intake in kg/a	Intake in kg/a				
			100	30	200	40	30	6	130	52
	> 17 a	< 1 a	> 17 a	< 1 a	> 17 a	< 1 a	> 17 a	< 1 a	> 17 a	< 1 a
U-238 Series										
Ra-226	2.80E-07	4.70E-06	24.2	122.0	19.7	66.2	2.1	7.1	4.9	32.9
Rn-222	NA	NA								
Po-218	NA	NA								
Pb-214	1.40E-10	2.70E-09	0.0	0.1	0.0	0.0	0.0	0.0	0.0	0.0
Bi-214	1.10E-10	1.40E-09	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Po-214	NA	NA								
Pb-210	6.90E-07	8.40E-06								
Bi-210	1.30E-09	1.50E-08								
Po-210	1.20E-06	2.60E-05								
U-235 Series										
Th-232 Series										
Ra-228	6.90E-07	3E-05								
Ac-228	4.30E-10	7.40E-09								
Th-228	7.20E-08	3.70E-06	5.3	82.3			0.6	6.2		
Ra-224	6.50E-08	2.70E-06	4.8	60.1			0.5	4.5		
Rn-220	NA	NA								
Po-216	NA	NA								
Pb-212	6.00E-09	1.50E-07	0.4	3.3			0.1	0.3		
Bi-212	2.60E-10	3.20E-09	0.0	0.1			0.0	0.0		
Po-212	NA	NA								
Tl-208	NA	NA								
Total µSv/a			34.9	267.9	19.7	66.3	3.3	18.0	4.9	32.9

ANNEX 1

Title: Fingerprinting of various foodstuffs from the Witwatersrand area, South Africa, for essential and toxic element composition, using INAA

Client: Radioanalysis
Project Leader: Nicholas Sackitey Opata

DESCRIPTION

1. BACKGROUND

An ongoing project in the Radioanalysis laboratory (RA-TA-072) is the investigation of the possible presence of naturally occurring radionuclides (NORM's) and essential and toxic elements in foodstuffs in South Africa, and more specifically in the Witwatersrand area, which is the economic hub of South Africa. Various foodstuffs have already been screened for their possible radioactivity content, but the element composition should still be investigated.
Furthermore, Radioanalysis has been accepted as participant in an IAEA Coordinated Research Project (Chief Scientific Investigator: Dr A Faanhof) on "The use of Nuclear and Related Techniques in Studying Health Impacts of Toxic Elements consumed through foodstuffs contaminated by Industrial Activities". Through this technology action, it is therefore planned to address at least part of the above (the CRP will run over 3 years).

2. DELIVERABLE

A project technical report, acceptable to the IAEA, which describes the study performed, results obtained, comments and recommendations for further investigations.

3. SPECIFICATIONS

(a) This initial study will be focussed on foodstuffs produced and consumed in the Witwatersrand (Gauteng) area of South Africa. It will also only focus on foodstuffs, and not environmental factors of influence (i.e. irrigation water, soil or fertilizers used for growing vegetables, etc.).
(b) Only Neutron Activation Analysis (NAA), including sample preparation therefore, will be used for this study. Other complementary analytical techniques such as XRF and ICP-MS, will not be investigated for this study. These techniques may be used through collaboration with interested participants from the Africa Region.

4. PROGRAM

4.1. Literature study

(a) Evaluation of the dietary intake of food by the South African population based on available statistics on local food production and consumption.
(b) In conjunction with (a), also collect information on the essential elements and toxic elements normally found in foodstuffs.

4.2. Sample preparation

(a) Assess the available routine sample preparation methods at NECSA on their applicability to various food matrices. The final aim is to obtain a dry powdered homogeneous material that has an acceptable shelf-life of at least three months, is not hygroscopic and can be dissolved for wet chemical processing. Advise on possible other equipment required for proper sample preparation and conservation if required.

(b) The final report should have comments/recommendations on the homogeneity of the materials at the 200 milligram level normally used for INAA. Homogeneity should be further evaluated at 1 gram and 10 gram levels for materials proven to be inhomogeneous at the 200 milligram level.

4.3. Analysis of foodstuffs for essential and toxic elements

A suite of samples from various food categories are already available for analysis. These, together with newly prepared samples should be analysed by INAA for the essential and toxic elements identified in 4.1 (b).

- Test irradiations are performed initially in order to optimise on the irradiation procedures applied.
- Individual element standards are prepared for irradiation and measurement together with the samples.
- The final report should include comments/recommendations on the possibility of using multi-element standards in order to reduce the total number of capsules irradiated and spectra accumulated.

5. SCHEDULE

#	Period	Activity	Detail						
1	6 - 8 March 2002(3 days)	Administrative arrangements	(a)	Registration as temporary NECSA worker(b)	Registration as radiation worker(c)	Registration as chemical worker			
2	11 - 15 March 2002(1 week)	Literature study	Ongoing, but dedicated time scheduled for one week						
3	18 March - 5 April 2002(3 weeks)	Sample preparation	(a)	Witness sample preparation by operational teams of Radioanalysis. This is done as and when samples are received for analysis	(b)	Perform sample preparation of further foodstuffs not already available	·	Witness microwave digestion of various sample materials·	First technical report to IAEA. Report to be reviewed by NECSA prior to release
4	8 - 16 April 2002	IAEA /AFRA Training course on QA/QC in radiochemistry, nuclear related analysis and NAA	Course presented by Radioanalysis at NECSA						
5	mid April - mid July 2002(3 months)	Analysis of essential and toxic elements by INAA	(a)	Perform test irradiations·	Prepare element standards, samples and quality control samples for analysis (approximately 70 irradiation capsules)·	Schedule irradiations and subsequent counting of samples·	Count samples ·	Mid-term technical report to IAEA by mid June 2002. Report to be reviewed by NECSA prior to release	
6	mid July - end August 2002(7 weeks)	Analysis of essential and toxic elements by INAA	·	Data processing: Analysis of spectral data and calculation of element concentrations in _g/g·	Quality control: Analysis of CRM's included in the study·	Compile final technical report. Report to be reviewed by NECSA prior to release to the IAEA			

POTENTIAL HUMAN EXPOSURE TO Pb, Cd, Zn, As and Hg TROUGH CONSUMPTION OF FOODSTUFFS GROWN OR BRED NEAR MINING AREAS IN SLOVENIA

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Abstract

Food contaminants and essential elements will be investigated in two Slovenian areas highly polluted with heavy metals due to former Pb and Zn mining (1424 - 1995) and a still active Pb smeltery using secondary Pb products in the Meža valley, and Idrija mercury mine activities from 1508-1994 in the Idrija region. For selected 'food' samples the present situation will be checked regarding the concentrations of contaminating metals (Pb, Cd, Zn and As or Hg). Determinations of Se will be included regarding its detoxifying role as an essential part of antioxidative enzymes and in forming insoluble complexes with some metals, either in food (especially of animal origin) or after digestion in humans. Since individual chemical forms of elements definitely determine bioavailability and toxicity, some speciation studies will also be performed on foodstuffs from contaminated areas, which exceed maxiumum permissible trace element levels. The speciation studies will include arsenic speciation since it is already known that inorganic forms are much more toxic than organic species, mercury speciation (MeHg, Hg) and biological speciation oregarding cellular distribution of metals between water soluble and unsoluble parts.

1. SCIENTIFIC BACKGROUND AND SCOPE OF PROJECT

Food contaminants and essential elements will be investigated in two Slovenian areas highly polluted with heavy metals due to former Pb and Zn mining (1424 - 1995) and a still active Pb smeltery using secondary Pb products in the Meža valley, and Idrija mercury mine activities from 1508-1994 in the Idrija region.

In these regions the soil is highly contaminated by past and/or present smelting activities particularly with Pb, Zn and Cd (to lesser extent also with As) in the Meža valley and mainly with Hg in the surrounding of Idrija. As most of the people eat locally produced food, special attention should be given to foodstuffs grown or bred in these areas. Especially since according to literature data, lead and mercury can be harmful (neurotoxicity) even in very low levels for children, who are the most critical and vulnerable group. This is because children have higher rates of respiration and metabolism than adults.

The Slovenian Institute of Public Health is largely concerned with routine annual monitoring of Hg, Pb, Cd in some vegetables, fruits, milk and meat products on the Slovenian market, but not with the investigation or monitoring of toxic elements in locally produced foodstuffs in risk regions. So there are no regular data about recent intake of Pb, Cd, Zn, As and Hg for people living in these contaminated areas. Some studies regarding soil and food contamination related to human health (total dietary intake) were performed previously in our institute and elsewhere, especially during intensive mining operations in the Meža valley (1, 2) and the town of Idrija (3, 4, 5). Nowadays we are included in the IAEA coordinated Research projects 'Speciation methods for As, Se and Cr using nuclear techniques'. Its subject is sampling, sample preparations and validation of methods developed for application in nutritional studies.

In present project a review of previous data regarding food contaminants (Zn, Cd, Pb, and Hg As) and essential elements (Se, Zn) will be made in areas of interest:

- The area around the lead and zinc mine and Pb smeltery in the Meža valley (Zn, Cd, Pb, As)
- The area near the Idrija mercury mine (Hg, Se, Cd)

Thereafter for selected 'food' samples the present situation will be checked and supplemented. In the Meža valley the total concentrations of Zn, Cd and Pb (FAAS/ETAAS) together with As and Se (RNAA/HG AFS) will be determined in crops grown in contaminated soils and compared to available data for the same crops from non-contaminated areas. In the area near the Idrija mercury mine Hg and Se (RNAA, CV AAS, HG AFS) concentrations will be followed in a similar way. Determinations of Se will be included regarding its detoxifying role as an essential part of antioxidative enzymes and in forming insoluble complexes with some metals, either in food (especially of animal origin) or after digestion in humans.

Further, the partitioning of Zn, Cd and Pb in sediments and soils from mining areas in the Meža valley and the area around the lead smeltery and "operational speciation" by the use of a sequential extraction procedure (BCR scheme) will be applied. On the basis of data on the distribution of these elements between easily and sparingly soluble sample fractions, estimation of the extent of metal pollution will be made and data compared to non-contaminated area. Speciation of Zn in aqueous soil extracts will also be performed in selected soil samples by applying anion-exchange convective interaction media (CIM) DEAE fast monolithic chromatography with FAAS and ES-MS-MS detection. The results obtained will be compared with total concentrations in crops samples from the same locations.

Since individual chemical forms of elements definitely determine bioavailability and toxicity, some speciation studies will also be performed on foodstuffs from contaminated areas, which exceed maxiumum permissible trace element levels. The speciation studies will include:

- Arsenic speciation since it is already known that inorganic forms are much more toxic than organic species, and
- Mercury speciation (MeHg, Hg)
  (For speciation studies IE/GC HPLC techniques will be combined with the above mentioned methods)
- Biological speciation of metal cellular distribution between water soluble and unsoluble parts

2. METHODS

Food samples: soil, different vegetables, fruits and domestic animals (laying hens) samples from contaminated regions

Metal analysis:

Neutron activation analysis - radiochemical, k_0 or cyclic instrumental: RNAA (Hg, Se), ko-INAA (multielemental – Cd, As, Zn, Se), CINAA (Se)

Cold vapour, flame and electrothermal atomic absorption spectroscopy: CV AAS (Hg), ETAAS (Pb, Cd – low levels), FAAS (Pb, Cd, Zn)

Hydrid generation atomic fluorescence spectroscopy: HG AFS (Se, As)

Speciation studies:

Gas chromatography (GC) and liquid high pressure chromatography (HPLC) with different gel or ionic exchange columns.
Water soluble cell fractions will be obtained by homogenisation and consequent ultracentrifugation.

3. RESULTS AND DISCUSSION

Regarding that slovenian research institute ERICO have already started with broader monitoring programe in Meža valley, we will wait to their results until next year and then start with speciation studies and selenium analysis in the samples found to be highly contaminated. In Idrija region the sampling was performed by us last year in october. We have collected different vegetable samples, some fruit samples and soil from 9 sampling stations from three different areas regarding the contamination as is shown on table 1. Three sampling stations were located near chimney of former smelting plant, six in different parts of Idrija city and one in the vilage next to Idrija town.

4. PLANS FOR FUTURE WORK

Until the end of this year and during the next year existing previous data on contaminated foodstuffs and dietary intakes for inhabitants of the Meža valley and the surroundings of Idrija will be collected. In order to assess the present status, the obtained samples from Idrija region will be analysed. Beside total concentrations of elements in samples with highly elevated levels, speciation studies of some elements will also be started.

TABLE I: SAMPLES OF VEGETABLES, FRUITS AND SOIL FROM DIFFERENT SAMPLING STATIONS IN THREE SAMPLING AREAS OF IDRIJA WITH SORROUNDING (THREE STATIONS NEAR FORMER SMELTING CHIMNEY, FIVE STATIONS IN IDRIJA CITY, ONE STATION IN VILAGE NEXT TO IDRIJA)

SAMPLES (oct. 2001)	**n**	*SAMPLING SITES*								
		SMELTING CHIMNEY			**CITY**					**Spodnja Idrija**
		1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
Potato	**2**	+		+						
Carrot	**8**	+	+	+	+	+	+	+	+	
Onion	**4**		+			+	+		+	
Red beet	**1**			+						
Radish	**1**		+							
Parsley	**9**	+	+	+	+	+	+	+	+	+
Celery	**1**				+					
Leek	**9**		+							
Lettuce	**5**	+	+	+	+	+	+	+	+	+
Cabbage	**1**	+	+	+	+			+		
Couliflo.	**1**								+	
Mangold	**1**					+				
Pumpikn	**3**				+		+			
Tomato	**4**	+			+		+	+		
Cucumber	**4**				+	+	+		+	
Paprika	**2**				+		+			
S.pepper	**1**			+						
Bean	**4**	+			+			+	+	
Apple	**1**									+
Pear	**1**									+
Soil	**6**	+	+			+	+	+	+	

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TRACE ELEMENTS IN FISH FOR CONSUMPTION

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Abstract

The presence of toxic elements in fish may constitute a health hazard for consumers in general as well as for people with specific consumption patterns. The levels of lead, cadmium, total mercury, total and inorganic arsenic and certain other, primarily essential, metals will be determined in a large number of fish species and originating from freshwater lakes, brackish water and marine waters. The results will be used to make a risk assessment of their impact on human food consumption.

1. INTRODUCTION

Fish is a major food in many countries and the fishing industry supports the livelihood for a vast number of people. Certain population groups may have specific consumption patterns due to geographical conditions. Traditions may also give rise to large consumption of certain fish species, which may leave them exposed to certain contaminants. Other population groups may be at risk at specific times, e.g. during pregnancy. It is thus of major importance that fish and fish products are safe for consumption.

Contamination of fish by toxic elements may be caused by effluent from populated areas, which drains into fish habitats. It can also be due to specific industrial activities involving metal handling, e.g. Cd in metal plating industries and Hg from chlorine production plants, from which wastewater may contaminate local waters. Mining activities are also known to contaminate local waters with an array of elements, including Pb, Cd and Zn. Another problem is the acidification of freshwater lakes making e.g. Hg more mobile (soluble) and available for accumulation, and enrichment, in the food chain.

Fish contaminated by trace elements caused by human activity is thus mainly a problem in coastal areas as well as inland lakes and rivers and is not affecting fish in the large oceans to any large degree. Fish from marine waters may however be affected by other problems. The level of As is invariably higher in marine fish, than in fish from fresh or brackish waters. Large predatory species from marine waters, e.g. sharks and tuna, may have high levels of Cd and Hg in the muscle tissue, probably due to their place at the upper end of the food chain and relatively long life span.

2. SCIENTIFIC BACKGROUND AND SCOPE OF THE PROJECT

The European Union (EU) has agreed on setting maximum residue limits (MRL) for Pb, Cd and Hg in certain foods [1], in order to protect the population from overexposure to these toxic metals. Codex Alimentarius are proposing MRLs for the same metals and along the same line [2]. Much of the background data for these MRLs is old and has not been produced under the analytical quality assurance (AQA) demands that are required today. It has been

shown that engagement in AQA-procedures may have a direct effect on the results of e.g. Pb and Cd in fish [3], I.e. the better the analytical control procedures are described in a published report the lower, and more consistent, are the results. It is thus important that such procedures are written in a transparent way.

Fish is one of the food groups that are generally high in As. It is by now well established that the total content of As in foods is perhaps of less interest than the species that are of toxicological concern, which are identified as the inorganically bound compounds. It has therefore begun to be questioned whether MRLs for As in (certain) foods should be set on total As or on the sum of the inorganic species [4]. The ratio between total and inorganic As in foods is, however, still largely unknown.

Due to these questions, i.e. the difficulty in collecting data and establishing if their analytical quality is satisfactory, the European Commission has decided to encourage scientific cooperation (SCOOP) between the member countries [5] in order to collect and validate national data for these elements. Acceptable data will be used to estimate the intake of these elements in the different Member States and an assessment of the risk these elements pose to the general public through food consumption.

The scope of this project is thus:

2.1. To produce data for Pb, Cd and Hg using modern analytical techniques and following the AQA procedures required today [6]. These data will be used when the current MRLs are due to be re-evaluated in 2003 [1] and for setting local (national) recommendations for consumption of fish by certain risk groups, e.g. pregnant women, with regards to Hg.

2.2. To analyse total As and inorganic As in certain fish species to elucidate if there is a difference in the ratio total/inorganic As for different species of fish. These data will provide part of the material used for future discussions on MRLs for As.

2.3. To produce data for Co, Cr, Cu, Mn, Ni and Zn, using modern analytical techniques and following the AQA procedures required today. Such data are important for estimation of intake of these metals from different sources. They are also important from an environmental point of view, for future comparisons.

The results for Pb, Cd, Hg and As will be included in the SCOOP-project to the extent they are available before the deadline.

3. METHODS

Samples of fish is collected from the different fishing districts with the aid of staff from the Swedish National Board of Fisheries and local fishery organisations. The fish is kept frozen until the time of analysis, when it is thawed. Samples of muscle tissue are freed from skin and bone using a stainless knife. The muscle samples are then homogenised in a mixer with a stainless steel blade and distributed to the participating laboratories.

The metals Pb, Cd, Co, Cr, Cu, Mn, Ni and Zn are determined by atomic absorption spectrometry (AAS) after either dry ashing [7] or microwave pressure digestion [8]. In most cases Pb, Cd, Co, Cr and Ni are determined by graphite furnace - AAS and Mn and Zn by flame-AAS. As a complement, inductively coupled plasma - mass spectrometry (ICP-MS) will be used, primarily for verification of results.

Total Hg is determined by Cold Vapour-ICP-atomic emission spectroscopy (CV-ICP-AES) after an open digestion procedure including perchloric acid [9].

Total As will be determined by ICP-MS after microwave digestion. The instrument is of the new generation that incorporates a "collision cell", in which a small amount of a selected gas (e.g. H) is introduced into the ion stream. The result is that many argon induced polyatomic ions are reduced or diminished [10, 11]

Inorganic As is determined by HPLC-ICP-MS after extraction with chloroform-methanol-water and separation by HPLC [12].

The laboratories taking part in the study are using ISO/IEC 17025 [6] as the basis of their AQA. They use appropriate CRMs at regular intervals and participate in relevant proficiency testing programmes at intervals.

4. RESULTS AND DISCUSSION

Only very few data are yet available from the present project for Pb and Cd in fish. A previous survey of trace elements in fish [3], carried out under strict AQA-procedures, indicate that the levels are very low in all the species analysed, as shown in table 1. All results for Pb are far below the MRLs (0.2 mg/kg for most fish species and 0.4 mg/kg for e.g. eel) decided by the EU [1]. For Cd the difference between the found levels and the MRLs (0.05 mg/kg for most fish species and 0.1 mg/kg for e.g. eel) is not very big [1]. A study of Pb and Cd in tuna, within this project, resulted in a consistently low level of Pb, whereas the Cd level showed a surprising degree of variation (Table 1) and may even exceed the MRL.

TABLE I: LEVELS OF PB AND CD IN CERTAIN SPECIES OF FISH. RESULTS IN MG/KG FRESH WEIGHT, N=NUMBER OF SAMPLES

Specie	**n**	**Study**	**Pb**		**Cd**	
			Min	**Max**	**Min**	**Max**
Tuna fresh	6	Present	<0.003	<0.003	0.005	0.056
Tuna canned	26	Present	<0.003	0.045	0.003	0.17
Atlantic herring	3	Previous [3]	<0.005	<0.005	0.005	0.020
Baltic herring	3	Previous [3]	<0.005	0.011	0.014	0.034
Pike	5	Previous [3]	<0.005	0.005	<0.0005	<0.0005
Plaice	4	Previous [3]	<0.007	<0.007	<0.001	<0.001
Eel	3	Previous [3]	0.002	0.003	0,0007	0.022

No new data are yet available for the metals Co, Cr, Cu, Mn, Ni and Zn in fish, with the exception of tuna which data are not presented here. Previous data are found in reference [3].

Previous results for Hg from a survey presented in 1993 (13) showed that fish from freshwater lakes had higher levels than the same species caught in the Baltic Sea, which

contains brackish water (Table 2). A new study from the Swedish lake Vänern gives light to the situation in a lake where previous industrial activities has left its mark [14]. It was also found that halibut and swordfish contained very high levels of Hg.

The few results available from this survey tend to verify that freshwater lakes constitute a greater problem than fish from the Baltic Sea with its brackish water. In tuna the Hg-level was much lower than in several other marine species. The MRL for Hg in fish is 0.5 mg/kg for perch, pikeperch, burbot and mackerel. In pike, halibut, swordfish and tuna the MRL is 1.0 mg/kg.

TABLE II: LEVELS OF HG IN CERTAIN SPECIES OF FISH ORIGINATING FROM DIFFERENT TYPES OF WATER. MEAN LEVELS IN MG/KG FRESH WEIGHT, NUMBER OF SAMPLES IN BRACKETS.

Species	**Study**	**Type of water**		
		Freshwater lakes	**Baltic sea**	**Marine waters**
Perch	Previous [12]	0.66 (7)	0.35 (8)	
Pike	Previous [12]	0.57(7)	0.31 (7)	
Pike	Present		0.11 (10)	
Pikeperch	Previous [12]	0.28 (7)	0.13 (7)	
Pikeperch	Present		0.11 (10)	
Burbot	Present	0.75 (9)		
Mackerel	Previous [12]			0.07 (7)
Halibut	Previous [12]			0.67 (12)
Swordfish	Previous [12]			1.5 (3)
Tuna	Present			0.21 (21)

The previous study of As in fish [3] showed that there is great difference in concentration depending on the type of water, and with the highest levels in fish from marine waters. As some species can survive in different types of water and have very different As levels, it is evident that the habitat may be the main factor for the As-concentration in the fish (Table 3). The results available, so far, from the determination of inorganic As, i.e. the sum of arsenite and arsenate, was below the limit of detection for salmon (Table 3).

TABLE III: LEVELS OF AS IN CERTAIN SPECIES OF FISH. MEAN LEVELS IN MG/KG FRESH WEIGHT. NUMBER OF SAMPLES IN BRACKETS. ALL RESULTS FOR TOTAL AS ARE FROM REFERENCE 3.

Species	**Freshwater lakes**		**Baltic sea**		**Marine waters**	
	Total	**Inorganic**	**Total**	**Inorganic**	**Total**	**Inorganic**
Mackerel					1.8	TBD*
Plaice					13	TBD
Salmon	0.10		0.98	<0.015		<0.015
Cod			0.43		4.8	
Perch	0.024		0.72			
Pike	0.052		0.31			

*To be determined

When the results for inorganic As becomes available for mackerel and plaice it will, perhaps, be possible to draw some conclusions regarding the general ratio between organic and inorganic As-species in fish. No MRLs for As in fish has yet been established.

5. PLANS FOR FUTURE WORK

For the near future, focus will probably be on the inorganic As-constituent in foods that are known to have considerable levels of total As. One such food is rice, which may contain levels in the order of 0.1-0.3 mg/kg, which considerably more than in wheat with levels of <0.05 – 0-1 mg/kg [15]. Although this level is not exceedingly high, it must be taken into account that rice is one of the most important foods on a global scale. Knowledge of the amount of inorganic As in rice may thus be of major importance when it comes to intake recommendations and setting of maximum residue limits for other foods than fish.

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USE OF NUCLEAR AND RELATED ANALYTICAL TECHNIQUES IN STUDYING HUMAN EXPOSURE TO TOXIC ELEMENTS CONSUMED THROUGH FOODSTUFFS CONTAMINATED BY INDUSTRIAL ACTIVITIES

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Abstract

Contaminated by industrial activities foodstuffs seem to be important but less studied source of human over-intake of trace elements including toxic ones. For Uzbekistan very important is that the typical local diet includes mainly the local food – meat, milk, rice, potatoes, vegetables, and fruits. Because of lack of irrigated arable lands and pastures many farms (state and private) are situated very close to the industrial sources of contaminants and roads (problem of leaded gas). Additional contamination of food is caused by application of phosphate fertilisers (fluorine, uranium, etc.). Making huge number of analyses in many cases we found significantly elevated concentration of some trace-elements (including toxic ones) in local foodstuffs. Quality of food is monitored very randomly for very limited number of toxicants like nitrates, pesticides, mercury, etc. The quality of food provided and sold on small markets (bazaars) by private producers is out of toxic elements monitoring. That means that having some information on average local diet in terms of proteins, carbohydrates, calories, etc. Uzbekistan practically has not systemised information about the body burden by over-intake of some trace-elements (including toxic ones) which could be compared with the regional medical statistics.

There are several heavily contaminated areas in Uzbekistan. For the proposed CRP should be chosen the following two – Amalyk (city with non-ferrous metals factory, phosphate fertilisers factory, chemical factory, etc. This city is situated close to row-cement factory, coal mines, and decommissioned uranium mines and mill sites), and, possibly, Samarkand (city with phosphate fertilisers factory and other sources. In addition this city is situated in Hg-Sb biogeochemical province with naturally elevated levels of some toxic elements). Available at present is information of an environment contamination, human hair composition, and health status. In process are other studies in these cities. The information available looks very alarming. To obtain more complete view of situation additional studies of food (mainly of local origin) and drinking water (also very important for Uzbekistan) should be extremely important. Taking into consideration growing consumption of preparations (salt, vitamins, garlic, etc.) containing additions of essential trace elements it should be also of interest to estimate role of these preparations as a source of additional uptake of elements (even essential elements should be harmful in overdoses. And final task should be comparison of data obtained with the local population health status.

1. SCIENTIFIC BACKGROUND AND SCOPE OF THE PROJECT

Contamination of the environment is one of the most important problems of the present century. Monitoring of the environment having the aim to determine the present situation, to detect sources of contamination, to propose measures for reduction of an environment contamination, and, finally, to reduce harmful impact on human health deals with surface (including drinking) water, atmosphere (regional, occupational, etc.), soil. Less widely is monitored biota (plants, human and animal samples, etc.).

Role of intake of toxic elements with foodstuffs is till now rather unstudied. Dietology works with the food quality (calories, carbohydrates, proteins, etc., and sometime with essential trace elements searching for nutritional elements deficiency.

Special importance of the starting Project for Uzbekistan is connected with peculiarities of the typical local diet which includes mainly the local food – meat, milk, rice, potatoes, vegetables,

and fruits. In difference to European countries there practically absents wide international exchange of foodstuffs. Most foodstuffs in Uzbekistan is produced in small private hose-farms. Because of lack of irrigated arable lands and pastures many farms (state and private) are situated very close to the industrial sources of contaminants and roads (problem of leaded gas). Additional contamination of food is caused by application of phosphate fertilisers (fluorine, uranium, etc.). Making huge number of analyses in many cases we found significantly elevated concentration in plants of some trace-elements (including toxic ones).

The quality of food is monitored very randomly for very limited number of toxicants like nitrates, pesticides, and mercury. The quality of food provided and sold on small markets (bazaars) by private producers is out of toxic elements monitoring. That means that having some information on average local diet in terms of its nutritional quality (calories, proteins, carbohydrates, etc.) Uzbekistan practically has not systemised information about the body burden by over-intake of some trace-elements (including toxic ones) which could be compared with the regional medical statistics.

There are several heavily contaminated areas in Uzbekistan. For the proposed CRP should be chosen the following two - Amalyk (city with non-ferrous metals factory, phosphate fertilisers factory, chemical factory, etc.). This city is situated close to row-cement factory, coal mines, and decommissioned uranium mines and mill sites), and possibly Samarkand (city with phosphate fertilisers factory and other sources. In addition this city is situated in Hg-Sb biogeochemical province with naturally elevated levels of some toxic elements). As a reference area Tashkent should be chosen. Available at present is information of an environment contamination, human hair composition, and health status. In process are other studies in these cities. The information available looks very alarming. To obtain more complete view of situation additional studies of food (mainly of local origin) and drinking water (also very important for Uzbekistan) should be extremely important. Taking into consideration growing consumption of preparations (salt, vitamins, garlic, etc.) containing additives of essential trace elements it should be also of interest to estimate role of these preparations as a source of additional uptake of elements (even essential elements should be harmful in overdoses. And final task should be comparison of data obtained with the local population health status.

2. METHODS

For many years (more than 40) Institute of Nuclear Physics works successfully in elaboration and application of nuclear analytical methods in many fields of science, industry, agriculture, medicine, environmental sciences, etc. The main method is Instrumental Activation Analysis but there are used also Activation Analysis with Radiochemical Separation and with Preconcentration. There are also used related methods like XRF-analysis, prompt gamma from neutron capture, analysis using accelerators and isotope neutron sources. For elements “difficult” for neutron activation analysis is used isotope dilution, AAS, fluorometry a.o. Existing possibilities as well as existing at the Institute of Nuclear Physics experience should be successfully used in the starting Programme.

Concerning to AQA/AQC it should be mentioned that the Institute for many years participates in certification of national and international Standard Reference Materials. The choice of proper SRM and intercalibration seems to be very important in the starting CRP especially to ensure comparability of data obtained by participating teams in different countries.

Extremely important is elaboration and harmonisation of the sampling protocol beginning from determination of the typical for participating country diet including analytical protocol and finishing by the data obtained statistical treatment procedure. It is necessary to underline that existing in dietology sampling protocols are unacceptable because dealing with foodstuffs nutritional quality they do not concern differences of elemental composition of this same food produced in different areas, and different biogeochemical conditions, and under different levels of the environment contamination. This stage should also include of protocol of samples treatment (cleaning, drying, storage, etc.).

3. PROGRAMME OF WORK FOR 2002

3.1. Selecting study and reference sampling sites within the study areas.

Uzbekistan is a country on the South of the FSU. It borders with Turkmenistan, Kazakhstan, Kirghyzstan, Tadjikistan, and Afghanistan. It has 447,000 sq. km area and nearly 25 million inhabitants. Uzbekistan is an agro-industrial country having more than 39 million hectares of agricultural lands from which more than 4.2 million hectares are irrigated lands (more than 2/3 of the FSU Central Asian region). Irrigated lands give more than 97% of the total agricultural production. Most industrially developed is Tashkent district (Tashkent is a capital of Uzbekistan) which is 15.6 thousand square km in size with about 4.5 million inhabitants. Most of the territory is submontane flatness depressed to the Syr-Darya river. On N and NE are Thian-Shian mountains. There are situated 16 cities. There are regular sources of contamination - concrete mixing plants, cable works, brick works, canning factories, engineering plants, metal-working plants, engine works, breweries, fruit-and-vegetable processing plants, assembly plants, tractor works, power-and-heating plants, etc., etc.

But there are also cities with beside regular sources the very specific sources of contaminants like:

- Chirchik – nitric fertilisers, factory of hard alloys (Mo, W, Cr, etc.);
- Yangi-Abad – decommissioned uranium mines and uranium ores milling site;
- Angren – coal mines (local coal contains elevated amount of uranium);
- Akchangharan – large power-and-heating plant working on coal, row cement factory;
- Bekabad – ferrous metallurgy;
- Almalyk – chemical factory, non-ferrous metals mines and factories (Cu, Zn, Pb, etc.).

That means that in this region is a lot of sources of contamination and it is not too easy to attribute the contamination to certain source.

According to data collected earlier high levels of contamination are found in Almalyk and it's vicinity. Almalyk has about 120 thousand of inhabitants. Total area is 97 square km. The main sources of contamination are:

- Non-ferrous integrated works (95% of contaminants).
- Ammophos factory.
- Chemical factory (washing powder, etc.).
- Factory of building materials.
- Furniture-making factory.
- Power-and-heating plants.
- Boiler houses.
- Vehicles (leaded gasoline).

The total exhalation into atmosphere from all sources of pollution in 2000 is about 100,062 in metric tons/year. There is a trend of elevation of the atmosphere contamination. The data on Almalyk suburban soil contamination by mobile forms of toxic elements also show increase of contamination. Near non-ferrous metals integrated works and the Ammophos factory sporadically were detected extremely high relative (to background level - BL) levels of mobile forms of Pb (to 206 BL), Cu (to 660 BL).

Almalyk is placed on left side of the Angren river. Most of factories have efficient water cleaning facilities or are using closed water circuit. Water of Angren river contains elevated concentrations of some elements (e.g. uranium) but it may be caused by decommissioned mines and milling sites and deposits of coal with elevated uranium contents. These sources of contamination are situated in upper stream of the river. Nevertheless in bottom sediments of irrigation system were found extremely high concentrations of some toxic elements (Sb, U, Cd). Under question is also composition of groundwater. There were found statistically very significant correlations for diseases frequency and total contaminants exhalation. For Almalyk the correlation coefficient for these diseases was 0.92-0.97. There is a trend of increase of the diseases frequency. That means that Almalyk may be considered as a first candidate of the area to be studied.

The second possible area may be Samarkand which is situated in natural biogeochemical anomaly province with naturally elevated levels of Sb and Hg. For this area the institute has several data on foodstuffs composition.

As a reference area the Tashkent district may be considered.

For all these three areas exists rich information on environmental situation but it should be underlined that there do not exist any systemised data on foodstuffs composition especially for toxic trace elements.

So, the first step of the Programme should be collection and systematisation of information on environmental situation and health status on the selected areas of the study.

3.2. Designing experimental protocol and sampling programme

Elaboration of sampling protocol seems to be the most important step because absence (or lack) of recommendation for foodstuffs study from the point of view of foodstuffs contamination. Probably the first step is to determine the typical local diet composition and to determine the most important components of local diet. We believe that the Programme should include the drinking water sampling too.

Analytical procedure depends on possibilities of participating teams. Obviously taking into account the novelty of the Programme it should be useful do determine as much elements as possible but it should be also necessary to determine by all participants the priorities of elements to be determined to obtain comparable data.

3.3. Validating analytical methods and procedures to be used within the project (neutron activation analysis, XRF-analysis, and other available methods)

This stage should include preparation of written analytical procedures and AQAS/AQAC. Institute of Nuclear Physics (as well as all participating countries) is for many years deeply involved into analysis of new developing SRMs. But to obtain reliable data the list of SRMs

to be used within the Programme should be also discussed with other participants. Preferably the first meeting should determine the type (types) of SRMs to be used by all participants. We believe that the IAEA may help to provide the most modern, most reliable SRMs most similar to the samples to be studied.

3.4. Collecting and analysing pilot samples to evaluate the appropriateness of the study design

Within the first year according to the results of the step # 3.2 the most typical samples of foodstuffs should be collected from one or two studied and one reference areas and analysed. This stage will allow to estimate the homogeneity of the diet components elemental composition to determine number of samples to be collected in the 2003 year and to determine significantly elevated elements to estimate of elements priority.

3.5. Choice and preparing appropriate software for data processing and evaluation

There exists a number of commercial and home-made programs for data processing (data bases, statistical treatment, etc.). This stage will include choice of existing programs and treatment of data obtained in the stage # 3.4. Despite small statistics this stage will allow to estimate the frequency distribution pattern and choice the linear or geometrical approximation, to detect possible correlations, to estimate acceptability (or fruitfulness) of multifactor statistical treatment procedures (principal components, Fisher discriminant analysis, trees, etc.).

4. EXPECTED OUTPUTS/RESULTS FOR 2002

Selection of the study area (areas) and reference area. Systemisation of available information on environmental situation and health status on the selected areas of the study. Determination of the typical local diet composition and determination of the most important components of local diet. Determination of priorities of elements to be determined to obtain comparable data. Preparation of written analytical procedures and AQAS/AQAC. Collection and analysis of most typical samples of foodstuffs. Estimation of the homogeneity of the diet components elemental composition to determine number of samples to be collected in the 2003 year and to determine significantly elevated elements to estimate of elements priority. Choice and preparing appropriate software for data processing and evaluation. Preparation of the 2003 Programme.

5. PROGRAMME OF WORK FOR 2003

According to the results of 2002 year in 2003 and final work Programme all samples should be collected and analysed. It will allow to start in 2004 the data statistical treatment and interpretation and to make final conclusion and proposal for further work in this extremely important and interesting field.

CONCLUSION

Idea of the started CRP seems to be very important and interesting. There is a knowledge on environmental contamination, on normal elements intake, on human health, etc. but we never met systemised data on trace elements (including toxic ones) intake in case of foodstuffs produced in industrially contaminated area. One can expect that the data obtained in various areas will be important contribution to the Life Sciences and will allow to prepare new recommendations for human health protection.

USE OF NUCLEAR AND RELATED TECHNIQUES IN STUDYING HEALTH IMPACTS OF TOXIC ELEMENTS (As, Hg, Cu, Pb, Zn, Se and Cd) CONSUMED THROUGH FOODSTUFFS CONTAMINATED BY INDUSTRIAL ACTIVITIES.

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Abstract:

Study and application of nuclear - related analytical techniques have been being one of main tasks at NRI since 1984 to now. With one reseach Reactor, some equipments for radioactivity measuring and also many physico-chemical anlysers (Polarography, Stripping Volt Ammetry, AAS, UV-VIS...), the nuclear – related analytical methods have developed and applying at our institute. The past of more than 18 years we have carried out some national scientific research projects, IAEA reseach contracts and many economic contracts for different scientific – technological fields including: environment, agriculture, geology, biology, mineral oil, industry....Obtained results have contributed for developing of our Institute, other scientific – technological sectors and also economic – social developments of Viet nam. These reseach directions will be continue in the future.

1. INTRODUCTION

Center for analytical Techniques and Environmental Research (CATER) has 21 persons, it belong to Nuclear Research Institute (NRI). After more than 18 years carried out of analytical actions, We are having some knowleges and experiences in research and applying fields for economic – social developments of our country.

We are having now some following analytical equipments:

1.1. Dalat Nuclear Reactor with thermal power about 500 kW, it is a kind of research Reactor: former TRIGA Mark II reactor. Construction of this reactor is including:

- Two dry channels: 7-1, 13-2,
- A thermal column,
- One wet channel: 1-4,
- Inside of the reactor there are a neutron trap and a rotary specimen rack in the graphite reflector consisting of 40 irradiation positions.

Since 1984 the reactor has been operated mainly for radioisotope production, neutron activation analysis and other related studies. The following NAA methods are being carried out at DNRI: Instrumental Neutron Activation Analysis (INAA), Radiochemical Neutron Activation Analysis (RNAA), Ko - standardization method (Ko-NAA), Delay Neutron Activation Analysis (DNAA) and Prompt Gamma Neutron Activation Analysis (PGNAA).

For analysing of the elements by NAA we have also 8 detectors Ge(HP) which are connected with 8 multichannel analysers (MCA) controlled by IBM/PC, among them there is one automatic analyser.

Neutron Activation Analysis (NAA) is one of the most sensitive, rapid, accurate methods for determination of major - minor - trace elements and heavy-toxic metals in different materials. This method has a very important role to study elemental compositions in geo – bio – environmental samples. For determination of elements which have short lived radionuclides the samples are irradiated in channels 13-2, 7-1 and thermal column from 3 seconds to 30 minutes and for determination of elements which have long lived radionuclides, the irradiation process of the samples is carried out in the rotary specimen rack or at neutron trap. The irradiation and cooling times depend on characteristics of the nuclide of elements and the sample to be analyzed.

The characteristics and the parameters of neutron spectrum of Dalat nuclear reactor are shown in Table 1.

TABLE I: IRRADIATION FACILITIES AND THEIR CHARACTERISTIC PARAMETERS OF DALAT REACTOR

Irradiation positions	Thermal neutron flux ($n.cm^{-2}s^{-1}$)	Average Rcd Value	Note
Neutron trap	2.21×10^{13}	2.93	Wet channel with beryllium moderator, diameter: 64 mm, length: 600 mm for RI and NAA
Rotary Specimen Rack	4.27×10^{12}	3.0	40 irradiation holes, diameter 40 mm, length: 30 mm for NAA and RI
Channel 1 – 4	1.28×10^{13}		Wet channel, diameter: 32 mm; length: 600 mm for NAA and RI
Channel 7 –1	4.5×10^{12}	2.1	Dry channel with pneumatic transfer system for NAA
Channel 13 – 2	4.6×10^{12}	2.2	Dry channel with pneumatic transfer system for NAA
Thermal column	5.5×10^{9}	1.94	Dry channel with pneumatic transfer system for NAA
Horizontal (tangential) beam tube No-3	2.3×10^{6}		For PGNAA

1.2. We having also physico – chemical analytical equipments such as: Polarograph 646 VA Processor with 1 mecury drop electrod and some kind of rotating disc electrod; Spectrophotometer (UV-VIS); Atomic Absorption Spectrophotometer (AAS);

The nuclear-related analytical equipments have been using for determination of radioactivity - nutritional elements and toxic - trace metals in geo-biological and environmental samples. The sensitivity of these analytical methods is very good.

Some obtained results of the R & D program on the nuclear - related analytical techniques to determine the content of elements of geo – bio and environmental samples has been being carried out at the Center for Analytical Techniques and Environmental Research, NRI since 1984 in following Table 2:

TABLE II: RESULTS OF ANALYSIS FOR GEO-BIO-ENVIRONMENTAL SAMPLES FROM 1986 TO 2001

Year	Number of samples
1986	100
1987	200
1988	490
1989	2400
1990	2600
1991	2700
1992	3300
1993	950
1994	834
1995	927
1996	821
1997	976
1998	773
1999	1120
2000	1097
2001	1176

We carrying out the environmental studies in the following directions:

- Analysing of nutritional and radioactivity elements in food – foodstuffs samples, among them there were one IAEA Research Contract and two National Projects.
- Analysing of air pollution by the toxic heavy metals such as Zn, Cu, Cd, Pb…through one IAEA Research Contract and three National Projects.
- Investigation of environmental pollution by heavy metals and other toxic elements coming from industrial manufacturing and development.

The main projects have been carrying out:

1. UNDP-IAEA Research Contract No. 8549/RO on air pollution monitoring studies in Vietnam using nuclear- related analytical techniques. (12 /1995 - 12/1997)
2. FAO/IAEA Research Contract No. 7477/R1/RB on Factors of Radionuclide Transfer from Air, Soil and Fresh water to the Foodchain of Man in Monsoon-tropical conditions of Vietnam (1994 – 1996).
3. UNDP-IAEA Research Contract No. 8923/RO on “Reference Asian Man” (1997-2000).
4. Study and development of analytical techniques to estimate the quality of fresh water with impact of ores – mining, National Project (1999).
5. Analysing of heavy metals in see- water and weeds; National Project (2000).
6. Separating and enriching of heavy – toxic metals in aerosol samples have colleced at Dalat and HoChiMinh Cities for environmental monitoring (since 1996 to now).
7. The concentration of toxic elements and radionuclides in environmental objects in different areas of Viet nam.
8. Supporting the sustainable development of agriculture and improving the quality of human life;
9. Investigation of environmental pollution by heavy metals and other toxic elements

coming from industrial manufacturing and development. The samples of soil, water, plant, aerosol have been collected in different areas of Vietnam for determination of toxic elements and radionuclides.

10. IAEA - RCA Project RAS/2/010 " QA/QC for nuclear – related analytical methods"
11. Study and development of radiochemistry Nuclear Activation Analysis (RNAA) to determine trace elements in some purity materials (2002 – 2003).

Some obtained analytical results of aerosol and water samples at environmental monitoring stations and lakes in Dalat, Nha trang and HCM Cities are given in Tables 3, 4 and 5.

TABLE III: COMPOSITION OF HEAVY METALS IN FRESH WATER OF DALAT, DETERMINATION BY RNAA AND RELATED METHODS (MG/L)

Sample	Pb	Cd	Cu	Zn	As	Hg
Suoi-vang Lake	6.33	0.94	7.16	12.8	2.64	1.22
Tuyen -lam Lake	10.6	1.41	5.75	22.1	3.95	0.98
Chien -thang Lake	10.8	0.86	7.50	12.8	5.60	1.66
Ta -in stream	15.3	1.65	9.95	12.5	6.90	1.22
VN. Standard (1995)	50	10	100	1000	50	2
Inter. Standard (1963)	50	10	1000	5000	50	-

TABLE IV: COMPOSITION OF HEAVY METALS IN SEAWATER OF NHA TRANG, DETERMINATION BY RNAA AND RELATED METHODS (μG/L)

Element	Drying season	Raining season
As	3.9	2.5
Co	5.3	7.1
Cu	3.1	3.1
Fe	13415	13651
Mn	258	288
Pb	0.9	0.4

TABLE V: ELEMENT COMPOSITION OF AEROSOL COLLECTED IN DALAT AND HO CHI MINH CITIES, DETERMINATION BY NAA AND RELATED METHODS

Element	Concentration range (ng/m^3)	Element	Concentration range (ng/m^3)
Al	1200 – 7200	Mg	320 – 880
Ba	12 – 40	Mn	24 – 64
Br	10 – 18	Na	450 – 1150
Ca	1600 – 5600	Nd	0.6 – 2.2
Cd	0.004 – 0.030	Sb	800 – 4400
Ce	1.6 – 4.2	Sc	4 – 44
Cl	1000 – 1200	Se	0.3 – 0.8
Co	0.5 – 1.5	Sm	0.02 – 0.06
Cu	0.8 – 6.8	Ta	0.04 – 0.10
Fe	160 – 40000	Tb	0.02 – 0.06
Hf	0.08 – 0.35	Ti	160 – 400
Hg	0.004 – 0.04	U	0.06 – 0.20
I	0.3 – 0.4	V	8 – 42
K	600 - 2200	Yb	0.024 – 0.092

The nuclear - related analytical methods have been used to determine the heavy – toxic metals; radionuclides and trace elements in biological meterials for investigation of their distribution in plants, foods, foodstuffs… such as U, Th, Cd, Zn, Pb, T- Hg and Hg(methyl) in human urine and hair of women living in different areas of Viet nam. The main directions of application of these methods in present and future at DNRI are:

- Determination and assessment of the nutritional roles of microelements in agriculture plants growing in different kinds of soil.
- Determination and assessment of the concentration and distribution of elements in food used for feeding domestic animals and livestock.
- Quality control for heavy and toxic metals in foodstuffs including products for export.

2. SCIENTIFIC BACKGROUND OF THE PROJECT

2.1. Basis conditions

- DNRI having a good policy for scientific and technical analytical development in present and also in the futrue, such as: adding some new analytical equipments, carrying out QA/QC for NAA...
- Now there are 21 persons whose working in CATER. After more than 18 years of analytical activities, we have carried out 14 national scientific research projects, 4 IAEA reseach contracts and many other applying contracts, among some projects have relating with this research contract.

2.2. Analytical methods have been using at the DNRI

- Instrumental Neutron Activation Analysis (INAA).
- Radiochemical Neutron Activation Analysis (RNAA).
- Delay Neutron Activation Analysis (DNAA).
- Promp Gamma Neutron Activation Analysis (PGNAA).
- Measuring of α, β, γ.
- X-Ray fluorescene.
- Physico-chemical analytical methods: Polarography, Stripping Voltammetry, UV-VIS, Atomic Absorption Spectrophotometry (AAS), ...

The sensitivity of these methods is very good to determine the content and distribution of the elements in many kind of different sample.

2.3. The typical specialities of sampling stations of this project are

- Ho Chi Minh City is a biggest city of Vietnam with population of about five millions, Dongnai and Baria-Vungtau are also population Cities and are besides Ho Chi Minh City.
- These Cities are the biggest industrial zones of Vietnam where having many factories, processing zones that can made pollution of the living environment. Those are: refine of Iron, Tin, Petroleum; Production of battery; textile industry; make shoes; process food... These activities have been made contamination of air, water and in particular for foodstuffs such as: Vegetable (Salat, Celery, Tomato, Waterconvolvulus...); fresh-water fish (Carp, Snacke-head, Tench...); meat (Chicken, Duck, Pork, beef...).

The evaluation of concentration of toxic heavy metals (As, Hg, Se, Cu, Pb, Zn and Cd) in foodstuffs is very necessary because of the health impacts of these metals.

3. CONCLUSIONS

After more than 18 years of nuclear and related analytical activities by using Dalat reactor and other analytical equipments for determination elemental composition in geo – bio – environmental samples with thousands samples have analyzed every year for different sectors of science and technology in Viet nam it has seen that these methods have very important roles to study and apply. Those are very good conditions to carry out the contents of research contract No-11931/Regular Budget Fund (RBF).

For the further achievements in the development and application of these techniques, DNRI wishes to strengthen the co-corporation with other Institutions which belong to Agency as following problems:

- To introduce and implement the new nuclear - related analytical techniques and also procedures in the practice (RNAA, INAA, PGNAA,...).
- To exchange the experience in the applications of used analytical methods in different fields of science and technology such as geochemistry, environmental, biology, purity materials etc. by research contracts, scientific visits, training courses and workshops.

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PART IV:
APPENDICES

APPENDIX 1: AGENDA OF THE MEETING

FIRST RESEARCH CO-ORDINATION MEETING (RCM) FOR THE CO-ORDINATED RESEARCH PROJECT (CRP) ON USE OF NUCLEAR AND RELATED ANALYTICAL TECHNIQUES IN STUDYING HUMAN EXPOSURE TO TOXIC ELEMENTS CONSUMED THROUGH FOODSTUFFS CONTAMINATED BY INDUSTRIAL ACTIVITIES

AGENDA

MONDAY, 18 MARCH 2002

9:00 – 9:10 Registration

9:10 – 9:40 Opening of the meeting

Representative of the Division of Human Health (NAHU)
Representative of the Nutritional and Health-Related Environmental Studies Section (NAHRES)
Election of the rapporteur
Adoption of the agenda
Administrative arrangements for the meeting
Status report on the CRP

9:40 – 10:00 Coffee break

10:00 – 12:30 SESSION 1: PROJECT REPORTS

Chair: A. Kist

Brazil (*M. A. Menezes*):
Iron Quadrangle, Brazil: Assessment of health impact caused by mining pollutants through chain food applying nuclear and related techniques

Canada (*A. Chatt*):
Studies of organohalogen contamination of fish using neutron activation, liquid chromatography, nuclear magnetic resonance, and mass spectrometric techniques

China (*Z. Chai*):
Evaluation of halogen element level in foodstuffs contaminated by pesticides and herbicides in Beijing and its health impact on children by nuclear analytical and related techniques

12:15 –13:30 Luncheon

13:30 – 15:00 SESSION 2: PROJECT REPORTS (continuation)

Chair: V. M. Nguyen

Czech Republic (*J. Kučera*):
Use of NAA, PAA, PIXE and PIGE in studying human exposure to toxic elements consumed through foodstuffs contaminated by industrial activities in the Czech Republic

Ghana (*D. Bansa*):
Industry-related contamination of peri-urban fresh vegetables

15:00 – 15:30 Coffee break

15:30 – 17:00 SESSION 3: PROJECT REPORTS (continuation)

Chair: M. A. Menezes

India (*V. Prakash*):
Al, Cd, Hg. and Pb level in human food chain (in Kamataka, India) and their interaction with micronutrients Cu, Fe Zn and vitamin A

Nigeria (*J. Ojo*):
Dietary intakes of essential and toxic elements by several groups of Nigerians consuming food exposed to specific industrial pollution sources

17:00 RECEPTION

TUESDAY, 19 MARCH 2002

9.00 – 10:30 SESSION 4: PROJECT REPORTS (continuation)

Chair: A. Chatt

Peru (*P. Bedregal*):
Determination of trace elements and heavy metals in agricultural products cultivated at the Rimac river in the city of Lima

Russian Fed. (*M. Frontasyeva*):
Use of INAA, AAS and XRF in studying health impacts of toxic elements consumed through foodstuffs contaminated by industrial activities in Russia

10:30 – 11:00 Coffee break

11:00 – 12:30 SESSION 5: PROJECT REPORTS (continuation)

Chair: Z. Chai

South Africa (*A. Faanhof*):
Analysis of food by nuclear and related analytical techniques

Slovenia (*I. Falnoga*):
Potential human exposure to Pb, Cd, Zn, As and Hg through consumption of foodstuffs grown or bred near mining areas in Slovenia (Pb, and Zn mine Mezica and Idrija mercury mine)

12:30 –13:30 Luncheon

13:30 – 15:45 SESSION 6: PROJECT REPORTS (continuation)

Chair: J. Kučera

Sweden (*L. Jorhem*):
Trace elements in fish for consumption

Uzbekistan (*A. Kist*):
Studying human exposure to trace elements (including toxic ones) consumed through foodstuffs contaminated by industrial activities in Uzbekistan studied by nuclear techniques

Vietnam (*V. M. Nguyen*):
Use of nuclear and related techniques in studying health impacts of toxic elements (As, Hg, Cu, Pb, Zn, Se and Cd) consumed through foodstuffs contaminated by industrial activities

15:45 – 16:15 Coffee break

16:15 – 17:30 SESSION 7: SEMINARS (see separate list of seminars)

Chair: D. Bansa

WEDNESDAY, 20 MARCH 2002

8:30 – 10:30 SESSION 8: GENERAL DISCUSSION
(See separate list of discussion topics):
Chair: V. Prakash

10:30 – 11:00 Coffee break

11:00 – 12:30 SESSION 9: GENERAL DISCUSSION (continuation)
Chair: J. Ojo

12:30 –13:30 Luncheon

13:30 – 17:30 SESSION 10: GENERAL DISCUSSION (continuation)
Chair: P. Bedregal

15:30 – 16:00 Coffee break

16:00 – 17:30 SESSION 11: GENERAL DISCUSSION (continuation)
Chair: M. Frontasyeva

THURSDAY, 21 MARCH 2002

8:30 – 12:30 SESSION 12: GENERAL DISCUSSION (continuation)
Chair: A. Faanhof

- Drafting of the Meeting Report

12:30 – 13:30 Luncheon

13:30 – 17:30 SESSION 13: GENERAL DISCUSSION (continuation)
Chair: I. Falnoga

- Drafting of the Meeting Report (continuation)

FRIDAY, 22 MARCH 2002

9:00 – 12:30 SESSION 14: GENERAL DISCUSSION (continuation)
Chair: L. Jorhem

- Drafting of the Meeting Report (continuation)

12:30 – 13:30 Luncheon

13:30 – 15:30 SESSION 15: CONCLUDING SESSION

- **Final discussion and adoption of the Meeting Report**

Chair: L. Jorhem

15:30 Open end, personal discussions

APPENDIX 2: LIST OF DISCUSSION TOPICS

FIRST RESEARCH CO-ORDINATION MEETING (RCM) FOR THE CO-ORDINATED RESEARCH PROJECT (CRP) ON USE OF NUCLEAR AND RELATED ANALYTICAL TECHNIQUES IN STUDYING HUMAN EXPOSURE TO TOXIC ELEMENTS CONSUMED THROUGH FOODSTUFFS CONTAMINATED BY INDUSTRIAL ACTIVITIES

LIST OF DISCUSSION TOPICS

PURPOSE AND SCOPE OF THE CRP

1. Review of individual Summaries

2. Identification of research areas following the review

3. Comparison of identified areas with the proposed CRP plan

- 3.1. Review of specific CRP objective
- 3.2. Review of the expected research outputs
- 3.3. Review of the proposed research plan
  - 3.3.1. The core programme
    - 3.3.1.1. Topics
    - 3.3.1.2. Priorities
  - 3.3.2. The supplementary programme
    - 3.3.2.1. Topics
    - 3.3.2.2. Priorities

4. Review of the proposed action plan (activities)

5. Review of individual project plans to comply with the adopted overall CRP plan

TECHNICAL ASPECTS

6. Selection of sampling sites and types of samples to be collected

- 6.1. Criteria for the selection of sampling sites
- 6.2. Types of samples to be collected
- 6.3. Number of samples to be collected
- 6.4. Sampling frequency

7. Sampling techniques and equipment

8. Analysis

8.1. Sample preparation

8.2. Analytes to be determined versus specific sources of pollution

8.3. Recommendations for nuclear analytical techniques

8.4. Recommendations for other analytical techniques

8.5. Reference analytical laboratories

8.5.1. As sources of specialised advice
8.5.2. To assist less advanced participants for more samples and/or analytes
8.5.3. For cross-checking purpose

9. Data processing and evaluation

9.1. Database management (quality, outliers, software)

9.2. Data evaluation and presentation (techniques, software)

10. Quality assurance and control

10.1. Existing written protocols for (1) sampling, (2) sample preparation, (3) analysis

10.2. Existing in-house QA/QC procedures

10.3. Recommended QA/QC for sampling each type of sample

10.4. Recommended QA/QC for analysis

10.4.1. In-house
10.4.2. External

10.5. QA for data reporting and evaluation

10.6. Interlaboratory comparisons to be organised by IAEA

ORGANISATIONAL ASPECTS

1. Co-operation within the group

2. Co-operation with other institution within a country

3. Co-operation among countries and with international organisations

4. Next RCM

APPENDIX 3: LIST OF PARTICIPANTS

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