DETERMINATION OF TRACE ELEMENTS AND HEAVY METALS IN AGRICULTURAL PRODUCTS CULTIVATED AT THE RIMAC RIVER VALLEY IN LIMA CITY USING NUCLEAR AND RELATED ANALYTICAL TECHNIQUES

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ABSTRACT

There are strong indications that the Rimac river valley is being contaminated with heavy metals and an excess of trace elements that come from some industrial and mining activities developed along the Rimac river valley. The agricultural products cultivated there in 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 for 100 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 Rimac river 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. Figure 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].

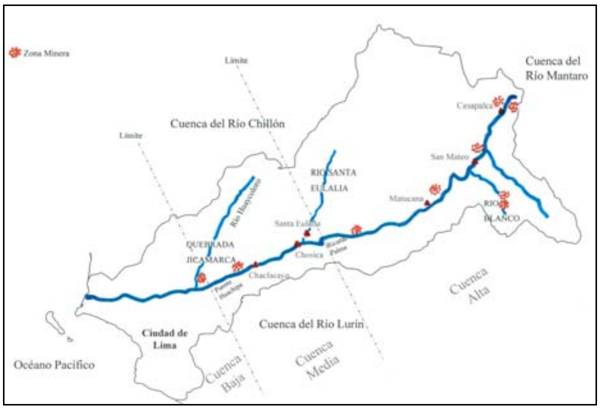

Figure 1. Map of the River Basin [3].

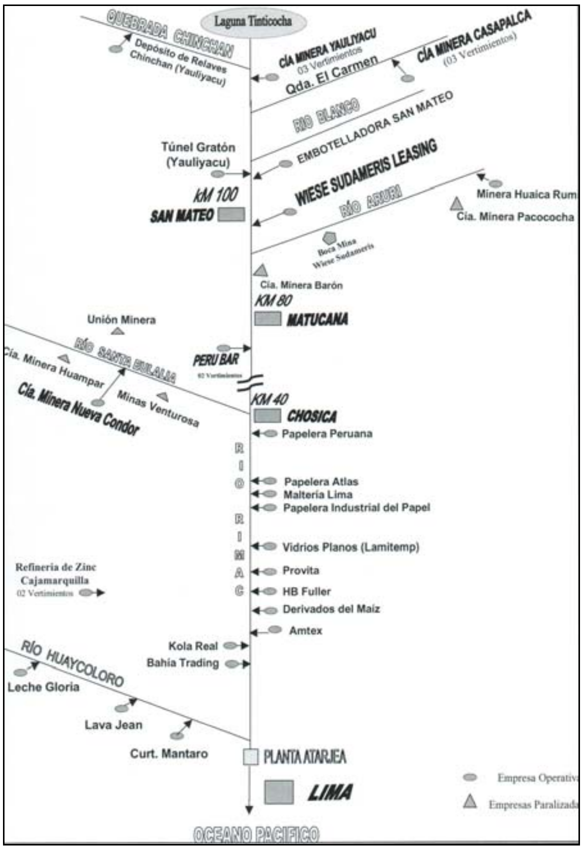

Figure 2. Industries and other activities at the Rimac River Valley [4].

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 1. 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, Br, Rb, Sr, Zr, Cs, W, Pt, Au, La, Pr, Sm	Be, Al, Y, Nb, Ru, Rh, Pd, Ag, Cd, In, Sb, Te, Ba, Hf, Ta, Re,Os, Ir, Hg, Tl, Bi, Ce,Nd, Eu, Gd, Tb, Dy, 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 Rimac River in Lima City 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 2.

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.

Table 2. 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

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 3. 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 analyzed by INAA: Table 4 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 4. 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	20 (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 5 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 5. 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 PLANS 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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