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DOTTORATO DI RICERCA INTERNAZIONALE IN SPETTROSCOPIA ATOMICA E MOLECOLARE

CICLO XXVI

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Spectroscopic investigation of toxic heavy metals in environmental samples from coastal area of Vlora in Albania using XRFS, AAS and LIBS

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SPECTROSCOPIC INVESTIGATION OF TOXIC HEAVY METALS IN ENVIRONMENTAL SAMPLES USING XRFS, AAS, LIBS

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Chapter 1 Historical and environmental background of the research

Introduction

The environment

We live in a world where the environment is of major concern. The environment must include the place where we live or work, the atmosphere which we breathe and the water which we drink, unspoilt areas of the world which could soon be ruined, parts of the atmosphere which shield us from harmful radiation, and anywhere else which could affect the well-being of living organisms. Concern must extend over any process which would affect this well-being, whether it is physical (e.g. global warming and climate change), chemical (e.g. ozone layer depletion) or biological (e.g. destruction of rain forests).

In order to understand the environment, we must first realize that it is never static. Physical forces continuously change the surface of the earth through weather, the action of waves and natural phenomena, such as vulcanoes. At the same time, they release gases, vapor and dust into the atmosphere. These can return to the land or sea a great distance away from their sources. Chemical reactions high up in the atmosphere continuously produce ozone which protects us from harmful ultraviolet radiation from the sun. Living organisms also play a dynamic role through respiration, excretion, and ultimately, death and decay, thus recycling their constituent elements through the environment.

There are similar cycles for all elements which are used by living organisms.

Reasons for concern

The current interest in the environment stems from the concern that the natural processes are being disrupted by people to such an extent that the quality of life, or even life itself, is being threatened. Many indicators would suggest that the world is at a crisis point.

Pollution

The pollution definition is from the Organization of economic Cooperation and Development: "Pollution means the introduction by man, directly or indirectly, of substances or energy into the environment resulting in deleterious effects of such a nature as to endanger human health, harm living resources or interfere with amenities or other legitimate use of the environment."

If a pollutant is discharged into the environment, the effects on individual living organisms will be caused by the concentration which is of concern with respect to individual living organisms. Some metals, which are necessary for plant growth when found in small concentrations in the soil, would kill the plant growth when found in larger concentrations on, let us say, a waste dump.

If we are considering the effect of a particular pollutant on the global environment, we would have to consider the total quantity emitted. [1]

the key issue is the level of the pollutants and the new discovery of a dangerous chemical in air, the public water supply, or food.

As analytical instrumentation becomes more highly developed, detection limits push steadly lower. Hence pollutants thought to have rather local distribution are turning up in very small amounts almost everywhere. The urgent problem is then whether these levels are harmful to humans and other organisms in a ecosystem. Thus the following questions must be answered:

What are the effects on plants and animals of long-term low-level exposure to harmful substance?

What are the pathways of these substances in the environment?

The analytical chemistry should be the cornerstone of a multidisciplinary team who must answer these questions.

It is only in relatively recent times that man has greatly disturbed the geochemical environment. The metallurgical extraction of metals has greatly increased human exposure to rock and dusts, metal vapors, and other toxic vapors. It was the Industrial Revolution and particulary the large demand for metals generated by World Wars I and II that focused great attention on geochemical toxic hazards.

Of the toxic elements, arsenic, lead, mercury and cadmium have been studied the most closely. Arsenic, mostly as arsenic oxide, has during the course of history been frequently administrated ad a poison and many a mercury compound, such as mercurochrome, has been widely used as a drug and yet it was discovered in several parts of the world, that ingestion (from shellfish) of mercury compounds exhausted by industry resulted in the poisoning of large numbers of people. This metal causes severe neurological impairment.

Of the toxic elements, it is lead, however, that has received the widest dispersal worldwide, mostly as an antiknock additive to gasoline.

Lead poisoning causes symptoms similar in some respects to those of mercury poisoning. The most obvious message to emerge from this facts is the need for accurate and reliable analytical techniques. There are some official methods for metal and trace metal analysis in the environmental field. . it is often necessary to develop e suitable method to have trace metal analytical data. It is essential that ample research be devoted to trace metal analytical procedure development.

Transport of Pollutants in the Environment and approaches to their Analysis

The environmental effects of compounds are dependent on their concentration and also that the environment is not static. Materials are constantly being transported between the three spheres of the environment – the atmosphere, the hydrosphere and the lithosphere (the earth's crust). At each stage of the transportation, the concentration of the compounds will be altered either by phase transfer, dilution or, surprisingly, reconcentration. Before discussing analytical methods, we need to understand these processes so that we can:

to predict where large concentrations of the pollutant are likely to occur;

To assess the significance of measured concentrations of pollutants in different regions of the environment.

Sources, Dispersal, Reconcentration and Degradation

It is very easy, for instance, for solid particulate material to be dispersed ion distances via the atmosphere. There has been, for example, an approximately equal quantity of lead entering in a sea off from the atmospheric particulates as from rivers or the dumping of solid waste. Distances which are travelled by pollutants in the atmosphere may be as long as hundreds or thousands of kilometers. When Mount st. Helens volcano erupted in the USA, the particulate material which was discharged resulted in the production of vivid sunsets several thousand kilometers away Dispersal of a pollutant in water or in the atmosphere will inevitably lead to a dilution of the pollutant.

Accumulation in Sediments

This is related to the low solubility of high-molecular –mass organic compounds in water, together with the hydrophobicity of organic compounds not containing polar groups. Undisolved or precipitated organic material in water will adhere to any available solid. The larger the solid surface area, then the greater will be its ability to adsorb the compound. Suitable material is found in sediments. This is particularly true within estuaries where there are often discharges from major industries and fine sediment is in abundance. *It is often the case (as may be expected from surface area considerations) that the smaller the particle size, then the greater is the accumulation of organic compounds in the sediment. These organics may then be ingested by organisms which feed by filtration of sediments (e.g. mussels, scallops, etc.) or, if the solid is sufficiently fine to be held in suspension, by "bottom-dwelling' fish.*

Transport and Reconcentration of Metal ions

The metals which are of most environmental concern are first transition series and post transition metals.

Cr, Mn, Fe, Co, Ni, Cu, Zn, Al, Cd, Sn, Hg, Pb

Table. The metals which are of most environmental concern, from the Periodic table of elements. (atomic number and atomic mass)

24 Cr 51.996	25 Mn 54.938	26 Fe 55.847	27 Co 58.933	28 Ni 58.71	29 Cu 63.546	30 Zn 65.37	13 Al 26.98	48 Cd 112.4

30 Zn 65.37	13 Al 26.98	48 Cd 112.4	50 Sn 118.69	80 Hg 200.59	82 Pb 207.18			

Solubilization

Metals entering the environment are often in an insoluble form inindustrial waste in discarded manufactured products, or as part of naturally occurring mineral deposits. Deposition from the atmosphere is often in the form of soluble salts. However, the solubility of metals increases with a decrease in pH. Some of the problems of "acid rain' in causing the death of fish have been attributed to the leaching of toxic metals from the soil, as well as the direct effect of pH on the fish.

Solubilization is often aided by the formation of complexes with organic material. These may be anthropogenic but may also occur naturally. Humic and fulvic acids produced by the decay of organic material can help soluble metals.

Deposition in Sediments

This can occur when there is an increase in pH. The pH at which this occurs may vary from metal to metal, although ***under sufficiently alkaline conditions all transition metals will precipitate. Deposition of relatively high concentration metals may result in traces of other metal ions also being deposited*. *This is known as cooprecipitation.*** Metal ions may also interact with sediments by a number of mechanisms, including the following:

- Adsorption
- Ion exchange (clay minerals are natural ion exchangers Complex formation within the sediment
- A change in the oxidizing or reduction nature of the water (i.e. the redox potential)may lead either to solubilization or deposition of metal ions. Most transition metal ions can exist in a number of different ixidation states in solution (e.g. iron can exist as Fe^{2+} and Fe^{3+}). Iron in solution under slightly acidic conditions is predominantly Fe^{2+}. Under alkaline oxidizing conditions, the iron is oxidized and precipitates as $Fe(OH)_3$. Under reducing condition, all sulfur-containing ions (e.g. SO_4^{2-}) are reduced to S^{2-}, and this may lead to the deposition of metals such as lead and cadmium as their insoluble sulfides.

Qualities for a trace analysis procedure

A trace analysis procedure should, ideally, have the following qualities:

Have suitable detection limits,
Be relatively fast,
Be relatively low in cost,
Be applicable to a wide range of samples,
Be relatively specific,
Be applicable in most analytical laboratories (not need special equipment),
Be simultaneous multielement,
Have relatively long linear working range, and

Be accurate (tested on SRMs).

The elements

Industrial processes have resulted in the introduction of metals into the environment. Subsequently these metals can be ingested by humans and other animals.

Ingested metals may invoke no response, act as a stimulant, or result in toxic response. Even essential metals in high enough dosage can be toxic. Metals can react with protein and DNA and RNA, affecting the metabolic processes, and with other substances, resulting in physiologic changes. Metals may cause enzyme inhibition and produce changes in the rates of catalytic decomposition of metabolites.

The action of a metal in an animal system depends on its ability to absorbed and excreated, its valence, and its electrochemical behavior. Toxicity due to metals results in changes, some of which may be irreversible. Acute toxicity, caused by a large dose of metal, produces sudden symptoms, often with irreversible damage. Cumulative effects of metals or chronic poisoning occurs as a result of long-term exposure to lower levels of metal. The trace metals of present biological and clinical interest and essential elements are as follows: Li, be, Ti, V*, Cr*, Mn*, Fe*, Ca*, Ni*, Cu*, Zn* B*, Al*, Si*, As*, Se*, Mo*, Ag, Ce, Sn*, Sb, Te, Ba, Pt, Au, Hg, Tl, Pb, Bi. As more and more research is carried out on the role of trace elements in biological systems the clearer it becomes that there is often no way to make a definite distinction between essential and nonessential trace elements. Arsenic has recently been found to be essential. Even elements such as cobalt, iron, zinc, and copper, which are well established as essential, become toxic at high levels. Other elements such as nickel, selenium, flourine, and vanadium are now known to be essential, but at very low levels. The presence of these elements at only slightly higher levels results in toxicity.

The well-known toxic elements include arsenic, beryllium, cadmium, mercury, lead, antimony, tellurium, and thallium. Of these there are certainly some data to suggest that arsenic, cadmium, and lead may be essential at very low levels. In fact, one might hypothesize that, because living systems developed in the sea (which contains all elements at some level), most if not all elements may ultimately be shown to be essential. Indeed, here is a challenge for metal analytical chemistry, to improve detection limits so that it is possible to determine the less common elements at the very low concentrations in which they occur naturally in living systems. This will then allow research into their biological behavior.

research has shown that the presence of selenium results in some protection against heavy metal (e.g., mercury and cadmium) toxic effects. This problem emphasizes the importance of being able to do multielement analysis. It must be stressed that it is the form of metal that determines its biological and environmental effects. A striking example is the case of chromium. Trivalent chromium is an essential element and yet extremely low levels of hexavalent chromium are known to be carcinogenic. Thus it will be very important analytically to b e able to determine the chemical forms of elements in biological and environmental samples.[2]

Uptake by Organisms

There are same rods by which metals may disperse and reconcentrated in the environment and in organisms. From the above consideration, an obvious route into the food chain is from sediments via filter feeders. Many metals are retained in the organism as a simple ion. Others, particularly cadmium and mercury, can be converted into covalent organometallic compounds. and will preferentially accumulate in fatty tissues. The distribution of the metal within an organism is thus dependent on the individual metal and its detailed chemistry.

The mode of action of environmental contaminants

The toxic effect of a potentially dangerous chemical substance is a function of several factors which depend on the intrinsic characteristics of the test substance, the characteristics of the biological system exposed, both at individual and at a higher level of organization.

Absorption, distribution and excretion

The toxicity is a function of the internal dose of a substance and of his stay at the target. The term toxicity can be defined as the impairment of one or more functions of a given biological system (survival, growth, motility, reproduction, photosynthesis, etc..) exposed to a substance. The pattern and the destination of a chemical in a biological system is: exposition, absorption, metabolism or accumulation site, active action site, excretion.

In mussels the site is the gastrointestinal apparatus, respirator surface, the principal forms is food, water.

The main mechanisms by which a toxic exceeds the membranes are: 1) passive transport, which can occur by simple diffusion (predominat) through the membrane or filtration (only in specific tissues such as liver or kidney where the membrane are pores about 70nm); 2) active transport, which uses, for toxic substances, the same specialized transport systems by which the sugars, amino acids and nucleic acids across nuclear membrans and is of particular interest in the processes of excretion or elimination; 3) endocytosis a phenomenon rarely studied from a toxicological point of view, which seems important in the process of elimination of toxic substances from the blood

Biological membrane and transport

In an animal cells, this active transport system is primarily responsible for setting and maintaining the intracellular concentrations of Na+ and K+ and for generating the transmembrane electrical potential. It does this by moving three Na+ out of the cell for every two K+ it moves in. the electrical potential is central to electrical signaling in neurons, and the gradient of Na+ is used to drive the uphill cotransport of solutes in many cell types.

Toxic effects occur at the molecular level. The molecular interactions between the contaminant and the active site lead to toxic manifestations. In vertebrates and invertebrates the nervous system is very sensitive regarding the interaction with some contaminants which have as targets the nervous system. In all the effect is expressed disturbing the mechanisms that the transmission of impulses along nerves and /or along the synapses. It comes to effects because the mechanisms are different.[14]

CONCLUSIONS OF RECENT STADY OF HEAVY METALS IN VLORA

Several monitoring studies have been carried out to evaluate the contamination levels (with particular regard to mercury pollution) in marine sediment, water, biota, and soil sampled from Vlora Bay

1 (S1) Heavy metals distribution in suspended particularte matter and sediment collected from Vlora Bay (Albania). This work was undertaken as part of the Interreg III Italia- Albania CISM Project (Progetto di Assistenza Tecnica alla Realizzazione e alla Gestione di un Centro Internazionale di Scienze del Mare in Albania) funded by Regione Puglia and by National Interuniversity Consortium for Marine Sciences (CoNISMa). {Department of Chemistry and Industrial Chemistry University of Genoa, Department of Chemistry, Faculty of Natural Sciences University of Tirana, ARPA Puglia–Regional Agency for the Environmental Prevention and Protection}

2 (S2) Ecotoxicological assessment of Vlora Bay (Albania) by a monitoring using an integrated approach of of sublethal toxicological effects and contaminant levels in bioindicator species, May, 2007

3 (S3) Analytical investigation of heavy metals in sediments of Albanian coast and Vlora Bay. *This study is made possible in the framework of MEDPOL II Program of UNEP Mediterranean Action Plan (Athens) with support of Marine Environmental Laboratory of IAEA in Monaco*.

4 (S4) Environmental situation of Vlora bay after mercury pollution, Tirana 2008. Study by Universiteti i Tiranes, Fakulteti I Shkencave Natyrore, Departamenti i Kimise, Akademia e Shkencave, Universiteti i Vlores

5 (S5) MED POL 2 and 3 of UNEP (UNEP-MAP, 1998)

6. Determination of trace metals in sea water of the albanian coast by Energy Dispersive X-ray fluorescence.

Conclusion S1

The distribution of heavy metals in suspended particulate matter of Vlora Bay in southern Albania reveals that the Vjosa River flow, which carries discharge from industrial and mining activities, is one of the main sources of Ni, Cr, Al, and Fe in this coastal environment. Moreover, the distribution of the suspended particulate matter and of the associated metals is conditioned by the circulation scheme of this half closed basin.

According to the described scientific approach used in this research, the sediment falls in categories defined as unpolluted to moderately polluted for almost all metals, with the exception of As and Hg, for which some stations were moderately to highly contaminated. These comments partially agree with the analysis of data according to the quality standards reported in the national and international laws and regulations.

The small divergences are to be found in the different approaches; in fact, while the existing national and international regulations consider the metal total content only, in this paper other variables and parameters have been used, such as the Igeo (a useful tool providing complementary information on the pollution processes caused by anthropogenic inputs), the SQGs, and the metal speciation in the sediments.

Moreover, the values reported in this paper can be considered as useful information for the judgment of sediment quality in the Albanian investigated area; in fact, as it was stated in the existing laws (Italian Law Decree no. 152/2006 [Italian Government, 2006], EC Directive no. 105/2008 [European community, 2008], Italian Environmental Ministry Decree no. 56/2009 [Italian Government, 2009]) the threshold values to preserve the environment and human health from the pollution have to be revised according to the effective background values found in a particular area and related to the natural geobiochemical processes.

Conclusion S2

This integrated approach combining bioaccumulation and biomarker responses has thus a good potential for the evaluation of environmental assessment of a marine coastal area and appears to be the most suitable approach for future pollution and environmental stress monitoring. This first study on Vlora Bay generated important data that could be used as a baseline for future monitoring programs related to accumulation and effects of both organic and inorganic pollution along the continental coasts of Albania.

Conclusions S3

In specific areas along the Albanian Coast, significantly high levels of heavy metals are noticed. There are certain anthropogenic and natural factors that probably affect their distribution in sediment samples.

- Very high levels of mercury in Vlora Bay are received due to the past industrial activity of the chlor-alkali plant.
- The emissions of Mati River are significant sources, affecting the Cu, Fe, Zn, Cr, Ni in the sediments of the North part of the coast. The high concentrations of these metals in marine sediments of this area are mostly related to natural factors.
- The very high levels of Cr and Ni in our marine sediments, particularly in the estuarine samples taken from the deltas of Shkumbini, Semani and Vjosa river (near Vlora Bay) present a special interesting phenomena and needs a further more complete study.

Conclusion S4

Very high concentrations of mercury in the territory of former plant present a real thread to the residents living very near this territory. The most contaminated area remains PVC and Electrolysis plant. Due to transport of soils from seaside to PVC and Electrolysis plant, the contents of Hg in seaside is smaller. After this process, the content of Hg in different deepness appeared to be very critic: till 1.5 m deep Hg content is very high (PVC and Electrolysis plant)

The estimate volume of the soils with concentration of Hg higher then 20 $mg.kg^{-1}$, amounts to 32,750 m^2 in the area concern.

Compare with previous monitory studies (the period 1992-2005), the content of total Hg in seawater samples appeared to be in the same level (110-140 ng/ml). it means that Hg pollution in Vlora Bay, remain to be problem for a long time in the future (Vlora Bay is a half closed bay).

The monitoring studies proved that there was not any distinct contamination from mercury in Vlora Bay caused by former Soda –PVC plant. The concentrations of mercury compare with levels in the polluted areas of Northern Adriatic, in the sediments, seawater and biota (fish, mussels and algae) samples were found to be lower, except the site near the former plant. There are two factors controlling the process of mercury distribution. Metal form of mercury in contaminated soils and hydrological factors that actually control the distribution of Hg in the sediments of the Bay are not favorable for the transportation of Hg to the open sea, because Vlora Bay is a semi closed area having just little communication with open sea. These factors necessities a long term monitoring program for mercury levels in sediments, water and biota samples of Vlora Bay.
About the mercury content in hair samples, the highest value found is 1.953 µg/g, but compare with overall mean of mercury content in hair samples of un-exposure people are two times higher. The most critical group is the group of children 2-12 years old. Same medicinal controls are necessary to be done to the people living inside contaminated area.

Conclusion 5

Map of mercury pollution and contour lines of "salt sands" surface depth 1:5000 (Area of PVC-SODA plant , in Vlora), August 2000 [13]
Map of mercury pollution and contour lines of "salt sands" surface depth 1:5000 (Area of PVC-SODA plant , in Vlora), August 2000

Conclusion 6

The increased values for Fe, Cu, Zn in Durres and Golem samples may be due to small industrial and urban discharges, 1994

Conditions of Vlora

Vlora Bay is located in the southwest of Albania. It is in front of Karaburuni Peninsula and Sazani Island, and has a wonderful view and beach, close to various sandy and rocky beaches and the scenic nearby mountains. It represents the natural boundary between the Adriatic and the Ionian Seas. It is a half-closed bay having a reduced water exchange with the Adriatic Sea throughout the Mezocanal inlet. The Bay of Vlora represents one of the most attractive coastal zones of Albania, and it has been defined as a top-priority tourism area.[3]

The Vlora Gulf is a wide inlet 9 km long, 10 km wide and includes the Karaburun Peninsula, the Triport Cape, and the harbor, which opens on the west by northwest toward the Adriatic Sea. The Saseno Island, with its steep rocky coasts, closes to the gulf mouth, makes the area one of the safest natural landings in the south Adriatic Sea. The Vjosa Delta, along with the Narte Lagoon, represents the northern boundary of the Vlora Gulf. The height of the Karaburuni Peninsula, characterized by steep cliffs along its sides, hides the interior of the gulf. The presence of low coasts with sandy and gravelly beaches represents the main morphological features of the southern and eastern internal sides of the inlet. The bathymetry of the gulf, which reaches its maximum depth (50 m) in the central zone, shows it to be, on average, 20 m. The presence of a sill between the Saseno Island and the deepest area of the gulf influences the circulation pattern of water masses in the gulf without producing suboxic conditions. Finally, the natural composition of the waters could be affected by human pollution through water discharges from the surrounding cities.[25]

Unfortunately, this area has suffered from some anthropogenic impact in recent years. From 1967 to 1992 (when the production stopped), a chloro-alkali plant (producing soda and polyvinyl chloride [PVC] using very outdated technology), lying 4 km to the north of Vlora city, discharged relatively large amounts of liquid wastes containing mercury and other pollutants directly into the sea.

Four miles north of Vlore is the site of a ex former chemical complex that produced chlorine alkali, vinyl chloride monomer and polyvinyl chloride. The plant was closed in 1992, and its buildings have been completely destroyed since that time. Families now live on and around the industrial site. The factory encompasses approximately one km^2 and is located directly on the Adriatic Sea. A major environmental problem is posed by the destroyed former chlorine-alkali electrolysis plant. UNEP observed drops of metallic mercury in the hall of the electrolysis plant and in all of its drainage canals. A UNEP soil sample found mercury levels > 10,000 mg/kg in the area[37]

Chapter 2 Spectroscopic methods

EDXRFS, AAS, LIBS

During this study has been used 3 spectroscopic methods to analyze the environmental samples collected in the coastal area of Vlora as follows:

- EDXRFS Energy Dispersive X-ray Fluorescence Spectroscopy
- AAS, Atomic Absorption Spectroscopy (GFAAS & FAAS graphite and flame atomic absorption spectroscopy)
- LIBS, Laser Induced, Breakdown Spectroscopy

1. X-ray fluorescence spectroscopy

Experimental method

In XRF the ejection of the core electron from the atom to produce the ion may be by X-rays or by an electron beam of appropriate energy. The usual source of X-ray is the Coolidge tube. Electrons are generated from a heated tungsten filament (the cathode) and accelerated towards the anode which consists of a target of such metals W, Mo, Ag, etc., depending on the range of wavelength required. The Coolidge tube source can cover wavelength up to 1nm, beyond which the intensity becomes too low. This restricts XRF investigations to atoms with atomic number Z greater than 12 (Mg) since XRF spectra of light atoms are often broadened and are not very useful for analysis. this is not a serious limitation. The fluorescence may be detected by a scintillation counter, a semiconductor detector or a gas flow proportional detector. An alternative type of spectrometer is the energy dispersive spectrometer which the detector receives the undispersed X-ray fluorescence and outputs a series of pulses of different voltages that correspond to the different wavelength (energies) that it has received. This energies are than separated with a multichannel analyzer. An energy dispersive spectrometer is cheaper and faster for multielement analytical purposes but has poorer detection limits and resolution.

Processes in X-ray fluorescence

A 1s (K-shell) electron has been ejected from the atom and X-ray fluorescence is caused by an electron falling from another shell and filling the vacancy in the K shell. Forming a K emission spectrum. The transitions forming the L emission spectrum is caused from filling a vacancy created in the L shell. The quantum yield XRF decreases as the nuclear charge increases and also from K to L emission. The transitions in lower energy group are the transitions α (α1, α2,...,.) and the higher energy group β (β1, β2,…,.). the splitting between α1 and α2 transitions is due to the spin – orbit coupling (coupling of the electron spin and orbital angular momenta). This coupling increases with nuclear charge Z and decreases as the orbital angular momentum quantum number l increases. The α1, β1, are the strongest transitions in their respective groups.

The selection rules which apply[29] to XRF transitions are:

$\Delta n \geq 1,\ \Delta l = \pm 1,\ \Delta j = 0, \pm 1$

where the quantum number refer to the electron that is filling the vacancy.

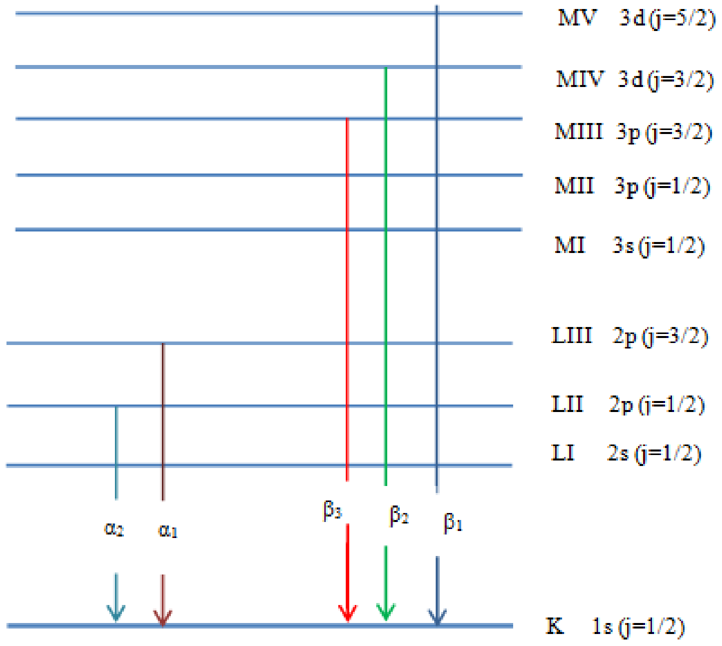


Fig. X-ray fluorescence transition forming a K (Kα, Kβ) emission spectrum

1. LIBS, Laser induced breakdown spectroscopy

Laser-induced breakdown spectroscopy (LIBS) is a method of atomic emission spectroscopy (AES) that uses a laser-generated plasma as the hot vaporization, atomization, and excitation source. Because the plasma is formed by focused optical radiation, the method has many advantages over conventional AES techniques that use an adjacent physical device (e.g. electrodes, coils) to form the vaporization/excitation source. Foremost of these is the ability to interrogate samples in situ and remotely without any preparation. In its basic form, a LIBS measurement is carried out by forming a laser plasma on or in the sample and then collecting and spectrally analyzing the plasma light. Qualitative and quantitative analyses are carried out by monitoring emission line positions and intensities.

LIBS is the only technology that can provide distinct spectral signatures characteristic of all chemical species in all environments. It is the simplicity of LIBS that allows this diversity of applications; simply strike any sample with a pulsed laser beam and measure a distinct optical spectrum. The laser beam initiates a tiny luminous plasma from ablated sample mass. The plasma spectrum is a signature of the chemical species in the sample; spectral data analysis provides the chemical species composition and relative abundance.

LIBS is one method of atomic emission spectroscopy (AES). The purpose of AES is to determine the elemental composition of a sample (solid, liquid, or gas). The analysis can range from a simple identification of the atomic constituents of the sample to a more detailed determination of relative concentrations or absolute masses. Basic steps in AES are:
_ atomization/vaporization of the sample to produce free atomic species (neutrals and ions),
_ excitation of the atoms,
_ detection of the emitted light,
_ calibration of the intensity to concentration or mass relationship,
_ determination of concentrations, masses, or other[68] information.

The optimization of LIBS system event timing is important for efficient capture of high resolution line spectra. During the first microseconds after the focused laser pulse initiates a plasma “spark”, the resulting plasma energy is dominated by a strong “white light” continuum also described as broadband black body or bremsstrahlung radiation emission, or deceleration radiation. This is essentially electromagnetic radiation that is produced by the acceleration and collision of charged particles (read electrons) with other charged particles such as atomic nuclei. The initial few microsecond after plasma ignition is followed by a longer period when elemental line spectra emission shows up as the dominating broadband emission decays.
This is essentially electromagnetic radiation that is produced by the acceleration and collision of charged particles (read electrons) with other charged particles such as atomic nuclei. The initial few microsecond after plasma ignition is followed by a longer period
when elemental line spectra emission shows up as the dominating broadband emission[67] decays.

2. AAS methods (FAAS, GFAAS, AAS/CV

Atomic absorption spectroscopy (AAS) is complementary to atomic emission spectroscopy. The main problem in this technique is getting the atoms into the vapor phase. The method used is to spray, in a very fine mist, a liquid molecular sample containing the atom concerned into a high-temperature flame. Air mixed with coal gas, propane or acetylene or other, produce flames in the temperature range 2100K to 3200 K. The source radiation which passes through the flame is not a continuum, but a hollow cathode lamp which contains a tungsten anode, a cup-shaped cathode made from the element to be analyzed, and a noble gas at about 5 Torr. When a voltage is applied a coloured dsischarge appears, in which mainly neutral atom emission occurs, is confined to inside of the cathode. The radiation emited, apart from the noble gas, is from the atom to be observed in absorption. The dispersing spectrometer is set so that the photoelectric detector receives radiation of wavelength of the atoms,[29] selected atoms of heavy metals in this study.

Calibration is achived by spraing a mist of a solution, containing a known concentration of the atom concerned, into the flame.

Chapter 3 Identification of sampling sites and sampling

During this study 2011-2013, were collected and analyzed the environmental samples: marine sediment, sea water, suspended material and Mediterranean mussels.

The samples were collected in the Vlora coast area: Bay of Vlora, Narta & Orikumi Lagoon and Delta of Vjosa river

Principal goal
Investigation of the toxic heavy metals, trace and total content in environmental samples applying absorption and emission techniques like EDXRF, AAS and LIBS with the aim to assess

the presence and the variation of concentration of toxic heavy metals in marine sediment, sea water and bioindicators such Mediterranean Mussels in Bay of Vlora, Narta referring to the precedent study.

1. Geologic, Hydrologic and geographic view. General information

Albania is a small country with a total surface of about 28’748 km2 located in the Western part of the Balkan Peninsula in South-Eastern Europe. It borders to Montenegro, Kosovo, Macedonia and Greece, and joins the Adriatic and the Ionian Sea.

Fig. Satellite map of Albania, indicating the political borders with the main check points, prefectures, towns and national road (with permission[27]) (http://maps, google.com/maps, modified, Miho at al)

Vlora, is the most southern district in the Western Adriatic Coastal Lowland, holds about 150 km of coastline. It borders on both the Ionian and the Adriatic coast.

Overview on Vlora nature

The relief of the Albania is characterized by very diverse topographic textures, with flat lowlands in the West and mountains in the East. the altitude increases gradually from West to East. The west of the country with hills of altitudes up to about 200 m a.s.l. Deep valleys often squeeze through narrow gorges forming canyons such as the Kelcyra Gorge (Permeti) one of the biggest in Albania; there Vjosa River finds the way towards the Western Lowland.

The climate is mainly of a Mediterranean subtropical character with high humidity. The winter is relatively short, mild and wet, while the summer il long, hot and very dry. Precipitation is heavy, ranging from about 1300 - 2000 mm per year, increasing from West to East. upon sudden strong rain events, brooks and torrents often develop with extreme erosion capacity. The number of sunny hours is high. The geology shows multifaceted rock formations. In the Adriatic Lowland is composed of Quaternary depositions of marine, lagoon and alluvial origin.

Vlora marine coast

Vlora is a coastal town with 120 000 inhabitants situated just where the Adriatic meets the Ionian Sea, close to the channel of Otranto.

Physic and geographical features of the Vlora coast.

Albania isa coastal country with a coastline of about 427 km, of which 273 belong to the flat Adriatic coast and 154 km to the rocky Ionian coast. Strong currents in the sea move the water along the coast; in summer large masses flow from the greek Ionian sea into the Adria while Adriatic water exist mainly along the Apulian coastline.

Based on the geomorphology, the Albanian coast is divided into four main sectors, the Buna delta (Shkodra) – Shengjini (Lezha) part, the coast between Shengjini and Vlora bay, the vlora (cold Water) – Saranda and the Saranda –Stillo cape part towards Greece.

Fig. Satellite map of Albania with the main prefectures; the predominant sea currents for June are shown (with permission, Miho at at) (modified from http://maps.google.com/maps,)

The Shengjini – Vlora part comprises about two thirds of the Albanian Adriatic coastline; it is characterized by a high morphologic diversity and coast, by wind and wave activities, and particulary by the vast amounts of solid matter transported to the sea by the main rivers, Mati, Ishmi, Erzeni, Shkumini, Semani and Vjosa. This zone is the most populated part of the country, and human impact, urbanization, water pollution and other activities have continuously degraded the natural values of the landscape.

The part from cold Water (Vlora town is a fraction of mostly the Ionian Rivera with high and steep cliffs, rocky mountains and gravel beaches formed by the river mouths of mountain torrents, like the Dukati torrent (Orikumi)**.**

Informations about the most important sites in Vlora

The Narta Lagoon together with Dajlani Cape marsh and coastal dunes are situated about 14 km North of Vlora. The Vjosa-Narta region comprises the largest and the most important coastal wetlands of Albania.

The Orikumi wetland, also called Pashalimani marsh or Dukati pond, is situated near the town of Orikumi, just at the south end of the Vlora bay. The wetland is close to the military zone of Pashalimani that was heavily fortified after the 2nd World War and sheltered military submarines of the Warszawa Pact. The

The Vlora part of Vjosa delta and Narta lagoon plain rose from the end of the Pilocene and during the Quaternary and turned gradually into a continental plain. The ground is of alluvial material deposited by the river Vjosa which showed a strong sedimentation regime from the Pilo-quaternary to the present.

Major morphological features of the zone are the fluvial delta of Vjosa, the sandy dunes and the *Narta lagoon*.

The largest dunes are in Zverneci where they are half moon shaped, about 3-4 m high and 400-500 m distance from the coast. A chain of three hills, about 5 km interlinked by sundy belts, cover the Treporti cape. They are of sandy layers of the Tortonian time (Miocene) and mixed with lime-clay formations.

The sandy coast of Vlora extends about 8 km away from Vlora town (Skela) towards the Treporti cape in Zverneci, known as the Soda Forest. The Narta coastal area has much suffered in the past from pollutions by the industrial zone in Vlora. Most of these activities stopped in1990. However in recent times, the wetlands became polluted by urban wastes of the Vlora town.

Orikumi

Orikumi is situated at the foot of Rreza Karaburuni mountain chain, just at the south and of the Vlora bay. The Orikumi lagoon is of tectonic origin. It has surface area of 1,5 km2 and it is connected with the sea by two channels. The gravel coast is 6 km long. The water exchange with the sea is rather poor and does not ensure optimal hydrological condition. The marine national park of Karaburuni-Sazani is 16 km long and includes scenic marine and coastal areas and is characterized by outstanding canyons and caves and by a high diversity of landscapes. The rocky coastline holdes steep and inaccessible cliffs fissures, caves, small gravel beaches and bays, especially on the western slopes. Small dry river canyons descend almost vertically to the sea.

Like along the whole Albanian coast the climate of Vlora coast is strongly influenced by the Adriatic Sea with high mean temperatures, high sunny irradiation (1644 kWh m^{-2}) and many sunny days. Eastern and south-eastern winds dominate; about 22 days with breezes during winter are reported. The multi annual mean temperature varies between 9.2°C in January and 24.6°C in august, with an annual mean temperature of 16.5°C. The mean annual precipitation is around 1000 mm.

About 2 km south of Vlora town at the beginning of the rocky coast more than 30 carstic springs discharge about 900 L/s of very cold water into the sea. The place is known as cold water. The water used as drinking water source for Vlora town.[27]

2. Identification of Sampling stations

Sampling approaches

Planning of the sampling strategy in area of Vlora, defining the objective.

Bay of Vlora, Narta & Orikumi Lagoons and Delta Vjosa river are the sites chosen to be investigated during this study. This area is in the most tourist area, but in this area are situated the Harbor or Vlora, and industrial plants as TEC and Petrolifera.

Summary of the sampling approaches in according to IAEA, International Atomic Energy Agency adapted for this study:
Approach – Judgmental
Relative number of samples – larger
Basis of selecting sample sites – prior to history & visual judgment.

Some of the trace metals as well as rapidly scavenged by the particulate matter in the water body which eventually settles down to the bottom sediment. And hence the determination of these elements in sediments can play a key role in detecting the sources of pollution. Although sediment analysis does not represent the extent of intoxication, they may be employed on a semi-quantitative basis in comparative studies to trace the sources of pollution such as surreptitious discharges from the nearby industries. *Since many of the toxic pollutants affect sediment-dwelling organisms and in turn may get transferred through the food chain to humans, attempts have been made to set up guidelines for pollutant contents in aquatic sediments in order to protect environmental health*.[59]
Trace elements in seawater can be limiting factors of biological productivity ,tracers of ocean circulation and biogeochemical processes, and proxies for paleoceanography.[62]
Surveillance of the coastal tourist area in Vlora, of the marine environment and the assessment based on the precedent study have provided preliminary information about the site on the material to be analyzed in the coast area of Vlora.

Objective of collection
The objectives of the sampling program:
To collect environmental samples of the sites from Vjosa Delta river to Orikumi Lagoon including the Bay of Vlora and Narta Lagoon with the aim to investigate the actual level and the variation of the levels of heavy metals in these areas referring to the precedent study.
In according to this objective considering the cost of the study and the technical support, the collection of the environmental samples selected, was defined as follows:

1). Marine sediment
Sampling in Bay of Vlora in front of the coastline, 100, 300 and 700 m from the shore.
Sampling in Narta and Orikumi Lagoons and in the collecting channels between the lagoons and the sea and in discharged channels The aim is to assess the actual level of toxic heavy metals and the variation of the levels of toxic heavy metals in these areas referring to the precedent study.
Sampling in Vjosa Delta River 3 stations, one on the delta and 2 other along the river to see the changes in the presence of heavy metals in diverse positions.
The marine sediment samples were collected in two seasons:
in the end of the summer season in the area most accessible for the public
in the later autumn

2). Sea water

Sampling in Bay of Vlora from Triport Cape to Pashaliman in Orikum, in the same station as the sediment samples in the surface of the sea (about 50 cm in depth) and about 50 cm from the bottom sediment (the bed of the sea) in the end of summer seasons in the area most accessible for the public.

3). Suspended material

Collection in the same time and sites as the water samples

4). Mediterranean mussels (bioindicator species)

Collection was carried out along the coastline in sites in which the mussels are present in their natural beds. Seven sampling sites along Vlora Bay cost, characterizing by different anthropogenic impacts and identified by the surveillance of the area precedent studies effectuated in this area.

SAMPLING

the collection of samples in area of Vlora coast has been realized in total in 6 cruises and represented in the table below.

Sediment samples were collected in later autumn 2011, in the end of summer season 2011, and in later autumn and during2012

Sea water samples were collected in later autumn 2012 and in the end of summer season 2013

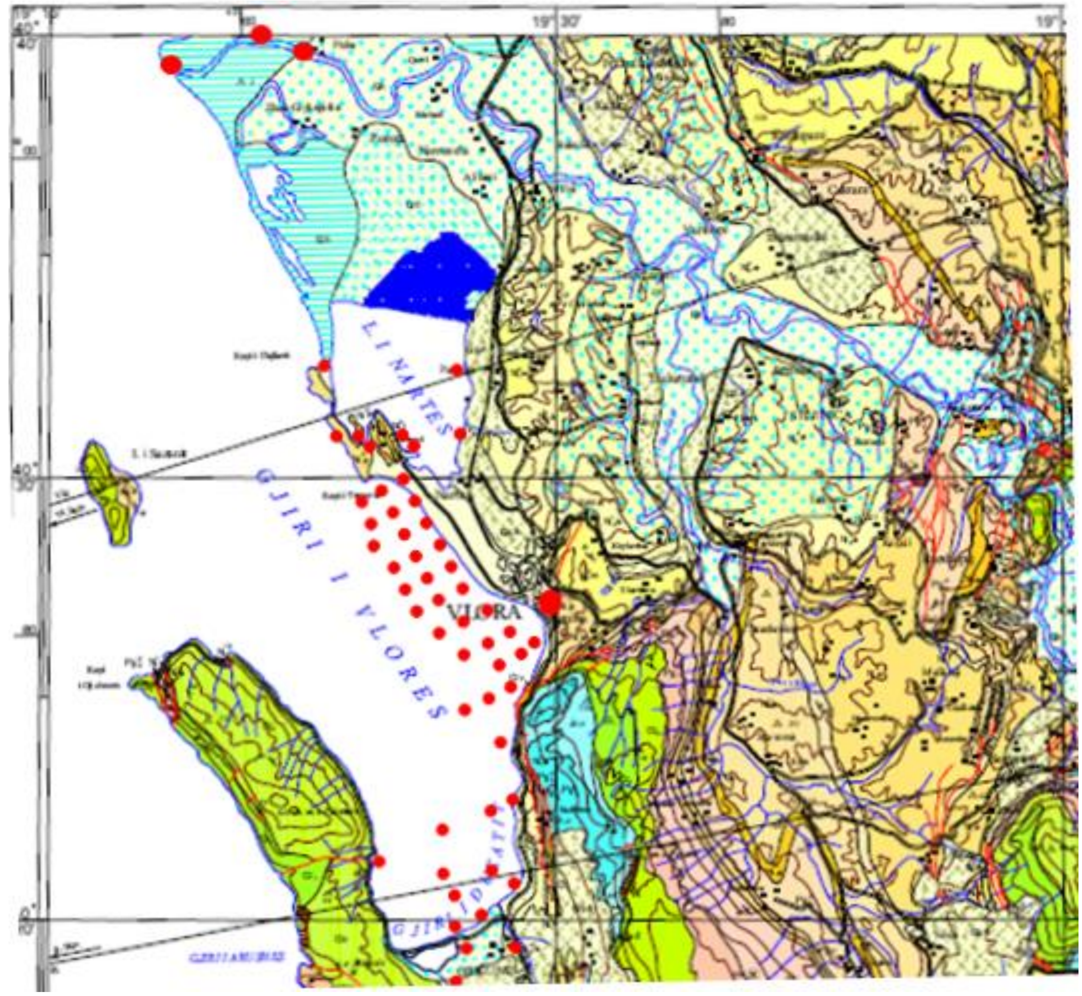
Mussels samples were collected in the end of summer season 2013 (analyzed) and in the end of summer season (10 samples) during 2012 (was not analyzed, because of difficulties in the laboratory technical conditions).

Sampling time and atmospheric conditions (2011-2013)

Sediment	atmospheric conditions	Sea water	Atmospheric conditions	Mussels	Atmospheric conditions
Summer 2011	☼	Autumn 2012	☼	Summer 2012	☼
Autumn 2011 later	⛅	Sumer 2013	☼	Sumer 2013	☼
Autumn 2012	☼				

During this study, in total were collected in the area under investigation 107 marine sediment samples , 63 in the first phase (22 in summer and 41 autumn season) , 44 in the second phase, sea water 44 samples during the second and third phase in summer & autumn season (24 analyzed) and 17 samples of Mediterranean mussels (Mytilus galloprovincialis) during the second phase (10samples) and 7sample during the third phase (7 analyzed, because of technical difficulties and laboratory conditions).
During the first phase of this research marine sediments from the Vlora area were collected analyzed. Samples were collected specifically in the bottom marine sediments of the Bay of Vlora, Orikumi Lagoon, Narta Lagoon and in the delta of Vjosa river. In the
During the second phase 2012 of this research study, marine sediments sea water and mussels from the coastal of Vlora at the same area were collected, specifically in the Bay of Vlora, Orikumi Lagoon and Narta Lagoon. During the third phase, 2013 this study will be completed in full analysis of the marine sediment, sea water and bioindicator samples. (Mediterranean mussels).

The map of geographical position of sampling stations for all samples collected in the area of Vlora coast. (Topographic map by Institute of geological research, Tirana, Albania)


19° 30'
L I NARTES
GJIRI I VLORES
VLORA

Chapter 4 Marine sediment samples

Sampling, sample preparing and analyzing

Sampling of marine sediment

The sampling stations of marine sediment samples collected during this study are presented in the tables and the maps below.

Table. The sampling station of marine sediment are reported in the table below.

Sediment sampling stations in Vlora Bay, 2011	
1	In front of Soda - PVC- plant: S (S1, S3, S7, S_0, H)
2	In front of ex junior campus: Kampi K (K1, K3, K7)
3	Moli,in front of harbor of Vlora (M1, M3, M7)
4	Vlora, New beach V (V1, V3, V7)
5	Petrolifera P (P1, P2, P3)
6	TEC T (T1, T2, T3)
7	Narta Lagoon L (Ln, Lm, Dv, Dm, D)
8	Zvernec Z (Z1, Z2, Z3)
9	Orikumi Lagoon O (O1, O2, O3, O4, O5)
10	Delta of Vjosa River L (L1, L2, L3)
11	Jonufra J
12	Rradhima R

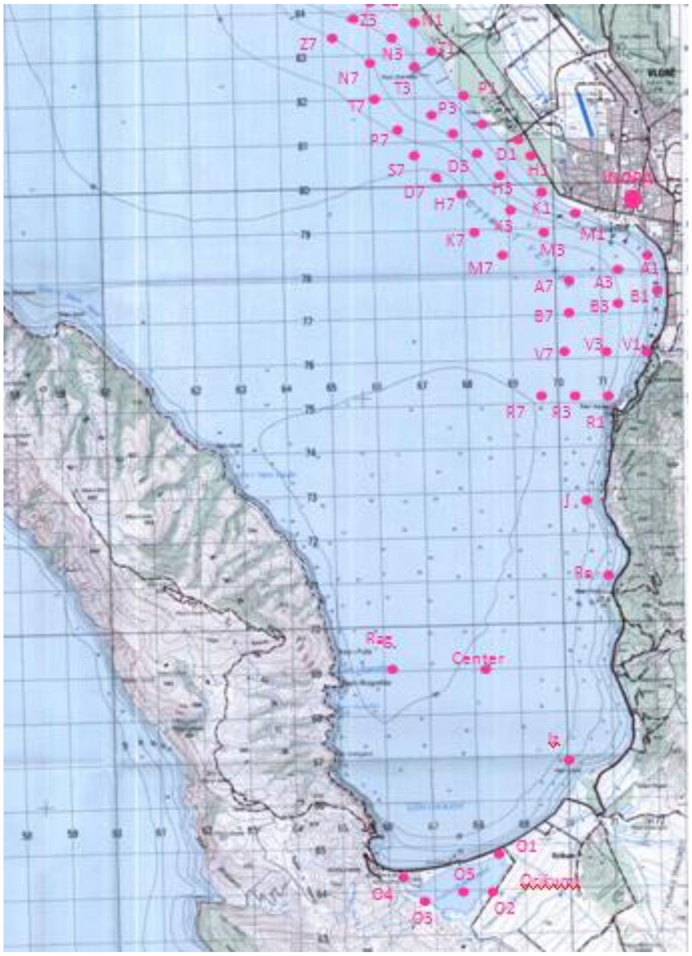
Position of sampling stations

S stations in front ex Soda – PVC plant, destroyed (S1, S2, S3, S_0)
S1 – 100 m from the shore coordinates: N- 40°28’05” E- 19°27’11’’
S3 – 300 m from “ “ “ N-40°28’03” E – 19°27’
S7 – 700 m from “ “
S0 – near the shore
H- near the shore

K stations in front ex junior Campus (old beach):	N- 40^{O}27’3’’	E 19^{O}28’2”
K1 – 100 m from the shore		
K3 – 300 m “ “		
K7 – 700 m “ “		
M stations in front the harbor of Vlora:	N- 40°26’30’	E 19°28’15”
M1 – 100 m from the shore		
M3 – 300 m “ “		
M7 – 700 m “ “		
V stations in betwen Uji I Ftohte& new beach in Vlora:	N- 40^{O} 26’8”	
V1 – 100 m from the shore	E -19^{O} 29’5”	
V3 – 300 “ “		
V7 – 700 “ “		
P stations in front Petrolifera (area near Soda –PVC plant)		
P1 – 100 m from the shore	N –40°28’33’’	E- 19°26’30”
P3 – 300 “ “	N-40°28’30”	E – 19°26’25”
P7 – 700	N-40° 28’22”	E – 19°26’16”
T station in front TEC in Treport of Vlora		
T1 – 100 m from the shore	N- 40°29’8”	E- 19°25’47”
T3 – 300 m	40°29’05”	19°25’36”
T7 – 700 m	40°29’01”	19°25’24”
N stations in front Narta town		
N1 – 100 m from the shore: coordinates:	N – 40°29’31’’	E – 19°25’24”
N3 – 300 m	40°29’31”	19°25’25”
N7 – 70 m	40°29’26”	19°25’26
Z station in front of Zvernec		
Z1 – 100 m from the shore	N- 40°29’51”	E- 19°25’
Z3 – 300	n-40°29’50”	19’25”
Z7 – 700	N-40°19’48”	19°25’03”
Ln - Narta Lagoon	N – 40° 31”	E 19° 21’1”
Lm - Narta Lagoon, Monastery		
Dv – Narta Lagoon, Small Dajlan	N - 40^{O} 30’8”	E 19° 23’8”
Dm – Narta Lagoon, Big Dajlan		
D - Dajlan, near the shore		
O stations in Orikumi Lagoon		
O1, O2, O3, around the lagoon		
O4 in the center of lagoon	N- 40°19’1”	E 10°26’4”
O5 located on the Orikumi beach		

L1 - on the river , 3km from delta of the river
L2 – on the delta of Vjosa river (on the river) near the sea
L3 – station in the delta of Vjosa river (on the see)

J- Jonufra (located after Uji i Ftohte)	N 40°24’2” E 19°28’9”
R- Rradhima (located between Jonufra & Orikumi	N 40°23’ E 19°29’



Map of sediment sampling stations in Vlora Bay (summer and autumn season) and Orikumi Lagoon, autumn 2011, (Geographical Map by geographic institute in collaboration with NIMA)

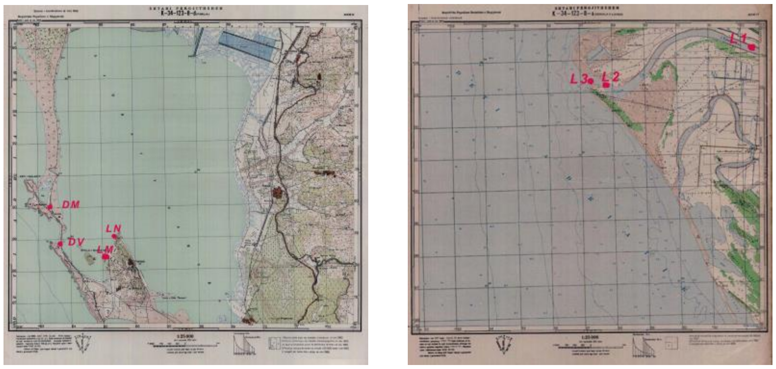
Figure 12-3: Vlora town from the Kanina castel with the Soda forest and the new harbor (with permission, Miho at al, Photo: L. Kashta).

Table. Depth of sampling stations, autumn 2011.

Depth of the sediment sampling stations in Vlora Bay, 2011						
Station	S1	S3	S7	K1	K3	K7
Depth (m)	1.9	3	5.3	1.4	2.7	6.3
Station	M1	M3	M7	V1	V3	V7
Depth (m)	1	3.5	1.5	1.3	5	12.6
Station	P1	P3	P7	T1	T3	T7
Depth (m)	1.8	3.4	5	1	2.5	5
Station	N1	N3	N7	Z1	Z3	Z7
Depth (m)	1.5	2.5	5.5	1.5	2.5	3

Table. Sampling stations of marine sediment in Vlora Bay, Summer season, 2011,

Sampling stations, distance from the shore in Vlora Bay, Summer season, 2011,											
sample	B_0	B_1	B_3	B_7	M_0	M_1	M_3	M_7	K_1	K_3	K_7
distance	0	100	300	700	0	100	300	700	100	300	700
sample	D_1	D_3	D_7	H_3	H_7	S_1	S_3	S_7	N_1	N_3	N_7
distance	100	300	700	300	700	100	300	700	100	300	700



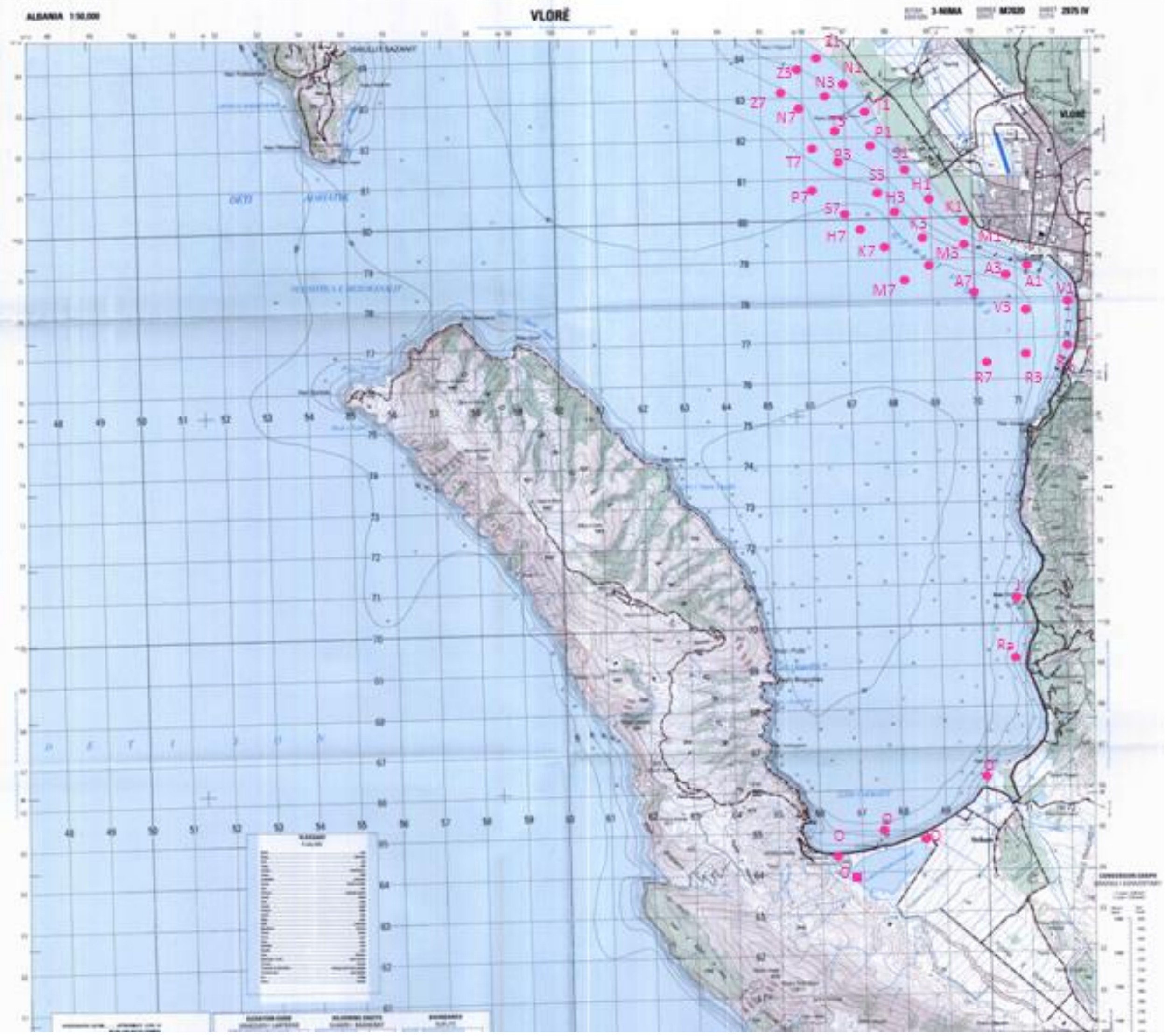
a. b

Fig. Map of Sediment sampling stations: a. Narta Lagoon b. Delta of Vjosa River, autumn 2011 (Military map, scale 1:25 000, Photo I. Sino).

Fig. Map of sampling stations of marine sediment in Narta Lagoon and Delta Vjosa river. Google Map of Narta lagoon and Vjosa delta in Vlora (modified, with permission, Miho at al)
Marine sediment sampling stations in Vjosa Delta and Narta Lagoon

Second and third phase (2012-2013)

Map of sampling stations of marine sediment in Vlora



Map of sediment sampling stations in Vlora Bay (summer and autumn season) and Orikumi Lagoon, autumn 2012, (Geographical Map by geographic institute in collaboration with NIMA)

Table. Sediment sampling stations in Vlora and Lagoons, 2012

Sediment sampling stations, in Vlora bay,Narta & Orikumi lagoon, 2012	
1	In front of Soda - PVC- plant: S (S_1, S_3, S_7)
2	In front of ex junior campus: Kampi K (K_1, K_3, K_7)
3	Moli,in front of harbor of Vlora (M_1, M_3, M_7)
4	Vlora, New beach V (V_1, V_3, V_7)
5	Petrolifera P (P_1, P_3, P_7)
6	TEC T (T_1, T_3, T_7)
7	Zvernec Z (Z_1, Z_3, Z_7)
8	Hidrovori (H_1, H_3, H_7)
9	Aulona (A1, A3, A7)
10	Orikumi Lagoon O
11	Jonufra J
12	Rradhima R
13	Narta Lagoon (Lm, Ln, Dv, Lu, Lp)

33 O_1 – Orik Pasha Liman (shore)
34 Ra – Rradhima (shore)
35 J - Jonufra (shore)
36 O_2 – Orikumi lagoon, derdhja, dalan (shore)
37 O_3 orikumi plazh (shore)
38 O_4 - Orikum derdhja 1, Izvori (shore)
39 O_5- Orikum derdhja (shore)
40 Lm Monastery S. Mary.N lagoon Zvernec
41 Ln, Narta Lagoon
42 Dv Dalan Narta lagoon
43 Lu, Narta lagoon (ura) bridge
44 Lp, Narta lagoon (west)

Table. Sampling stations distance and depth, 2012

Distance from the shore and depth of sampling stations in Bay of Vlora, autumn 2012									
Stations	1/Z_7	2/Z_3	3/Z_1	4/N_1	5/N_3	6/N_7	7/T_3	8/T_1	9/T_7
Distance)m)	700	300	100	100	300	700	300	100	700
Depth (m)	5	3.4	2	2	4	1.5	3.6	2	9
Stations	10/P_1	11/P_3	12/P_7	13/S_1	14/S_3	15/S_7	16/H_1	17/H_3	18/H_7
Distance (m)	100	300	700	100	300	700	100	300	700
Depth (m)	2.5	4	5.3	100	300	700	100	300	700
Stations	19/K_1	20/K_3	21/K_7	22/R_1	23/R_3	24/R_7	25/V2	26/V_1	27/A_1
Distance (m)	100	300	700	100	300	700	300	100	100
Depth (m)	1.9	7.8	13.3	0.8	5	12.5	12.5	1.8	1.8
Stations	28/A_3	29/A_7	30/M_7	31/M_3	32/M_1	33/O_1	34/Ra	35/J	36/O_2
Distance (m)	300	700	700	300	100				
Depth (m)	8	12	13.3	9	2.5				
Stations	37/O_3	38/O_4	39/O_5	40/Lm	41/Ln	42/Dv	43/Lu	44/Lp	
Depth									

Map of Orikumi lagoon. (Miho at al., with permission)

The first MPA in Albania, Sazani island – Karaburuni peninsula, as a regional priority conservation area for marine biodiversity http://www.slideshare.net/mkazani/kashta-sazan-islandkaraburun-albania Kashta L., Beqiraj S., Tilot V., Zuna V., Dodbiba E. (2011) (with permission)

Marine Sediment Sampling Device

The marine sediment samples were collected using:

1) stainless-stil grab and sampled from the centre of the grab with a plastic spoon to avoid contamination by the metalica parts ,

2) Sludge and sewage sludge in lagoons and il Vlora Bay were collected using a Eijkelkamp product, device of auger sets for heterogeneous soils and water (50m in depth), length 1m, volum 1000ml with the threaded portion at the end, which allows getting the sediment.

"Using this device, a cilindrical tube is first driven into the sediment. On withdrawal, the valve system closes which allows the sample to be withdrawn from the sediment. Just before breaking the surface of the water, the tube is then sealed to preserve the sediment structure".[1]

All sediment samples were placed in polyethylene bags and carefully labeled and transported to the laboratory in an ice packet cooler for further analysis. Marine sediment samples for elemental analysis were preliminarily subject of dredging (used for coarse sediments). "After draining off the excess water the sediment samples were stored deep-frosen".

Sampling equipment used to collect marine sediment are shown in the figure below. In estuarine or coastal waters, grab and corer sampler were used to collect sediments. For this pollution assessment, a sampler that collects material at the water-sediment interface without loss or disturbance have been selected. *The upper section of the samples were carefully taken in order to assess the most recent contributions of contaminants to the surface*.

Photos from marine sediment sample collecting in Vlora are presented below.

Photos. Narta Lagoon sampling station 1. In wiev Near the Monastiry of S.Mary) 2. Eastern part of the lagon

Photos from Zverneci sampling station. Wiev of Karaburuni Penusula and Sazani Isle

Photo Harbor of Vlora sampling station Triport sampling stations

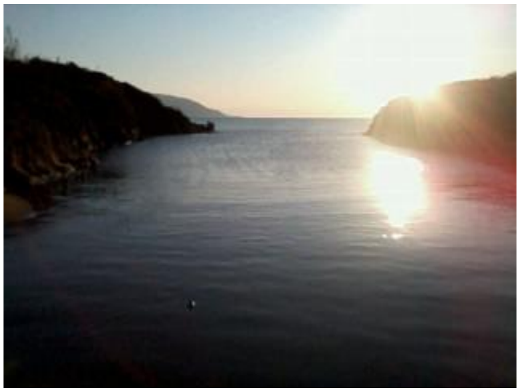


Photo. Sampling station Dajlani I Vogel, communication Channel between Narta Lagoon and the sea.

Photo. Sampling station near ex-PVC-Soda plant in Vlora where now is situated TEC-i and Petrolifera


Photos. The bay of Vlora, view of the New Beach. Sewage is discharged into the sea, in areas frequented by the public. This situation si all along the coast of new beach; in the second picture, waste at see, in the area 300m from University of Vlora and near harbor of the city where there is a more intensive activity, 2011

SAMPLE PREPARATION AND ANALYSIS USING EDXRF, AAS, LIBS TECHNIQUES

The analysis of the all the samples were performed at the institutions as follows:

EDXRF analysis performed at the Center of Applied physics, University of Tirana, Albania (marine sediment, sea water, suspended material, quantitative analysis)

AAS analysis were performed in the Toxicology & Quality department, Food Safety & Veterinary Institute, Tirana, Albania (sea water, mussels, marine sediment quantitative analysis)

LIBS analysis were performed in Physics Chemistry department, University of Florence, Italy (marine sediment, qualitative analysis)

Pretreatment procedure

The pretreatment procedure in marine sediments included the following.

The main difference between marine sediment samples and other samples is: it is the high water content. On return to the laboratory the sample is thawed and screened to remove large contaminants such as stones and twigs.

After draining off the excess water the sediment samples were well homogenized and after that went through a nylon sieve.

Finally were placed in polyethylene bags and stored at <5° C until analysis. These samples for heavy metal analysis were oven dried at 100°C.

EDXRF TECHNIQUE

Marine sediment sample preparation technique for heavy metals quantitative analysis by Energy Dispersive X-Ray Fluorescence Spectrometry (EDXRFS) and Laser Induced Breakdown Spectrometry (LIBS) qualitative analysis.

The preparation techniques applied in this study are faster and well established as existing techniques. A large number of samples was analysed for many heavy metals and a simple and rapid sample preparation procedure, with reasonable cost and low detection limits was used.

Marine sediment sample preparation technique for EDXRF heavy metals analysis

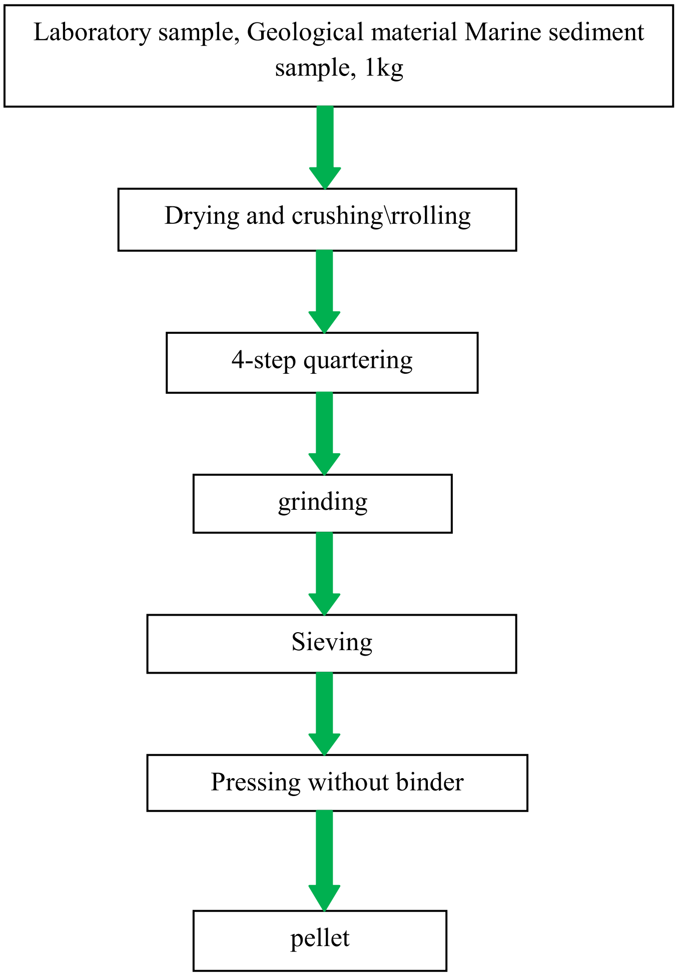


Fig. Comminution of sediment prior to sample pelletizing according to IAEA. Marine sediment sample preparation technique for XRF

The powder were pressed at 25 ton for 3 min. The quality and reproducibility of the pellets are very acceptable and they can be prepared in 20 min.

The samples were ground in SPEX MIXER/MILL, grinding device for 10 min. To reduce particle size effects the samples wasd ground to pass a >150-mesh sieve.

Photo 1. Pressing devices used for marine sediments. 2. Marine sediment pellets prepared until analysis in EDXRFS in the Center of Applied Physics, XRF lavoratory,Tirana, Albania (For XRF and LIBS analysis)

All Sediments containing a mixture of all fractions are analysed by two methods EDXRF & AAS (GFAAS, FAAS and AAS/CV VGA-77 system) and for 10 samples were qualitatively analyzed by LIBS.

Measurement procedure

EDXRF Analysis

X-ray fluorescence method in this work consists of exciting samples by photons and measuring the intensities as fluoresced.

For analysis of environmental samples, photon excitation has been demonstrated to be more practical and advantageous[59] than the particle excitation.

The excitation efficiency and detector sensitivity for any element is dependent on excitation energy, Therefore excitation energy that provides reasonable sensitivity for a range of elements is adopted in this study. In X-ray tube source used, it was possible to vary the energy by using different secondary targets (Mo, Ag). The elements like As, Cr, Cu, Fe, Ni, Pb, Mn, Zn, Se, Rb, and Sr, were measured using X-ray tube with Mo or Ag secondary target. The measurement times were 1500- 2000 seconds.

Instrumentation

Measurements were performed at the Center of Applied Physics, Tirana, Albania, using experimental EDXRF system. This system, which uses the secondary target excitation mode, consists of a Philips 1729 X-ray generator equipped with a W-anode X-ray tube, a 30 mm^2 PGT Si(Li) detector with a resolution of 180 eV at 5.9 keV (Mn Kα), a Canberra Model 2024 fast spectroscopy amplifier, a Canberra Model 8706 fast ADC and a PC-based Canberra S-100 multichannel analyser. The system use a 90° sample-detector geometry and a thin filter is placed between the target or source and the sample. In the secondary target excitation system, a thin filter of the same material as the target is used to filter the tube anode lines and the scattered radiation from the primary beam. The high voltage of the X-ray tube was selected to have a good excitation of the secondary targets and the tube current was adjusted to limit in each case the dead time of the system to less than 15%. The operating conditions and acquisition times are given in table below.

Excitation conditions for EDXRF					
Year	Voltage (kV)	Current (mA)	Time (s)	Source	Filter
2012	35	20	1500-2000	Mo	Mo
2013	40	40	1500-2000	Ag	Mo
Element range	As, Cr, Cu, Fe, Ni, Pb, Mn, Zn, Sr, Rb, Ti, Ca, Y				

Photo. Analysing marine sediment pellet in EDXRF system, XRF laboratory, Institute of Applied Physics, Tirana, 2013

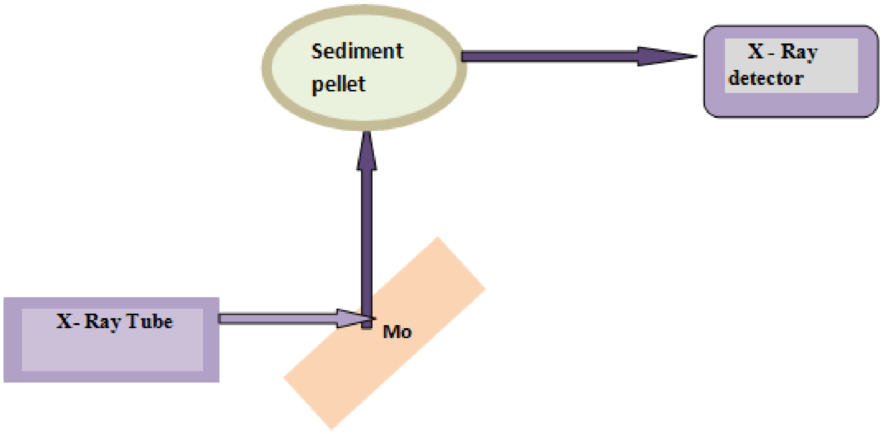


Fig. Secondary source (Mo secondary target) for XRF instrument

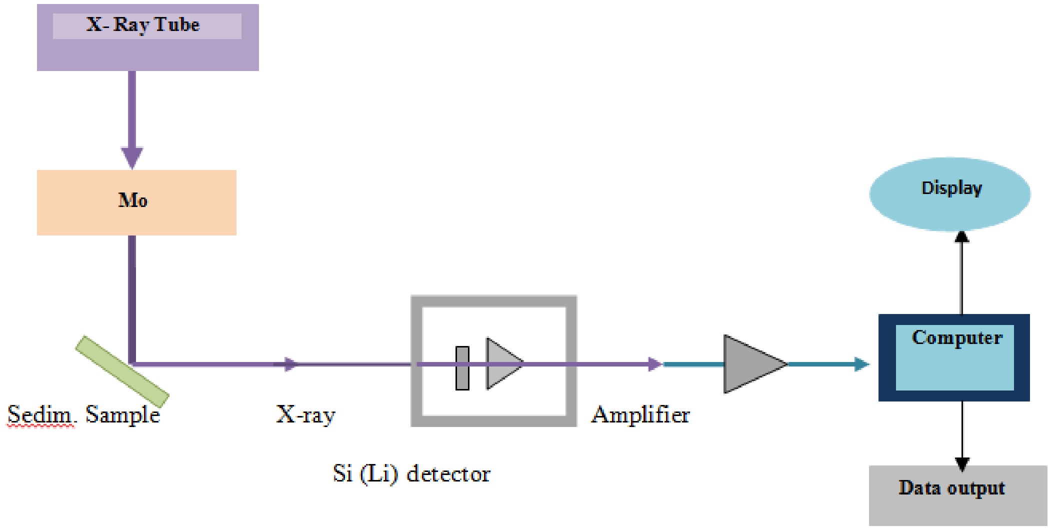


Fig. Schematic view of EDXRF spectrometer with 3D optics.
The x-ray path is in two perpendicular plans. The sedondary target radiated from the tube, emits characteristic X-rays irradiating the sample. The sample emits their characteristic radiation measured by this EDXRF detector.

Photos During analysis of heavy metals in marine sediment. Production X-ray system , analyzes and elaboration XRF system in the XRF laboratory of the Center of Applied Physics, Tirana, Albania are represented below.

Photo. Philips 1729 - X-ray generator system in Tirana. Analyzing environmental samples by Energy Dispersive X-Ray Fluorescence

Photo 1. The Detector of X-ray used for sample analysis and EDXRF spectrum of heavy metals in sediment samples

Photo. X ray fluorescence detection & elaboration system in the XRF laboratory, Center of Applied Physics, Tirana, Albania

The intensities of analyte lines were determined by the program AXIL. An approximate sample composition and peak shape correction, were introduced in the fitting model, (when required) with other needed parameters.

Calibration Procedure of EDXRF system for heavy metals determination in marine sediment from Vlora

The program COREX, which uses backscatter peaks and fundamental parameters, was first used for calculation of concentrations. As fundamental parameters, mass absorption coefficient was used In this program, while the others parameters such as excitation – detection efficiencies and scattering coefficients for coherent and incoherent peaks are determined by measurements, under the same conditions, using a set of standards prepared (pressed pellets) from pure elements or compounds.

Thesee artificial standard were used for the calibration of the excitation detection efficiency.

20 reference materials are used for quality control of the apparatus. The calculated concentrations of each element of the standards were plotted against respective recommended values as reported in the table below.

T

Reference material	**Ca rec value**	**Ca analysed**	**Ti rec value**	**Ti analysed**
GSS1	**1.16**	1.12	**0.45**	0.38
GSS2	**1.60**	1.45	**0.25**	0.19
GSS3	**0.86**	0.65	**0.21**	0.17
GSS4	**0.17**	0.16	**1.02**	0.93
GSS5	**0.06**	0.042	**0.59**	0.57
GSS6	**0.15**	0.11	**0.41**	0.37
GSS7	**0.10**	0.087	**1.91**	1.76
GSS8	**5.61**	5.26	**0.36**	0.3
GSD1	**3.12**	2.62	**0.55**	0.46
GSD2	**0.16**	0.11	**0.13**	0.09
GSD3	**0.14**	0.09	**0.60**	0.48
GSD4	**5.10**	4.68	**0.50**	0.44
GSD5	**3.62**	3.46	**0.51**	0.43
GSD6	**2.62**	2.41	**0.44**	0.38
GSD7	**1.12**	0.83	**0.42**	0.35
GSD8	**0.16**	0.12	**0.34**	0.28
GSD9	**3.63**	3.37	**0.52**	0.45
GSD10	**0.47**	0.41	**0.12**	0.1
GSD11	**0.31**	0.25	**0.19**	0.15
GSD12	**0.78**	0.64	**0.14**	0.11

	G95-12	**2.08**	1.34	**0.29**	0.23
	G95-17	**2.89**	1.98	**0.47**	0.38
	SL - 1	***0.25***	0.22	***0.51***	0.41
IAEA	***Soil - 5***	***2.21***	2.09	***0.46***	0.44
	Soil - 7	***17.00***	15.85	***0.31***	0.17

	Reference material	**Mn rec value**	**Mn analysed**	**Fe rec value**	**Fe analysed**	**Cr rec**	**Cr anal**
	GSS1	**1671.9**	1732.2	**3.44**	3.65	**58.9**	157.5
	GSS2	**484.5**	536.73	**2.33**	2.5	**44.6**	180.92
	GSS3	**288.8**	253.49	**1.33**	1.43	**30.4**	101.03
	GSS4	**1348.9**	1565.9	**6.84**	6.86	**351.5**	463.68
	GSS5	**1291.9**	1395	**8.38**	8.41	**112.1**	213.7
	GSS6	**1377.4**	1533	**5.37**	5.42	**71.2**	171.34
	GSS7	**1691.0**	1635.4	**12.46**	12.07	**389.5**	474.15
	GSS8	**617.5**	694.4	**2.97**	3.08	**64.6**	142.2
	GSD1	**874.0**	895.7	**4.88**	4.91	**184.3**	216.59
	GSD2	**228.0**	262.76	**1.25**	1.29	**11.6**	113.53
	GSD3	**380.0**	418.36	**4.32**	4.35	**82.6**	108.14
	GSD4	**783.7**	812.55	**3.91**	4.01	**76.9**	121.97
	GSD5	**1101.9**	1080.1	**3.89**	3.91	**66.5**	138.76
	GSD6	**921.5**	964.1	**3.90**	4.06	**180.5**	300.8
	GSD7	**655.5**	669.68	**4.31**	4.37	**115.9**	175.56
	GSD8	**318.2**	311.09	**1.46**	1.53	**7.2**	74.27
	GSD9	**589.0**	585.29	**3.23**	3.37	**80.7**	161.81
	GSD10	**959.5**	1032.96	**2.56**	2.73	**129.2**	232.89
	GSD11	**2365.4**	2294.4	**2.91**	2.96	**38.0**	121.2
	GSD12	**1329.9**	1231.1	**3.23**	3.25	**33.2**	106.72
	G95-12	**1800**	1621.5	**7.67**	7.57		4233.65
	G95-17	**4300**	4197.3	**6.45**	6.51	**520**	593.04
	SL - 1	***3461.9***	3576.6	***6.74***	6.57	***104***	121.45
IAEA	***Soil - 5***	***851.9***	948.05	***4.48***	4.55	***28.9***	90.56
	Soil - 7	***627.0***	466.82	***2.58***	1.85	***58.4***	115.01
						5580	

	Reference material	**Ni rec**	**Ni anal**	**Cu rec**	**Cu anal**	**Zn rec**	**Zn anal**
	GSS1	**19.4**	43.4	**19.9**	55.2	**646.0**	654.9
	GSS2	**18.4**	23.21	**15.5**	32.35	**40.2**	34.95
	GSS3	**11.6**	22.42	**10.8**	34.12	**29.8**	29.03
	GSS4	**61.0**	74.05	**38.5**	57.73	**199.5**	193.92
	GSS5	**38.0**	47.28	**136.8**	152.11	**469.3**	474.89
	GSS6	**50.3**	66.65	**370.5**	402.02	**91.8**	101.44
	GSS7	**262.2**	247.47	**92.2**	106.99	**134.9**	127.09
	GSS8	**29.9**	46.81	**23.1**	48.54	**64.6**	67.48
	GSD1	**72.2**	88.72	**20.7**	48.3	**75.0**	90.76
	GSD2	**5.2**	14.31	**4.7**	16.01	**41.8**	41.58
	GSD3	**24.3**	25.14	**168.1**	185.13	**49.4**	54.17
	GSD4	**38.0**	54.69	**35.4**		**95.9**	97.42
	GSD5	**32.3**	39.29	**130.1**	133.67	**230.8**	224.04
	GSD6	**74.1**	86.77	**363.8**	394.1	**136.8**	144.52
	GSD7	**50.3**	77.9	**36.1**	64.66	**226.1**	234.63
	GSD8	**2.6**	3.75	**3.9**	22.71	**40.8**	36.02
	GSD9	**30.7**	49.62	**30.5**	52.11	**74.1**	74.01
	GSD10	**28.7**	45.74	**21.5**	46.02	**43.7**	50.64
	GSD11	**13.6**	32.16	**74.7**	87.39	**354.3**	353.83
	GSD12	**12.2**	27.86	**1168.4**	1148.5	**473.1**	467.82
	G95-12		1775.5	**66**	74.35	**85**	76.99
	G95-17	**314**	306.7	**181**	193.08	**238**	228.37
	SL - 1	***44.9***	59.08	***30***	55.17	***223***	215.6
IAEA	***Soil - 5***	***13***	25.91	***77.1***	105.12	***368***	372.08
	Soil - 7	***29.5***	37.01	***12.4***	29.59	***111***	100.93
		2010			212.12		

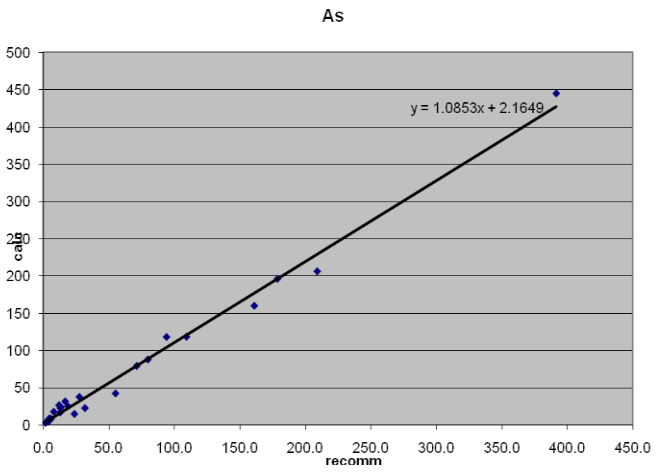
	Reference material	**As rec**	**As anal**	**Rb rec**	**Rb anal**	**Sr rec**
	GSS1	**31.8**	23	**133.0**	145.6	**147.2**
	GSS2	**13.0**	23.15	**83.6**	88.35	**177.6**
	GSS3	**4.2**	5.14	**80.7**	83.97	**361.0**
	GSS4	**55.1**	42.68	**71.2**	69.71	**73.1**

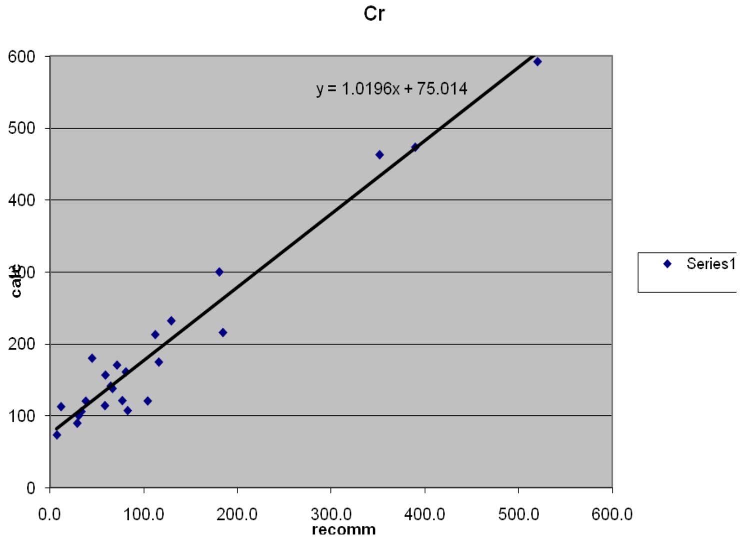
	GSS5	**391.4**	445.28	**111.1**	118.47	**39.4**
	GSS6	**209.0**	206.54	**225.1**	230.54	**37.0**
	GSS7	**4.6**	9.09	**15.0**	17.59	**24.7**
	GSS8	**12.1**	26.89	**91.2**	93.61	**224.2**
	GSD1	**1.9**	3.26	**110.2**	117.83	**498.7**
	GSD2	**5.9**	8.66	**446.5**	444.99	**26.6**
	GSD3	**16.7**	31.91	**75.0**	75.98	**85.5**
	GSD4	**18.7**	25.51	**123.5**	125.6	**134.9**
	GSD5	**71.2**	79.55	**112.1**	115	**193.8**
	GSD6	**12.9**	17.18	**101.6**	108.68	**252.7**
	GSD7	**79.8**	88.2	**139.6**	144.23	**209.0**
	GSD8	**2.3**	4.24	**125.4**	124.18	**49.4**
	GSD9	**8.0**	18.09	**76.0**	83.62	**157.7**
	GSD10	**23.7**	15.13	**8.7**	10.55	**24.0**
	GSD11	**178.6**	196.4	**387.6**	387.48	**27.5**
	GSD12	**109.2**	118.71	**256.5**	263.14	**23.2**
	G95-12		9.15	**31**	37.66	**46**
	G95-17	**161**	160.31	**102**	105.44	**105**
	SL - 1	***27.5***	38.04	***113***	107.68	***80***
IAEA	***Soil - 5***	***94***	118.46	***138***	129.95	***330***
	Soil - 7	***13.4***	24.38	***49.8***	61.27	***108***

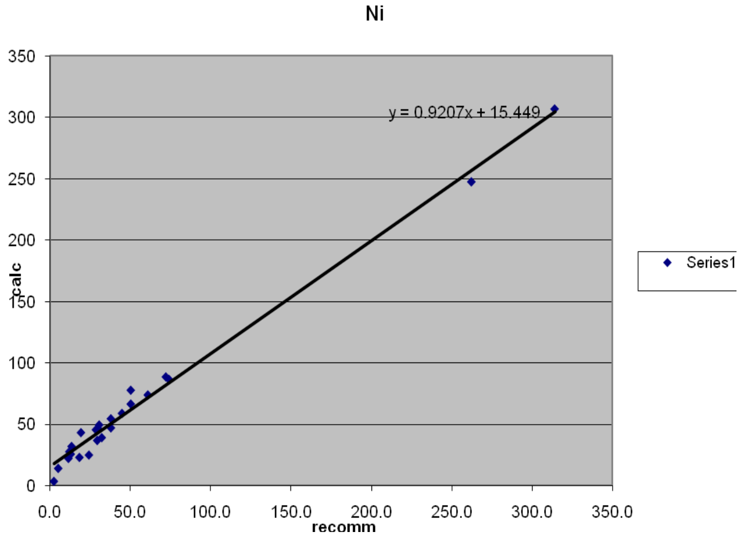
	Reference material	**Y rec**	**Y anal**	**Zr rec**	**Zr anal**	**Pb rec**	**Pb anal**
	GSS1	**23.7**	23.6	**232.7**	196.7	**93.1**	122.6
	GSS2	**20.6**	19.4	**208.0**	157.75	**19.2**	2.82
	GSS3	**14.2**	14.35	**233.7**	245.44	**24.7**	21.38
	GSS4	**37.0**	39.36	**475.0**	451.76	**55.6**	65.39
	GSS5	**19.9**	20.94	**258.4**	227.41	**524.4**	451.71
	GSS6	**17.9**	21.39	**209.0**	170.44	**298.3**	305.73
	GSS7	**25.3**	26.34	**302.1**	298.1	**12.9**	8.91
	GSS8	**24.7**	26	**217.6**	173.22	**20.0**	

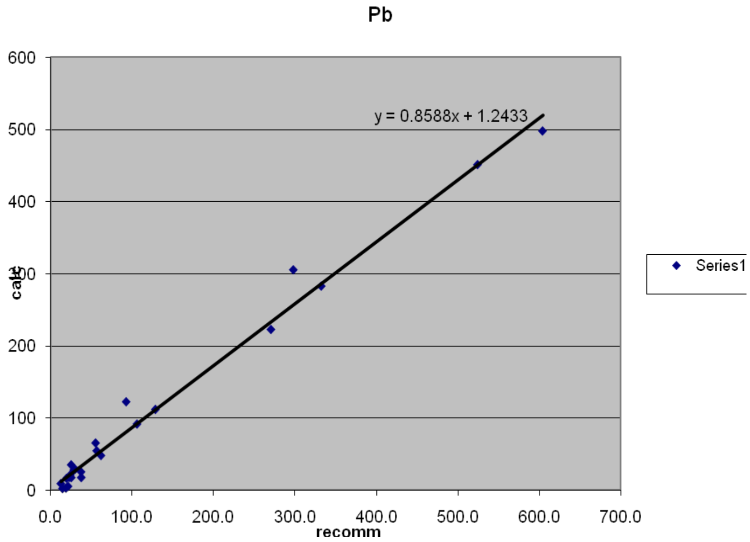
	GSD1	**21.4**	21.82	**294.5**	261.41	**23.2**	17.69
	GSD2	**63.6**	65.3	**437.0**	365.81	**30.4**	29.01
	GSD3	**20.9**	22.6	**209.0**	157.26	**38.0**	17.45
	GSD4	**24.7**	26.45	**178.6**	159	**28.9**	28.04
	GSD5	**24.7**	24.94	**209.0**	181.86	**106.4**	91.68
	GSD6	**19.2**	19.59	**161.5**	123.75	**25.6**	17.39
	GSD7	**22.6**	24.96	**153.9**	132.31	**332.5**	283.09
	GSD8	**17.1**	12.51	**465.5**	413.43	**19.9**	16.35
	GSD9	**25.3**	26.49	**351.5**	319.25	**21.8**	5.24
	GSD10	**13.1**	14.99	**66.5**	5.85	**25.6**	35.1
	GSD11	**40.6**	41.42	**145.3**	99.51	**604.2**	498.36
	GSD12	**27.8**	30.05	**222.3**	199.72	**270.7**	222.93
	G95-12	**16**	15.46	**107**	49.03	**15**	2.22
	G95-17	**30**	34.68	**148**	102.33	**57**	54.55
	SL - 1	***35***	34.11	***241***	216.78	***37.7***	25.34
IAEA	***Soil - 5***	***21***	22.82	***221***	167.8	***129***	111.97
	Soil - 7	***20.8***	26.53	***190***	172.12	***62.2***	48.02

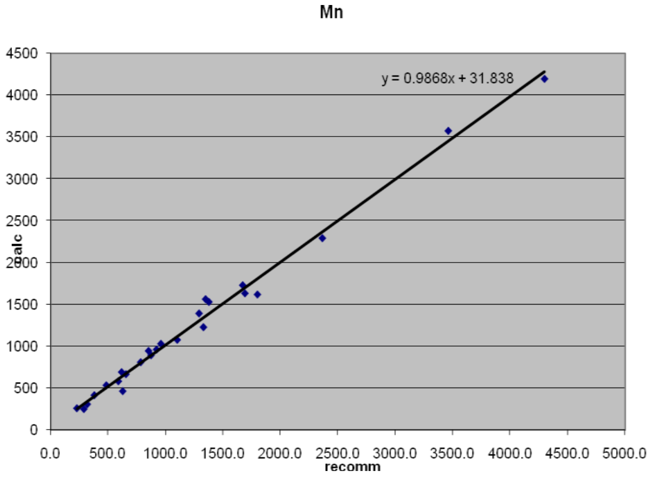
The calculated concentrations of each element of the standards were plotted against respective recommended[38] values and data from IAEA standards soil and GSD standards were used.
Generally the fitled regression lines have slopes close to 1 and intercepts close to 0. Cr, Ni, Cu shows high intercept values that are related with the respective intensities emitted by the metallic parts surrounding the detector. The relative error of the fit was about 10%.
The parameters of these lines were used to correct the calculated concentration of the elements in the samples. Measured detection limits (ppm) for Mo secondary target:
Ti- 65, Cr-38, Mn-27, Ni-10, Cu-8, Zn-7, As-6, Rb-6, Sr-7, Y-9, Zr- 13, Pb- 12.

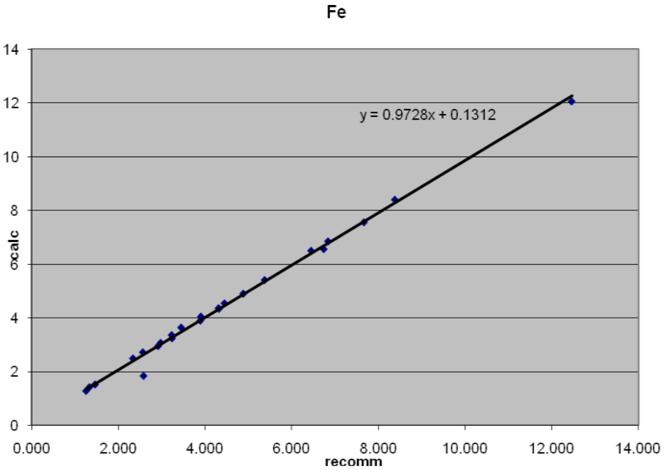

As
y = 1.0853x + 2.1649
calc
recomm
0
50
100
150
200
250
300
350
400
450
500
0.0
50.0
100.0
150.0
200.0
250.0
300.0
350.0
400.0
450.0

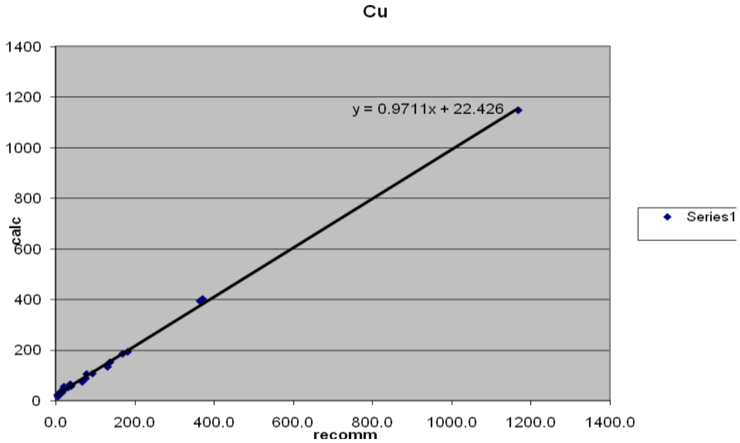

Cr
y = 1.0196x + 75.014
calc
recomm
Series1
0
100
200
300
400
500
600
0.0
100.0
200.0
300.0
400.0
500.0
600.0

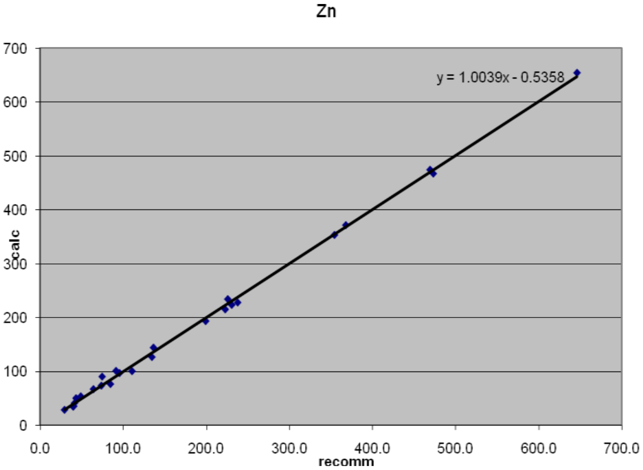

Ni
y = 0.9207x + 15.449
calc
recomm
Series1
0
50
100
150
200
250
300
350
0.0
50.0
100.0
150.0
200.0
250.0
300.0
350.0

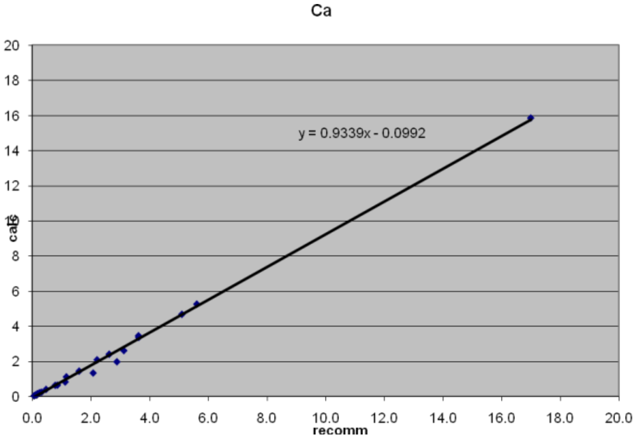

Pb
y = 0.8588x + 1.2433
600
500
400
300
200
100
0
calc
0.0
100.0
200.0
300.0
400.0
500.0
600.0
700.0
recomm
◆ Series1

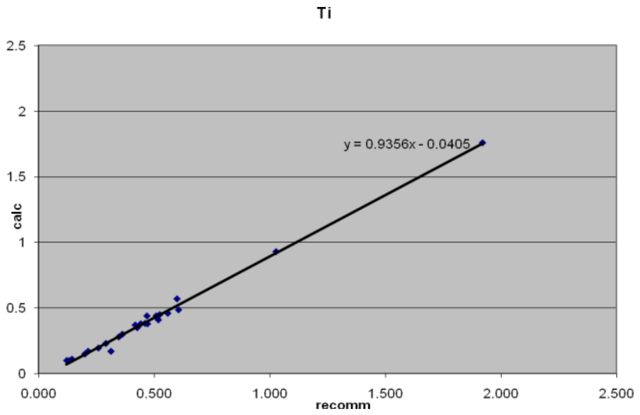

Mn
y = 0.9868x + 31.838
4500
4000
3500
3000
2500
2000
1500
1000
500
0
calc
0.0
500.0
1000.0
1500.0
2000.0
2500.0
3000.0
3500.0
4000.0
4500.0
5000.0
recomm


Fe
y = 0.9728x + 0.1312
14
12
10
8
6
4
2
0
calc
0.000
2.000
4.000
6.000
8.000
10.000
12.000
14.000
recomm

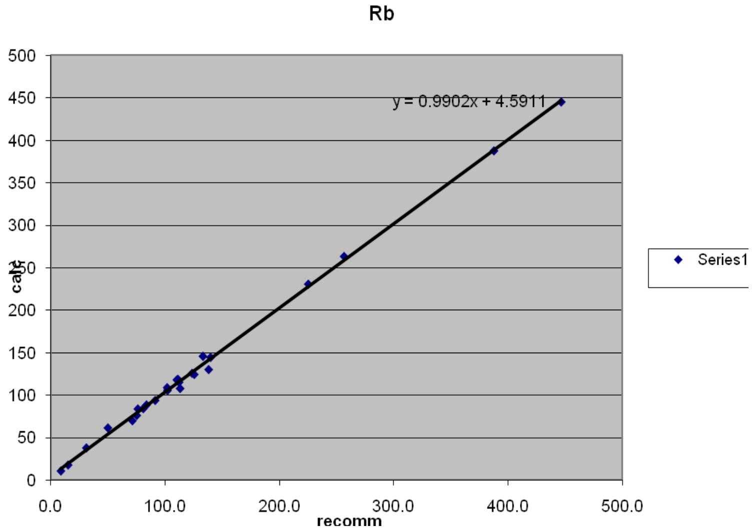

Cu
1400
1200
1000
800
600
400
200
0
calc
y = 0.9711x + 22.426
Series1
0.0
200.0
400.0
600.0
800.0
1000.0
1200.0
1400.0
recomm


Zn
700
600
500
400
300
200
100
0
calc
y = 1.0039x - 0.5358
0.0
100.0
200.0
300.0
400.0
500.0
600.0
700.0
recomm

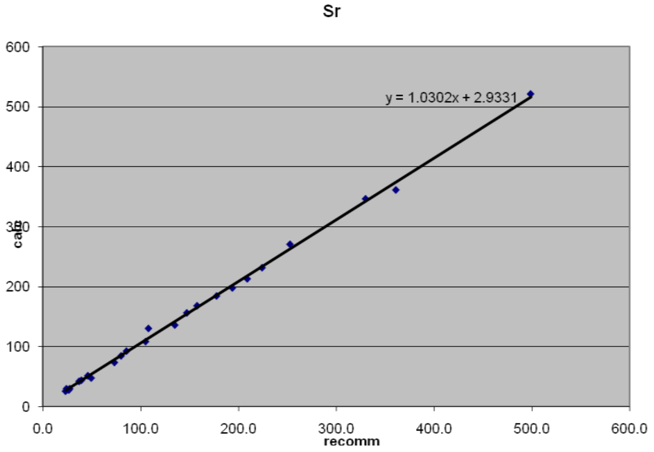

Ca
20
18
16
14
12
10
8
6
4
2
0
calc
y = 0.9339x - 0.0992
0.0
2.0
4.0
6.0
8.0
10.0
12.0
14.0
16.0
18.0
20.0
recomm



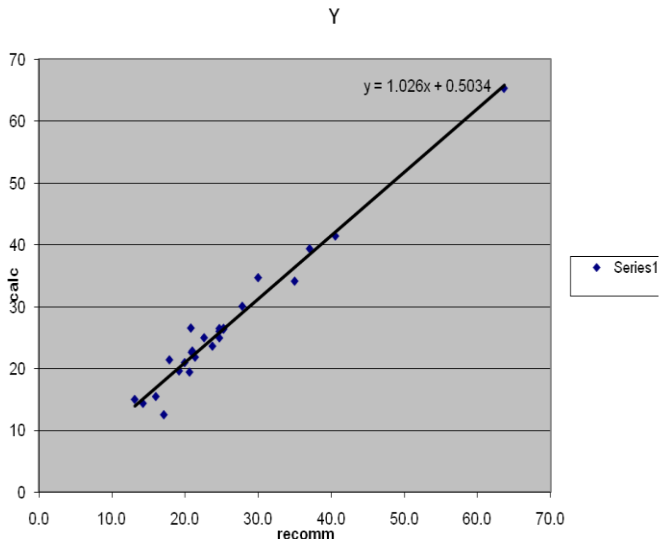
Ti
y = 0.9356x - 0.0405
calc
recomm
0
0.5
1
1.5
2
2.5
0.000
0.500
1.000
1.500
2.000
2.500

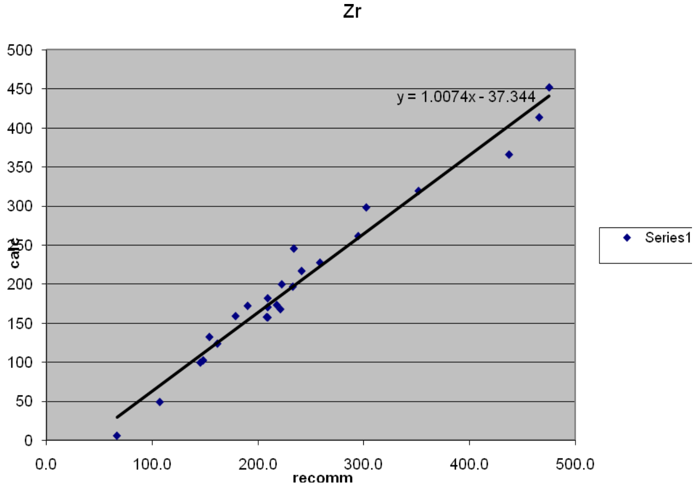


Rb
y = 0.9902x + 4.5911
calc
recomm
Series1
0
50
100
150
200
250
300
350
400
450
500
0.0
100.0
200.0
300.0
400.0
500.0



Sr
y = 1.0302x + 2.9331
calc
recomm
0
100
200
300
400
500
600
0.0
100.0
200.0
300.0
400.0
500.0
600.0





For all heavy metals analyzed by their Kα lines, the precision of the technique were evaluated by the repetition of measurements of the same standards as below.

Concentration of total metals in marine sediment standards (ppm) and (%Fe,Ca)									
	Ca	Ti	Cr	Mn	Fe	Ni	Cu	Zn	As
gss1a	1.13	0.49	122.62	1929.7	3.72	17.81	60.02	776.68	45.46
gssb	1.18	0.5	166.04	1936	3.71	18.88	52.72	752.75	24.54
gss1	1.11	0.52	134	2158	3.89	9.61	50.24	788.8	41.11
gss1	1.06	0.5	49.16	2117.46	3.7	13.38	30.13	738.18	40.49
gss1d	1.12	0.51	81.71	2089	3.89	11.71	53.48	818.64	27.4
Average	1.12	0.504	110.706	2046.032	3.782	14.278	49.318	775.01	35.8
St deviation	0.043	0.011	45.758	106.213	0.099	3.964	11.319	31.418	9.231

Conc. (ppm) (%Fe, Ca), of sed. Standards				
Rb	Sr	Y	Zr	Pb
143.17	166.88	28.67	243.54	72.68
139.87	161	27.15	237	103.97
146	166.49	26.9	246.05	86.14
136	163.54	26.85	236.95	69.64
152.28	171.74	27.71	253.38	101.45
143.464	165.93	27.456	243.384	86.776
6.182	4.031	0.760	6.878	15.841

AAS METHOD

Marine sediment sample preparation technique for heavy metals quantitative analysis by Atomic Absorption Spectrometry, AAS

Standard and sample preparation

Chemical sample preparation is a very important aspect of the trace metal analysis of environmental (sediment) and biological samples. Basically, the two approaches to sample decomposition that employed are acid attack or fusion. In the case of acid treatment, mineral acids or mixtures of mineral acids are commonly utilized. In this study it was used acid attack method for sample decomposition.

Digestion procedure

The digestion procedure were performed using the alternative technique wichi is both quicker and safer: microwave digestion techniques. The microwave system functions by using a combination of acid temperature and pressure. It was been successfully used as well as for the samples under investigation, biological tissue of bioindicator like mussels and for geological species such as marine sediments and for metal from sediment. The sample matrix was treated with concentrated nitric acid until and after the digestion and presented to the instruments used for analyzing, AAS/CV, GFAAS and FAAS in solution. All the samples are introduced in AAS instrument in solution form and reagents used of analytical quality

Microwave digestion program for sediments and sewadge sludge in 5 steps was applied in BERGHOF Microwave digestion system until analyzes.

The speed wave MWS-3+ microwave system is designed for pressure digestion at temperatures up to 230^{o}C (446^{o}F) in continuous use (500oF) and, depending on the type of the vessels employed, pressures up to a max of 100 bar. The microwave made from stainless steel is equipped with a swiveling safety lid with vent connectionand a circular sample chamber, keypad and display. for The measurement physically determines the temperature radiation emitted by the vessel contents, that is, the digestion solution. Radiation components emitted by the vessel walls are completely filtered out. Sub sample from marine sediments for heavy metals Cr, Cd, Cu, Hg, Ni, Fe, Pb, determination were treated with 7 ml acid nitric 69% (puriss p.a) until digestion. Special reagents for mercury analysis from Merck were used

Foto. Digestion in Microwave oven BERGHOF, ISUV, (Toxicology & Quality department, Food Safety & Veterinary Institut, Tirana, Albania).

Table Marine sediment digestion program drown in 5 steps

Program	Step 1	Step 2	Step 3	Step 4	Step 5
Temp (^{o}C)	145	175	175	100	100
Pressure (bar)	35	35	35	1	1
Time (min)	5	12	15	10	10
Slope (min)	2	2	2	1	1
Power (%) of infrared radiation	80	80	80	10	10

Meterial of vessels	Volume	Max pressure	Max temperature	Max sample weight	Min fill volume (acid)
dAP-60T	60 ml	40 bar	230^{o}C	≤ 500mg	➢ 5ml

Sample	Weight	Vessel	Acid	Temp
Sewage sludge	500 mg	DAP-60 T	HNO$_3$	175^{o}C

After the digestion procedure the content of the vessels (after cooling) was filtered and transferred in 50 ml balloons adding nitric acid 2%.

Determination of Mercury (Hg)

Reference material (CRM) used for determination of Hg concentration: Mercury solution etalon1000mg/L (ppm) ($Hg(NO_3)_2$ in HNO_3, 2 mol/l. concentration from MERCk

Reference material used for determination of Cd concentration: Traceable to SRM from NIST ($Cd(NO_3)_2$ in HNO_3, 0,5 mol/l concentration 1000 ml Certipur.


1


2

Photo 1. Subsample in Vessels after digestion in microwave system & 2. The subsamples prepared for analyze

Sub sample for Hg determination were analyzed by Atomic Absorption Spectrometer, Instrument type VARIAN Specter AA200 & VGA 77 vapor Generation Accessory.

The Cd determination was carried out by Graphite Furnace Atomic Absorbtion Spectrometry (GFAAS) and Flame Atomic Absorbtion Spectrometry (FAAS)

Heavy metals Cr, Cu, Fe, Ni, Pb, Mn, Zn in marine sediment sub samples were analyzed in FAAS instrument.

Calibration of the device for the Mercury (Hg) determination
Operating Parameters for the instrumentation laboratories model Varian Specter AA200

Method type: and Mode
Element - Hg
Units - µg/kg
Sampling mode – manual
Vapor mode – cool vapor
Measurement Parameters
Calibration mode – concentration
Minimum reading 0.0000
Smoothing
Time (s) – measurement 5 s
Total reading 45 s

Standard
Replicates 3
Sample standard 3
LOD Hg instrument - 0,2 ppb (µg/L)

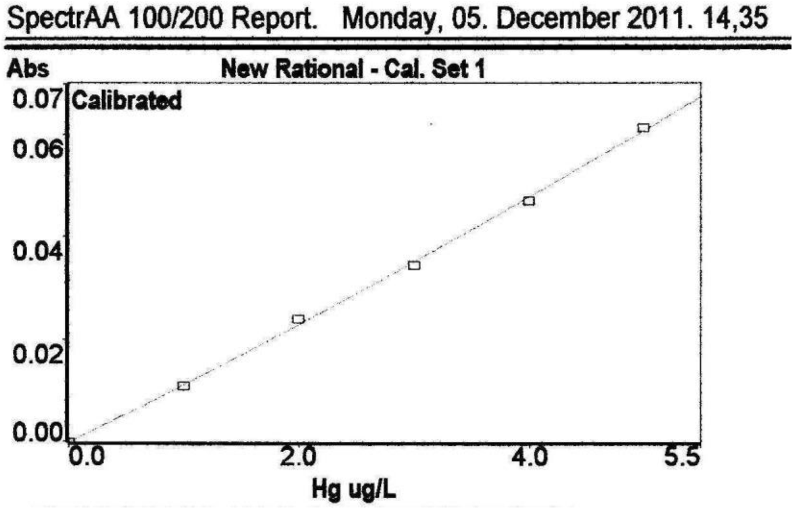

SpectrAA 100/200 Report. Monday, 05. December 2011. 14,35

Fig. Calibration curve obtained during the Hg analysis in samples collected in autumn 2011.

Optical parameters:
Lamp position 2
Lamp current (mA) 4
Wavelength (nm) 253,7
Slit (4) width (nm) 0,5
Background correction BC off
Reductant: stanor chloride 25%

Solution prepared: nitric acid 2%, stanor chlorur 25%, standart Hg 10ppm, standard Hg 100 ppm, standard Hg 1ppb

Standard 1	1.00µg/L
Standard 2	2.00 µg/L
Standard 3	3.00µg/L
Standard 4	4.00 µg/L
Standard 5	5.00 µg/L

Foto AAS System of cold Vapor for analysis of mercury in marine sediment of Vlora.
The device for the determination of mercury with cold vapor atomic absorption (photo I.Sino)

a.

b.

Photo 1 Atomic absorbtion Spectrometer (photo I.Sino) Varian SpecterAA 200, b. Analyzing Hg in marine sediment samples

Determination of Hg by AAS/VGA-77

Analytycal notes

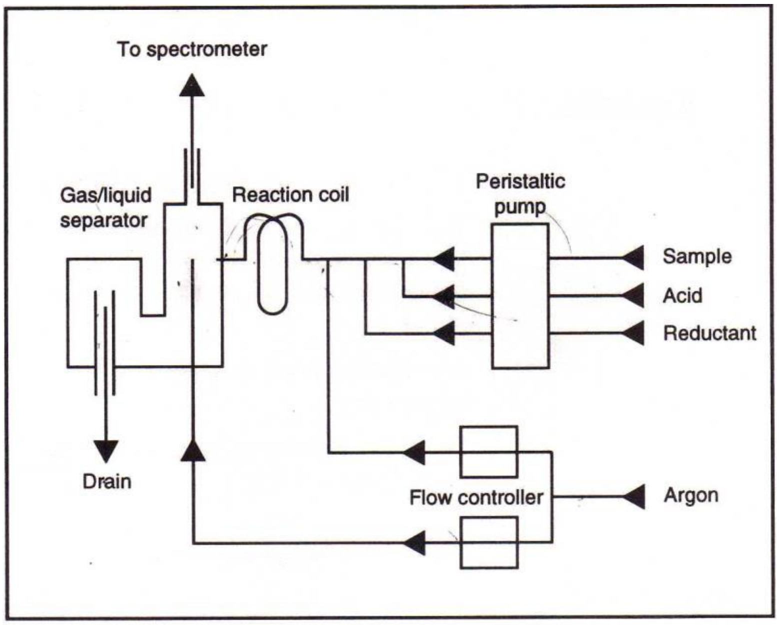
The VGA-77 employs continuous flow technology where samples and liquid reagents are pumped together and mixed. The gaseous reactions products are swept by a flow of argon gas into the spectrometer.

The following figure shows a schematic diagram of the VGA-77.

The peristaltic pump maintains a constant flow of analytical solutions into the accessory. The sample and acid are allowed to merge first before the reductant, $SnCl_2$ enters the stream. For mercury analysis, $SnCl_2$ solution was used (is recommended). Argon is then introduced into the liquid stream and the reaction proceeds while the mixture is flowing through the reaction coil. Vigorous evolution of hydrogen assists the stripping of the hydride (or mercury vapor) from the liquid into the argon.

The gas is then separated from the liquid in the separator. The liquid drains away to waste. At this point a second stream of argon is introduced to ensure that the gas stream is not saturated with water vapor and so does not condense in the sample introduction system.

The gas containing the element of interest then passes out of the separator into the spectrometer where it is analyzed. With VGA-77, a continuous signal is produced. In this is necessary (should) use the integration mode with SpectrAA or Liberty systems. (SpectrAA users can also use PROMT mode).



Schematic of the VGA

Fig Schematic of the VGA

<u>Sources (AA only)</u>

Hollow cathode lamps was used for VGA-77 methods for AAS analysis of Hg. Its main feature is the narrow absorbing spectral line. The hollow cathode lamp is stable, reliable, has a long operating life and is the standard source in AAS and may be expected to run in 5000 mA hours without failure.


Hollow cathode lamp (photo I. Sino)

Photo. The Hollow cathode lamp used for Hg determination (in sediments of Vlora) in AAS/VGA77. Current lamp used, 4 mA, wavelength used for atomization of Hg, λ=253.7 nm (Photo I. Sino)

Atomization in AAS

When a voltage of between 300-400 is applied between the anode and cathode the discharge is set up and argon is ionized by the anode and becomes a positive argon ion by the mechanism of:
$Ar + e^- = Ar^+ + 2e^-$
The positive Ar+ ion is attracted and accelerated toward the metal cathode where it dislodges or "sputters" excited Hg atoms (or excited metal atoms of the interest Cd, Cr, Ni, Pb, Mn, Fe, Cu). present in cathode) into the space inside the hollow cathode. Argon collides with the metal cathode knocking metallic Hg atoms into the discharge, which improves the sensitivity of the discharge. The excited mercury atoms emit energy of their own characteristic wavelength before returning to the ground state and the emitted light is used as the light source λ= 253.7 nm for the AAS/CV system. After the atoms return to the ground state they form a cloud of free atoms which return either to the walls of the glass lamp or to the metal cathode. If the atoms in the cathode are hot they produce spectral line broadening caused by the Doppler effect.(manual of AAS) [59]

Standards

The calibration standards were prepared from 1000 μg/mL stock solutions.

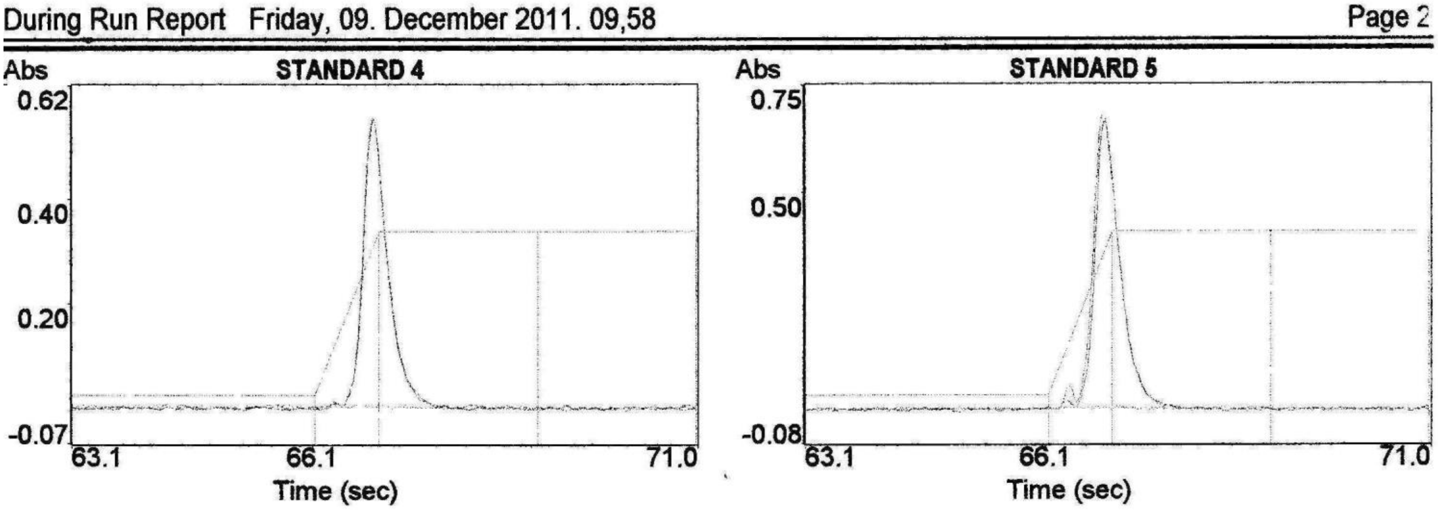
Acid concentration

The concentration of acid will affect the efficiency of hydride formation in the VGA-77. It was necessary that the acid concentrations of blank, standard and sample solutions to be the same.

Determination of Cd by Graphite Furnace Atomic Absorption Spectrophotometer GFAAS

Reference material were used to prepare the work standards for determination of Cd concentration: Traceable to SRM from NIST ($Cd(NO_3)_2$ in HNO_3, 0,5 mol/l concentration 1000 ml Certipur.
The determination of Cd was carried out by atomic absorption spectrophotometer by flame and by furnace. LOD instrument for Cd is 0,0066μg/l

Photo. Graphite Furnace Atomic absorption spectrophotometer used for determination of Cd in marine sediment collected in Vlora (photo, I. Sino)



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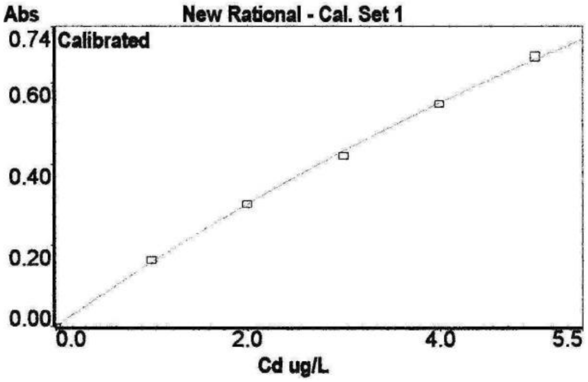


3
Fig. Calibration procedure, calibration curve for the determination of Cd by GFAAS

To measure the absorbance are used both peak hight and peak area.

Determination of Cr,Cu, Cd, Fe, Ni, Mn, Pb by Flame AAS

Standard acqueous metal solutions (1000 ppm metal) were prepared from reagent grade metals or metal salts.Working solutions were prepared by diluting approximately by volume.to determinate the Cd concentration.

We prepared four standard solutions (using reference solutions from Merck) with known concentration to built the standard courve and to calibrate the apparatus.

Calibration of the device

Table Concentrations of standard solutions

Element	Concentrations of standard solutions (mg/L)
Cr	0.5mg/L, 1mg/L, 1.5mg/L, 2mg/L
Pb	1, 3, 5, 7
Cd	0.25, 0.5, 0.75, 1
Mn	0.3, 0.6, 0.9, 1.2
Fe	0.8, 1.6, 3.2, 6.4
Cu	0.4, 0.7, 2.8, 5.6
Ni	0, 1.5, 3, 6

These concentration are given because are specified by lineare curve. In four ballons were dropped check concentration (0,1 – absorbance for calibration of the device). One is check solution and its absorbance must be 0,1. In this way the calibration of device is done. In four ballons added deionizated water up to 100ml and adding HNO_3 1:3. Cr added according to the above concentrations. The ballon filled with deionizated water and well mixed for having the homogenized solution.

Table 4.5 Concentrations band of standard solution for elements under study

Element	Concent.of standard solution zone	R^2
Cr	0-2	0.996
Cu	0-5.6	0.999
Cd	0-1	0.994
Fe	0-6.4	0.999
Ni	0-6	0.996
Mn	0-4	0.997
Pb	0-7	0.996

a.Burner of FAAS b. Analytic Jena NOV AA400

Photo. Instrument type: Atomic absorption spectrometer by flame (acetilen flame) Analytic Jena NOV AA400 used for analyzing of heavy metals in sediment of Vlora (photo, I. Sino)

Operating Parameters of the instrument FAAS model Analytic Jena NOV AA400

Procedure in atomic absorption spectrometer:

Activated Cr lamp controlling the other parameters.

Lam current = 5 mA

Pressure of acetilen in exit = 1,2 bar

Compresor of absorption = 5 bar.

Was done a combination of the acetylene – airflow

Tab. General analytical conditions for the flame absorption spectrometer used for determination of concentration of heavy metals

Element	Wavelength	Type of flame	Lantanit chloride	The main interferences	Background correction
Cd	222.8	Oxidant air/acetylene			Deuterium

Cr	357.9	Reductant flame air/acetylene NO2	yes	Fe, Al, Ca, Mg	Halogen
Cu	324.8	Oxidant Air/acetylene			Deuterium
Pb	217	Oxidant Air/acetylene			Deuterium
Mn	279.5	Oxidant Air/acetylene/ NO2		Fe, Si	Deuterium
Ni	232	Oxidant Air/acetylene		Fe	Deuterium

Caracteristics of instrument

Instrument type: Atomic absorption spectrometer by flame (acetilen flame) Analytic Jena NOV AA400

The atomic absorption spectral photometer novAA 400 is a Pc- controlled multielement automatic machine for sequentialdetermination of traces and ultra-traces of metals and semi-metals in liquid, solution and solid samples. novAA works in flame and in graphite tube.

NovAA 400 flame

Compact spectrometer for flame – AAS in signle and double beam mode

The flame –AAS instrument with deuterium background correction is designed as double beam instrument and allows for operation in single or double beam mode, as selected.

Measurement Principle:

Light change technique with deuterium background compensation

Single and double-beam mode

Photometer

Double –beam layout with rotating mirror for inserting the reference beam

High light yield and bse line stability

Quartz-improved mirror optics

Wide range photomultiplier

Monochromator

Table

Assembly	Modifier Czerny-turner layout with a flat holo-grating, automatic wavelength and slit width setting
Effective grating surfaces	54x54mm^2, 1600 lines /mm

Blaze wavelength	220 nm
Focal distance	350 mm and 389 mm
Wavelength range	185 to 900 nm
Slit width	0,2nm, 0,5 nm, 0,8nm, 1,2 nm
Reciprocal linear dispersion	2nm/mm

Hollow cathode lamps HCl: lamp type: luminiescence discharge lamps with additional discharge for 68 elements with line radiation in the UV-VIS range, current lampl: 2 to 30 mA, mode: electrical timing 150 Hz.

Were analysed heavy metals: Cd, Cr, Pb, Cu, Mg, Ni, Fe, with the flame technique (from manual of AAS Analytic Jena NOV AA400)

LIBS QUALITATIVE ANALYSIS OF HEAVY METALS CONTENT IN MARINE SEDIMENT

To evaluate and to compare the results obtained by EDXRF, qualitative analysis of heavy metal were perfomed using Laser Induced Breakdown Spectroscopy, LIBS in marine sediment collected in Vlora bay was performed applying LIBS, Laser Induced Breakdown Spectroscopy, at Department of Physics Chemistry, University of Florence..

The qualitative analysis to identify the heavy metals was performed applying a compact (84x94.32 cm) nanosecond Q-swiched Nd: YAG laser (model CRF 200-GRM, Big Sky Lasers, 8 ns, 20 Hz, 0.005-115mJ/pulse for the 532 nm emission). the instrument was used as an irradiation source. The laser has a top-hat profile with a spot of constant energy density. The emitted light from the sample is collected through the same lens used to focus the laser beam, and subsequently is focused into a 0.30 m imaging spectrograph (model SP-2358i, Action Research) equipped with three interchangeable diffraction gratings with 150, 300 and 1200 grooves/mm. the ICCD is a 1024x256 imaging pixels detector (model P.I. Max-1024/RBPTG, Princeton Instruments) with a minimum gate speed of 1ns. LIBS spectra were acquired using a gate width of 700 ns and a delay time of 740 ns.

LIBS system

A general scheme of the pulsed laser setup used is showed in the figure below.

The laser pulses are guided to the sample through a convenient set of mirrors, a KDP crystal may be placed in front of the laser so as to produce the forth harmonic at 260 nm and so two alternative optical paths must be available. The emitted light from the sample is collected through the same lens used to focus the laser beam, and subsequently is focused into a 0.30 m imaging spectrograph. The ICCD isa 1024256 imaging pixels detector that allows time resolved acquisition, essential for LIBS measurements and to discriminate Raman signal from background radiation or luminescence contribution (or particular interest for measurements done in outdoor environments). For Raman spectroscopy analysis the light back-scattered from the sample is filtered by a notch filter that is placed before the focusing lens in front of the slit of the spectrograph.

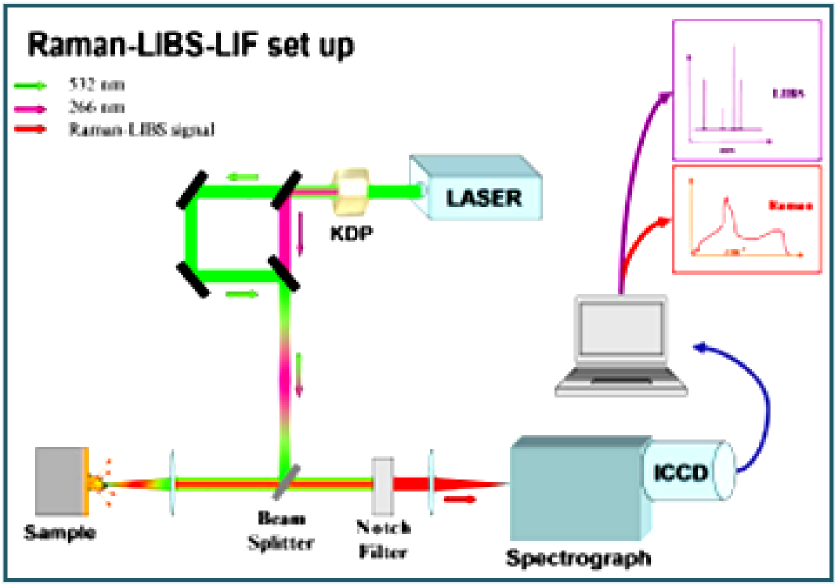


Fig. the scheme of the pulsed laser setup for LIBS used for qualitative analysis of heavy metals in marine sediment

Laser

The laser used was a CRF 200 Q-switched Nd:YAG laser supplied by the “Big Sky” (Quantel) company. it has a pulse duration of 8 ns, a repetition rateof20 Hz, and an energy of200 mJ/pulse for the first harmonic. Nd:YAG lasers is the most used type of solid –state laser and low cost, the host medium is a crystal of Y3Al5O12 inwhich someof theY3+ ions are replaced by ND3+ ions, when a Yttrium Aluminium Garnet (YAG) crystal is doped with a small amount of neodymium the crystal becomes slightly red and achieves goog laser qualities. The laser has a top-hat profile with a spot of constant energy density. The profile emage can be obtained by cutting the laser beam with a small iris along the x and y directions and measuring the energy of the part of the beam uncat by the iris.

Detector

The detector used in the setup is an ICCD model PI MAX 1024/RB-PTG supplied by the Princeton Instruments Company. The CCD array is constituted by 1024 x 256 pixels of 26x26 µm. In full vertical binning mode, hte detector can work at a repetition rate of 185 Hz working up to 630 Hz for a 200 µm tall spectrum. The minimum gate speed applicable in normal conditions is on the order of 2 ns but with the "fast gate" option it is possible to work up to gate times on the order of 500 ps. The detector is provided with an RB (Red –Blue optimized) intensifier active in a wide spectral range from 180 up to 900 nm.

Monochromator

A spectra Pro 230i monochromator supplied by Acton Research corporation Company has been used, it is a 300 mm (f/4 aperture0 monochromator with triple grating. Three different grating have been mounted in order to achive an efficient light througput over a broad spectral region and to strike a balance between spectral resolution and the spectral range width: 150 g mm-1 (300 nm blazed) grating with a dispersion of 21 nm/mm and wavelength coverage of 568 nm; a 300 gr mm-1 (500 nm blazed) grating with a dispersion of 11 nm/mm and a wavelength coverage of 279 nm; 120 gr mm-1 (300 nm blazed) with a dispersion of 1.5 nm/mm and a wavelength coverage of 38 nm. The changing of the gratings is controlled by software.

Measurement

The results were obtained by 6 repeating measurements, taking the measurements after a certain ablation time when the signal was at a more stable level. During the time the laser beam was focused on the sediment pellet, the sample absorbs the energy melting and vaporizing in that point of the surface. After the vapor absorbed the energy of laser and the created plasma expanded highly ionized lines was found near the pellet surface. The analyte signal obtained[66] is proportional to the laser energy.

Chapter 5 Results of Marine sediment samples

1. EDXRF RESULTS

Total heavy metals concentration (as dry weight) in marine sediment samples collected in the area of Vlora Bay and Lagoons, autumn 2012 determined by EDXRF

Total heavy metals concentration (mg/kg) in sediment - XRF analysis														
Station	Ca	Ti	Cr	Mn	Fe	Ni	Cu	Zn	As	Rb	Sr	Y	Zr	Pb
Z7/1	113000	3200	2180	888	22900	201		32	12	31	203	16	85	
Z3/2	111500	2800	1247	905	25400	246	8	38	11	37	199	14	110	
Z1/3	118400	2000	681	735	24300	247	9	28	8	35	198	14	23	
N1/4	101900	2900	1362	833	22000	181		35		35	190	18	198	
N3/5	104200	2100	949	871	24200	223	8	35	10	37	196	15	103	
N7/6	105600	2200	1047	827	24900	245	12	35	8	37	194	15	97	12
T3/7	112500	2100	781	824	24700	234	10	34	20	38	203	13	61	
T1/8	112100	1600	603	937	24600	270	9	35	6	35	216	14	17	28
T7/9	98500	2600	1016	862	24500	209	18	39		40	196	17	117	17
P1/10	123200	2000	1259	839	21200	191		33	14	32	215	13	95	
P3/11	76300	2900	803	878	39900	299	32	74	12	71	196	16	71	
P/712	104500	2600	2254	872	23200	203	8	37	19	35	205	16	232	
S1/13	140600	2500	2650	935	19700	167		35		25	245	13	115	

S3/14	123200	1500	712	812	22300	274	8	29	21	30	216	12	7	
S7/15	113900	3000	1881	804	20000	173		37	20	31	199	17	168	
H1/16	135200	2000	1657	824	19500	194		27	11	26	234	13	95	
H3/17	132000	3400	3757	935	22000	180		33	9	28	217	14	179	
H7/18	119300	4900	7844	1022	26000	186		50	14	28	205	29	682	
K1/19	147900	1700	1425	891	19500	199		29	15	25	243	13	78	
K3/20	129100	1700	936	896	20800	186		32	18	31	225	12	4	
K7/21	86700	2500	742	674	29400	258	21	60	6	50	190	18	96	18
R1/22	127100	1000	364	928	22300	255		32	39	30	220	11	0	
R3/23	125200	1600	532	941	18900	164		25	21	28	233	12	0	
R7/24	110000	2100	572	691	25100	211	13	46	14	45	264	16	43	
V3/25	96100	2700	613	675	29200	294	25	64		53	236	19	79	43
V1/26	137500	1300	480	939	22200	260		27	19	27	230	13	0	14
A1/27	153200	1300	484	831	17700	188		26	16	25	244	10	0	
A3/28	87300	2800	465	620	34200	231	26	77	22	73	207	18	96	
A7/29	87900	2900	479	677	35100	228	27	72	12	69	207	20	63	12
M7/30	100900	2500	446	671	30200	269	15	51	18	48	202	14	56	
M3/31	92600	2200	650	772	59900	251	53	153	9	48	217	16	48	31
M1/32	111300	2100	600	642	24200	206	10	54	14	44	240	13	69	
O1/33	170100	400	93	183	2800	11		23		16	144			16
R/34	186000	100	46	155	1300	12		9		18	137			
J/35	282700	400	112	266	1900				15	10	180			
O2/36	14.35	100	102	119	2200	11		85	56	10	238			
O3/37	12.99	100	100	66	600			9		8	75			
O4/38	22.76		47	145	1300	12		8		10	129			
O5/39	25.87			104	500		86	39		7	137			
DL (Mo)	120.00	65	38	27		10	8	7	6	6	7	9	13	12

DL (Mo) Measuret detection limits (ppm) Mo secondary target

These results in the table above represent the concentration of the element equivalent to three standard deviations of the background counts at the energy of its characteristic line. The values of the background under the peak of each element and the corresponding sensitivities were calculated by COREX. As the values of the background depend on the composition of the sample, the average of the background values, from some standards with different composition, was used for the calculation of detiction^2 limits.

As and Pb lines are not always separated appropriately at this concentration level.

Accomplished studies to date using XRF indicate that it is very difficult to distinguish between As and Pb, because of the interferences. These two elements are present in small percentages. Their values will be accepted reluctantly.

Cr, shows values larger then those obtained with AAS method^4 in 2011, during this study.

Table. Total toxic heavy metals concentration (as dry weight) under the study in marine sediment samples collected in the area of Vlora, Vlora Bay and Orikumi lagoon, autumn 2012

Concentration (ppm) of total toxic heavy metals in study collected in autumn, 2012 (XRF analysis)								
Station	Cr	Mn	Fe	Ni	Cu	Zn	As	Pb
1/Z7	2180	888	22900	201		32	12	
2/Z3	1247	905	25400	246	8	38	11	
3/Z1	681	735	24300	247	9	28	8	
4/N1	1362	833	22000	181		35		
5/N3	949	871	24200	223	8	35	10	
6/N7	1047	827	24900	245	12	35	8	12
7/T3	781	824	24700	234	10	34	20	
8/T1	603	937	24600	270	9	35	6	28
9/T7	1016	862	24500	209	18	39		17
10/P1	1259	839	21200	191		33	14	
11/P3	803	878	39900	299	32	74	12	
12/P7	2254	872	23200	203	8	37	19	
13/S1	2650	935	19700	167		35		
14/S3	712	812	22300	274	8	29	21	
15/S7	1881	804	20000	173		37	20	
16/H1	1657	824	19500	194		27	11	
17/H3	3757	935	22000	180		33	9	
18/H7	7844	1022	26000	186		50	14	
19/K1	1425	891	19500	199		29	15	
20/K3	936	896	20800	186		32	18	
21/K7	742	674	29400	258	21	60	6	18
22/R1	364	928	22300	255		32	39	
23/R3	532	941	18900	164		25	21	
24/R7	572	691	25100	211	13	46	14	
25/V3	613	675	29200	294	25	64		43
26/V1	480	939	22200	260		27	19	14
27/A1	484	831	17700	188		26	16	
28/A3	465	620	34200	231	26	77	22	
29/A7	479	677	35100	228	27	72	12	12
30/M7	446	671	30200	269	15	51	18	
31/M3	650	772	59900	251	53	153	9	31
32/M1	600	642	24200	206	10	54	14	
33/O1	93	183	2800	11		23		16
42/Ra	46	155	1300	12		9		

35/J	112	266	1900				15	
36/O2	102	119	2200	11		85	56	
37/O3	100	66	600			9		
38/O4	47	145	1300	12		8		
39/O5		104	500		86	39		
DL (Mo)	38	27		10	8	7	6	12
DL (Mo) measured detection limits (ppm) Mo secondary target								

Result on the table above were obtained from the stations as follows:

In front of Soda - PVC- plant: S (S_1, S_3, S_7)
In front of ex junior campus: Kampi K (K_1, K_3, K_7)
Moli,in front of harbor of Vlora (M_1, M_3, M_7)
Vlora, New beach V (V_1, V_3, V_7)
Petrolifera P (P_1, P_3, P_7)
TEC T (T_1, T_3, T_7)
Zvernec Z (Z_1, Z_3, Z_7)
Hidrovori (H_1, H_3, H_7)
Orikumi Lagoon O
Aulona (A1, A3, A7)
Jonufra, J
Rradhima, Ra
O_1 – Orik Pashaliman (shore)
O_2 – Orikumi lagoon, derdhja, dalan (shore)
O_3 Orikumi plazh (beach)
O_4 - Orikum discharge Izvori (shore)
O_5- Orikum discharge (shore)
Lm Monastery S. Mary.N lagoon, Zvernec
Ln, Narta Lagoon
Dv Dalan Narta lagoon
Lu, Narta lagoon (ura) bridge
Lp, Narta lagoon (west)

Table. Total toxic heavy metals concentration mg/kg (as dry weight) in samples collected in Narta Lagon, 2012

Concentration of total toxic heavy metals (ppm) (Fe%), in marine sediment for Narta Lagoon (XRF analysis)								
Station	As	Cr	Ni	Pb	Cu	Mn	Zn	Fe (%)
Lm		74	60	12	40	343	46	7.71
Ln		591	154	14	36	625	57	2.13
Dv		517	130	20	25	1315	50	2.21
Lu		1474	156	15	11	721	40	1.71
Lp	21	330	106		22	587	40	1.12
Min	21	74	60	12	11	343	40	1.12

Max	21	1474	156	20	40	1315	57	7.71
Mean	21	510	121	15	27	750	47	2.98

Table. Total heavy metals concentration mg/kg (as dry weight) in samples collected in Narta Lagon, 2012

Total heavy metals concentration (mg kg-1) (Ca,Ti%), Narta Lagoon, 2011						
Station	Ca (%)	Ti (%)	Rb	Sr	Y	Zr
Lm	27.75	0.03	12	1042		69
Ln	20.03	0.18	26	643	9	150
Dv	8.43	0.24	56	221	16	161
Lu	7.80	0.20	27	163	13	228
Lp	28.04	0.06	9	842		70

According to the results for heavy metals obtained by EDXRF (analyzing the mixture of all fractions in marine sediments 2012) were identified three the most polluted samples, number 11, 18, and 31. These samples are subsequently analyzed in terms of the sizing characteristics of the grains of which they are composed. The results from the particle size analysis are used to generate size distribution plots.

Via sieving methods, the sediment samples were separated in different fractions using the analitycal sieve shakers. The grains are separated in 4 fractions and a grain size distribution constructed in fractions (layers) as follows:

Fraction 1 - grain size 90 µm
Fraction 2 – grain size 250 µm
Fraction 3 – grain size 800 µm
Fraction 4 – grain size > 800 µm

EDXRF heavy metals analysis performed in three first fraction fractions various grain size (after granulometric analysis) in marine sediment sample as follows: 90 µm, 250 µm and 800µm grain size fraction were analyzed and the results are reported in the table below.

Table. Total toxic heavy metals concentration (as dry weight) in marine sediments fractions in samples collected in Vlora Bay, autumn 2012.

Total toxic heavy metals concentration (mg kg^{-1})of total toxic heavy metals in sediment of Vlora according to the granulometric layer								
Station/sed.frac.	As	Cr	Ni	Pb	Cu	Mn	Zn	Fe (%)
P3/11-1	33	1535	378		131	1209	123	4.29
P3/11-2		704	316	35	122	1259	98	3.68
P3/11-3	38	875	351		88	1141	92	4.51
H7/18-1		17496	248	24	52	1913	168	4.60
H7/18-2		2358	194	19	25	986	58	2.15
H7/18/-3	37	902	401		45	1198	109	4.85

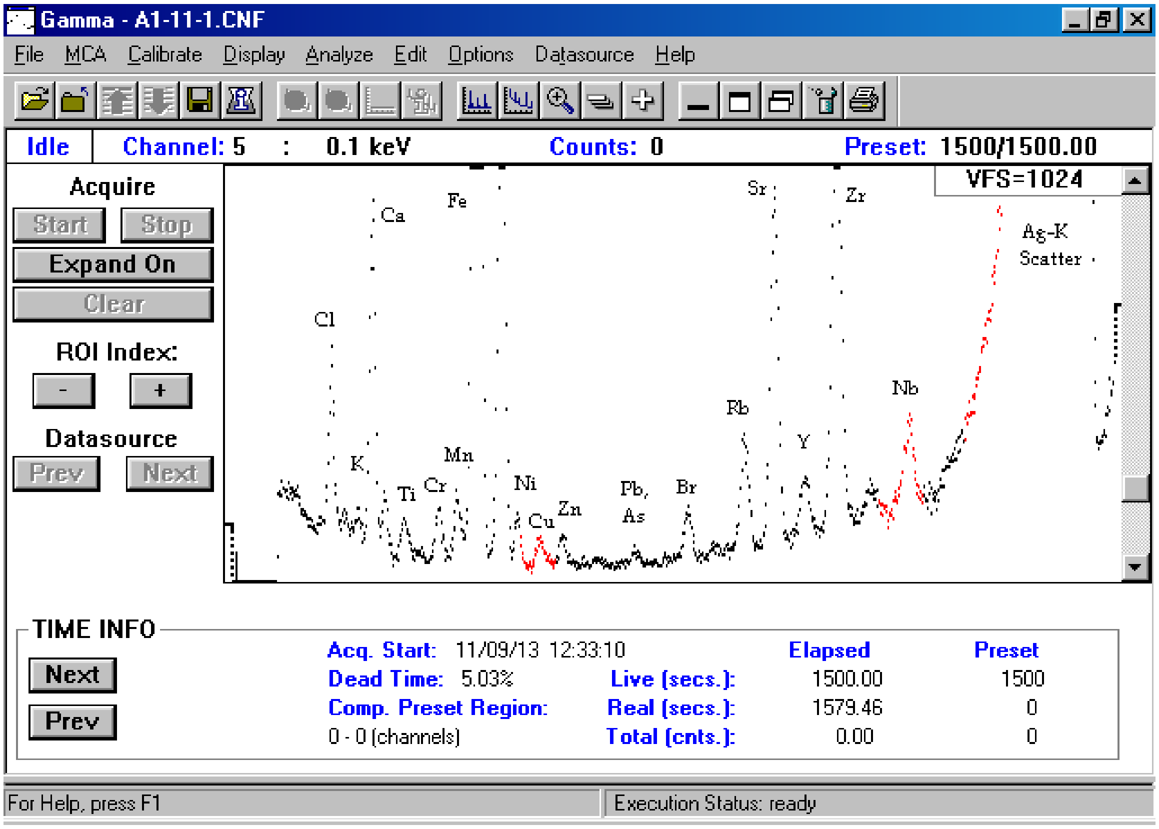
M3/31-2	26	484	279	20	150	1002	100	3.17
M3/31-3		564	290	57	86	919	135	3.85
Min	26	484	194	19	25	919	58	2.15
Max	38	17496	401	57	150	1913	168	4.85
Mean	34	3115	307	31	88	1203	105	3.89

Table. Total heavy metals concentration (as dry weight) in marine sediments fractions in samples collected in Vlora Bay, autumn 2012

Total heavy metals concentration (mg kg-1) (Ca,Ti%), granul.fract., 2012						
Station	Ca (%)	Ti (%)	Rb	Sr	Y	Zr
P3/11-1	7.18	0.36	69	199	20	207
P3/11-2	8.87	0.26	45	209	18	140
P3/11-3	6.72	0.34	66	197	17	156
P3/18-1	8.08	1.16	15	191	58	1899
H7/18-2	11.79	0.30	19	213	17	188
H7/18-3	7.85	0.29	77	212	19	169
M3/31-2	9.70	0.13	38	245	15	106
M3/31-3	9.14	0.21	41	244	17	147

M3 - Harbor of Vlora, 300 m from the shore
H7 - Hidrovori, situated 700 m from the shore, near and on the left of ex Soda PVC plant
P3 - Petrolifera situated 300m from the shore in the same place of ex- Soda &PVC plant

The first fraction, grain size 90 um of sample number 18 (H7) situated on the left of ex Soda-PVC plant 700 m from the shore , in the same direction with the Vlora discharge, resulted the most polluted in Cr than the others. The pollutions as resulted in the table is more stabilized in the small grain size, fractions, of marine sediments.



Idle | Channel: 5 : 0.1 keV | Counts: 0 | Preset: 1500/1500.00

Acq. Start: 11/09/13 12:33:10

Dead Time: 5.03%

Comp. Preset Region: 0 - 0 (channels)

	Elapsed	Preset
Live (secs.):	1500.00	1500
Real (secs.):	1579.46	0
Total (cnts.):	0.00	0

For Help, press F1

Execution Status: ready

Fig. EDXRF Spectrum (Kα lines) of marine sediment measured for 1500 s with a Ag secondary target, Sample 11-1, grain size 90 µm, fraction of sample 11 collected in P3, positioned in front and between of ex-PVC-Soda plant and the sea.

In EDXRF spectrum the area of peak profile determines the concentration of respective element as in the figure above.

The secondary target selected (Mo) has a fluorescent line with an energy just above the absorption edge of the analytical line.

In EDXRF the analysis of the samples has been done in two steps[66]: Qualitative analysis and Quantitative analysis. The first determine which element are present and the net intensities for each element from the measured spectra. The net intensities are used in the quantitative analysis to calculate the concentration of each element present. The surface under the peak gives the intensity. The detector used, has measured the different energies of the characteristic radiation coming directly from the sample and separate the radiation from the sample into the radiation from each element present, doing in this way the dispersion.

Table. Total toxic heavy metals concentration in marine sediments of Vlora collected in summer, 2011 (Fe %)

Concentration of total toxic heavy metals (mg kg^{-1}), in marine sediment, summer 2011								
Station	As	Cr	Ni	Pb	Cu	Mn	Zn	Fe (%)
P0	15	331	218	20	7	1031	41	1.88

P1	16	732	279	14		1100	51	2.27
P3	15	577	272	12	5	928	65	2.47
P7		701	249	25	6	1038	55	1.98
M0		938	229	19	13	1126	48	1.98
M1	21	597	270		29	872	82	2.96
M3		712	287	19	23	969	92	2.96
M7		606	288	22	27	842	91	3.46
K1	28	1270	243			1057	47	2.17
K3	14	855	267		10	1023	56	2.11
K7	13	2459	202	10	6	1108	53	2.27
D1		1392	234	16	9	1059	56	2.14
D3		1220	232	20	12	1010	45	2.12
D7		874	237	15		1100	47	1.98
H3	16	1013	236		15	1131	39	2.08
H7		2035	241	31	10	1078	53	2.27
S1		1527	268	31		1010	55	2.39
S3		1150	293	21	20	1051	55	2.55
S7	28	766	272		18	1024	64	2.75
N1	12	1948	258		20	1265	58	2.42
N3	18	1607	254		8	1183	51	2.35
N7	17	571	302		10	1186	59	2.80
Min	12	331	202		5	842	39	1.88
Max	28	2459	302		29	1265	92	3.46
mean	18	1093	256		14	1056	58	2.38

Table. Total heavy metals concentration mg/kg in marine sediment samples collected in Vlora Bay, Narta and Orikumi Lagoons, summer 2011

Content of heavy metals in marine sediment (ppm)(Ca,Ti %), 2011						
sample	Ca (%)	Ti (%)	Rb	Sr	Y	Zr
P0	15.81	0.10	11	253	12	76
P1	13.70	0.18	16	225	14	95
P3	12.65	0.17	25	226	13	116
P7	15.81	0.14	17	244	12	80
M0	13.70	0.17	16	250	14	108
m1	11.59	0.21	32	298	14	133
M3	10.54	0.28	37	220	16	135
M7	8.43	0.32	57	194	20	169
K1	12.65	0.21	18	220	13	191
K3	13.70	0.16	17	234	13	129
K7	11.59	0.28	20	213	16	212

D1	14.76	0.18	19	235	14	153
D3	14.54	0.18	19	235	13	153
D7	14.76	0.19	18	231	13	98
H3	14.44	0.20	18	237	11	134
H7	13.70	0.26	18	222	16	266
S1	12.65	0.24	26	227	15	216
S3	11.59	0.25	30	224	14	173
S7	10.54	0.26	28	202	15	163
N1	13.72	0.28	26	246	22	226
N3	12.48	0.21	25	247	18	211
N7	7.17	0.19	32	209	14	42

Table. CRM

	SL – 1	JSD-2	JSD-3	GSD-3	GSD-5
	lake sediment	stream sediment	stream sediment		
Fe (%)	6.743	8.052	3.071	4.55	4.098
Mn (mg/kg)	3461.9	952.6	1115.2	400	1160
Cr (mg/kg)	104	104	35	87	70
Ni (mg/kg)	44.9	94	19.6	25.6	34
Cu (mg/kg)	30	1114	426	177	137
Zn (mg/kg)	223	2070	139	52	243
As (mg/kg)	27.5	39.4	261	17.6	75
Pb (mg/kg)	37.7	151	82	40	112
Cd (mg/kg)	0.26				
Hg (mg/kg)	0.13				

2. AAS RESULTS

Heavy metal concentration mg/kg in sediment samples collected in Bay of Vlora in autumn 2011

Nr.	Station	Cd	Cr	Cu	Fe	Hg	Mn	Ni	Pb
1	S1	<DL	164.7	6.2	<DL	0.167	242	147.9	0.54
2	S3	<DL	142.5	12.3	49550	0.064	119.6	50.3	<DL
3	S7	<DL	147	12	40150	0.07	102	243	8.58
4	K1	0.084	206.9	10.1	45320	0.07	310	156.2	<DL
5	K3	0.045	580	11.7	50210	0.05	290	162.2	<DL
6	K7	<DL	211	16.1	3042	0.06	310	158.8	<DL
7	M1	0.085	186.1	27.4	53400	0.488	1180	228	<DL
8	M3	<DL	117.2	27.7	58180	0.144	720	155.3	9.2

9	M7	0.39	173.7	28	66120	0.476	1058	81.6	<DL
10	V1	0.028	165.4	20.4	55710	0.083	897	191.8	24.7
11	V3	0.025	177.9	12.6	45530	0.05	1266	60.6	20.3
12	V7	<DL	150.4	29.3	61530	0.212	75	197.7	16.7
13	P1	<DL	153.3	10.6	49660	0.016	960	166.5	<DL
14	P3	<DL	153.6	12.1	50300	0.023	1160	167.4	<DL
15	P7	<DL	144.4	14.8	52420	0.07	1320	201.8	<DL
16	T1	1,2	152.4	10	47800	0.08	1274	152.6	10.7
17	T3	<DL	181.3	6.7	48550	0.105	826	12.8	37.2
18	T7	<DL	171.7	22.1	57810	0.11	1160	220.6	36
19	N1	<DL	899.5	90	47180	0.066	1280	153.3	51.5
20	N3	<DL	597.5	23.5	63730	0.098	1157	229.2	58
21	N7	0.12	745.7	8.9	46850	0.05	736	153.4	16.4
22	Z1	<DL	852.7	10.4	47000	0.04	992	163.1	84.3
23	Z3	<DL	463.6	12.5	54640	0.04	1101	163.4	29.2
24	Z7	<DL	839.3	12.7	48430	0.03	1066	165.9	5.38
25	Ln	<DL	108	31.5	57390	0.035	926	144.8	66.6
26	Lm	<DL	53	15.2	25090	0.029	879	51	<DL
27	Dv	<DL	78.3	19.8	32170	0.025	640	70.1	20.6
28	Dm	<DL	171.6	26.9	57660	0.112	733	234.4	<DL
29	D	<DL	123.1	2.1	20890	0.02	570	62.7	29.6
30	O1	0.129	29.26	2.1	543	< D.L	406	4.5	5.5
31	O2	<DL	19	<DL	4450	< D.L	391	3.4	5
32	O3	<DL	39.66	1.7	<DL	< D.L	529	2.5	0.13
33	O4	0.066	52.03	17.9	63730	0.05	306	42	26.3
34	O5	<DL	66.87	7	449	0.013	335	3.9	70
35	L1	<DL	208.1	30.5	57650	0.03	1154	268	<DL
36	L2	<DL	181.5	25	62050	0.03	1234	31.3	3.8
37	L3	<DL	856.4	16.7	48170	0.01	940	225.4	25.7
38	J	<DL	88.59	10.3	18210	0.01	424	23.6	42
39	R	<DL	116.1	12.1	28190	0.01	521	34.2	69
40	H	0.029	786.8	12.5	44430	0.09	1020	193.4	82
41	S0	<DL	207.7	5.4	38430	0.023	115	143.5	38.1
B*		NR	90	45	47200	0.07+	850	68	20
MAC*		0.3	50	-	-	0.3	-	30	30
MAC**		-	150	120	-	-	-	-	-

B* - Metal background values (except Hg) from Turekian and Wedepohl (1961) for average shale
+ Hg values from Buccolieri et al. (2006)
MAC* = MAC-D.M. 56/09 Maximum allowable concentration (MAC) as reported in the Italian Environment Ministry Decree no. 56/2009 (Tables 2/A-3B) (Italian Gorernment 2009)
MAC** - MAC-D.L.GS. 152/06 Maximum allowable concentration of (MAC) as reported in the Italian Legislative Decree no. 152/2006 (Table 1, annexed 5, session IV) (Italian Government, 2006)
NR= Not reported

Table . Concentration of total heavy metals in sediments in stations of Vjosa River, autumn 2011

Concentration (mg/kg) of heavy metals, autumn 2011								
Station Delta of	Cd	Cr	Cu	Fe	Hg	Mn	Ni	Pb

Vjosa River								
L1	<D.L	208	30.5	57650	0.03	1154	268	<D.L
L2	<D.L	181	25	62050	0.03	1234	31	3.8
L3	<D.L	856	16.7	48170	0.01	940	225.4	25.7

Table Concentration of total heavy metals in stations of Narta Lagoon autumn 2011

Concentration (mg/kg) of heavy metals in Narta Lagoon autumn 2011							
Stations Narta Lagoon	Cd	Cr	Cu	Fe	Hg	Mn	Ni	Pb
Ln	<D.L	108	31.5	57390	0.035	926	144,8	66.6
Lm	<D.L	53	15.2	25090	0.029	879	51	<D.L
Dv	<D.L	78.3	19.8	32170	0.025	640	70,1	20.6
Dm	<D.L	171.6	26.9	57660	0.112	733	234	<D.L
D	<DL	123.1	2.1	20890	0.02	570	62.7	29.6

Table Concentration of total heavy metals in stations of Orikumi Lagoon

Concentration (mg/kg) of heavy metals in Orikumi Lagoon, autumn 2011								
Stat. orikumi Lagoon	Cd	Cr	Cu	Fe	Hg	Mn	Ni	Pb
O	<0.129	29.26	1.6	543	< D.L	406	4.5	5.5
O2	< D.L	19.	<D.L	4450	< D.L	391	3.4	5
O3	< D.L	39.66	1.7	<D.L	< D.L	529	2.5	0.13
O4	<0.066	52.03	17.9	17540	0.05	306	42	26.3
O5	< D.L	67.87	7	449	0.013	335	3.9	70

Table Concentration of total heavy metals in stations of J(Jonufra), R(Rradhima)

Concentration of total heavy metals in J(Jonufra), R(Rradhima), autumn 2011								
Stations	Cd	Cr	Cu	Fe	Hg	Mn	Ni	Pb
J	<D.L	88.59	10.3	18210	0.01	424	23.6	42
R	<D.L	116.1	12.1	28190	0.01	521	34.2	69

Table. Cd content determinate by GFAAS

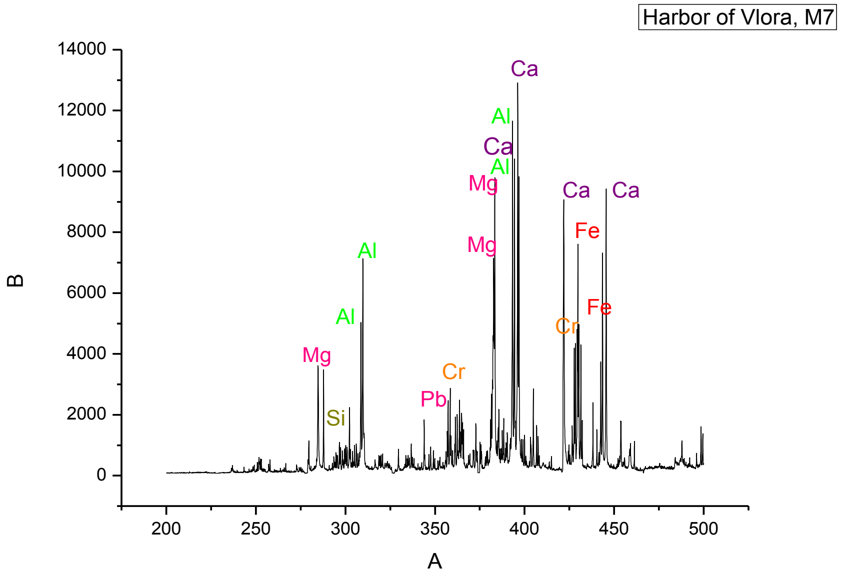
Concent of Cd determinate by atomic absorption spectrometer by furnace									
Sample	M1	M3	K1	K3	V1	V3	O1	O4	H

Vlora	0.085	0.043	0.084	0.045	0.028	0.025	0.129	0.066	0.029

Stations: M1, M2 (in front harbor of vlora), K1, K2 in front ex junior campus, old beach in Vlora, V1,V1, infront new beach in Vlora, O1, O4 (Orikumi Lagoon), H (near soda – pvc).determinatet by grafit furnace. In other stations values were <DL and determinate by FAAS Cd content determinated by flame Atomic Absorbtion Spectrometry by Flame: M7 (0,39mg/kg, T1 (1,2mg/kg), N7 (0,12mg/kg and the other values were under the detection limit.

3. LIBS RESULTS

Qualitative chemical analysis of marine sediments with LIBS were obtained by the identification of the stronger emission lines, persistent lines, provided by LIBS spectra, associated with heavy metals under the study, using the NIST Database of NIST. The results for some samples obtained during this qualitative analysis are reported in the graphs and tables below.



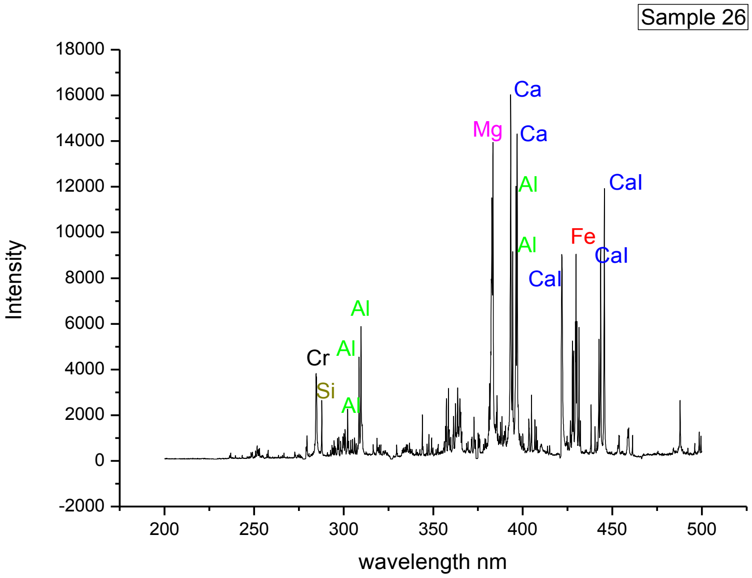
Sample number 30

Graph. LIBS specter of heavy metals in marine sediment , stations M7, Harbor of Vlora , sample number 30, autumn 2012

Element	Wavelength (persistent lines (nm), sample 30, 2012
Ca	393.4, 422.67, 421.7, 443.5, 445.4
Al	393.4, 396.1 308.21, 309.7
Cr	427.48, 357.8

Pb	357.5
Fe	428.2, 429.2
Mg	383.23, 383.82, 285.213

Sample number 26

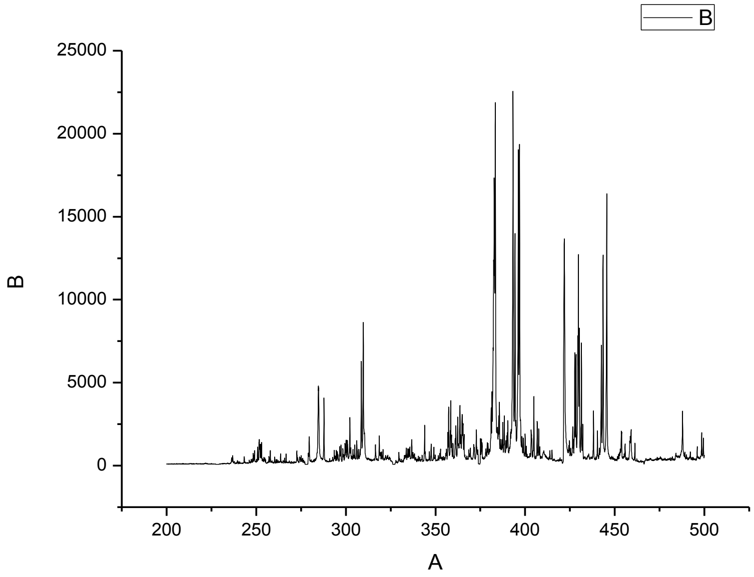


Graph. LIBS specter for the station New beach V1, sample number 26, autumn 2012

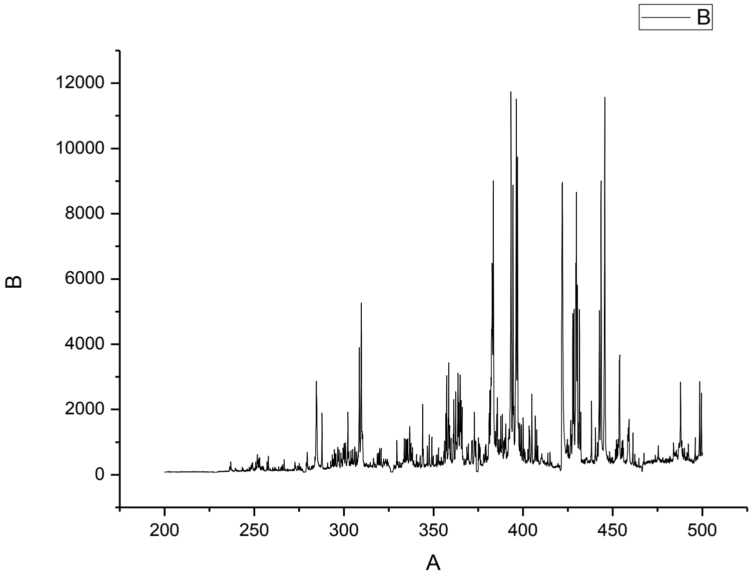
Table. Wavelengths (persistent lines) of elements detected in sample 26

Element sample26	Wavelength (persistent lines) nm , sample 26, 2012
Ca	393.36, 396.8
Ca II	284.3, 284.9
Al	393.43, 396.1
Cr II	284.3, 284.9
Si	288
Fe	428.2, 429.2
Mg	383.23, 383.82
?	487.5

Sample 1



Sample 2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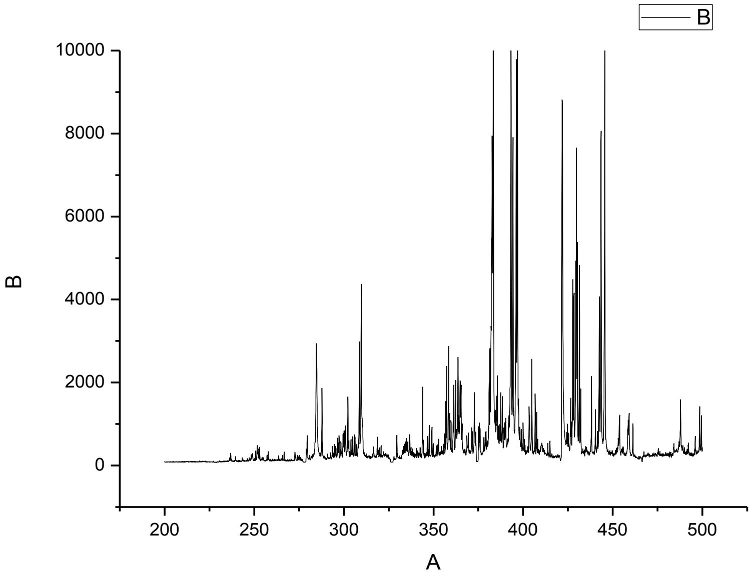
300
350
400
450
500
A

Sample 8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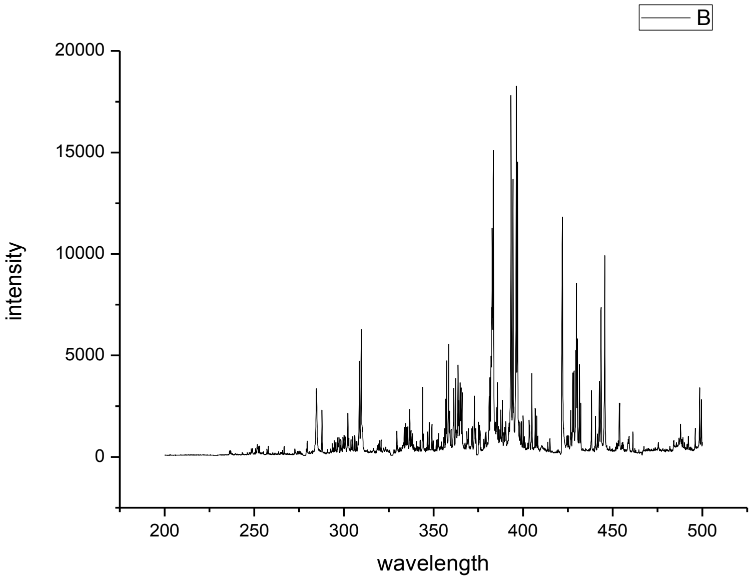
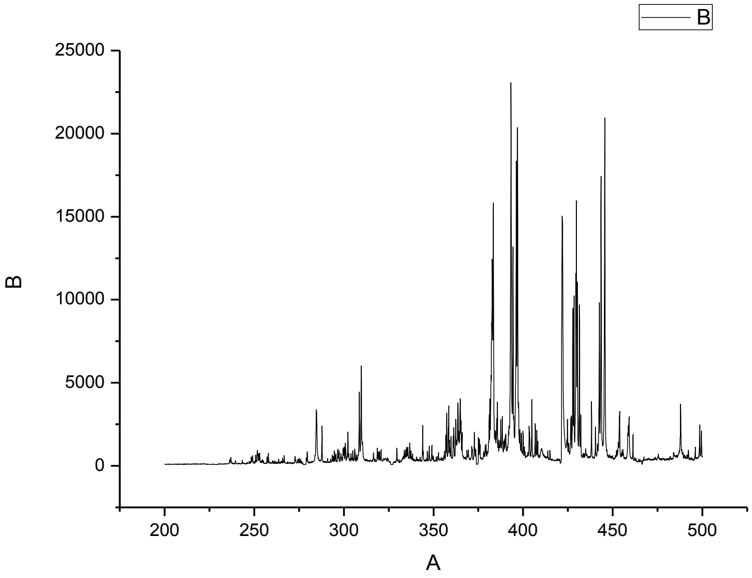
400
450
500
A

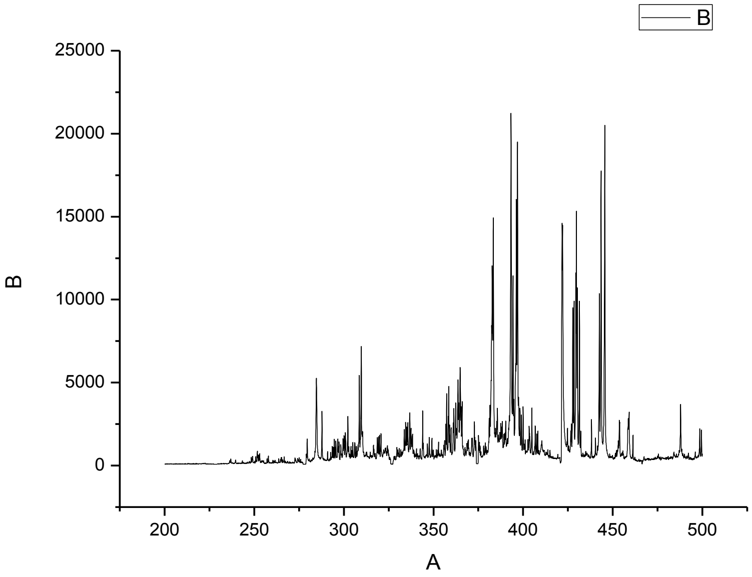
Sample 11



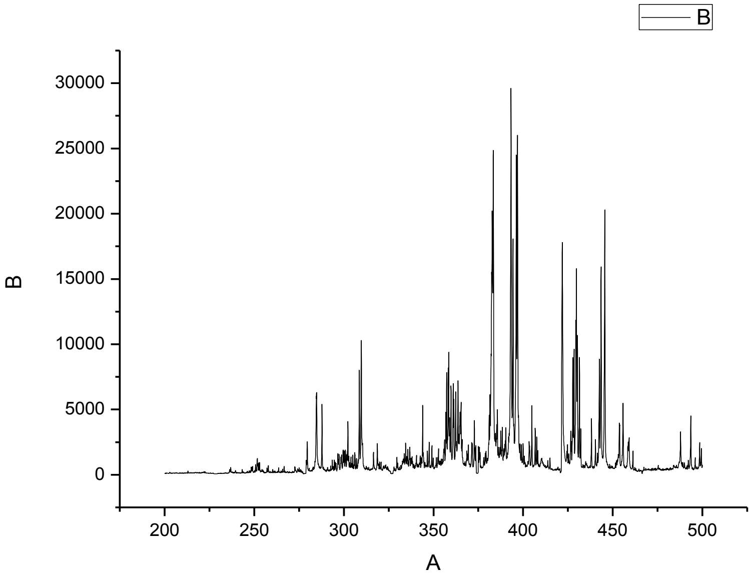
Sample 12



Sample 13



Sample 18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B
200
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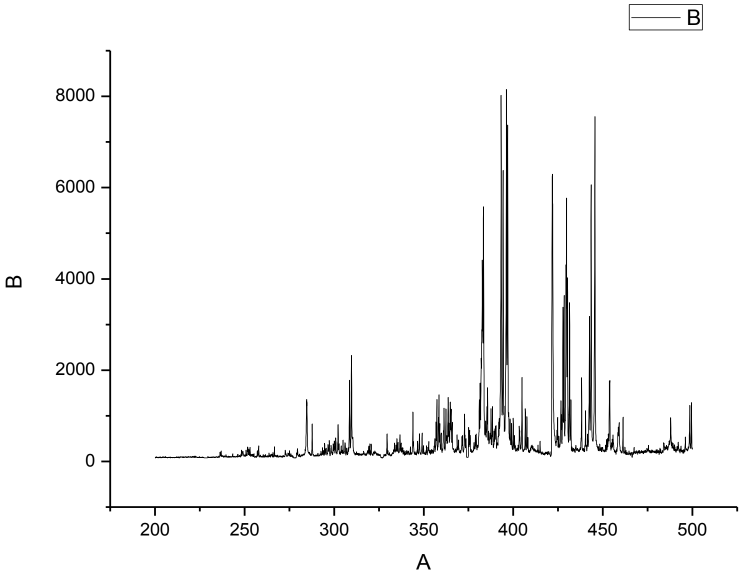
300
350
400
450
500
A

Sample 25


B
8000
6000
4000
2000
0
B
200
250
300
350
400
450
500
A

Chapter 6 Sea water & suspended material samples

Sampling
Filtration and preservation
Sample preparation procedure for sample analysis using two analytical method:
1 X Ray Fluorescence Spectrometry (miltielemental analysis) Determination of Trace transition and heavy metal ions by precipitation with APDC combined with XRF
2 Atomic Absorbtion Spectrometry AAS (Coold Vapor Atomic Absorbtion Spectrometry) (elemental analysis) Determination of mercury, Hg, in seawater by Cold Vapor Atomic Absorbtion Spectrometry (CV-AAS)

Introduction

Natural waters are dynamic systems containing living as well as nonliving, organic together with inorganic, and dissolved as well as insoluble substances. Events can occur during or after sampling that may change the sample composition drastically from its original form.

Natural waters vary greately in matrix constituents. A single analytical method for a metal will not necessarily be applicable to such a wide range of composition.. Table lists the concentrations of some selected trace elements in normal seawater.

Table Concentration of selected trace elements in Seawater [2]

Element	Chemical form	Conc. (µg/L)
Al		0.01
As	AsO_4H^{2-}	0.003
Cd	Cd^{2+}	0.00011
Cr		0.00005
Cu	Cu2+	0.003
Fe	Fe(OH)3	0.01
Hg	$HgCl_4^{2-}$	0.00003
Mn	Mn^{2+}	0.002
Ni	Ni^{2+}	0.0054
Zn	Zn2+	0.01

Sampling

Filtration and preservation
Sample preparation procedure for sample analysis using two analytical method:
1 X Ray Fluorescence Spectrometry (miltielemental analysis) Determination of Trace transition and heavy metal ions by precipitation with APDC combined with XRF
2 Atomic Absorbtion Spectrometry AAS (Coold Vapor Atomic Absorbtion Spectrometry) (elemental analysis) Determination of mercury, Hg, in seawater by Cold Vapor Atomic Absorbtion Spectrometry (CV-AAS)

Sampling

Sampling of seawater was carried out at 16 covering the Bay of Vlora with the aim to analyse heavy metals in sea water and in particular matter. In total were collected and analysed 34 samples in autumn and at the end of tourist summer season 2013.

The selection of the area under investigation, the stations were choosen in base of relative knowledge in according to some results obtained by precedent monitor programs, to individuate areas under study.

The samples represent surface and sub surface coastal water collected in cleaned plastic and glass bottles, from 50-300 m from dhe coast. Sea water samples were collected at the same profile as the marine sediments under the study and 15-50 cm above the marine sediment.
The sampling sea water stations (a samples are surface samples, b & c samples are above the sediment samples.

1 Qendra e gjirit te Vlores
2 Raguza 2
3 Pasha Liman, near Orikumi Lagoon, 100 from the shore, O1
4 Pasha Liman, near Orikumi Lagoon, 300 from the shore, O2
5 Orikum, near Izvori river, 100 m from the shore, O3
6 Orikum, near Izvori river, 300 m from the shore, O4
7 Radhima, 100 m from the shore, Ra1
8 Radhima, 300 m from the shore, Ra 3
9 Uji iftohte, Tuneli-Belvedere100 m from the shore, R1
10 Uji I ftohte Tuneli-Belvedere 300 from the shore, R3
11 Marina 100 m from the shore, A1
12 Marina 300 m from the shore, A3
13 Moli 100 m from the shore,M1
14 Moli, 300 m from the shore,M3
15 Soda, 100 m from the shore, S1
16 Petrolifera, 400 m from the shore, P3

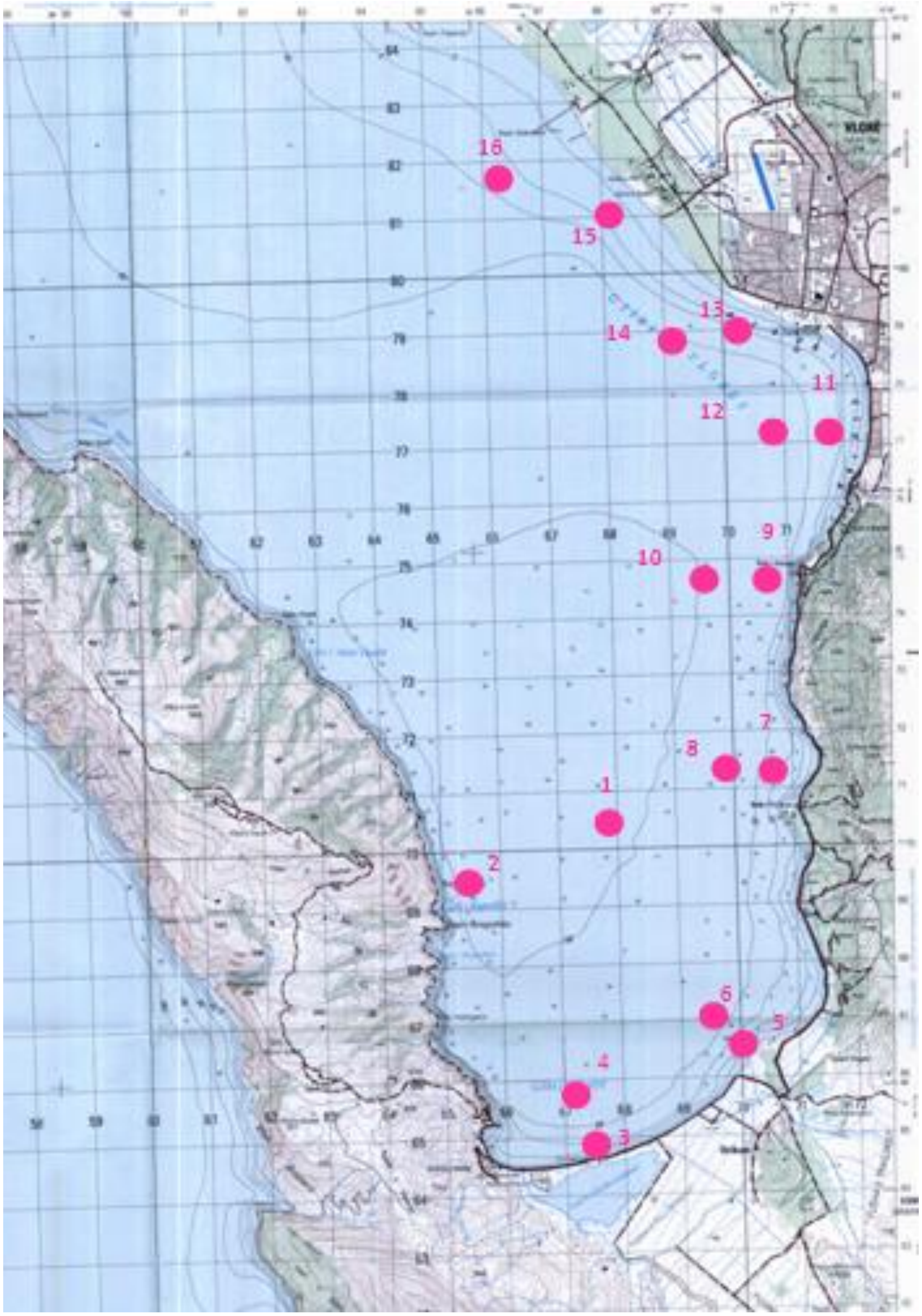


Fig. Map of sea water sampling in Vlora Bay and Orikumi Lagoon

Legend:

1 the center of bay of Vlora , (1/a, 50 cm under the surfacec1/b and 1/b’ sample 50 cm from the bottom of the sea, above the marine sediment,

2 Raguza 2, near Fish Farm, 2/a
3 Pasha Liman, Discharge of Orikumi Lagoon on the sea, (3/a, 3/c)
4. 4/c
5 Discharge of the Izvori river on the sea (5/a)
6. (6/c)
4 Radhima (7/a, 8/c)
5 Uji I Ftohte (Cold Water) (9/a, 9/c, 10/a, 10/c)
6 Marina (11/a, 12/a, 12/b)
7 Moli –Kampi (13/a, 14/a, 14/c)
9 Soda 15/a
10 Triport (16/a, 16/c)
The samples: 1/a, 1/b, 1/b', 2/a,3/a, 3/c, 4/c, 5/a, 6/c, 7/a, 8/c, 9/a, 9/c, 10/a, 10/c, 11/a, 12/a, 12/b, 13/a, 14/a, 14/c, 15/a, 16/a, 16/c.

Nr//samp.	Station	Samples	Distance from coast (m)	Depth (m)	pH	Water temp (T^oC)	Air temp (T^oC)
1	1	1/a	CBV	Surf	8.04	23	30
2	1	1/b	CBV	20			30
3	1	1/b'	CBV	depth			30
4	2	2/a	100	surface			30
5	3	3/a	100	surface	8.07	24.5	30
6	3	3/c	100	8			30
7	4	4/c	300	8			30
8	5	5/a	100	suface	8.01	23	30
9	6	6/c	300	12.5			30
10	7	7/a	100	surface			30
11	8	8/c	300	8.5	8.07	22.5	30
12	9	9/a	100	surface	8.11	24	30
13	9	9/c	100	6			30
14	10	10/a	300	surface			30
15	10	10/c	300	13.5			30
16	11	11/a	100	surface	7.86	24	31
17	12	12/a	300	Surface			31
18	12	12/b	300	5.5			31
19	13	13/a	100	surface	8.14	24	31
20	14	14/a	300	Surface			31
21	14	14/c	300	5.5			31
22	15	15/a	100	surface	8.05	24.5	29
23	16	16/a	400	surface	8.04		29
24	16	16/c	400	5.5			29

CVB – Center of the Bay of Vlora

Per each station were collected 2-3 samples in surface or at a specific depth. Emmersing the sampler to the required depth. The water samples collected has had suspended material. The samples was filtered and were taken the suspendetd particulate matter and before the preservatives are added.   By the general definition the soluble portion of a water sample is that which passes through a 0.45 µm membrane filter. There is no universal preservative available, the most common technique that is effective for many system being to bring the sample to a pH below 2, and to refrigerate the sample at 4°C. The low pH stops much of the biological action and retards the adsorption of many cations on the container wall. Some parameters require a special preservative system.[56] For example: for Mercury HNO_3 and $K_2Cr_2O_7$ was added.

Sea water sampling stations are presented in the map of Vlora, below.

Each location was be sampled in duplicate. Seawater samples are taken according to some international

standards **ISO 5667/1-80** [37, 54, 55], The subsurface sampler (Ruttner standard water sampler collector, HYDRO-BIOS,Germany is shown in foto. The sampler is an open cylinder with valves at each end and produce less disturbance to the sea on sampling. The sampler is sealed by using a weight dropped down the attachment line to activate the valve mechanism.[37, 48 & 52]

Photo. Sampling with Ruttner standard water sampler collector

In the table are represented some physical characteristics of the samples collected at the mos important points

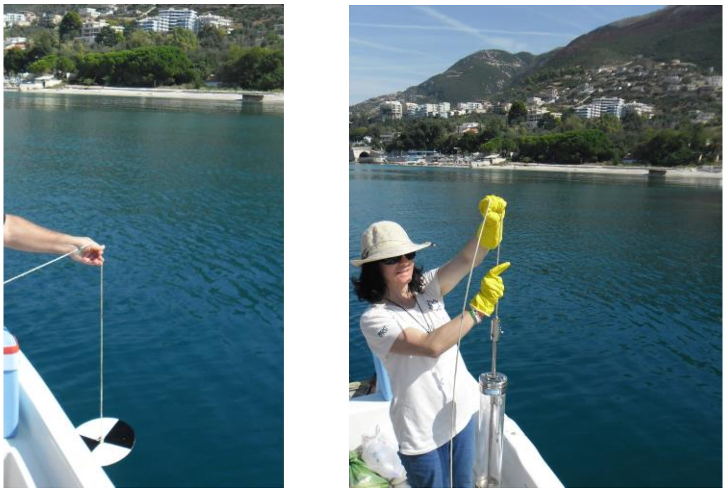


Photo. Sea water sampling in Vlora, near Uji I Ftohte

Preservation of water samples

Particulate matter

Filtration

The first step in this procedure consisted in separation of the suspended material by filtration under vacuum through 0.45 µm millipore membrane filter filtration unit. The filtration apparatus consists of a Plexiglas vacuum chamber. The chamber was connected by a silicone tube directly to the sampling bottle, through the filtration cartridge containing the PC filter. The volume of the filtered water, varied from 1.5 to 2L.The loaded filters after filtration, until analysis was placed in special Teflon supports and after being dried at room temperature, were weighed and presented to the X-ray system for the determination of trace metals by Energy Dispersive X-Ray Fluorescence.

Water samples

The sea water samples after the filtration were immediately acidified with concentrated HNO_3 to pH <2. Per 1L sample about 2ml concentrated nitric acid, analytical reagent, to bring the sample to a pH 1-2.

Preservation procedure for mercury for atomic absorption spectrometry analysis, AAS : per 100 ml sample, 1ml of a 5% solution $K_2Cr_2O_7$ are added and about 2ml nitric acid concentrated to bring the sample to pH 1-2.[22]

X Ray Fluorescence Spectrometry (multielemental analysis) - Determination of Trace transition and heavy metal ions by precipitation with APDC combined with XRF

Some transition and heavy metal ions, are treated as contaminants and from environmental pollution point of view their analysis is of great interest. The concentration of these elements are so low that multielemental analyticaltechniques usually require a prior concentration step which ideally nrighes the transition and heavy metal ion exclusively and efficiently, while leaving the abundant alkali and alkaline earth ions in solution.[39]. It represents interes the procedure for multielement preconcentration[47] of trace elements prior to X-ray fluorescence analysis of water.

Sea water sample preparation

Preconcentration

Preconcentration is a rapid method for determination of trace amount. It bring the element of interest, (heavy metals) into the working range of the instrument, and it will be necessary to concentrate the sample. Consisted in 2 steps: in separation of suspended material by filtration as described above and precipitation of dissolved trace metal ions with APDC (Ammonium-pyrrolidin-dithiocarbomat, für laborator only) [39,47,64,65] with optimal conditions for this procedure. The formation of a rather coarse precipitate aids in the filtration step, by reducing the filtration time from hours to minutes without any loss of analyte. The control of pH is crucial to the successful use of this method [63]. The procedure has been realizet in optmal condition as follows:

To a 250-500 ml water sample 500 µl of Mo ion, molybden standard solution (Molybdän standardlösung, gebrauchsfertig), was added for coprecipitation. The pH was adjusted to 4 adding Ammonia solution obtained 25% NH_3 (Ammoniakalösung etwa 25% NH_3) and 5-10 ml of freshly prepared 1% water solution of APDC was added. After mixing for 15-20 min the solution was filtered using Millipore polycarbonate membrane filters. 0.45µm. Filters with the precipitate were placed in the Teflon supports and dried at room temperature before analysis.

Photo. Preconcentration procedure
a) Millipore polycarbonate membrane filters with the precipitate obtained by the preconcentration procedure, b) Precipitate preparation

Instrumentation and calibration.

The X-ray fluorescence system consisted of a Philips PW 1729 high voltage generator and a tungsten anode X- ray tube. The excitation of the samples was done with a secondary target excitation system (90° geometry) using the fluorescent K radiation from silver Ag, secondary target. The measuring system consisted of a Si (Li) detector, having a resolution of 180 eV at 5.895 keV (Mn Kα), and Canberra Series 80 multichannel analyzer. The samples were measured for 5000 sec and the intensities of the analytical lines were calculated by fitting the spectra with a Fortran program, AXIL. [20(2012)] on a Digital PC-350 computer.

Thin Mylar foils covered with known deposits of elements and compound were used for calibrating the system.

Millipore polycarbonate membrane filters with the precipitate, analyzing

Fig. Analysing trace heavy metals ion in EDXRF system, XRF laboratory, Institute of Applied Physics, Tirana 2013

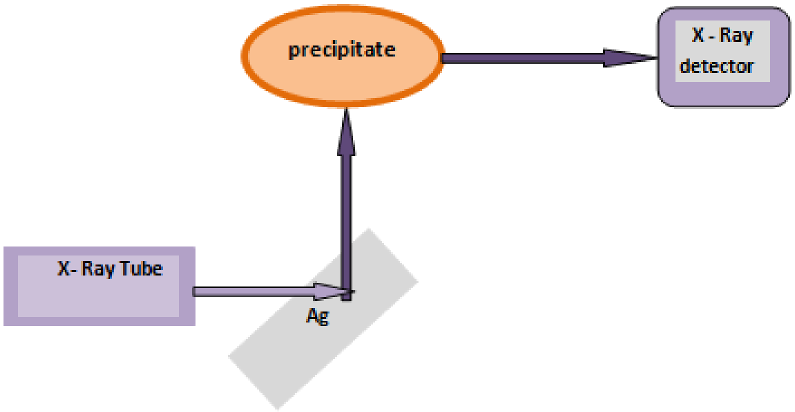


Fig. Secondary source (Ag secondary target) for XRF instrument

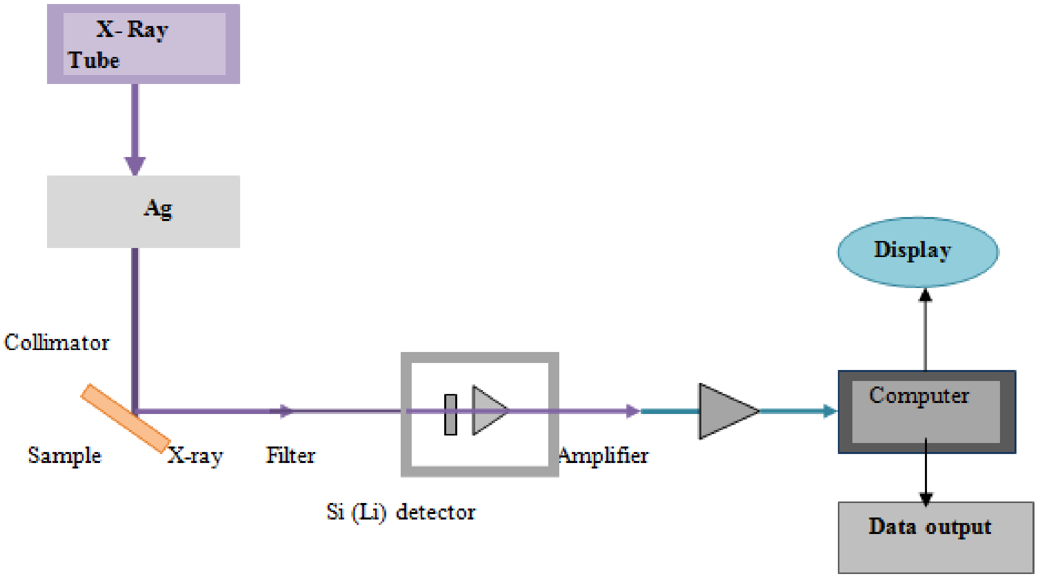
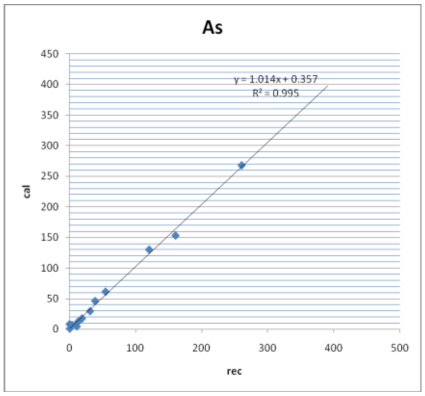
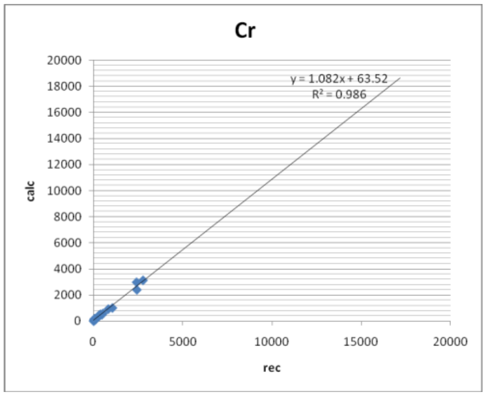


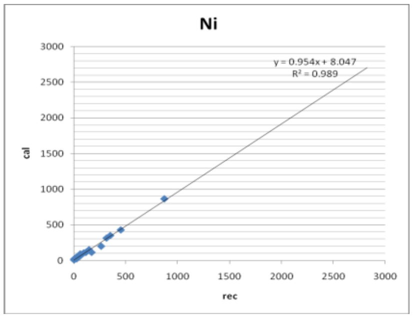
Fig. Schematic view of a Si EDXRF spectrometer

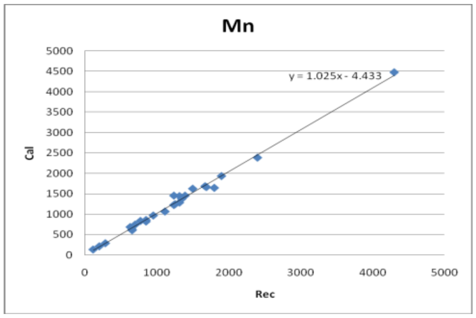
This trace analysis procedure has suitable detection limits, is relatively fast, is relatively low in cost, is applicable to a wide range of samples, is relatively specific.

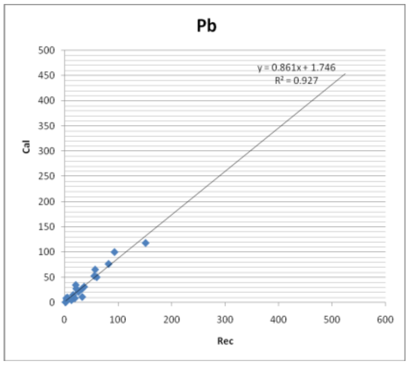
Calibration
Some calibration curves using Ag secondary target, below.

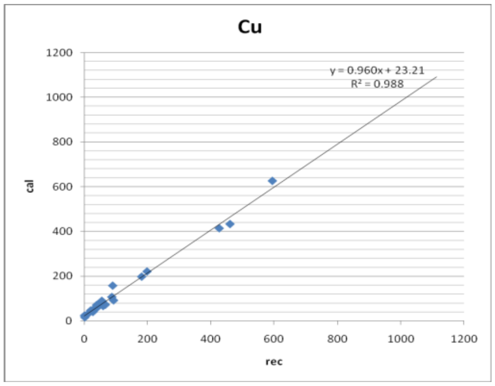

As
y = 1.014x + 0.357
R² = 0.995
cal
rec
0
50
100
150
200
250
300
350
400
450
0
100
200
300
400
500

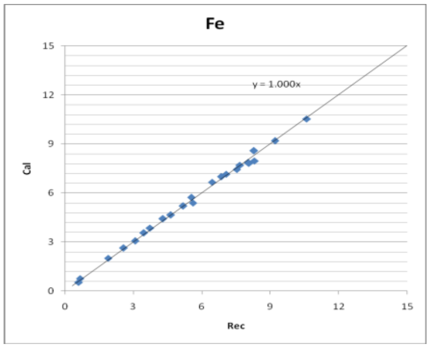

Cr
y = 1.082x + 63.52
R² = 0.986
calc
rec
0
2000
4000
6000
8000
10000
12000
14000
16000
18000
20000
0
5000
10000
15000
20000

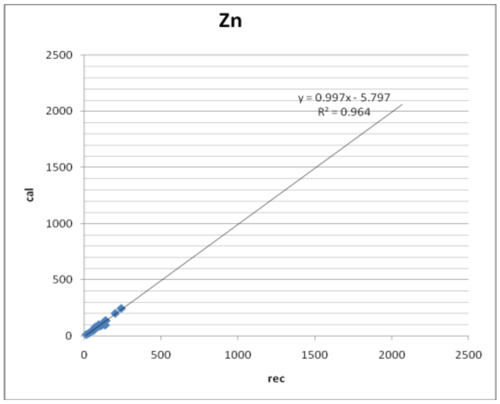

Ni
y = 0.954x + 8.047
R² = 0.989
cal
rec
0
500
1000
1500
2000
2500
3000
0
500
1000
1500
2000
2500
3000


Mn
y = 1.025x - 4.433
Cal
Rec
0
500
1000
1500
2000
2500
3000
3500
4000
4500
5000
0
1000
2000
3000
4000
5000


Pb
y = 0.861x + 1.746
R² = 0.927
Cal
Rec
0
50
100
150
200
250
300
350
400
450
500
0
100
200
300
400
500
600


Cu
y = 0.960x + 23.21
R² = 0.988
cal
rec
0
200
400
600
800
1000
1200
0
200
400
600
800
1000
1200


Fe
y = 1.000x
Cal
Rec
0
3
6
9
12
15
0
3
6
9
12
15


Zn
y = 0.997x - 5.797
R² = 0.964
cal
rec
0
500
1000
1500
2000
2500
0
500
1000
1500
2000
2500

For the calibration of the system were used Mylar foils covered with known elements. For all heavy metals analyzed by their Kα lines, the sensitivities were calculated by the repetition of measurements of the same standards

Until the analysis prove 1 and prove 2 were performed to test the instrumentation. To a 500 ml and 250 ml water sample from the center of bay of Vlora (20 m in depth, h_{max}= 40 m) was added 500 µl to prove 1 and 250µl to prove 2, of Pb, Zn and Mn standard and treated in the same way as well as the samples. The filters of prove 1 and 2 were measured until analysis of the samples.

1 XRF SEA WATER RESULTS

Results and discussions

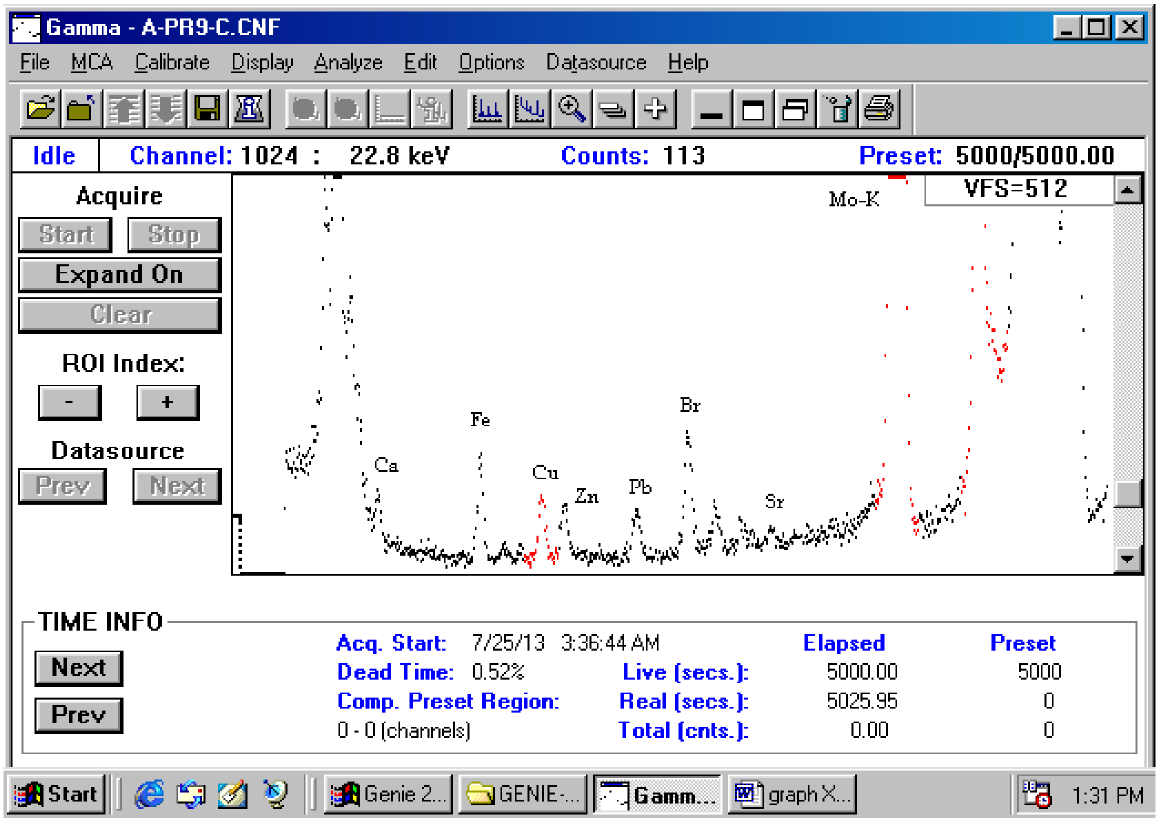
Water samples

Table. Trace heavy metal ion concentration in sea water samples collected in Vlora Bay, determined by EDXRF, 2013 The results in the table above are calculated taking under consideration the standard deviation.

Trace heavy metal ion concentration in sea water samples (µg/l), Vlora Bay, 2013					
Sample	Fe	Ni	Cu	Zn	Pb
1-a	2.7	5.2	10.0	21.6	4.0
1-b	4.4	14.2	8.9	23.6	6.2
2-a	3.2	1.5	9.3	10.9	2.2
1-b’	1.7	14.2	11.0	40.0	5.8
13-a	16.4	2.7	10.3	18.0	1.7
6-c	77.6	3.3	11.7	19.2	1.5
16-a		13.1	18.4	8.1	
15-a	5.7	5.3	9.0	34.3	1.4
14-a	1.2	1.6	7.4	17.1	
12-b	16.5		2.8	16.5	
12-a	2.5	3.8	6.8	4.5	
11-a			4.5	4.5	
10-c	50.6	4.5	9.9	9.7	14.0
10-a	3.8	3.6	6.7	14.2	
16-c	61.3		6.1	17.0	
9-c	28.2	1.9	11.4	8.1	11.0
9-a	6.5	2.3	5.4	6.1	

8-c	51.6	3.5	7.4	16.8	4.5
7-a	6.2	3.1	7.7	35.4	
5-a	15.5	3.0	7.0	10.3	
4-c	29.1	5.5	4.6	22.2	
3-c	21.0	3.7	6.4	18.5	2.4
3-a	7.7	2.8	10.4	19.3	3.3
14-c	54.8	1.7	2.8	12.5	
min	1.2	1.5	2.8	4.5	1.4
max	77.6	14.2	18.4	40	14
mean	21.3	4.8	8.2	17	4.8

Table. Trace heavy metal ion concentration in sea water samples collected in Vlora Bay, determined by EDXRF, 2013 The results in the table above are calculated taking under consideration the standard deviation.



Idle Channel: 1024 : 22.8 keV Counts: 113 Preset: 5000/5000.00

Acq. Start: 7/25/13 3:36:44 AM

Dead Time: 0.52%

Comp. Preset Region: 0 - 0 (channels)

	Elapsed	Preset
Live (secs.):	5000.00	5000
Real (secs.):	5025.95	0
Total (cnts.):	0.00	0

Fig. EDXRF specterum (Kα lines) of trace heavy metal ion in sea water measured for 5000 s with a Ag secondary target. sample 9/c, station 9, collected in Cold water (Uji I ftohte)

The analysis of the samples has been done in two steps[66] in the same way as well as the sediment analysis: Qualitative analysis and Quantitative analysis. The first determine which element are present and the net intensities for each element from the measured spectra. The net intensities are used in the quantitative analysis to calculate the concentration of each element present. The surface under the peak gives the intensity. The detector used, has measured the different energies of the characteristic radiation coming directly from the sample and separate the radiation from the sample into the radiation from each element present, (the dispersion).

2. RESULTS (SUSPENDED MATERIAL)

RESULTS by EDXRF analysis for the suspended material collected

On the table below are reported the concentrations of heavy metals resulted by analysis in suspended material collected from Vlora Bay.

Table. Concentration (µg/L) of heavy metals in suspended materials in sea water collected in Bay of Vlora

Concentration of heavy metals in suspended material (µg/l), Vlora bay, 2013								
sample	Fe	Cu	Zn	Sr	Ti	Mn	Ni	Pb
1-a	2.8	1.0	2.6	3.0				
1-b	15.3	0.3	0.7	0.6			0.3	
2-a	35.4	0.4	1.1	2.0				
3-a	2.6	0.5	0.8	1.1				
3-c	123.5	0.7	4.6	3.0				
4-c	41.7	1.9	2.9	2.8			0.2	1.0
4-d	119.9		1.7	2.6				
5-a	11.5							
6-c	96.7	0.1		1.5	14.2			
7-a	3.5		0.5	1.2				
8-c	2.7		0.8	0.6				
9-a	5.1	0.3	0.5	1.1				
9-c	8.1		0.7	1.0				
10-a	11.4	0.6	1.5	1.1				
10-c	14.2	0.4		1.1				
12-b	7.0		1.1	1.6				
13-a	8.4	0.1	0.8	1.5				
14-a	3.6		0.4	1.2				
14-c	5.3			0.7				
15-a	28.9	0.8	0.9	1.2		1.5	0.8	
16-a	34.1	1.3	0.8	1.4			1.7	

Sp-16c	18.7		0.5	1.1				
min	2.6	0.1	0.4	0.6				
max	123.5	1.9	4.6	3				
mean		0.7	1.3	1.5				

For the determination of heavy metals in suspended material, were analyzed the Millipore filters obtained from the procedure of sea water filtration. The analysis were performed using the same calibration, no matrix correction was used and taking blank values in account for Millipore filter.

Determination of Hg in sea water samples applying AAS/CV

Instrument type: Varian Atomic Absorption Spectrometer AA200 / VGA 77 vapor Generation Accessory

Atomic Absorbtion Spectrometry AAS, sea water (Hg) analysis

Determination of Mercury concentration for the sea water samples was performed using Atomic Absorption Spectrometer VarianAA200, equipped with Cold Vapor/AAS technique (VGA 77). The calibration and quantification was carried out by working out standard solutions 1ppb, 2ppb, 5ppb, prepared by proper dilution of Hg standard solution for AAS (1000mg/L, purchased from Meck, Germany). In this study was analysed the content of Hg in sea water, collected in Bay of Vlora and near Karaburini Penisula, Pasha Liman near Orikumi Lagoon, collected during the year, in autumn and in the end of the touristic summer session. The method used for analyzing Hg in water samples, was in according to AOAS (Official method of analysis), some modifications were applied according the laboratory conditions, adapted in ISUV, (Toxicology & Quality department, Food Safety & Veterinary Institut, Tirana, Albania).

Blank analysis was performed on deionised water following the same procedure of the samples and showed no contamination being in the same order of magnitude as the detection limits.

Sample preparation procedure

Sea water samples was filtered and stored before AAS analysis according to the analytical procedure below:

Analysis was performed on 100 mL seawater samples. The samples were transferred to a 250 mL separative flask, adding analytical reagents of analytical grade per each sample:

5ml H_2SO_4cc, 2,5mL $HNO3_{cc}$, 25 mL $KMNO_4$ 5% were added in 100 ml sea water sample. The blank was treated in the same way, using the same reagents as well as the samples.

(HNO_3 is one of the most useful acids for digestion. The nitrate ions produced in solution are an acceptable matrix for both AAS & ETA, Electro Thermal Atomization. HNO_3 is sufficient to oxidize easely oxidized samples. Combination of HNO_3/H_2SO_4, HNO_3/HCl, are suitable for easily oxidized organic matter[57].)

Digestion procedure

15 minutes after this analytical procedure per each sample was added 8 ml $K_2S_2O_8$, 5% and putting them in the digestion strumentation“Bagnomari”, at 95°C for 2 hours. After cooling, per each sample was added, 25 ml of 5% solution hydroxilamine for reducing $KMnO_4$ (to the standard and the banks was added 15 ml of 10% solution hidroxilamine), and 5 ml of 25% solution $SnCl_2$ and was immediately analyzed.
(Sea water is a high salt solution and require as much as 25 m of 4% m/V KMNO4 to break up organo-mercury compound. The chlorides are converted to free chlorine gas during the oxidation step. The free chlorine can be removed by adding excel hydroxylamine sulphate and passing clean nitrogen through the sample, before the Hg is reduced.[57])

Sea water sample preparation for digestion procedure

a) b)

Fig. Sea water Sample preparation a) until digestion b) after digestion in “bagnomari”

a) b)

Fig. a)Sea water samples after digestion until analysis. b)Analysing Hg in sea water in AAS/CV system VGA-77

Varian Atomic Absorption Spectrometer AA200 / VGA 77 vapor Generation Accessory
Determination of Hg concentration in Sea water . Mercury cold vapor technique. Analysing Hg in sea water in AAS/Cold vapor system (VGA-77)

The determination of Hg concentration was performed by using AAS/CV system. Hg is the only element with appreciable vapour pressure at room temperature. Hg can be reduced according to the following reaction

$Hg^{2+} + Sn^{2+} \leftrightarrow Hg + Sn^{4+}$

The Hg vapour is flushed out of the system into the T piece and measured. The longer residence time in the tube also increases the sensitivity 100 times compared with flames AAS. Background conection is not normally required. Detection limits of < 1 ng/ml are obtained by this technique.

3. AAS RESULTS

For Hg determination were analysed 20 samples most of them collected to15-50 cm above the marine sediment. Sea water samples collected in autumn 2012: Orikumi (O) Lagoon, Marina (B), Rrapi, Uji I ftohte, Aulona, Moli, Hidrovori, and the samples coallected in the end of summer season 2013: 1/b, 8/c, 9/a, 9/c, 10/a, 10/c, 11/a, 12/a, 13/a, 14/a, 14/c, 15/a,16/c.

Hg concentration in sea water samples, collected during years 2011 and 2012 years resulted to be under the detecton limit. The absence of the detectable levels of heavy metals Pb & Hg in samples from Vlora bay might suggest a low level of contamination in marine coastal waters. Values detected of heavy metals are similar to those reported for low impact sites in an previous study.

Chapter 7 Mediterranean mussels samples

MATERIAL & METHODS

Study area and sampling, criteria for the selection of sampling area

Mediterranean mussel were investigated in Seven sampling sites along Vlora Bay cost, identified by using precedent studies effectuated in this area, characterizing by different anthropogenic impacts. Within each area of investigation was carried out sampling along the coastline in sites in which are present mytilus galloprivincialis (mussels) in their natural beds. Mussel samples between 3-5 cm in length were collected using a small bout from the shore line to the seven stations. Three replicate per station in various distance from each other were collected and performed for determinate Hg and Pb concentration.

Fig. Map of Mytilus galloprovincialis (mussels) samapling, in Vlora Bay

Mytilus galloprovincialis, (mussels) sampling Stations

1. U, Uji I Ftohte (Cold water)
2 . R, Rrapi
3. V, Vefa
4. B, Marina (New Beach)
5. A, Aulona
6. M, Moli (Harbor of Vlora)
7. T, Triport (Port of Zverneci)

Analytical Protocol

Sample preparation

The samples was prepared 100 mussels per stations (between 2- 5 cm in length), about 100 (three replicate) for each station. The mussels samples were washed e rinsed in deionizate water and were removed the soft tissues with a scalpel. the samples were prepared for analyzing within 24 hours, homogenized, weighted in vessels and degested in microwave digestion system.

***Digestion*.** The digestion procedure was performed in Microwave digestion system, BERGHOF. The samples were weighed into Teflon digestion vessels and 2.0 ml HNO_3 (65%) and 0.5 ml H_2O_2,hydrogen peroxide (30% m/v) were subsequently added. The sealed Teflon vessels were placed in Microwave Digestion BERGHOF and the sample were hated according to the program in 5 steps.

Digestion program	Step 1	Step 2	Step 3	Step 4	Step 5
Temp (^oC)	145	175	175	100	100
Pressure (bar)	40	30	30	1	1
Time (min)	25	20	1	1	1
Slope (min)	1	2	2	1	1
Power (%) of infrared radiation	80	80	80	10	10

Table. Digestion program for determination of heavy metals Pb & Hg in mussels

After the digestion the vessels were cooled for 20 minuts at the room temperature and were diluted with deionized water to the total volume 50 mL until analyses. The trace of heavy metal determination was carried out following standardized methods for the analysis of Hg& Pb such as SSHEN 14 084: 2003, CR 1881/2006

Photo. Mussel samples in Teflon digestion vessels

Determination of heavy metals Hg & Pb concentration in mussels samples in Atomic Absorption Spectrometer.

- AAS equipped with graphite furnace system, THERMO SOLAR Graphite Furnace GF 95, Autosampler, was used to determine the Pb concentration

- AAS/cold vapour AA system (VGA-77) Generation accesory was used to determine Hg concentration.

THERMO SOLAR GF 95, Pb analysis in Mediterranean Mussels

High sensitivity in solar graphite furnace system analyzing Pb in mussels, was achived using the autosampler or microprocessor controlled furnace autosampler which use a precision syringe, with sophisticated wash routine, leaving the furnace running unattended for prolonged period. The furnace autosampler has the following features: a carousel layout for wash, matrix modifier, master solution and position for up to 50 samples, reprogrammable calibration for each elemental analysis, reprogrammable injection volumes from 1µ to 70 µ, automatic ecc. THERMO SOLAR Graphite Furnace GF 95, Autosampler system prepared standards from a master solution (CRM, Pb standard for AAS, 1000mg/L, by Fluka, Switzerland)which are diluted with a blank-diluent (dilution of 10 ppb solution was prepared from 1000mg/L. The work standards 2.5, 5, 7.5, 10 ppb., were prepared by Solar system) . The matrix modifier used for Pb analysis: Mg(NO3)2 for graphite furnace AAS by Fluka,Switzerland. The advantage of the autosampler, is the reproducible injection of the sample once the correct position of the pipette tip has been determined. This is very important to achieve precision.

Photo THERMO SOLAR Graphite Furnace GF 95, Autosampler, AAS used Pb determination

Nr replicate 3/sample
Wavelength – 217 nm
Bandpass – 0.5 nm
Background correction – D2 Quadline
Signal – transient high
Technique - furnace

Determination of Hg concentration in mussels samples in Atomic Absorption Spectrometer

Instrument type: Varian Atomic Absorption Spectrometer AA200 / VGA 77 vapor Generation Accessory
Mussel Sub samples for determination of Hg concentration were treated in microwave (BERGHOF and were analyses in AAS/CV system.

Preleminary procedures for calibration of the device for the determination of Hg concentration is the same as the other matrixes analysed in AAS/CV during this study , marine sediment and sea water samples.

(CRM, Hg standard solution for AAS, 1000mg/L,was used to prepare the work standards 1, 2, and 5 ppb. Wavelength 253,7 nm, Nr replicate3/sample, replicate standard 3, slit width 0,5nm, lamp current 4 mA, background correction:BC off.. LOD of instrument 0,2 ppb (μg/L).

Results and discussions

The levels of heavy metals Pb and Hg and the mean values in soft tissues of mussels are reportet in the table below. Mussels collected in station B, Marina and Triport showed higher levels than those of the from the other stations

Table. Concentration of Hg & Pb in Mytilus galloprovincialis (Mussels) along the coastal line of Vlora city determined by AAS Thermos Solar GF 95

Stations	Concentration of Hg, mg/kg wet weight	Concentration of Pb, mg/kg wet weight.
U, Uji I ftohte	0.04	0.41
R, Rrapi	0.03	0.27
B, Marina	0.20	0.17
V,Vefa	0.05	0.19
M,Moli	0.07	0.16
Aulona	0.05	0.14
Triport	0.10	0.24
Mean	0.1	0.23
min	0.03	0.14
max	0.2	0.41

Hg concentration reported in soft tissues of Mytilus galloprivincialis, mussels, ranged from 0.03 to 0.2 mg/kg wet weight. This concentration were lower than upper limit (0.5mg/kg wet weight), within the normal range for human consumption set by CE 1881/2006. The level of Hg and Pb reported in table, various between stations investigated. Hg content observed is higher in samples collected in Marina station (0.2 mg/kg) near Vlora city and in Triport station near ex-PVC-Soda plant.

This significant contamination of Hg in Vlora Bay has been alredy known is due to the presende of Soda production industry, from 1978-1992. Due to the electrolytic method based on Hg, a huge amount of Hg was discharged in the sea, which is reflected by the high levels detected in marine sediments[25],Celo et al., 1999; MWH Consulting and in according to the Ecotoxicological assessement of Vlora Bay, Albania, by a monitoring study using an integrated approach of sublethal toxicological effects and contaminant levels in bioindicator species.

Concerning Pb levels founded in soft tissues of mussels, it shows variation between stations inside and outside Vlora city. Higher level of Pb is detected in samle from Uji I Ftohte (0.41mg/kg), Rrapi (0.27 mg/kg) and Triport (0.24mg/kg). the higher level of

The concentration of Pb in mussels ranged between 0.14-0.41mg/kg wet weight. The Pb content resulted to be higher in Uji I ftohte, in samples collected in southern part of the bay of Vlora, but lower than the upper limit of 1.5 mg/kg wet weight on the basis of the recommendation of CE, 1881/2006.

CONCLUSIONS

AAS conclusions 2011

Heavy metals content in sediments from various stations on Vlora bay, lagoons and in estuarine of delta of river Vjosa were analysed. The results obtanined for eight elements in each type of stations (Estuarine, Coastal and Lagoon) are presentet in the tables and are illustrated the diagrams below.
In specific areas along Vlora Coast, significantly high levels of heavy metals are noticed. There are certain anthropogenic, industrial and natural factors that probably affect their distribution in marine sediment samples.
Variation observed in the metal distribution from the stream sediment and marine sediment, could be attributed to environmental content of the different tourist areas of Vlora, such as intense activities around the studied area, population density, traffic volume, atmospheric fall-out and natural origin and a contribution from industrial effluent since these areas are industrially develop. The mos abundant heavy metals in all the studied marine sediments are: Ni,Cr, Hg, Pb, Cd.

In the bay of Vlora, along Old beach and New Beach (stations V1, V2, V3), sewage is discharged into the sea, in areas frequented by the public. This situation si all along the coast of new beach; in the second picture, waste at see, in the area 300m from University of Vlora and near harbor (station M1, M2, M3) of the city where there is a more intensive activity. This area results very polluted.

The levels of Hg in Vlora Bay are recived due to the past industrial activity of the PVC-Soda Plant. The highist level of Hg concentration were found in stations M1(0.488),M7 (0.476 mg/kg), S1 (0.167mg/kg), T7 (0.11mg/kg), V7(0.212mg/kg) Dm (0.112mg/kg), in proximity of the sewage distribution in Marine deposits near harbour of Vlora (M1, M7), near old and new beach(V7), along the coast of the city and outlet from the PVC. The situation of Hg content in sediments has changed relatively compared with recent studies. The station of marine sediment infront of PVC-soda was the most contaminated, but now there is bilt Petrolifera Italo-Albanese where currently performing civil and industrial works.Petrolifera to exploit the environment in which it operates has covered with inert material part of the area of marine sediment contaminated with Hg. By the other hand the level of Hg concentration may be related with the transport of contaminated soils from seaside to other places and by underwater currents.

Due to underwater currents and winds direcionto the specific weight and structure concentration Hg is increased toward the new beach and Cold Water (Uji I Ftohte) in Vlora. It appears from obtained values of concentration Hg at stations M1(100m)& M7(700m) from shore (in front of Harbor of Vlora)& V7 (700m) from the shore between Uji I Ftohte and new beach of Vlora.

High level of Ni was find in estuarine samples collected in the delta of Vjosa River, which originates in Greece and runs through the whole southern part of Albania and in stations located in Vlora city , in samples collected in front of harbor, in front of TEC-I, in front of Petrolifera. Vjosa river flows into the north of the bay, transporting eroded suspended material containing relatively high levels of nickel and chromium as well as most urban and agricultural pollutants.

Their distribution depends on te specific weight and structure as the underwater current and the wind.

The most high level of Ni was observed in this stations: L1 (268), Dm (234 mg/kg), S7(243mg/kg)L1 (268mg/kg), M1, T7, T3, P7, L3 (228.4mg/kg). The trend in nickel distribution in stations of Vlora Bay in order of decreasing average concentration in all the studied sediments were as follow: L1>S7>Dm>L3>N3 >M1>T7>P7

The most high level of Cr was observed in stations: L1, N3, L3, H, K3, K1, K7, S_0, N1, N7, Z1, Z3, Z7.

The most high level of Pb was noticed in stations: H (82mg/kg), Z1 (88mg/kg) R (68mg/kg), O5 (70mg/kg), Ln (66,6mg/kg)

High levels of Cr, Ni, in estuarine of delta of Vjosa river and in marine sediments taken from the deltas of Vjosa river have found.

The emission of Vjosa river affects the sediments of the Adriatic sea in Vlora.

In estuarine sediments are: Ni, Cr

In lagoon sediments are: Pb,

The trend in heavy metals distribution in order of decreasing average concentration in all the studied sediments were as follow Ni, Cr, Pb, Hg

Therefore, the most abundant metals in all the studied streams sediment are Ni, Cr, Hg.

STATISTICAL DATA

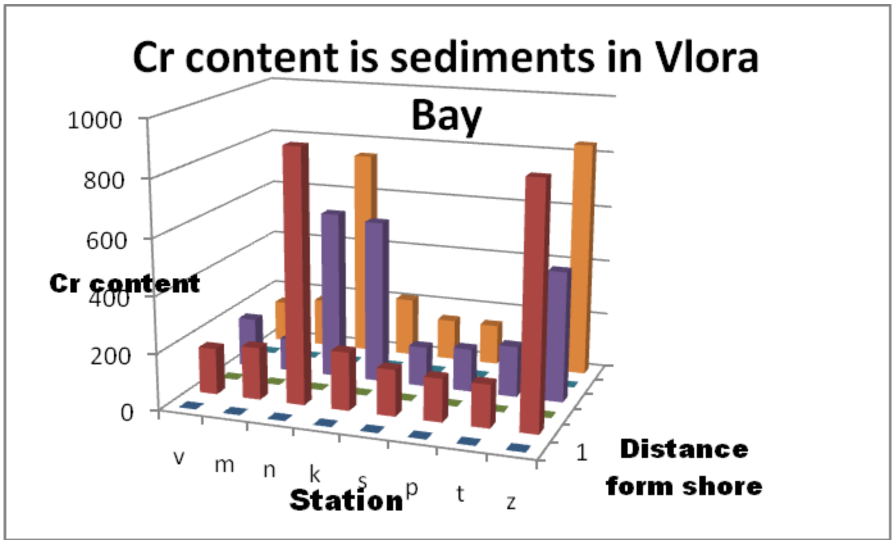


Fig. The diagram of Cr distribution in different stations (marine sediments in the area of Vlora Bay)

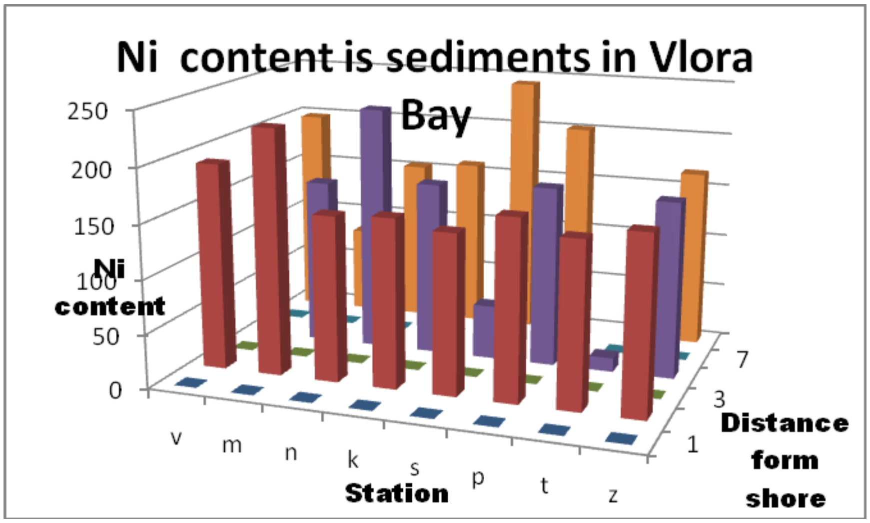


Fig. The diagram of Ni distribution in different stations (marine sediments in the area of Vlora Bay)

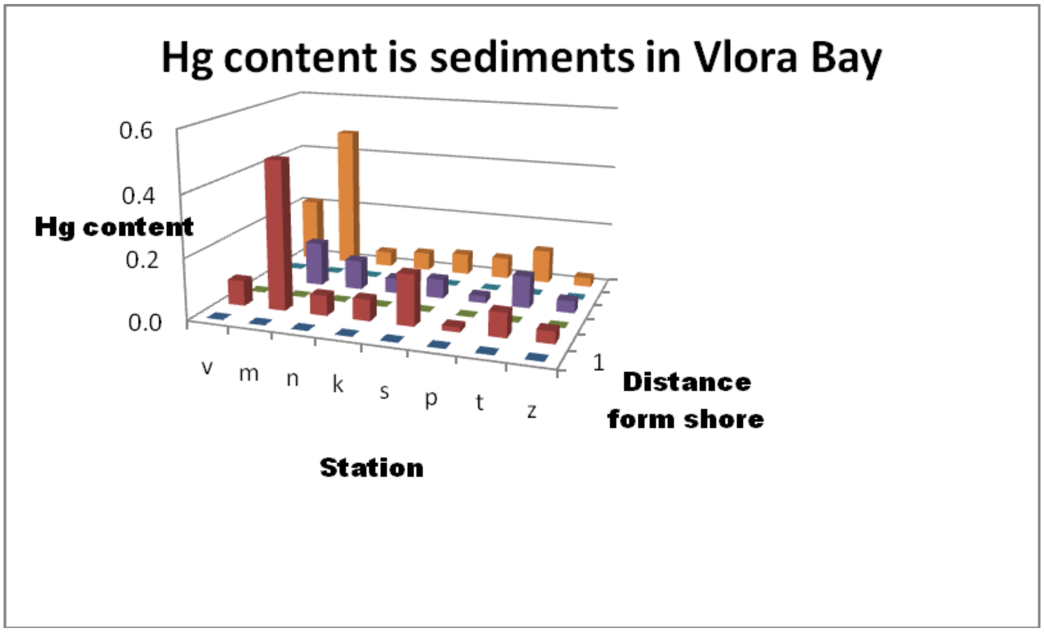


Fig. The diagram of Hg distribution in different stations (marine sediments in the area of Vlora Bay)

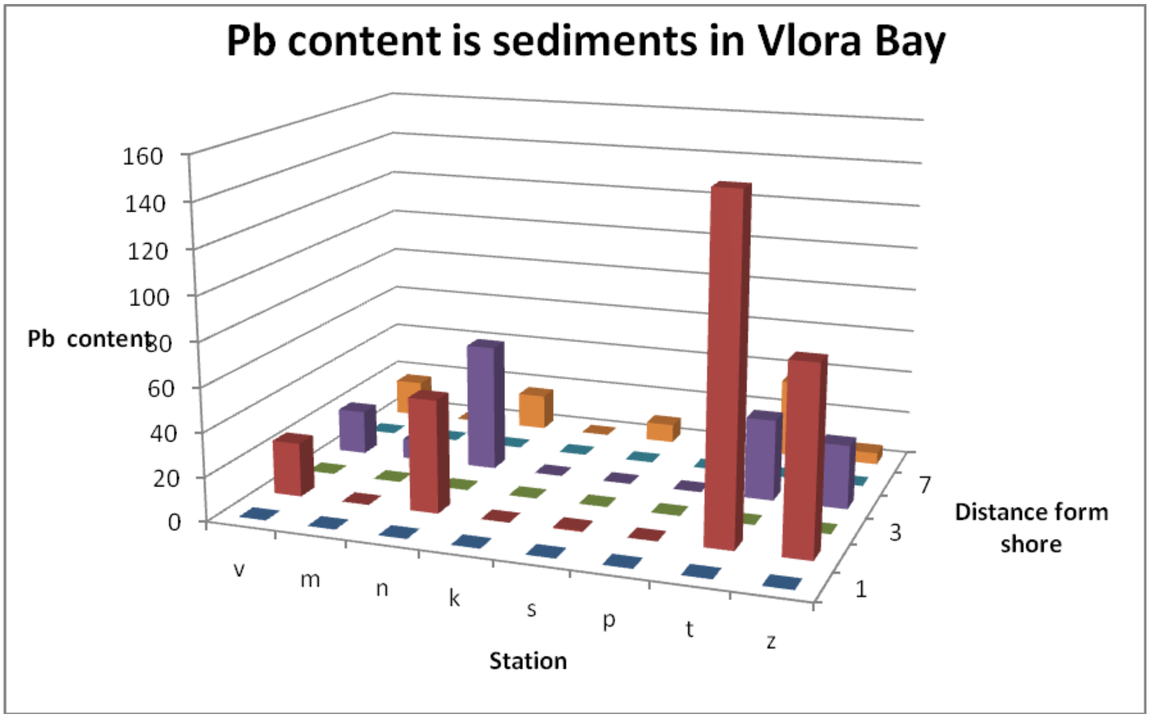


Fig. The diagram of Pb distribution in different stations (marine sediments in the area of Vlora Bay)

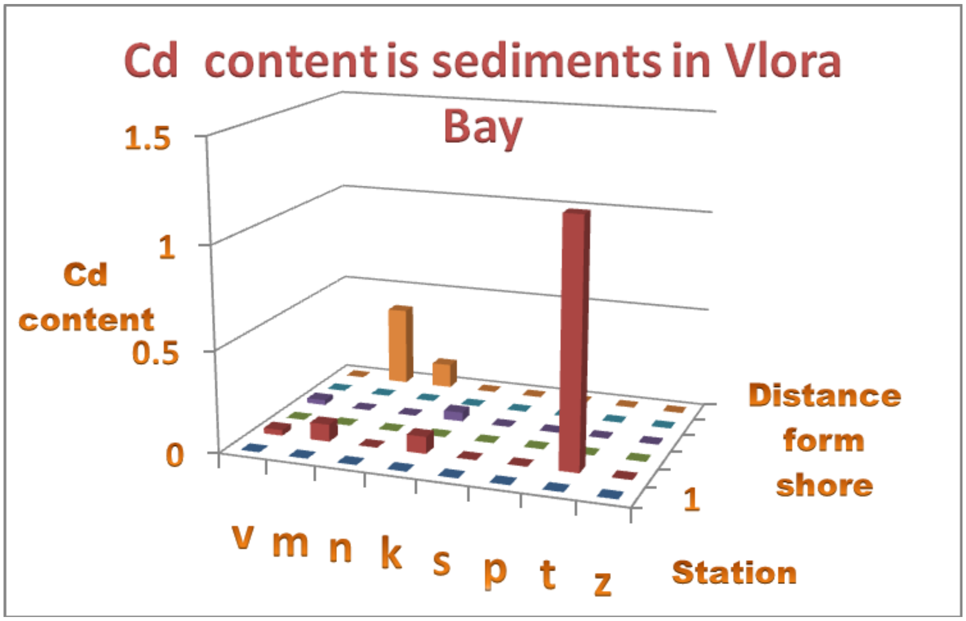


Fig. The diagram of Cd distribution in different stations (marine sediments in the area of Vlora Bay)

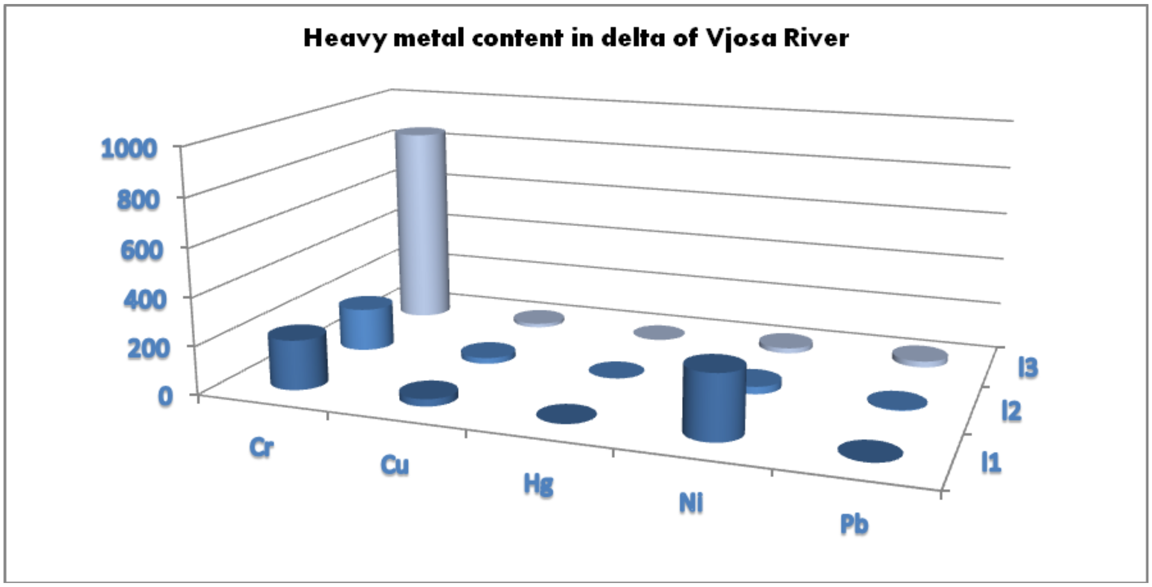


Fig. The diagram of Cr, cu, Hg, Ni, Pb distribution in different stations of marine sediments in the area estuarine in delta Vjosa River

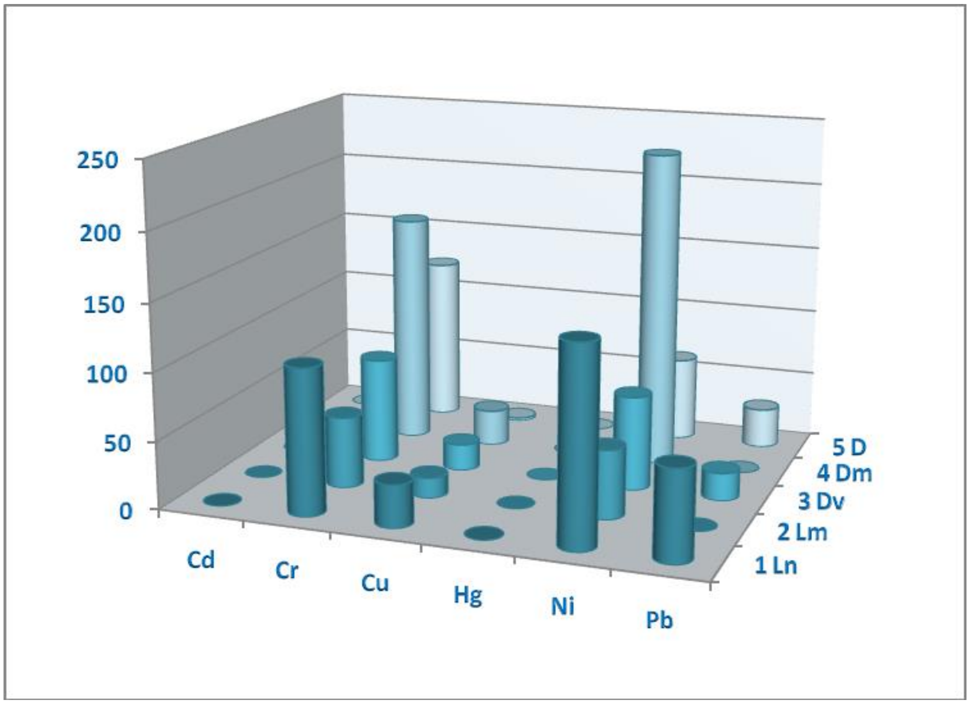


Fig. The diagram of Cd, Cr, Cu, Hg, Ni, Pb distribution in different stations of marine sediments in the area of Narta Lagoon

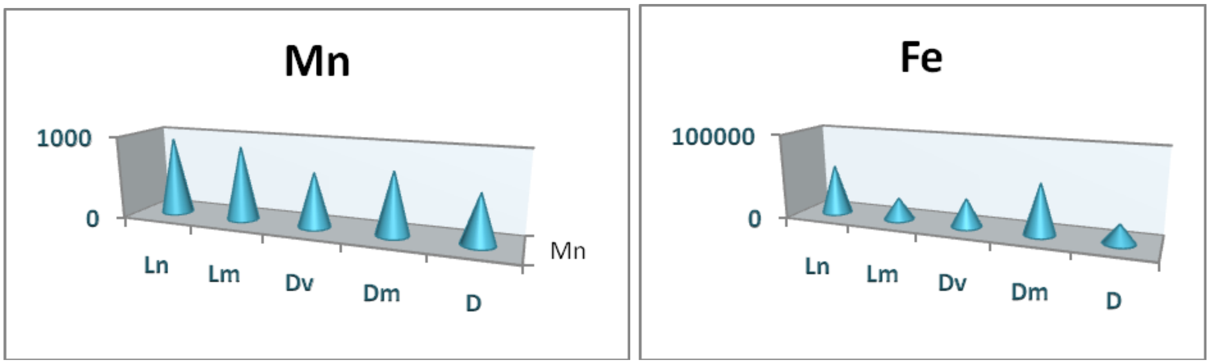


Fig. The diagram of Mn and Fe distribution in different stations (marine sediments in the area of Narta Lagoon

EDXRF Conclusions 2012

Three techniques were used for the qualitative and quantitative of toxic heavy metals such as As, Cr, Ni, Pb, Cu, Hg, Cd, Fe, Mn etc., in marine sediment, sea water particulate matter and mussels. Total Heavy metals in sediment and trace heavy metals ion in sea water were determined by EDXRF, AAS and LIBS (qualitative analysis).

Heavy metals content in sediments from various stations on Vlora bay, lagoons and in estuarine of delta of river Vjosa were analysed with EDXRF method. The results obtanined for eight elements in study and some others in each type of stations (Coastal and Lagoon) are presentet in the tables and are illustrated the tables with the comparison of some elements.

EDXRF was used for the determination of major and trace elements in sediment and will used to determine water samples etc. Using experimental systems with source and secondary terget excitation and pressed pellets, some major and trace elements can be determinated. The time needed to analyse one sample about 1 h, including sample preparation, measurement and calculation of the results. The sample preparation procedure is simple, fast and cost effective.

Variation observed in the metal distribution from the stream sediment and marine sediment, could be attributed to environmental content of the different tourist areas of Vlora, such as intense activities around the studied area, population density, traffic volume, atmospheric fall-out and natural origin and a contribution from industrial effluent since these areas are industrially develop.

The most high level of Cr was noticed in stations in front of Teci & Petrolifera.probably this concentration is due to this industrial activity & the emission of Vjosa river which originates in Greece and affects the sediments of the Adriatic sea in Vlora. Sampling stations are located near the city, and in samples collected in front of harbor (Moli) in front of TEC-I, Petrolifera the concentration of some heavy metals is very high. This is probably due of Vjosa river which transporting eroded suspended material containing relatively high levels of nickel and chromium as well as most urban and agricultural pollutants.

We are continuing to analyze marine sediment and water samples with other methods and the same methods to have a right conclusion.

We can compare our results of our work using XRF and AAS methods with results obtained by other study undertaken in region of Vlora with the aim to monitoring the evolution of the environmental situation.

LIBS Conclusions 2013

LIBS resulted an very effective method to analyze qualitatively the marine sediments. It gives a good results for the presence of the heavy metals in the marine sediment samples analyzed in the same time by the EDXRF method.

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