Session 4. BIOMEDICAL, BIOTECHNOLOGICAL AND ENVIRONMENTAL APPLICATIONS OF METAL IONS

HEAVY METAL EVALUATION IN ATMOSPHERIC FINE PARTICLES FROM GUAYNABO (URBAN) AND FAJARDO (RURAL), PUERTO RICO

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Several studies have revealed a direct association between particulate air pollution with increased in risks of respiratory, cardiovascular, and cancer related deaths as well as pneumonia, lung function loss, asthma, and other respiratory problems. Atmospheric fine particles (PM_{2,5}) include aerodynamic diameter equal to or below 2.5 µm. There is an increased interest in PM_{2.5} because they are thought to poses a greater risk to human health. Recently, the Environmental Protection Agency of United States extended its regulations from the particulate matter standard of diameter $< 10 \mu m (PM_{10})$ to a more stringent PM₂₅. Consequently, an understanding of the chemistry associated with PM_{2,5} and research in this field particularly in Puerto Rico is needed. We have sampled PM₂₅ at the Guaynabo Basin (an industrialized area) from September 2000 to September 2001 and in Fajardo (reference site) from November 2000 to September 2001. Sampling was performed using a Speciation Sampler from Andersen Instruments for periods of 72 hours. A composite of PM_{2.5} was created for each month (using material obtained from the station during the sampling period) and digested for metal analyses. Field filter blanks, laboratory filter blanks and laboratory prep blank were also digested for Ouality Control. Five heavy metals (Ni, Cu, Pb, As and Cd), organic and elemental carbon concentrations analyzed from particulate matter collected at the Guaynabo station were compared with those obtained at the reference site throughout a period of a year. Average levels of PM_{2.5} in Guaynabo were significantly higher (11.7 μ g/m³ versus 8.5 μ g/m³) in Fajardo. Average levels of Organic Carbon in Guaynabo were 3.0 μ g/m³ compared to 0.8 μ g/m³ in Fajardo. Average levels of Elemental Carbon in Guaynabo were 1.6 μg/m³ compared to levels below the measurement uncertainty at Fajardo. Arsenic, Cadmium, and Lead (0.38, 0.045, and 2.7 ng/m³ respectively) in Guaynabo were significantly higher than in Fajardo (As 0.10, Cd 0.018, and Pb 0.45 ng/m³). Significantly higher levels of all parameters tested in PM_{2.5} were obtained for the Guaynabo Station.

THE LOW VOLGA BASIN'S MICROORGANISMS CAPABLE TO ACCUMULATE IRON COMPOUNDS

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Processes of bacteria interaction with iron compounds have been attracting microbiologists attention for more than 100 years. It was established not long ago that several bacteria are able to accumulate ferromagnetic minerals – magnetite, greigite in environment and also in their cells – the last case stipulate their capability to magnetotaxis. The purpose of the research became the investigation of natural water basins in the area of the Low Volga for availability of magnetotactic bacteria (MTB). The following tasks were established: to study physical and chemical parameters that help compounds' biomineralization; to investigate the species content of water and silt microecosystems that have magnetic characteristics; to single out accumulating culture of MTB, determine its magnetic characteristics and establish the species belonging of determined MTB. In the research the following methods were used: photometrical, atomic and absorbing method, chromate-mass-spectrometric, phylogenetic and also analytical scanning and enlightening electronic microscopy. Investigation showed that there can be iron compounds' biomineralization in the Low Volga basin in the condition of low content of diluted organic substance and higher iron concentration both in water and silt and in low alkaline environment. Silt microorganisms with high parameters of magnetic repletion are presented by 23 species of bacteria that belong to 19 families. Accumulating culture of MTB was determined in the model system of Lake Belyachnoye that is characterized by low alkaline environment, low content of diluted organic substance, higher content of general iron and also by high magnetic silt repletion. It was established that the determined MTB have magnetic characteristics: capability to magnitotaxis and biomineralization of intercellular iron compounds. The carried phylogenetic analysis proved that the investigated bacteria belongs to aa-subclass of proteobacteria. Inside this group the bacteria was most close to representatives of Magnetospirillum family showing not less than 96% similarity of sequences. The investigated bacteria belongs to phylogenetic subclass that contains the typical species Magnetospirillum magnetotacticum.

The level of similarity in gene sequence 16s rRNA of determined bacteria and typical species Magnetospirillum magnetotacticum was quite high (99.6%), which proves its belonging to the species M. magnetotacticum.

SOIL AND BLOOD LEAD ASSOCIATION AMONG CHILDREN LIVING ON A FORMER MUNICIPAL WASTE SITE IN VEGA BAJA-PUERTO RICO

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Approximately 215 families live on a former municipal waste site that received wastes from domestic, commercial and industrial sources in Vega Baja-Puerto Rico. Various state and federal agencies became concerned of the health risk and the serious environmental problem faced by this community, especially children, after soil sampling detected the presence of lead (Pb) with concentrations $> 3,000 \mu g/g$. Despite studies conducted by government agencies to evaluate Pb concentrations in soil, there is a lack of information on the relationship between Pb levels in soil and children's blood. Knowing this relationship is very important because soil-Pb concentrations are a known contributor to high blood-Pb levels in children. The objective of this study was to determine the relationship between Pb levels in soil and blood of children age 1 to 6 years old living in a metal-contaminated former municipal waste site. In addition, arsenic (As) and cadmium (Cd) concen-

trations were determined in soils. Soil samples were acid digested according to the United States Environmental Protection Agency (USEPA) method sw2051 and analyzed using a Perkin Elmer atomic absorption spectrophotometer Analyst-model 800. Soil metal levels in ug/ g dry weight ranged as follows: 1.8 to 3,752 for Pb, 15 to 122 for As, and 5 to 35 for Cd. Thirty-three percent of the homes sampled (n=40) had soil Pb values higher than the USEPA lead hazard standard in soil of 400 µg/g. Blood lead values, ranging from 0.97 µg/dL to 7.79 µg/ dL, were below the blood-lead standard (10 ug/dL) of the US Center for Disease Control and Prevention. A linear regression model showed a positive statistically (p < .05) weak linear relationship between soil and blood lead levels accounting for 16% of the variation. Therefore, other predictors of blood-lead levels such as indoor dust and drinking water will be included for future correlation analysis.

DETERMINATION OF OCCUPATIONAL EXPOSURE TO DEPLETED URANIUM BY ISOTOPIC ANALYSIS OF URANIUM IN URINE

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Background: Depleted uranium (DU) is a byproduct of the 235U enrichment process for nuclear fuel. Thus, natural uranium contains 0.72% of 235U and 99.27% 238U whereas DU usually contains ~0.2% 235U and 99.8% 238U. DU is used commercially and in the military because of its high density, availability, and low relative cost. Occupational exposure to depleted uranium causes a decrease in the isotopic percentage of 235U in urine samples resulting in measurements that vary between natural uranium's 0.72% 235U and depleted uranium's 0.2% U235.

Aims: To develop a method based on high pressure liquid chromatography-inductively coupled plasma mass spectrometry (HPLC-ICP-MS) and/or ICP-MS with a dynamic reaction cell to identify occupational exposure to depleted uranium by measuring the isotopic composition of uranium in urine.

Methods: Urine samples from a non-exposed group and a suspected depleted uranium exposed group were processed and analyzed to determine whether depleted uranium was present in the urine. Sample preparation involved a deproteination step with nitric acid followed by centrifugation. The sample preparation can be completed within 2 hours.

Results: The ion intensity of 235U and 238U were measured using ICP-MS. The analysis was completed in less than 8 hours. The detection limit was below 10 ng uranium/L urine. By calculating the percent composition of 235U from the isotopic quantities of 235U and 238U in urine samples, this method rapidly identifies exposures to depleted uranium.

Conclusion: This method has the capability of identifying exposures to depleted uranium down to levels of uranium in urine normally found in control groups.

GEOECOLOGY OF COPPER IN THE LAKE SUPERIOR PROVINCE, NORTH AMERICA

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Background: The North American Lake Superior region contains a world-class copper (Cu) province nearly 300,000 km². Geologically, the area hosts a variety of life forms, including 2.6–2.75 billion year old microbial fossils.

Aim: Although Cu origins in this region were metagenic and epigenic, palynological and microbial research (Robbins, E.I., Tectonophysics, 94:633, 1983; Robbins, E.I. et al. Geol. Assoc. Canada/Mineralogical Assoc. Canada Annual Mtg., p. A94, 1994) prompts discussion about the concurrence of Cu and biota in the Province. Cu, an essential miconutrient, provides catalytic and electron transfer functions in almost every known group of organisms. Excess biological Cu is normally excreted, and some bacteria can precipitate excess Cu externally. As an organism enters the fossil record, its metal components accompany it to deposition (Honjo, S., Oceanographic Research Papers, 29:609, 1982).

Methods and Result: Interpreting relationships between fossil organisms and their associated metals relies on a variety of microtechniques, including palyno-

logical analysis, scanning electron microscopy, and isotopic analysis. Black opaque Cu sulfide mineral(s) were shown enmeshed in organic tissue fragments within regional black shale, and Cu mineralization accompanies microfossils of bacteria and fossilized algal filaments and probable fecal pellets of simple multicellular animals (Robbins, E.I. et al., Proc. Nat. Acad. Sci., 82:5809, 1985), fossil cyanobacterial sheaths, fungal hyphae-sized tissues, and aquatic algae. Despite multiple physical sources of Cu, Zhu (Zhu, X.K., Chem. Geol., 163:139, 2000) interprets wide isotopic variability as biological fractionation at low temperatures. Underground, brine pools are coated with films of Cu²⁺ minerals and petroleum; the bacterial role in forming these oxidized Cu chloride minerals is presently under study.

Conclusions: Research thus suggests biological interactions with Cu over geologic time. Current redox conditions and microbial action may contribute to elevated Cu in food stuffs and has raised concern that additional bioavailable Cu may react synergistically with other metal ions to exceed toxicity thresholds.

MERCURY TOXICITY: A CLINICAL PERSPECTIVE

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Throughout recorded time, mercury has held the dubious distinction as both a valuable resource in medical, agricultural, industrial, and household uses, as well as a toxin causing immense morbidity and mortality. The above passage by Fracastorius not only described and named the scourge of "syphilis" as it swept across Europe, but also vividly illustrated the poisonous nature of mercury (note the salivation, sweating, and mucosal ulcers) even as a medicinal cure.

The clinical presentation of excessive mercury exposure can vary tremendously, depending on the form of mercury, route of exposure, dose, duration of exposure, and susceptibility of the exposed individual. Since treatment options are limited, prevention remains the mainstay of therapy.

SAFETY ASSESSMENT FOR CHILDREN FROM BE CONTAINED IN ATMOSPHERIC DUST

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Background: The research of environment influence on a human health was investigated in South-Eastern Administrative District of Moscow City (Russia). This area (112 km²) is the territory with the highest concentration of polluting industries in all Moscow. The research is from the point of view of methodology

developed by US EPA (assessment of hazard quotient from substances intaking in the human organism by inhalation rout).

Aims: Adaptation of method of hazard quotient account from Be, intaking in human organism with inhaled dust, for use of the snow dust sampling data

instead of atmospheric air dust sampling data. Detection of the correlation between the hazard quotient assessment and Be concentration in children hair.

Methods: The snow sampling (scale 1:50000). The Be concentration in the dust contained in snow samples was analyzed by emission spectrometry method. The Be concentration in children hair (215 samples) was analyzed by local laser emission method.

Results: The spatial correlation between areas with hazard quotient above 1 and areas with the increased Be concentration in children hair is detected.

Conclusions: It is more preferable to use the snow sampling data at account of hazard quotient. Hazard quotient designed at such method correlates with the Be concentration in children hair.

ZEOLITES WITH SUPPORTED SILVER AND COPPER SPECIES AS A NOVEL MICROBICIDE MATERIALS

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The discovery of microbicide action (MBA) of the ion-exchanged zeolites has been reported [1,2]. The MBA is attributed to the ionic state of the metals released from the zeolites by ion re-exchange; zeolites are known to be the carrier and slow releaser of the heavy metals with olygodynamic properties [3]. Purified natural Cuban clinoptilolite (Cli) used for the present study is permitted and certified for application as external and internal medicines by Ministry of Public Health of Cuba [4]. The aim of the present work is to clarify if low cost Cli could be a substrate for copper and silver in different states with similar or better MBA than exchanged forms.

Chemical analysis showed that Cli contains ca. 10 wt. % of a non-toxic admixture of Fe₂O₃, FeO, MgO,

CaO, Na₂O, K₂O and P₂O₅. The concentration of toxic elements (F, Pb, Cd, and Hg) always appeared to be lower than 3 ppm [5]. Ion exchange was carried out from 0.1 M solutions of Ag and Cu nitrates. Then the samples were washed and dried at room temperature, and reduced in hydrogen to obtain dispersed metal species. The state of oxidation of the exchanged metal in zeolite could determine the microbicide effectiveness. Variation of the copper and silver state (Cu²⁺, Cu⁺, Ag⁺, clusters, sub-colloidal, colloidal and large particles) in zeolites might allow regulating the release of active species from the medical preparations. Influence of metal state on microbicide activity will be discussed.

HEALTH RISK ASSESSMENT AND MANAGEMENT OF ARSENIC TOXICITY AND CARCINOGENESIS

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Background: Acute and chronic exposure to arsenic has been reported in several countries of the world, with major outbreaks of arsenosis occurring in Argentina, Bangladesh, India, Mexico, Thailand, and Taiwan, where a large proportion of drinking water (groundwater) is contaminated with high concentrations of arsenic. Research has also pointed significantly higher standardized mortality rates for cancers of the bladder, kidney, skin, liver, and colon in many areas of arsenic pollution. The current literature indicates that arsenic poisoning represents a major public problem. There is therefore a great need for developing a comprehensive risk assessment model that should be used in the effective management of health risks associated with arsenic exposure.

Aim: With a special emphasis on arsenic toxicity and carcinogenesis, this paper aims at developing and

presenting a conceptual risk assessment and management model for toxic metals in the environment and human health.

Methods: Using the National Academy of Science's risk assessment and management framework as a guide, a thorough review of literature has been made. All critical information has been analyzed, and will be presented with respect to the health hazards associated with arsenic exposure, the sources and pathways of human exposure, the concept of dose-response relationship in arsenic poisoning, the characterization of both systemic and carcinogenic effects, and the potential strategies and methods to control and/or prevent arsenic poisoning.

Results: A comprehensive analysis of published data indicate that arsenic exposure induces cardiovascu-

lar diseases, developmental abnormalities, neurologic and neurobehavioral disorders, diabetes, hearing loss, heamatologic disorders, and various types of cancer. There exist various sources of exposure. Although exposure may occur via the dermal, and parenteral routes, the main pathways of exposure include ingestion, and inhalation. The severity of adverse health effects is related to the chemical form of arsenic, and is also time- and dose-dependent. From a management point of view, several control and treatment technologies, as well as regulatory guidelines have been developed to address the issue of arsenic toxicity and carcinogenesis.

Conclusions: Arsenic poisoning appears to be one

of the major public health problems of pandemic nature. The development of a comprehensive risk assessment and management model for arsenic requires a thorough understanding of its physical and chemical properties, production and use, fate and transport, toxicokinetics, systemic and carcinogenic health effects, regulatory and health guidelines, analytical guidelines and treatment technologies.

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LEAD AS A THREAT TO THE HEALTH OF CHILDREN FROM THE CITY OF VLADIVOSTOK

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Background: Lead poisoning (saturnism) is the widespread dangerous illness linked with the influence of the environment. Lead (Pb) intoxication is dangerous, not only because of the many overt clinical manifestations, but also because of delayed or subtle effects such as changes in higher cognitive functions, including social maladaptation.

Aims: To develop the science-based recommendations to decrease the Pb level in children from Vladivostok, and to prevent its adverse influence on children's health. The survey was conducted within the framework of the ecological project between the Administration of Primorski Krai and US Pacific Air Force Command – "Studying the influence of environmental factors and bioindicator estimation of health status of the risk groups among the population of Primorski Krai".

Methods: Pb detection in blood of 203 children from 3–10 years old by a "Lead Care" analyzer; clinical

method; laboratory method; sociological method; and statistical method.

Results and conclusion: Blood lead concentration exceeded the allowable level (8 µg/dl) in 27.6% of those surveyed. The average blood lead level of boys was higher than that of girls (p < 0.05). The tendency of increased blood lead level with increasing age of the children was revealed. Health examination of the children with raised Pb level revealed various changes consistent with saturnism manifestations. Digestive system, nervous system, and peripheral blood changes were more frequently diagnosed. Frequent and chronic respiratory diseases inflicted 54.2% of those surveyed. One-third of the children had retardation of biological and psychological development. A program of intervention for the children was developed. It included nutritional intake optimization. Pb elimination measures, correction of the somatic conditions, and regular medical check-ups.

HUMAN – MADE IMPACT ON WILD ANIMALS IN URBAN AREAS

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Wild animals whose habitat is urban areas are as object for sport hunting due to high levels of toxicant in their biological media. The only possibility to preserve wild animal populations is to set favorable environmental conditions. Studies in this filed remain episodic. In 2001, an experimental investigation of three species of wild ducks for the content of essential and toxic chemicals in animal organs and tissues was conducted. The ultimate aim of the study was to determine environmental exposure level and interspecies differences in the

accumulation of organogenic elements in ducks. The methods used contained pesticides gas-liquid chromatography, radionuclide spectrometry analysis, metal atomic-absorption spectrometry. The presence of zinc, cadmium, mercury, and arsenic in bird organs at concentrations not exceeding the permissible exposure limits (Sanitary rules and standards 2.3.2.560-96) has been detected. An exceeding of the permissible limit for lead has been recorded in the lung tissue of redhead pochards and grey ducks. Ducks of the given habitat are exposed

to lead mainly via air. This metal is accumulated in bone tissue and feather. The content of copper in muscular tissue of river ducks is two times higher than in pochards which may be assessed as an exceeding of the standard due to human-made impact in accordance with hygienic standards. However as the duck were caught within one habitat and had similar food. The enhanced accumulation of copper in muscular tissue of the given duck species is probably their specific feature. We believe that the study on microelement balance of water fowl exposed to high level antropogenic impact in suburb zones should be continued.

Conclusions:

- 1. Species of ducks studied in accordance with anatomic indices are characterized as healthy species.
- 2. Bird muscular tissues do not contain pesticides as the most typical pollutant for the region in question.
- 3. Bird environmental conditions do not contribute to the accumulation of radionuclides in their organs and tissues.
- 4. An exceeding of the permissible limit for lead recorded in lung tissues of redhead pochards and gray ducks.
- 5. An increased accumulation of copper is observed in muscular tissues of river ducks.
- 6. The use of ducks flesh in food allowance is not dangerous according to indices of technogenic pollution.

THE RELATIONSHIP BETWEEN FLUORINE I N DRINKING WATER AND DENTAL HEALTH OF OPPIDANS IN P. R. CHINA

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In this study, the relation of intake fluorine (including drinking water and main foodstuff) and the fluorine content in urine was evaluated. The incidence of DMF (mean number of decayed, missing and filled teeth), the ratio of dental caries and the index of dental fluorosis was evaluated and compared with the data of fluorine content in drinking water and in main foodstuff from 30

cities in China, where dental epidemiological investigation has been available since 1995. At concentration ranges between 1.0mg/L and 4.0mg/L of fluorine content in drinking water, the relative incidence of DMF and dental fluorosis was studied. Samples of drinking water and main foodstuff in 50 largest cities in China were selected and fluorine levels determined.

TRACE METALS IN EDIBLE FISH FROM VIEQUES-PUERTO RICO

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Since 1941, the eastern and western ends of Vieques have been mainly used by the United States (US) Navy for live ammunition practice and ammunition storage, respectively. The long use of live ammunition, and the potential exposure to chemical constituents (e.g., metals) of military artifacts are some major concerns of the consequences that military practices may have on both, the environment and human health, in Vieques. Marine fish could become exposed to toxic metals that may be present in contaminated soil that eventually reach aquatic system, or through the food web, accumulating high concentrations that could represent a health risk to the human population that consumes it. Despite the great concern that exists because of the potential for toxic metal contamination in Viegues, there is a lack of information about the extent of human exposure to metal from contaminated edible fish. Therefore, eight edible marine fish species (Diapterus plumieri, Gerres cinereus, Sparisoma sp., Caranax crysos, Acantharus coeruleus,

Holocentrus ascensionis, Lutjanus sp., and Haemulon sp.) were captured from seven locations around the island of Viegues for a total of 162 individuals. Fish muscle will be acid-digested with nitric acid in a microwave oven CEM-model 1000. After acid-digestion, concentrations of arsenic (As), cadmium (Cd), copper (Cu), mercury (Hg), lead (Pb), selenium (Se), and zinc (Zn) will be determined using a Perkin Elmer atomic absorption spectrophotometer Analyst-model 800. Metal concentrations will be compared to levels found in fish from other sites in Puerto Rico. For instance, metal levels (Sg/g dry wt) found in edible muscle of D. plumieri collected from two reference sites in southern and western Puerto Rico ranged as follows: As, 0.47–3.50; Cd, 0.002-0.029; Cu, 0.39-14.8; Hg, 0.017-0.090; Pb, 0.09-0.79; and Zn, 14.9-33.3. This study will provide important information about the risk posed to Vieques inhabitants consuming these potentially metal-contaminated fish.

STUDYING OF KINETICS OF ION-EXCHANGE SORPTION OF CATIONS CA²⁺ AND MG²⁺ ON THE CATIONIT

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In modern household and industrial filters cationits are used to make hard water, containing Ca²⁺ and Mg²⁺, softer. The degree of filtration depends on filter quality. However the conditions, of where the filtration takes place, play a significant role. To determine these condi-

tions we studied the Kinetics of ion-exchange sorption of Ca²⁺ and Mg²⁺ on the Cationit CU-2-8: the speed dependence (influence) of the given reaction from the nature of cation, its concentration and temperature.

ARSENIC ANALYSIS AND ISOTOPIC-LEAD TRACERS ON THE STUDY OF A 135-YEAR-OLD BODY

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Background: An autopsy of the 135-year-old body RXK was completed and materials were obtained for arsenic and lead analysis.

Aims: To determine arsenic and lead exposures of RXK before time of death. **Method:** Total arsenic and lead levels in adipose tissue from the liver area and stomach area, hair, and nail samples were determined employing electrothermal atomic absorption spectrophotometry with a Zeeman-background corrector (ETAAS). Isotopic lead analysis was preformed using inductively coupled plasma-mass spectrometry.

Results: High levels of arsenic and lead were measured all tissues analyzed. The arsenic levels were 24,

4.8, 0.24, and 1.18 PPM in hair, nail, adipose in liver area, and adipose in stomach area, respectively. Lead levels were 5813, 111.2, 388, and 636 PPM in hair, nail, adipose in liver area, and adipose in stomach area, respectively. Arsenic speciation on the adipose tissue in the liver area revealed that the majority of the arsenic was methylated. The isotopic analysis of the lead obtained from the casket did not match the lead in the tissues.

Conclusions: The methylation of arsenic indicates metabolism of inorganic arsenic before RXK deceased. The source of the high levels of lead in the tissues was believed to be from the casket; however, the isotopic analysis confirms the lead is from a different source.

ENVIRONMENT EFFECTS OF TRACE ELEMENTS CONCENTRATION IN SEA SNAILS USING ATOMIC ABSORPTION SPECTROMETRY

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Water pollution has increased in heavily industrialized areas where most industrial wastes end up in the sea. Sea water has to provide the essential elements for organisms living in it and through the food chain to man. Monitoring the elemental composition in marine organisms such as sea snails is of great importance. 30 samples of each of the two kind of snails has been collected from the west coast of

Libya. Samples were digested with nitric acid and the concentration of Copper, Iron, Magnesium and Zinc were determined by atomic absorption spectrometry. The results shows that Mg has the highest while the Copper has the lowest concentration level in both kind of snails. A pattern of the trace elements concentration were investigated regarding to the size and the kind of snails.

OCCURENCE OF HEAVY METALS IN SEDIMENTS, FISH SPECIES AND OYSTERS FROM MTWAPA, PORT REITZ, MAKUPA AND SHIRAZI CREEKS ALONG THE KENYAN COAST

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A comparative survey of elemental concentrations in abiotic and biotic compartments was carried out to

assess possible differential antropogenic influence on selected marine tidal creeks along the Kenyan coast.

Copper (Cu), zinc (Zn), Lead (Pb) and Cadmium (Cd) concentrations in acid digested samples were determined by atomic absorption spectrophotometry. The method of analysis was validated using IAEA/SOIL-7, MA-A-2 (Fish homogenate) MA-M-2 (Mussel tissue) International Atomic Energy Agency certified reference materials. In sediments, Cu concentrations (Mg/g, dry wt) ranged from 2.2 to 228.9, Zn ranged from 9.1 to 3196.2, Pb ranged from 8.4 to 164.5 while Cd ranged from 0.3 to 83.4. In fish, Cu concentrations (Mg/g, wet wt) ranged from ≤0.001 to 1.0 Zn ranged from ≤0.006 to 11.4, Pb ranged from ≤0.005 to 1.9 while Cd ranged from ?0.02 to 0.6. In oysters, Cu concentrations (Mg/g, wet wt)

ranged from 3.3 to 1090.7, Zn ranged from 46.8 to 1538.7, Pb ranged from ≤0.005 to 97.6 while Cd ranged from ≤0.002 to 19.6. Notably higher elemental concentrations which, in some cases exceeded the World Health Organization limit guidelines were observed in sediment and oyster samples from Makupa creek. In general, there was significant variation (p<0.05) in elemental concentrations between and within creeks and compartments. In order of most to least influenced, the creeks under investigation may be classified as follows, Makupa > Mtwapa > Port Reitz > Shirazi. However, further research into actual sources and fates of the elements investigated among others in warranted.

THE INFLUENCE OF METAL – IONS OF NATURAL ZEOLITHS OF TUZBEC LOCATION ON PHYSIOLOGICAL ORGANISM FUNCTIONS

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The natural deposits of alumosilicates on Russian territory are found everywhere, in every region of the country and are represented by mordentiths, shabasiths, clinoptiloliths and by other rare species of zeoliths. Such researchers as Valentina Krokhina, P. Mikhailov in 1998, Leonid Diyachenko, V. Lysenko in 1986, M. Malikova in 1997, 1998, I. Zukov, V. Androsov in 2001 learned the possibility of using them (zeoliths) in stock - raising practice as a fodder addition. As knowing, natural zeoliths have qualities of absorption and ion – metabolism; in their crystal fender they have peroxide bridges that have bactericidum and catholitic qualities. The goal of these researches was the learning of the influence of Metal – Ions of natural zeoliths on gematological index of calves. There were formed two groups of calves-7 analogous heads in each group. The experiments were taken according to the following scheme: 1.-control: basic ration-according to W.I.S. scheme. 2.experemental: basic ration +0.5 g of zeolith ofr 1 kg of living mass. In ration were 2.62 and 2.73 kg of dried substance accordingly; 2.92 and 2.96 of fodder units; 31.81 and 32.42 M J of metabolic energy; 480 and 492 g of raw protein; 348 and 352 g of digestible protein; 551.1 and 572.2 g of cellulose; 235 and 242 g of fat; 285 and 290 g of lactose; 24.8 and 26.2 g of calcium. The concentration of energy in dried substance of ration of calves in control group vas in average 12.14 MJ by, in experimental group -11.9 MJ by the norm of 10.1 MJ. The comparison of there facts shows that the concentration of energy in dried substance of ration of experimental animals was suitable to the exist norms of feeding. The clinic observations during the experiment show that experimental animals' temperature, frequency of breathing and pulse, scalp and general condition were within

the limits of physioligical norm. During the experiment gematological index of animals in control group and of those who was gotten zeoliths was studied. In experimental group the content of haemoglobin -g/1-92.3, red corpuscles $-10^{12}1 - 8.28$ and leucocytes $-10^91 -$ 8.32; in control group accordingly – 88.0; 6.86; 7.56. The results of researches show that morphological index of blood of experimental calves in the age of G months was within the limits of physiological norm, and characterize good progress in both groups. The zeolith feeding had good influence upon morphological index of blood. The mention the that there was increase of haemoglobin on 4.5%, red corpuscles on 13.1%, leucocytes on 10%. The increased content of red corpuscles, haemoglobin and leucocytes in blood of cubs in experimental group we can consider as improvement of ion-metabolic so oxidizing-reconstruction processes in comparison with control animals. Biochemical index of blood serum that characterize metabolic processes in organism of experimental animals was suitable to the physiological norms. In experimental group the content of protein was higher that in control group of animals on 10.4%, content of reserve alkalinity — on 2.5%, carotine — on 26.5%, calcium — on 18%, phosphorus — on 4.6%, A.S.T. index — on 17.2%, A.L.T. — on 15.5%. So, the using of natural zeoliths as a mineral feeding in rations of calves was conducive to the improvement of ionmetabolic, intensity of oxidizing-reconstruction processes, activity of reaminiration ferments in animals' organism. The increase of aminotransfer activity of calves, was gotten Metal-Ions of zeoliths, is an index of more intensive synthesis of protein, that was conducive, in its turn, of the increase of average daily growth of living mass.

IN-VITRO BIOACCESSIBILITY OF METALS IN SOILS FROM A FORMER LANDFILL IN PUERTO RICO

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The bioaccessibility of arsenic (As), cadmium (Cd), copper (Cu), mercury (Hg), lead (Pb), and zinc (Zn) in humans was tested by incubating metal-contaminated soil samples with artificial gastric juices. Three soil samples were obtained from a United States Environmental Protection Agency (EPA) Superfund site in Puerto Rico. In addition, a sediment sample from a metal-contaminated estuarine lagoon, and a standard reference soil (Montana SRM 2710) from the National Institute of Standards and Technology were included for comparisons. The EPA method 3050B was used to determine total metal concen-

trations in samples. Pb and Cd obtained the highest bioaccessibility values varying from 51–80% and 49–91%, respectively. Bioaccessibility values for As ranged from 4.5 to 55%, while values for Zn fluctuated from 29 to 67%. Cu, like As, showed large fluctuations in bioaccessibility values ranging from 4.6 to 73%. Hg levels were not determined in the artificial gastric juice because total concentrations in solid samples were low. In conclusion, results showed that a large fraction of the metals associated to soils is bioaccessible, potentially posing a health risk to humans, particularly children.

HEAVY METALS IN AIR PARTICULATE MATTER (PM₁₀) FROM VIEQUES-PUERTO RICO

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Viegues, a small island, inhabited by 9,000 civilian people, is located between Puerto Rico and Saint Thomas at latitude 18.5° North and longitude 65.3° West, consisting of 55 square miles. For over sixty years, the United States (US) Navy has been operating in Viegues using it as live ammunition target practice. The wind blows 65% of the time from the northeast potentially transporting particular matter to the human population. Therefore, there is a major public health concern that the population of Vieques is being exposed to toxic metals adsorbed to fine airborne particulate matter with a diameter < 10µm (PM₁₀). We will investigate levels of aluminum (Al), arsenic (As), cadmium (Cd), iron (Fe), lead (Pb), and vanadium (V) on airborne particulate matter (PM₁₀) in two locations on the island. Metal levels and composition on PM 10 will be compared before, during and after military practices. Two air sampling stations of PM₁₀ are located in northern and central location of the island. The PM₁₀ Partisol-Plus model 2025 sequentially collected air particles on a daily basis on a 47mm Teflon filter at a flow rate of 16.7 L/min. Collected air particles were removed from the field on a weekly basis and transferred to the laboratory. Samples from Fajardo (a reference site that receives airborne materials directly from the Atlantic Ocean) were obtained in parallel with those from Vieques. Unused clean filters, field and laboratory blanks, and an urban dust reference material (SRM-National Institute of Standards and Technology) were included to determine background contamination and recovery efficiencies. Filters with PM₁₀ will be digested in concentrated nitric acid, and analyzed for metals using a Perkin Elmer atomic absorption spectrophotometer, Analyst 800.

MEN'S AND WOMEN'S HAIR TRACE ELEMENT CONCENTRATIONS IN MOSCOW REGION

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There were 1206 20–40 years old human's hair samples, collected in Moscow region (excluding the Moscow city) by ICP-AES analyzed. According to obtained data we concluded that:

- in comparison to average data, obtained in our laboratory for European part of Russia and Moscow city, the

lower hair As and higher Mg, Mn, Ca and Fe concentrations in Moscow region men and women were observed; – comparison to Moscow city was observed increased Cd level in men and women hair and Pb, Sn – only in men:

– there are the significant differences between rural and

urban hair concentrations (higher Zn, P in women, living in rural part; lower Sn and higher Cu, Fe in men, living in rural part of Moscow region);

There is evident correlation between distance from Moscow city and elemental hair composition, more significant in men comparison to women. There are the significant variability in men hair concentrations of some important trace elements: concentration Ca, Mg, Na, Pb, Fe, Cu, Mn was increased in middle and far zone comparison to nearest to Moscow city part of region; concentration of As and Se in far and middle zone was lower. In hair

of women, living in far zone of Moscow region was higher concentration of Sn and lower concentration of Si comparison to nearest and middle zone.

Also, the dependence of hair element concentration from geographical direction was established. Hair Na, P, Fe, Pb, Cd concentration was significantly higher in men, living on south direction. Estimation of women's hair elemental content didn't show significant differences between inhabitants of different geographical directions.

So, as obtained data shows, men have more pronounced reactions on the environmental conditions changes.

THE PECULIARITIES OF GOITER CHILDREN HAIR ELEMENTAL CONTENT

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Previously we showed, that the children hair elemental content significantly due to biogeochemical picture in different regions of Russia and some specific disturbances of mineral metabolism could influence on the incidence of goiter (Skalny, 2000, Veldanova, Skalny, 2001).

In this study we tried to found some specific features of elemental status in goiter patients, independently to biochemical properties of their region. Totally, 304 12-16 years old boys and girls, suffering form goiter (G) and 112 children with normal dimensions of thyroid gland (K), living in 6 territories of Russia (Far East, Siberia, European part) were examined and investigated by ICP-

AES and ionometric methods.

It was revealed, that for G patients are typical significantly lower hair Cu, Al and Si $(11.5\pm0.4 \text{ vs. } 13.4\pm0.7 \text{ ppm}; 19.9\pm1.5 \text{ vs. } 23.8\pm1.5 \text{ and } 24.9\pm2.9 \text{ vs. } 34.8\pm2.8 \text{ ppm, respectively})$ and higher Pb, Co concentrations $(1.71\pm0.17 \text{ vs. } 1.59\pm0.11 \text{ ppm}, 0.18\pm0.03 \text{ vs. } 0.12\pm0.07 \text{ ppm, respectively})$ as compared to K group.

The hair Ca, Mg, P, K, Na, Fe, Zn, Mn, Cr, Se, Zn, Ni, Sn, As, Ti, V and I concentrations are the similar in both G and K groups. This study suggests the importance of epidemiological investigation of interelemental interactions in genesis of endemic goiter.

NERVOUS SYSTEM STATUS OF CHILDREN WITH POLYHYPERMICROELEMENTOSES

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Introduction: The nervous system (NS) of children is extremely sensitive to various external influences. Long, excessive exposure and accumulation of microelementoses (ME) possibly result in changes of the psychological status of children.

Aims: To study the NS status of the children with polyhypermicroelementoses (excessive accumulation in an organism of lead (Pb), cadmium (Cd), manganese (Mn), copper (Cu) and zinc (Zn)).

Methods: Bioindication method (detection of the levels of Pb, Cd, Mn, Cu and Zn by atomic absorption spectrometry in hair and urine); clinical method; laboratory method; sociological method; and statistical method.

Results: One hundred and thirty children from 3 to 14 years old were surveyed. Sixty-five of them were in the experimental group (children with polyhypermicroelementoses (PME)), and 65 were in the control group. In comparison with control group, children with PME showed increased somatic-vegetative disorders such as sleep disorders, appetite disorders, and stomachache.

Children with PME also had behavior disorders such as anxiety, tendency to disobedience, and fluctuation of mood. We noticed that the children with PME had a statistically significant decrease of the parameters describing their cognitive activity and socialization. Illnesses of the NS (asthenoneurotic syndrome, neurocirculatory dystonia) were more often diagnosed in children with PME (p < 0.01). Neurosis-like conditions were revealed in 7 children only from the experimental group. Children with PME had altered porphyrinic exchange (increase of the Δ -aminolevulinic acid in their urine, closely correlating with the level of Pb and Cd excretion). Since porphyrins are part of neuron myelinization, disturbances of neuron myelinezation and interneuronic communications in the brain are possible in children with PME.

Conclusion: Psychological disorders in children with PME are expressed in a greater degree than in the control group. Thus, it can be recommended as an additional diagnostic criterion for PME in children.