PREFACE

This book examines the environmental sources, geochemistry and human effects of trace elements. Topics discussed include an assessment of cancer and non-cancer health risk caused by trace element content in Belgrade; flow opto-sensing applied to the analysis of trace elements; trace metals in fruits and vegetables and their effect on human health; excessive livestock mineral supplementation on environmental pollution; assessing the geochemistry of trace elements in canal sediments; and trace element deficiencies in crops.

Chapter 1 – The urban atmosphere is subjected to large inputs of anthropogenic contaminants produced by both stationary (power plants, industry and residential heating) and mobile sources (related to traffic). Trace elements are widely dispersed in the environment and can have toxic effects on the biosphere and human health. The characterization of airborne trace elements is relevant to identification of variability and sources of atmospheric pollutants. The transport of trace elements has also attracted much attention. Extensively employed collection of atmospheric deposition using bulk sampling devices, or using air samplers of suspended particulate matter (PM) offer practical approaches for monitoring of atmospheric trace elements in the environment. However, the instrumental sampling methods are frequently limited by the high cost and difficulties in carrying out extensive monitoring in time and space. There has been increasing interest in the use of indirect monitoring methods, such as biomonitoring. Thus, mosses have been recognized as valuable airborne trace element biomonitors. In urban areas, where mosses are often scarce or even absent, the active biomonitoring (moss bags) has been developed with the aim of spatial and/or temporal assessment of atmospheric deposition. Since 2003 several studies have been carried out in the urban area of Belgrade using both instrumental and biomonitoring methods with the primary objective of assessing anthropogenic impacts on the environment by determination of trace element atmospheric pollution. Suspended PM_{10} were collected on filters using air sampler, while monthly atmospheric bulk depositions were collected monthly using bulk collectors. Active biomonitoring of trace elements with moss bags was performed with the aim to test the suitability of the moss, *Sphagnum girgensohnii* Russow, as an alternative method for air quality studies in urban areas. The elemental composition (Al, V, Cr, Mn, Fe, Ni, Cu, Zn, Cd, and Pb) of the moss samples was analyzed using instrumental neutron activation analysis (INAA), atomic absorption spectrometry (AAS), and inductively coupled mass spectrometry (ICP-MS). For the source apportionment purpose Unmix receptor model was used and the main source profiles were identified. Effects of regional sources were investigated using hybrid receptor models for identification of trace elements source regions: Potential Source

Contribution Function (PSCF) - describes the spatial distribution of probable geographical source locations inferred by using trajectories arriving at the sampling site; and Concentration Weighted Trajectory (CWT) model - determines the relative significance of potential sources. The impact of trace elements in PM_{10} on air quality and human health is considered as significant at receptor areas. PM_{10} penetrate into the human respiratory system, accumulate in human body and can exert health problems. The assessment of cancer and non-cancer health risk caused by the trace element content of PM_{10} in Belgrade was conducted using the US EPA health risk assessment model.

Chapter 2 – The determination of trace amounts of inorganic ions is of growing interest in several fields including environmental analysis, process control, biology, medicine, etc., and there is now a particular need for simple and fast field analytical tests. In contrast to well-established laboratory methods, such as atomic absorption or emission spectrometry, mass spectrometry or voltammetry, chemical sensors have attracted a great deal of interest in the last decade because of their great potential for in the field, *in situ*, continuous and remote, if required, applications. Flow-through optosensing emerged from the combination of Solid-Phase Spectroscopy (SPS) and Flow Injection Analysis (FIA). In SPS, an active solid support is used to pre-concentrate the target analyte and its spectroscopic detection is performed on the same solid support microbeads. The most remarkable features of SPS are its high sensitivity (it can be easily increased one hundred-fold due to the concentration of the target analyte on the solid beads) and selectivity (the interaction between the target chemical species and the solid phase beads is usually different from that one of co-existing species). In addition, the implementation of SPS in flow methods of analysis adds the inherent advantages of flow analysis, improving the analytical methods in terms of rapidity, commodity, automation, less consumption of reagents, etc. In these flow optosensors, the (micro) zone of the solid phase, where the signal is continuously monitored, is surrounded by a continuous stream flowing through it. The separation and retention of the species of interest on the solid phase takes place in the detection area itself and the spectroscopic determination is simultaneously performed. In this chapter, the authors will first describe the fundamentals of SPS from its origin, including some relevant examples. After that, they will focus on the versatility and potential of flow-through optosensing for the analysis of trace elements in a wide variety of samples related to human health, such as clinical samples (drugs, urine, and serum), food or environmental waters, emphasizing the most recent advances and future trends in this field.

Chapter 3 – Trace metals occur naturally in the earth's crust, but human activities have greatly increased the mobilization and bioavailability of metals and, therefore, the chance of exposure to harmful concentrations. In fact, they along with other pollutants are discharged in the environment through industrial activity, car exhaust, heavy-duty electric power generators, refuse burning and use of pesticides in agriculture etc. Natural baseline levels of trace metals in air, soil, rivers, lakes, and oceans are usually low, but in certain forms, and at sufficiently high concentrations, trace metals can be toxic to organisms. Trace elements play an important role in biological and biochemical reactions in the living cells. They are stable and cannot be metabolized by the organisms, so, through the food, they tend to bio-accumulate. If the accumulation rate is higher than the detoxification rate, they can reach toxic concentration levels. Toxic metals in the human body can "replacing" essential nutrients, especially if deficient; for example Pb can replace Ca, Al can replace Mg, etc.. The substitution allows the enzyme systems to continue its function, but, if the intoxication degree exceed the tolerable limits, serious diseases take over. The major source of trace metals for man is the food, in particular, fruit and vegetables that are essential components of the diet, by contributing protein, vitamins, iron, calcium and other nutrients in short supply. In recent years their consumption is gradually increasing, particularly in the urban community. However, because of the increased_environmental pollution, fruit and vegetables can also contain trace metals over a wide range of concentrations. That because the plants take off them from soil as well as from air particulate. In addition the contamination of fruit and vegetable products may be due also through irrigation with contaminated water, the use of fertilizers and metal-based pesticides, industrial emissions, transportation, the harvesting process, storage and/or at the point of sale. To monitor metal contents in these products is very important for crop yield technology, food nutrition and health impact. Many studies show that the trace metals at relatively high concentration may disturb the normal physiology (the normal functions of central nervous system, liver, lungs, heart, kidney and brain, produce hypertension, abdominal pain, skin eruptions, intestinal ulcer) until to produce different types of cancer.

Chapter 4 – Trace elements are essential to maintain physiological functions and it is well demonstrated that certain mineral supplementation in livestock can improve productivity. Mineral supplements are routinely incorporated into concentrate feed, even when not necessary, at doses largely (up to 10-fold) exceeding the physiological requirements; this is possible because there are fairly wide "safety margins" to avoid mineral toxicity, even though toxic effects on animals can appear when given at supra-optimal concentrations. A significant proportion of minerals that are given to livestock are excreted into urine and faeces, and this proportion increases as the margin of mineral supply over mineral requirement increases. This chapter addresses the main consequences of excessive livestock mineral supplementation on environmental pollution, the toxic effects on susceptible species when exposed to mineral enriched-slurries, and the pros and cons for human health of consuming animal products with a high mineral content.

Chapter 5 – Although trace elements are natural constituents of the environment, several of them present high toxicity, long persistency and quick accumulation in living organisms. For these reasons identification of trace element contamination sources and evaluation of their environmental impact are essential. Trace element pollution in estuaries has been considered a wide world problem for a long time. The principal pollution sources are atmospheric deposition (volcanic activity, combustion of fossil fuels, etc), land run-off (agricultural, mines, etc), direct industrial and urban inputs, fisheries and recreational uses. Once in water, trace elements are mainly adsorbed on suspended particle matter or colloids and deposited by flocculation in sediments, where they present different chemical forms. Thus sediments are important deposits of trace elements and hence an important tool to assess metal pollution in estuaries. Bibliographic data on the concentration of trace elements (As, Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn) measured in sediments from different estuaries of the world has been collected, summarized and compared with those experimentally obtained in two of the most important estuaries in the Basque Country (Urdaibai and Nerbioi-Ibaizabal). In general, it can be said that the concentration of trace element in sediments from the Nerbioi-Ibaizabal and Urdaibai estuaries are not alarming in comparison with other estuaries. Different tools have been used to identify diffuse and point sources in both estuaries.

Chapter 6 – The contamination of sediments by potentially harmful trace elements is of major concern, because of their toxicity, persistence and bioaccumulative nature. In many industrial and urban areas, sediments are the largest repository for, and potential source of these elements. Assessing trace element contamination of sediment is complicated since these elements are a ubiquitous, naturally occurring component of sediment, their concentrations in un-contaminated sediment can vary by orders of magnitude over relatively small spatial scales, and naturally occurring and anthropogenically introduced metals tend to accumulate in the same areas. Due to their particle reactivity, trace elements tend to accumulate in sediments and may persist in the environment long after their primary source has been removed. Element adsorption increases with decreasing grain size of the sediment. Thus, the metal concentrations significantly enriched in fine-grained sediment rich in clay minerals. Because of that, in geochemical and ecochemical studies, the normalization of elemental content using an immobile element is common practice for correcting grain-size effects and dilution by sedimentary phases such as carbonates and silica. The aims of the presented study were: (1) to assess the geochemistry of trace elements (Cr, Zn, Cd, Ni, Pb, and Cu) in canal sediments (Danube alluvial formation) and Tisa River sediments and its tributaries, after normalization of the elements data to a conservative element; (2) to discriminate natural and anthropogenic contributions; and (3) to identify possible sources of pollution. As the element for sediment normalization was used Al, since it represents aluminosilicates, the main group of minerals generally found in the fine sediment fractions. Flame atomic absorption spectrometry (FAAS) was used to determine the levels of the investigated elements. Multivariate statistical methods have been applied in this research to identify similarities in the sampling stations and to assess the relationship between the elements. The results from this study show that investigated sediments are affected by combined trace elements contamination. Also, there was shown a significance of applying geochemical normalization and statistical analysis for assessing trace element contamination and for distinguishing between natural and anthropogenic sources of trace elements in the sediments.

Chapter 7 – Zinc (Zn) deficiencies occur all over the world. Due to the naturally high soil fertility of the Pampas region, Argentina, macro and micronutrients have not been applied to soils through fertilization in a massive way. As a consequence, some trace elements deficiencies were noticed in some forage crops during the last years as a result of nutrient depletion. Trace mineral deficiencies were detected in dairy cows, causing a variety of suboptimal performances such as poor production and reproductive inefficiencies. Zinc and copper are the trace elements present in largest amounts in Buenos Aires City's biosolids. Soils amended with biosolids have been reported to have high Zn availability. Therefore, biosolids land application may raise the concentration of Zn in forage crops, reducing the need for mineral fertilisers or supplements in the diet of dairy farms. This chapter address sound soil and crop management practices that may not only enhance crop productivity but also help in reducing Zn deficiencies in dairy cattle.