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MEDICAL GEOCHEMICAL INVESTIGATIONS IN TAKING PRECAUTIONARY MEASURES AGAINST DISEASES. PROTECTION OF HUMAN HEALTH

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ABSTRACT

A considerable number of diseases are directly related to environmental impact. Toxic metals such as Hg, Pb, Cd, and As may damage significantly the human health when they exceed certain levels in the body. For example specific precautions should be taken for the diet of pregnant women and the children. Lead concentrations exceeding the safe values can cause severe damage to the development of central nervous system, as well as a general developmental delay of fetuses and young children, interfering with the functioning of almost every brain neurotransmitter. In particular for the pregnant women, it has been found that the exposure of the fetus on high lead values may cause, apart from neurological and behavioral problems, low birth weight, pre-term delivery, spontaneous abortion and stillbirth. Organic mercury (methyl mercury) is the most dangerous form of mercury, because it is the most easily absorbed orally and crosses into the brain and fetus so readily. Populations exposed to chemical compounds containing As, Ni, Cr, Cd, etc. are considered of high-risk in developing cancer.

Environmental geochemical studies can help in assessing the quality of the environment as well as the determination of the sources of pollutants, their behaviour and other characteristics. This knowledge is necessary in any application of remediation methodologies and waste management for the prevention of pollutants in getting into the food chain. It is also used in determining safe criteria regarding the quality of soils, drinking water, construction of schools, playgrounds etc. In this work the importance of environmental geochemical research and its applications towards the protection of human health is demonstrated.

KEYWORDS*:* Medical geochemistry, metals in human health, metals in cancer disease, metals in nervous diseases, Pb in fetus development, remediation methods, and job diseases.

1. INTRODUCTION

Results of epidemiological studies and laboratory experiments in combination with environmental geochemical studies have shown the impact of the environment on human health and development of diseases including cancer (Bennett, 1981; Spang, 1988; NIOSH, 1977). Environmental geochemical studies can help in assessing the quality of the environment as well as the determination of the sources of pollutants, their behaviour and other characteristics. In this work the importance of environmental geochemical research and its applications towards the protection of human health is demonstrated. On the basis of the results of geochemical studies remediation methodologies leading to prevention of toxic elements in getting into the food chain are applied, while criteria are put for the quality of soils, water etc. In addition decision makers are helped to make the necessary and right decisions in the management of toxic waste.

2. HEALTH RISKS

Populations exposed to chemical compounds containing As, Ni, Cr, Cu, Cd, etc. are considered of high-risk groups in developing cancer (EPA, 1984; Merian, 1991). The above and many other elements may cause various diseases in human beings (Merian, 1991; Nriagu, 1984).

High concentrations of manganese in human body can cause parkinson. Research in regard to the presence of Mn and other metals in the environment in relation to human health were carried out in Greece (Kondakis *et al.,* 1989, Leotsinidis and Kondakis, 1990). Similarly the levels of As in waters and sediments were investigated (Varnavas and Cronan, 1988; 1991; Aloupi *et al.,* 2009).

2.1. Toxic Metals in the Diet of Pregnant Women and the Children

Toxic metals such as Hg, Pb, Cd, and As may damage significantly the human health when they exceed certain levels in the body. Specific precautions should be taken for the diet of pregnant women and the children. During pregnancy, women need additional nutrient constituents in their diet. In an effort to take these with their food, there is a risk to get toxic elements, which may be very harmful for the health of both the pregnant and the fetus. During childhood, children may get toxic metals with their food present either in the preservatives or in the wrappings of the food.

The importance of the proper diet of pregnant women and the children in relation to the presence of toxic metals is given here, so as to avoid health risks. In order to achieve this, the necessary precautions are described, the knowledge of which is very useful for the protection of the health of pregnant women and the children.

Organic mercury (methyl mercury) is the most dangerous form of mercury, because it is the most easily absorbed orally and crosses into the brain and fetus so readily (Lappe and Calfin, 2002). The major source of organic mercury exposure is contaminated fish, particularly carnivorous fish such as swordfish, tuna, shark, and pike (Cook, 2001).

High amounts of lead present in the wrappers of food (i.e. sweets), in the printing ink on the surface of the food package, facilitate the uptake of lead by the children during eating sweets etc. In particular, it has been found that poly-vinyl-chloride (PVC) linings used for wrapping food contain lead, which can migrate from PVC to the food (Tarantino, 2006). For this reason FDA gives certain instructions to the manufacturers of PVC flexible lunchboxes. Lead concentrations exceeding the safe values can cause severe damage to the development of central nervous system, as well as a general developmental delay of fetus and young children, interfering with the functioning of almost every brain neurotransmitter (Farley, 1998). In particular for the pregnant women, it has been found that the exposure of the fetus on high lead values may cause, apart from neurological and behavioral problems, low birth weight, pre-term delivery, spontaneous abortion and stillbirth (Varnavas and Varnavas, 2007).

2.2.Specific Environments

2.2.1. Soils Adjacent to Major Roads

Car emissions may affect the quality of crops through metal accumulation and their distribution in various plant parts (Safaya and Gupta, 1979). The accumulation of metals in various plant parts of *Zea mays L.* has been reported in a number of studies (Jarausch – Wehrheim *et al.,* 1996; Xu *et al.,* 2002; Klejdus *et al.,* 2004). Heavy metal accumulation in edible plant parts may adversely affect consumers health. Maximum variability of metal concentration levels in the leaves and the normal, deficiency and toxicity levels have been reported by Pendias and Pendias (1992).

Critical levels of various heavy metals in plants and in the diet of animals, above which are considered to be toxic, have also been reported (Jones *et al.,* 1991; Sauerbeck, 1982). Significant production losses were reported for *Zea mays L*. when the zinc concentration in the leaves reached 792 μg g^{-1} (Safaya and Gupta, 1979). For many plant species, zinc concentrations in leaves have been found above 100 ppm. The sensitivity of *Zea mays L*. to zinc toxicity was investigated by White *et al.* (1976).

Several elements (Cd, Co, Cu, Mn, Ni, Pb, and Zn) in twelve different kinds of vegetables (tomatoes, eggplant, carrots, parsley, cucumber, marrow, potatoes, green pepper, lettuce, spinach, salad onions, leek, watercress and cabbages from Saudi Arabia were investigated (Muhammet *et al.,* 2003). The levels of total Cr in *Lycopersicum esculentum* were was determined to range between 0.008 – 0.026 μg g^{-1} (fresh weight of the edible fraction, Lendinez *et al.,* 2001). These levels are similar to those obtained by Vinas *et al*. (1995) and Chiffoleau and Bonneau (1994). The Cr levels tended to be higher in roots and tubers than in bulbs, whereas leaves and tender stalks had the lowest levels (Schuhmacher *et al.,* 1993). The excessive usage content of Cr in the vegetable products, but also in industrial contaminations, were also found (Zayed *et al.,* 1998). The diffuse pollution on agriculture product produced along the highways could be avoided by isolations distances suggested by Petit *et al. (*2009).

Several studies have demonstrated an apparent influence of traffic on both soil and crops grown in close proximity of major roads in Greece. Below two case studies are described one from the are a of Araxos with cultivations of: *Lycopersicum esculentum* and the other one from Lappas area with cultivations of *Solanum melongena*. The concentrations of heavy metals in soils and leaves of the plant species *Lycopersicum esculentum* and *Solanum melongena* at the edge of the road and 10 m from the road were determined. In general, the concentrations of heavy metals were found to be significantly lower when the plant species were cultivated at a distance 10 m from the major road. This is a result of the impact of road pollution on food-crops. Major sources of metals are the combustion of diesel and/or petrol, the wheels of the cars, as well as the dust from the limestone transported by the trucks.

The Mn concentrations measured in leaves of both species were lower in plants that were cultivated at a distance of 10 m from the major road. The concentration of Mn found in *Lycopersicum esculentum* cultivated at a distance of 10 m from the road was 87 ppm, (reduced by 51%, compared with that of 176 ppm in plants cultivated at the edge of the road). It is interesting to note that the decrease of Mn in the leaves of *Lycopersicum esculentum* is much greater, with regard to its decrease in *Solanum melongena* (Figure 1). In *Solanum melongena* cultivations, the reduction in Mn for plants at a distance of 10 m to the major road was 4 %. Decreases were observed in Cu concentrations of leaves of all species, when they were cultivated 10 m far from the major road. The percentage decreases of Cu levels in *Lycopersicum esculentum* and *Solanum melongena* were 19% and 2%, respectively. In plant species *Lycopersicum esculentum* and *Solanum melongena* the corresponding decreases of Zn were 7% and 0.3%, respectively.

Table 1. The decreases (%) in trace metal content of soils and leaves, grown 10 m from the road, with regard to samples at 0 m distance (Kalavrouziotis *et.al*., 2006)

Element	Trace element decreases (%) of soils and leaves, 10 m from the road (compared to samples at 0 m)			
	Lycopersicum esculentum		*Solanum melongena*	
	Leaves	Soils	Leaves	Soils
Mn	51	28	4	2
Al	9	17	10	12
Cu	19	47	2	37
Fe	4	25	20	4
Pb	8	7	54	8
Cr	30	23	13	16
Co	39	25	20	12

The decrease of Cr in *Lycopersicum esculentum* leaves was 30 %, but that in *Solanum melongena* leaves only 13%. Decreases in Co levels were observed to be 39% and 20% for *Lycopersicum esculentum* and *Solanum melongena*, cultivated at 10 m from the major road. The concentrations of Al in leaves of *Lycopersicum esculentum* and *Solanum melongena* were reduced by 9 and 10%, when cultivated 10 m far from the major road.

The concentrations of Fe in leaves of all plant species cultivated at a distance of 10 m from the major road were found to be lower than those in plants cultivated at the edge of the major road. In the leaves of *Solanum melongena*, the percentage decrease was found to be 20%, whereas that in *Lycopersicum esculenum* leaves was only 4%. Overall, it is shown that the concentrations of all elements studied in both *Lycopersicum esculentum* and *Solanum melongena* decrease from the edge of the road to 10 m distance. It is noted that the elemental concentrations in both soils and plants further decrease, away from the road edge and with distance from the road (Table 1, Figure 1). Therefore, it can be clearly deduced that there has been an input of these elements from the traffic. In conclusion the results demonstrated remarkable decreases in Pb, Zn, Cu, Ni, Cr and Co levels at 10 m distance from the road, compared to the examined samples from the edge of the road (Kalavrouziotis et. al., 2006). Other studies have shown increase in the concentrations of the (PGEs) =element group both in the soils and crops located in the vicinity of main roads (Kalavrouziotis and Koukoulakis, 2009). Therefore it is necessary that remediation methods should be applied on such soils and other precaution measures should be taken to prevent the pollutants to get into the food chain and protect the human health.

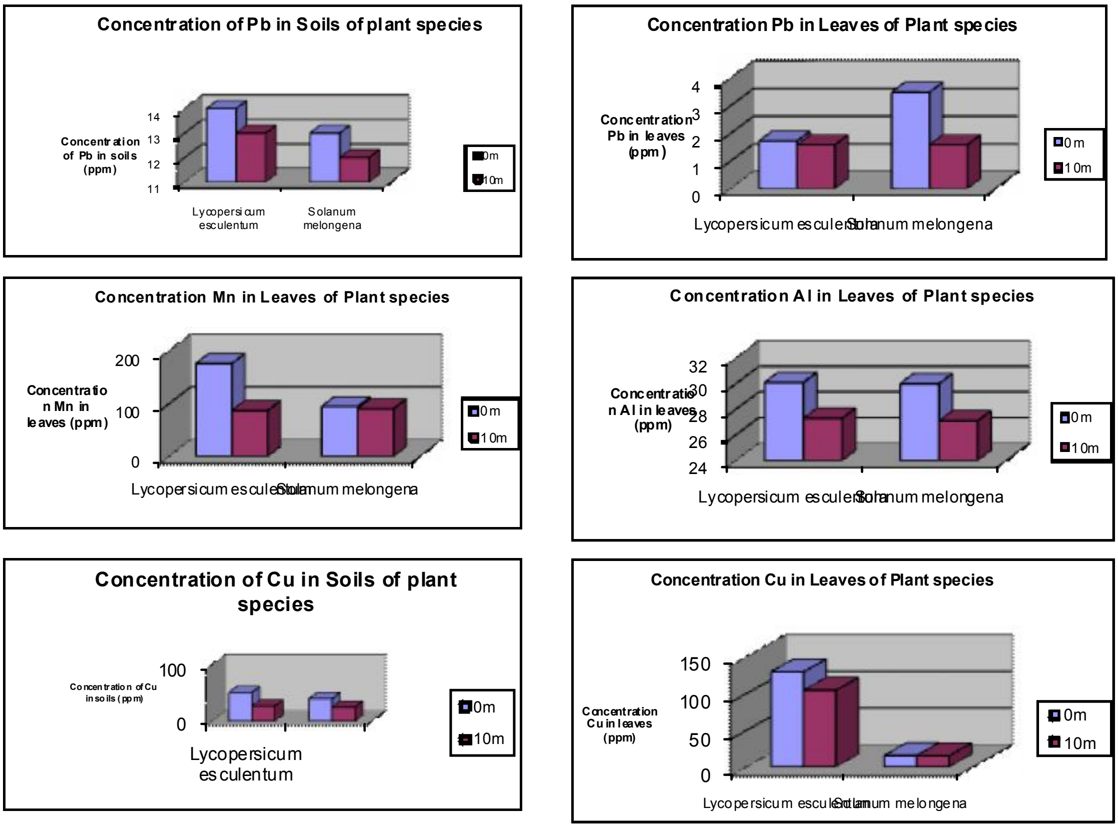


Figure 1. Concentrations of Mn, Cu, Zn, Fe, Al, Pb, Co and Cr in the soils and leaves of plant species which cultivated at the edge of the road and 10 m from the major road (Kalavrouziotis *et.al.,* 2006)

In relation to the vehicle road pollution of soil and plants, special models were obtained, under the assumption that the studied system has the structure "soil–roots–leaves" (Vissikirsky *et al.,* 2008). However, due to the insufficiency of the number of data samples at this initial stage of studies, as well as owing to the possible influence of other factors not included in the above structure, it was important to assess the level of uncertainty in the behaviour of chemical elements, in order to focus on unclear points in future experiments.

The qualitative analysis made possible to classify chemical elements according to the degree of similarity in their behaviour. Thus, the models (D, Ei (Cj)) → Ei (Ck)) used, enabled the preliminary solution whether an individual chemical element is the main factor of influence within the chains "soil–roots" and "roots–leaves". This makes possible to obtain initial classification of elements (factors) according to the degree of their influence, and to determine the level of certainty/uncertainty of the models. The obtained results could become the basis for the design of future experiments directed to resolve the uncertainties and obtain more detailed data about the behaviour of objects/elements.

Qualitative assessment simplifies the analysis of different combinations of subsets of analysed objects/factors, by considering them from different viewpoints, with the use of simple programming techniques.

This type of studies (modelling) could help significantly in the proper orientation of future research on road pollution of soil and food crops.

Investigations, related to vehicular pollution of highways, and its effect on food crop Zea *mays, L were also c*onducted in the highway of Araxos, area of Greece, An influence of vehicular emissions on the metal content of *Zea mays, L.* grown adjacent to the roadside, was exhibited, resulting in an increase of the dry matter heavy metal concentration of maize plants grown at the edge of the road. This increase however, did not exceed the critical metal toxicity levels. Nevertheless, higher levels of heavy metals accumulated in the roots of *Zea mays L.,* than the leaves, their effect being non-toxic to the plant growth (Kalavrouziotis *et al.,* 2007a; 2007b)

Linear regression showed that the soil heavy metal accumulation from the vehicular emissions was inversely related to the distance of soil sampling from the edge of the roadside, Also, quadratic fit to the data obtained, showed a further increase in the concentration of the metals with the increase of the distance above 40–50 m, suggesting theoretically, that the emitted metals could possibly be transported by the wind to greater distances. (Kalavrouziotis *et al.,*2007a.)

2.2.2. Mining Environments

Toxic solid waste occur in the area of Polis Chrysochous, near the Limni Mine mining area, 5 Km East of the town of Polis in the Paphos District, Cyprus (Figure 2). It was formed as a result of extended exploitation and mineral processing of sulphide minerals. Although the exploitation of copper deposits started in early times, it was more intensified between 1955 and 1979; then the mine was close down.

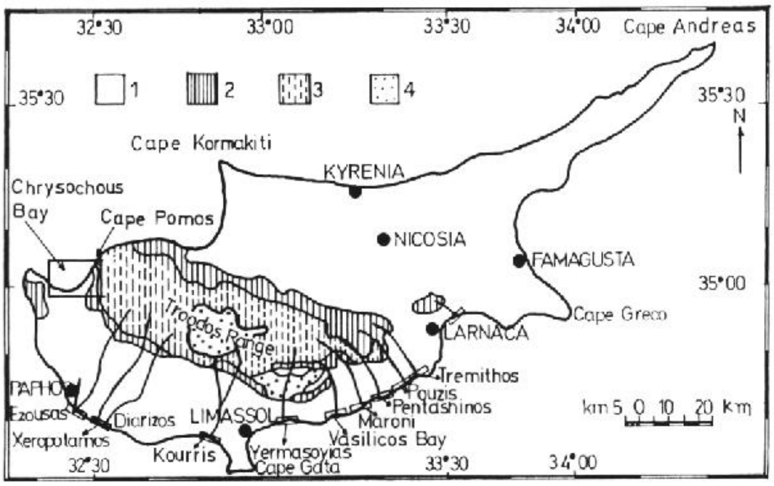


Figure 2. Map of Cyprus showing the geology of the Troodos massif 1: sedimentary rocks, 2: upper and lower pillow lavas, 3: basal group and diabase, 4: gabbro granophyre suite ultramafic suite (Constantinou, 1979) and the location of the area studied

During the above period, a total amount of 16,000,000 tons of ore was extracted, with an average content of 1.1% copper and 14.9% sulphur. In addition to the mining tailings present in the area, metal rich solid waste resulted from the mineral processing form distinct mounds. Also, remainings from metallurgical processes such as slags of pebble size are scattered in the area. Such slags occur on the beach investigated here. Environmental geochemical and mineralogical investigations on Chrysochou mining region were carried out by (Varnavas *et al*., 1990; 1994).

The environmental impact of the Limni Mine Cyprus mining activities was assessed on the basis of a detailed geochemical study. It was revealed that the mounds of toxic solid waste occurring in the area have undergone a high degree of chemical weathering leading to a wide dispersion of metals such as Fe, Cu, Zn, As, Mn in the surrounding area, including the beach. As a result of these processes large quantities of "pyrite sand" and its oxidation products occur on the adjacent beach, being a permanent source of toxic metals for the seawater.

Considering the metal rich dust formed and food production taking place in this highly metal polluted area, it is suggested that immediate action should be taken towards its remediation for the protection of the human health (Varnavas *et. al.,* 2000; 2001). Similar remediation actions should be taken also for other areas such as the Hermioni mining area in Greece (Varnavas *et.al.,* 1992; 1994).

2.2.3. Port Environnent and Maritime Transport

Ship emissions derived from the combustion of petroleum products contain harmful organic and inorganic substances that remain in air for a long period of time. Under certain meteorological conditions they can be taken up by human beings via respiratory and other systems. As a result of this, respiratory inflammations and neurological problems, cancer, even death, are caused (Bailey and Solomon, 2004; Cooper, 2003; Corbett and Fishbeck, 1997; Isakson *et al.,* 2000; Moreno *et al.,* 2004; Saxe and Larsen, 2004; Stone and Donaldson, 1998; Wilson and Spengler, 1996).The impacts of maritime transport activities as well as the environmental conditions occurring in the port of Patras and in the surroundings are currently being studied (Apostolopoulou and Varnavas, 2011). Preliminary results show that the maritime transport has severely affected the air quality in the area during peak periods (Figures 3, 4).

2.2.4. Wood Production and Management

The production preservation and industrial use of wood has a lot of environmental impacts. In the industrial use of wood, a variety of chemical compounds are used as preservatives of wood against fungi. The chemicals used for the preservation of wood usually are metal rich organic compounds, biokillers, etc. which cause severe environmental impact on the human health as well as on the ecosystems. The most common preservatives are: Chromate-Copper-Arsenate (Cr, Cu, As- CCA) and Cu, Zn, As. These are used under specific directions of Environmental Protection Agency of the United States (EPA), being introduced in the wood under pressure. Additionally, for the same purpose chemicals containing Hg are used against fungi, as well as organic compounds such as pentachlorophenole, Curichnapthaline. As a result of this, human health is being influenced on a great extent. For this reason, the World Health Organization, the European Union and the Environmental Protection Agency (EPA) as well as other National and International Organizations have put regulations which control the safety of working people during the above processes. More specifically, such criteria give emphasis on the management of wood waste (Table 2).

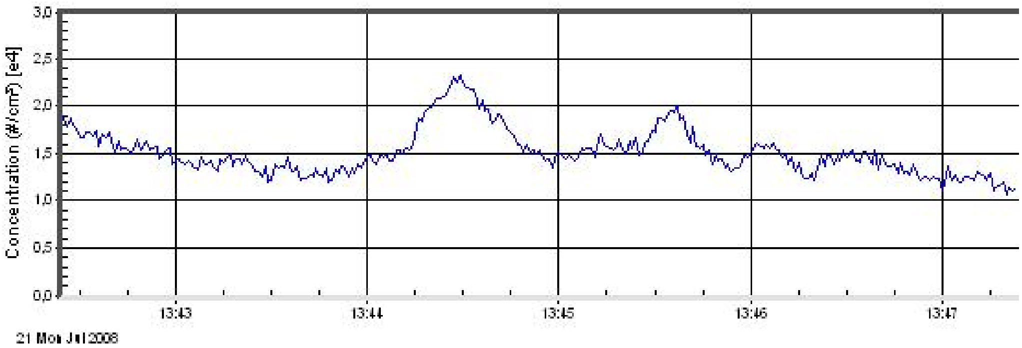


Figure3. Diagram showing the particulate content in air at the Patras port station. The peaks indicate approaching of ships

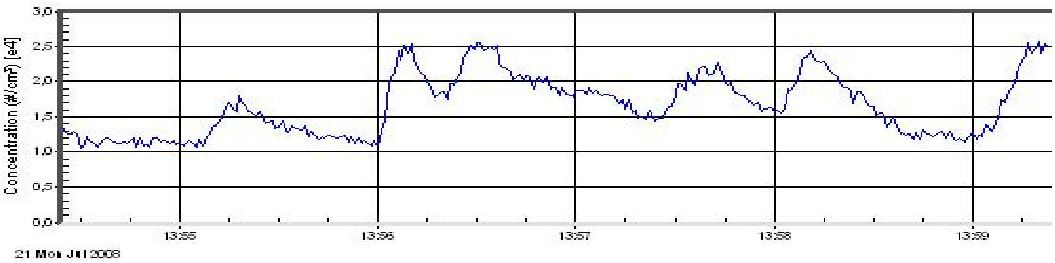


Figure 4. Diagram showing the particulate content in air at the Patras port station. The peaks indicate approaching of ships

Table 2. Chromium, Copper, and Arsenic Concentrations in Treated Wood and Treated Wood Ash Samples. Regulatory Levels Provided for Comparison (EPA, 2002)

Wood Type			Metals Concentration, mg metal per kg of wood or ash		
			Cr	Cu	As
Unburned Wood[a]	Untreated Wood		7.0	3.7	2.0
	CCA-Treated Wood at 0.25 pcf		2,060	1,230	1,850
	CCA-Treated Wood at 0.60 pcf		4,940	2,950	4,435
	CCA-Treated Wood at 2.50 pcf		20,600	12,300	18,500
Ash[b]	Non-CCA-Treated Wood		141	212	28
	CCA-Treated Wood at 0.25 pcf		20,600	11,200	11,400
	CCA-Treated Wood at 0.60 pcf		51,100	32,300	42,800
	CCA-Treated Wood at 2.50 pcf		174,000	104,000	113,500
Regulatory Limits	Federal	Ceiling (mg kg^{-1})	Not Applicable	4300	75
		Pollution (mg kg^{-1})	Not Applicable	1500	41
	Florida[d]	Industrial (mg kg^{-1})	430	12,000	3.7
		Residential (mg kg^{-1})	290	105	0.8

[a] Computed values assuming that retention rating equals amount of chemical in wood;
[b] Measured values; [c] Federal Register 40 CFR Part 503.13, Standards for the Use or Disposal of Sewage Sludge, Subpart B, Land Application; [d] Florida Department of Environmental Protection, Proposed Chapter 62-777, F.A.C. Contaminant Target Clean-up Levels

The conditions in Greece under which all above processes take place need to be investigated in regard to the contaminants released in the environment. Emphasis should be given to the management of wood waste. Considering the fact that the industrial use of wood is increasing with time, it is expected that in the future health damages of human beings associated with wood processing will be more pronounced.

It is advised that the use of chemicals on wood preservation should be avoided and should be used only in the cases where no other possibilities are found. The most commonly used compound is Urea - Formaldehyde (UF). Formaldehyde has the ability to be released with time in the environment and it is responsible for the “syndrome of ill building”. The investigation of such buildings showed that the responsible factors controlling the above syndrome include: temperature, humidity, air exchange as well as in-house environment pollutants, like dust, noise, and lighting.

It is seen that during the industrial use of wood, the use of wooden products and the management of wooden waste significant environmental problems are caused. Environmental geochemical research is needed towards the environmental protection by investigating the possibilities of reducing the pesticides used for wood preservation (Karaberou and Varnavas, 2004; 2007).

2.2.5. Wetlands and Lagoons

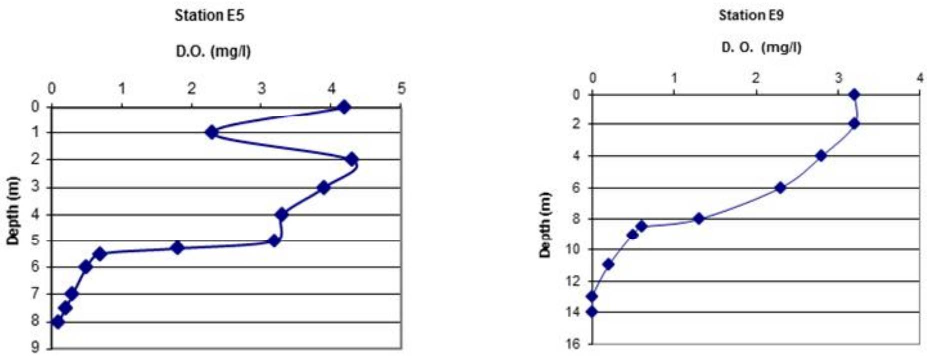
Wetlands and lagoon environments are important environments, both from economic and tourist point of view. Usually, a large number of human activities take place within or near these areas. Additionally, major natural processes and the results of wetland - land interaction processes lead to environmental changes, which have a negative influence on the life of people. Considering the fact that significant fishing activities take place in these environments and the environmental conditions influence the food production special attention should be taken on them.

The Aitolikon lagoon on the west Greek Coasts is an important marine environment (Voutsinou-Taliadouri and Satsmatsis, 1987) and the environmental conditions occurring there in relation to the behavior of pollutants are described as an example. Domestic sewage from the town of Aetolikon and from a number of adjacent villages are the main sources of pollutants in the lagoon. Another major source of pollutants is the existing pumping system on the west coast, bringing freshwaters in the lagoon. These are surface waters, which are collected in a pool prior to their discharge in the lagoon. Other sources of pollutants are related to human activities such as olive oil mills, the effluents of which are discharged in the lagoon through streams. Occasionally significant quantities of toxic gases are released from the seafloor, which escaping through the water column cause fish death and put in danger the health local people. Therefore, the study of the influence of these waters on the lagoon is of great importance. In order to achieve this, the following methodology was used:

a) in situ measurements were carried out for pH, conductivity, temperature; b) water sampling was carried out. Both, measurements and sampling were carried out at increasing distance from the site of discharge and at different seasons; c) The quantity of suspended solids in the waters at different sampling sites was measured. It was isolated and analyzed for a number of elements such as Cd, Pb, Cn, Cr, Zn, Mn, Al, Si, Fe and Ca.

An investigation of the fresh water - seawater interaction processes showed that at the transition from the freshwater to the seawater with slight increase of the salinity there is a sudden increase in the phosphorus value. This phenomenon was observed in December, January and May. Under the same conditions there is a tendency for metals to increase in the particulate matter. This is a result of increase of the degree of transfer of the ions from the dissolved to the solid form. The degree of incorporation of the metals studied in the solid form decreases in the following order: Mn>Zn>Cu>Cd>Fe. These are useful observations, which can be used in planning the decontamination of the lagoon.

Dissolved oxygen measurements were carried out in the hot period (June) in the deeper zone of the lagoon, which showed that D. O. decreases from the sea surface down to 8m depth. Just below this depth (8.5m) D.O. is below 1 mg l^{-1}, while below 9m down to the seafloor D. O. is zero (Figure 5).



(a) (b)

Figure 5. Vertical variability of dissolved oxygen at different stations (21.6.99, Varnavas, 2005)

2.2.6. Decontamination Methodology

In situ measurements (Figure 6) and laboratory work allowed the determination of the existing environmental conditions in the Aetoliko lagoon, which are of importance in planning its decontamination and management.

A major source of contaminants is the fresh water discharged in the lagoon by the pumping system. The study of the behavior of these contaminants, mainly phosphorous and toxic metals (i.e. Pb, Cd, Cr, etc.) suggests that removal of these contaminants will greatly improve the quality of the freshwater and in turn of the lagoon. Planning and construction of an artificial pond can achieve the removal of the contaminants.

It has been revealed that at intermediate water depths there is a cold layer at the top of which pollutants (i.e. Cd, Pb, Cr, Mn etc.) float in the form of particulate matter. Similar layer rich in pollutants also exists in shallow layers and near the seafloor. Sharp conductivity peaks characterize these.

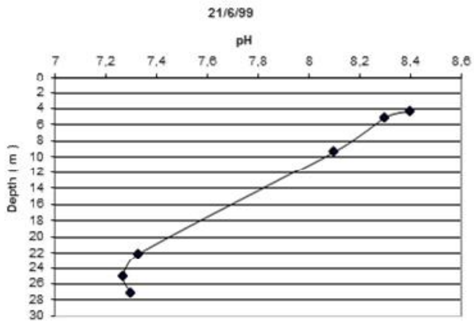


Figure 6. Vertical variability of pH (21.6.99, Varnavas, 2005)

The deep waters, where release of toxic gases takes place, are characterized by low pH relative to the waters of the upper part of the column. Further geochemical study is needed prior to take any action for improving the quality of the seafloor environment.
Below 9 m depth dissolved oxygen reaches zero value down the seafloor (32 m). It is therefore revealed that a large part of the water masses in the lagoon are under anoxic conditions.
It should be stressed that actions must be taken for decontamination of the lagoon for the following reasons:

i) The lagoon is a food source environment; fishing of large quantities of fish throughout the year takes place.
ii) Although it is not known whether toxic metals get into the food chain, their presence in large amounts may affect directly or indirectly the human health.(Varnavas,2005)

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