

## 2 Pollution in the environment

The past 200 years has seen a rapid increase in population's worldwide resulting in the need for even greater amounts of fuel and development of industrial chemicals, fertilizers, pesticides, and pharmaceuticals to sustain and to improve quality of life. Although many of these chemicals are utilized or destroyed, a high percentage are released into the air, water and soil, representing a potential environmental hazard (ALEXANDER 1995). A broad classification for pollutants based on their general characteristics or use is present on Table 2.1.

**Tab. 2.1: Classification of potential pollutants, the impacted media, and concerns (PIERZYNSKI et al. 2000)**

Pollutants	Examples	Medium impacted				Concern
		Soil	Water		Air	
			Ground	Surface		
Pesticides	Insecticides, herbicides, fungicides, etc.	*	*	*	*	Ecological risks, contaminated drinking water, human health
Hazardous organic chemicals	Fuels, solvents, volatile organic compounds	*	*	*	*	Ecological risks, contaminated drinking water, human health
Trace elements	Heavy metals, elements normally present at low concentrations in soils or plants	*	*	*		Human health concerns, ecological risk

Each pollutant category can impact more than one medium and each category can represent more than one process or member, e.g. the trace elements comprise more than 20 different elements (e.g. Pb, Cd, Zn, Cu, Fe, Ni, Mn, Hg etc.); the pesticides category represents a wide range of mostly organically based chemicals (e.g. PCBs, DDT, DDE, HCH). Hazardous organic chemicals (PAHs, HCB) represent a large number of organic chemicals, other than pesticides, that are commonly used as fuels and as materials for a variety of industrial processes.

Problems caused by contaminants depend on their distinctive characteristics and how these interact with biogeochemical pathways. Generally, pesticides, polyaromatic hydrocarbons (PAHs), and heavy metals have been produced and realised to the environment in large quantities. Once released, they are often long-lived and become dispersed. Pesticides are

distinct so, they can often be unequivocally associated with human activities as they have no natural sources.

### 2.1 Sources

#### 2.1.1 Sources of heavy metals

During the last two decades there has been a great progress in defining major anthropogenic and natural sources of Cd, Pb and other heavy metals (NRIAGU and PACYNA 1988; PACYNA 1996). It was concluded that high temperature processes, such as coal and oil combustion in electric power stations and heat and industrial plants, gasoline combustion, roasting and smelting of ores in non-ferrous metal smelters, melting operations in ferrous foundries, refuse incineration, and kiln operations in cement plants generate various heavy metals, which enter the atmosphere and the aquatic and terrestrial ecosystems. Practically every industry discharges one or more heavy metal in these ecosystems.

Pyrometallurgical processes in the primary non-ferrous metal industries are the major source of atmospheric As, Cd, Cu, In, Sb, and Zn, and important source of Pb and Se. Combustion of coal in electric power and industrial, commercial, and residential burners is the major source of anthropogenic Hg, Mo, Se, and a significant source of As, Cr, Mn, Sb, Tl. Combustion of oil for the same purpose is the most important source of V and Ni. Combustion of leaded gasoline is still the major source of Pb. Chromium and Mn are derived primarily from the iron and steel industry.

The estimates made by NRIAGU and PACYNA (1988) suggest that soils are receiving large quantities of heavy metals from disposal of a variety of industrial wastes. The two principal sources of heavy metals in soils worldwide are however, the disposal of ash residues from coal combustion and the general wastage of commercial products on land. Urban refuse represents an important source of Cu, Hg, Pb, and Zn with notable contributions of Cd, Pb, and V also coming via the atmosphere. The large volumes of wastes associated with animal husbandry, logging, as well as agricultural and food production can affect the heavy metal budget of many soils significantly. Although municipal sewage sludge may not be particularly important source on a global scale, it can be one of the most important sources of metal contamination of soils on a local scale.

A global assessment of natural sources of atmospheric heavy metals has been made by NRIAGU (1989). Biogenic sources can account on average for over 50% of Se, Hg, and Mo, and from 30 to 50% of the As, Cd, Cu, Mn, Pb, and Zn, released annually to the atmosphere from natural sources. Volcanic emanations can account for 40 to 50% of the Cd and Hg and 20 to 40% of the As, Cr, Cu, Ni, Pb, and Sb emitted annually from natural sources. Finally, soil-derived dusts can account for over 50% of the total Cr, Mn, and V emissions, as well as for 20 to 30% of the Cu, Mo, Ni, Pb, Sb, and Zn released annually to the atmosphere. Table 2.2 compare natural and anthropogenic emissions of trace elements.

**Tab. 2.2: Estimated natural and anthropogenic global emissions of trace metals to the atmosphere for selected elements (NRIAGU and PACYNA 1988; NRIAGU 1989; PACYNA 1996)**

Element	Natural (kt/year)	Anthropogenic (kt/year)	Approx. ratio anthropogenic/natural
Arsenic	1.1-33.5	12.0-25.6	1
Cadmium	0.1-3.9	3.2-12.0	4
Copper	2.2-53.8	19.7-50.8	1
Lead	0.9-23.5	287.5-376.0	27
Mercury	~2	3.5-4.5	2
Selenium	0.7-18.1	1.7-5.8	<1
Vanadium	1.6-54.2	30.0-141.8	3
Zinc	4.0-85.9	70.4-193.5	3

A comparison of the worldwide emissions of heavy metals from natural and anthropogenic sources suggest that human activities generate emissions of heavy metals in such quantities that they significantly exceed emissions from natural sources. For Pb, Cd and Hg the global anthropogenic emissions exceed global natural emissions by factors of 27, 4 and 2 respectively.

#### 2.1.2. Sources of organic pollutants

The groups of persistent organic pollutants that have raised most by concern internationally and determined as priority pollutants of the US Environmental Protection Agency (EPA, KEITH and TELLIARD 1979) are: the polycyclic aromatic hydrocarbons (PAH) and some of the persistent chlorinated organic compounds, such as DDX-group (o,p'-DDE; p,p'-DDE; o,p'-DDT; p,p'-DDT, o,p'-DDD, p,p'-DDD), PCB (polychlorinated biphenyls), HCB

(hexachlorobenzene) and HCH (isomers of hexachloro- cyclohexane including lindane,  $\gamma$ -HCH).

POLYCYCLIC AROMATIC HYDROCARBONS are widely distributed in the environment. They are produced at large quantities by natural processes with result that environmental samples may contain both natural and contaminant PAHs. Natural sources include: natural fires, volcanic activity (SUESS 1976; SHABAD and ILNITSKII 1979); natural losses or seeps of petroleum or coals deposits; and diagenetic production in soils and sediments (MACDONALD et al. 2000). They are both an important component of crude and refined oil and they are produced during the incomplete combustion of coal, wood, and oil (LOCKHART et al. 1992; YUNKER et al. 1993). Highly alkylated congeners, found in crude and refined oil (YUNKER and MACDONALD 1995), often have greater adverse effects than parent PAH (without alkyl substitutions) on biota (PACYNA and OEHME 1988; HELLOU et al. 1995). PAHs are semi-volatile and those of high molecular weight tend to become attached to particles. Concentrations in soil are considered as a useful indicator of air pollution levels, and this concentration in soil correlates significantly with the corresponding levels in air (VOGT et al. 1987), house dust (CHUANG et al. 1995), urban street dust (TAKADA et al. 1990) and plants (WANG and MERESZ 1982).

The group of organochlorines includes chlorinated industrial compounds and pesticides. The organochlorines were chemically persistent and semi-volatile. Their vapour pressures were sufficiently high to cause appreciable evaporation over a period of weeks to years, enabling the compounds to cycle between gaseous and condensed phases in the environment. The presence of chlorine in the organic molecule tends to enhance persistence. The low cost and efficacy of these pesticides has resulted in their intensive use over a large part of the globe, including tropical regions, from 1950s to present. Their use in warm climates enhances their global mobility (MACDONALD et al. 2000).

POLYCHLORINATED BIPHENYLS, examples of an industrial organochlorines, were used as hydraulic, transformer and heat-exchange (STRECK and WEBER 1982; TANABE 1988; HARRAD et al. 1994). Due to their low water solubility they remain in the environment although the PCB production and use has been significantly reduced since mid 70s or even stopped in some countries. However, large-scale release to the environment over several decades and their persistence has made them a ubiquitous contaminant. Currently, a major

source of them releases to air, water, and soil occurs from the cycling of PCBs remaining in the environment from one medium to another. This cycling process involves volatilization from aquatic and terrestrial surfaces into the atmosphere, and then subsequent redeposition of these compounds onto the Earth's surface (ATSDR 1996).

HEXACHLOROCYCLOHEXANE is an insecticide that was heavily used within Europe (BREIVIK et al. 1999) and other parts of the world (LI 1999;). Principally, two formulations have been made for use as an insecticide. One is technical HCH it is the unpurified technical mixture of various isomers (about 55-80 %  $\alpha$ -HCH, 5-14 %  $\beta$ -HCH, 8-15 %  $\gamma$ -HCH as well as minor quantities of  $\delta$ -HCH and  $\epsilon$ -HCH). Within this "raw" product, only  $\gamma$ -HCH has any significant insecticidal properties (BREIVIK et al. 1999). The other HCH-insecticide is lindane or essentially pure  $\gamma$ -HCH. Hexachlorocyclohexane has been used as a broad-spectrum contact and ingested insecticide against grasshoppers, cohort insects, rice insects, wireworms and other soil pests. It has also been used for seed protection, poultry and livestock treatment, household vector control, lumber protection, and even for rodent baits.

HEXACHLOROBENZENE has been regarded over many years as an ubiquitously occurring persistent environmental chemical. Since 1945 it has largely been used as pesticide and fungicide in seed dressings, in particular for wheat (BALLSCHMITER et al. 1985). Its use as plasticiser and flame protection agent in plastics and the development of HCB during the production of wood preservatives on the basis of pentachlorophenols, during chlorination and several technical combustion processes (waste incineration, incineration of chlorinated wastes) must also be considered as relevant sources of HCB input into soil (KORTE 1992).

DDT is an organochlorine insecticide used mainly to control mosquito-borne malaria. It was introduced as a synthetic insecticide in 1939 (CLARK 1992). Although DDT have been banned or restricted for nearly three decades in some countries but it is still used in some countries (FEDEROV 1997). Commercial DDT is actually made from a mixture of DDT, DDE and DDD. The properties that make it good pesticide (persistence, low solubility, and low price) also make it hazard to the environment. DDT is often applied to fields as a dust or suspended in water. It may be mobilized in runoff, adsorbed to fine-sized particulate and

enter the water supply. DDT also enters the atmosphere during spraying and from evaporation of treated surfaces. It adsorbs strongly onto particles and is transported by atmospheric dust and smog (JENSEN et al. 1997). Once ingested, DDT and its metabolites accumulate in the fatty tissues of organisms and bioconcentrate up the food chain.

### **2.2 Transport and deposition**

Physical, chemical, and biological processes influence the fate and the transport of pollutant in the environment. The tendencies and the rates at which these processes occur, depend on the physical and chemical properties of individual component and their mixtures and site-specific environmental conditions. For a long time it has been recognised that the atmosphere is an important pathways for the transport of pollutants from industrialized and densely populated areas to ecosystems near to, or far from these areas (VAN JAARSVELD et al. 1997).

Following the release into the atmosphere, heavy metals can be either deposited in the vicinity of the emission source or subject to long-range transport via air masses. In most cases (except for Hg and some extent Se), emission of heavy metals occurs on particles. The size of emitted particles containing heavy metals as well as the temperature and speed of exhaust gases and the height of the emission source are the major factors influencing the relative proportion of metals, deposited locally and transported over long distances. The atmospheric deposition of heavy metals dominates by dry deposition (BERGKVIST 1986; LINDBERG et al. 1989; FERGUSSON 1990). The mobilisation of heavy metals from smelter and mine spoil by transport with seepage waters or by windblown dust may also be an important source of soil contamination in some industrial regions.

Many organic pollutants are susceptible to dispersion on a regional and global scale because they are both persistent in the environment and have a volatility that enables them to move between the atmosphere and the Earth surface in repeated temperature-driven cycles of deposition and evaporation (WANIA and MACKAY 1995). This cycling process has important consequences for the global distribution process of POPs. The atmospheric residence time of those attached to particles is typically for a few days. These POPs can be modelled in a similar way as the aerosol bound pollutants such as heavy metals. However,

many of these components are semi-volatile under atmospheric conditions and may occur both in the gas phase and as attached to particles depending on the vapour pressure of the compounds. Atmospheric deposition of persistent organic pollutant to soils occurs by the processes of wet and dry deposition which can occur in either of two phases. In the case of wet deposition, the compound is either dissolved in the precipitation, or it is associated with atmospheric aerosols that are scavenged by the precipitation. For dry deposition the compound is deposited to soils by atmospheric turbulence and molecular diffusion, and if it is associated with particles also by gravitational settling or impaction. Soils with vegetated surfaces will receive an important additional input from decaying plant material because vegetation has been shown to be an effective scavenger of both particle- and gaseous-phase from the atmosphere (ALDER et al. 1997).

Once deposited to the soil, the compounds will be subject to various partitioning, degradation and transport/mixing processes, which will ultimately control their vertical distribution in the soil. Metals accumulated in soils are depleted slowly by leaching, plant uptake, erosion or deflation (KABATA-PENDIAS and PENDIAS 1984). Metal mobility in soils is influenced by various factors such as pH and redox status, type and quantity of soil present, the concentration and type of competing ions and mainly the presence of complexing ligands both organic and inorganic. Complex formation between metal and soluble organic matter affects metal adsorption and hence their mobility. BOLTON and EVANS (1991) reported that dissolved organic matter in leaches of municipal waste materials is one important factor in relation to the solubilisation and further migration of heavy metals through the soil. However, in systems when the organic ligand is adsorbed by soil surface, metal adsorption may be enhanced by the complexation of metal to the surface adsorbed ligand (MCLEAN and BLEDSOE 1995). Runoff and erosion losses of trace elements can be also a major transport mechanism in environment (PIERZYNSKI et al. 2000).

Organic compounds are accumulated mainly in the humus layer of soil (STREK and WEBER 1982). The further pathways of component dissipation in contaminated soil may be volatilisation, irreversible sorption, leaching, accumulation by plants, and biodegradation (REILLEY et al. 1996). Strong sorption coupled with very low water solubility and very low vapour pressures made leaching and volatilisation insignificant pathway of PAH dissipation (PARK et al. 1990). Also plants hardly take up any PAH from soil (SHABAD and

ILNITSKII 1979; SIMS and OVERCASH 1983). Soil bacteria are the primary degraders of PAH in soil (GIBSON and SUBRAMANIAN 1984; BOLDRIN et al. 1993). Only a small fraction of the less hydrophobic PCBs and PAHs is likely to partition into soil-water and can be transported by convection (i.e. leaching) or diffusion, although transport in the dissolved-phase may be enhanced by association of those components with dissolved organic matter or organic colloids (COUNCIL OF THE.. 1996; BERSET and HOLZER 1995). Small fractions of the lighter weight PCBs and PAHs will also partition to soil-air and can be transported in that medium. As PCBs and PAHs will predominantly partition to the soil organic matter the transport in the solid-phase is likely to be very important. The concentrations of PCBs in soils generally increases as particle size decreases (SCHARPENSEEL et al. 1977; PIERARD et al. 1996).

Two processes that are likely to be important are displacement of the sorbed compounds by burrowing animals (bioturbation) and transport of particles downward by water moving through the soil. In agricultural soils it is mostly earthworms that play a significant role in material displacement. OEHLENSCHLÄGER (1986) estimated that it takes only 5-20 years for earthworms to turn over the top soil once in grasslands, resulting in more or less homogeneous mixing. The movement of particles through the soil will be dependent on soil properties (e.g. soil organic matter content and texture) and on the nature of the particles (e.g. diameter).

### **2.3 Persistence in environment and ecotoxicology**

The persistence of contaminants in soil is much longer than in other components of the biosphere, and contamination of soil appears to be virtually permanent. The first half-life of heavy metals, as calculated by IMURA et al. (1977) for soils in lysimetric conditions, varies greatly – for Zn, 70 to 510 years; for Cd, 13 to 1100 years; for Cu, 310 to 1500 years; and for Pb, 740 to 5900 years. The range of half-lives for PAH in soil estimated by different researchers is quite large. They vary, dependent on the compound, from 2 months to 2 years (MACKAY et al. 1992) and from 8 to 28 years (WILD et al. 1990). Microbial degradation of DDT, DDD, and DDE is generally slow, resulting in environmental persistence of these compounds. Under certain conditions DDT may degrade to DDD with a half-life of a few days (GARRISON et al. 2000).



An increase in the concentration of chemicals (pollutant) in organisms that live in environment contaminated by a wide variety of organic and inorganic contaminants was result of pollution. These compounds are not usually decomposed in the environment (i.e. they are not biodegradable) or metabolized by the organisms, so that their rate of absorption and storage is greater than their rate of excretion. Therefore these chemicals are persistent and their go along food chain.

Heavy metals are easily incorporated into biological molecules and exert their toxic effects by displacing essential metals of a lower binding power in biologically active molecules or by acting as non-competitive inhibitors of enzymes. Regarding the heavy metals considered, it is important to realise that Cu and Zn are essential to all living organisms, being a co-factor in numerous enzymes. Apart from toxic levels, Cu and Zn deficiencies may also occur in terrestrial ecosystems, such as forests. There are also indications that Ni may be essential to plants (found in *Urease* enzyme), whereas Cr may be involved in the sugar metabolism in mammals. With respect to Pb and Cd, no biological function is known (MCBRIDE 1994). Specifically Cd and to a lesser extent Pb are thus toxic. All metals, however, can become toxic to various living organisms in a terrestrial ecosystem.

CADMIUM accumulates in the kidney and the liver. Kidney damage leads to a loss of proteins and essential minerals, even at modest exposures. Cadmium-induced kidney damage is irreversible (SEILER et al. 1988).

The exposure pathways for LEAD are air, food, and drinking water are the major sources. Lead is toxic to the process that builds red blood cells, leading to anemia. The most disconcerting damage, however, is on children's neurological development (SEILER et al. 1988).

Persistent organic compounds convert into carcinogens through metabolic activation in the organism. In many circumstances the environmental occurrence of these components has been associated with adverse effects on public health.

HEXACHLOROCYCLOHEXANE is accumulating in fatty tissues and people are exposed via food. The body excretes them slowly via breast milk, feces, and urine. The most toxic form,  $\gamma$ -hexachlorocyclohexane, also called lindane, can affect the liver, the nervous sys-

tem, the kidneys, the reproductive system, and perhaps also the immune system. Lindane is a possible human carcinogen (TOMLIN 1994).

In humans, animals, and the environment, DDT is converted to DDE. Both substances accumulate in fat. People may be exposed through the food they eat or directly when the pesticide is sprayed. The human body can only get rid of DDT and DDE very slowly, mostly via urine and feces. DDT and DDE have a range of effects, the most serious of which relate to reproduction, development, the nervous systems, and cancer (TOMLIN 1994).

HEXACHLOROBENZENE has a range of toxic effects including damage to the liver, the skin, and the immune system. It can also cause neurological changes, cardiovascular effects, and reproductive effects.

PCBs are highly persistent and accumulate in fatty tissues. They are only slowly excreted, mainly via breast milk. Some PCBs have dioxin-like effects. These compounds have been implicated in effects on the liver, reproduction and birth weight of infants, neurobehavioral development, and the immune system. PCBs may also cause cancer (STRECK and WEBER 1982; TANABE 1988; HARRAD et al. 1994).

PAH are important environmentally because many individual compounds are genotoxic (WHITE et al. 1998) and may cause mutations and certain types of cancer. The important sources for humans are local, with tobacco smoke as the main exposure route. Wood smoke and smoke from other fuel sources also contribute to exposure both indoors and outdoors.

### 2.4 Bulgaria

The Republic of Bulgaria is situated on the Balkan Peninsula between 44°13' and 41°14' northern latitude and between 22°21' and 28°36' of eastern length. Bulgaria is bounded on the north by Romania, on the east by the Black Sea, on the south by Turkey and Greece, and on the west by the federal Republic of Yugoslavia (Serbia and Montenegro) and the Republic of Macedonia. The area of Bulgaria is 110 912 km<sup>2</sup>. More than half of Bulgaria is hilly or mountainous; the average elevation is about 480 m. The Balkan Mountains cross the country from the northwestern corner to the Black Sea. The northern side of the Balkan Mountains slopes gradually to the northern Bulgarian plateau, which ends at the Danube River. The central portion of the southern side of the range is fringed by a series of narrow plains, notably the Thracian Plain, an important agricultural region. In the southern part of the country there are the broad and irregular Rhodopi Mountains, which delineate most of Bulgaria's southern boundary with Greece. At the western end of these mountains there are the Rila Mountains, which culminate at Musala (2925 m), the highest peak in the Balkans. Several smaller ranges lie westernly. The country can be divided into three parallel east-west zones: the Danubian tableland in the north; the Balkan Mountains in the centre; and the Thracian Plain and the Rhodope and Pirin Mountains in the south.

#### 2.4.1 Soil types

Bulgaria is situated in a transition-zone of the Mediterranean, the continental and the oceanic-central European climate. Thus transitions between the Mediterranean expect Eastern European and Central European soil types. The soils of Bulgaria have a long history of the development while also to climatic conditions changed. The soil formation (profile differentiation) consequently is very intensive (KOINOV 1986). The soil map of Bulgaria according FAO classification is presented in Figure A3 (appendix). The Cambisols (35.6%), Chernozems (19.89%) and Luvisols (17.36%), are the most widely spread in the territory of Bulgaria, followed by the Kastanozems (7.08%), Vertisols (6.64%) and Planosols (6.18%). The Fluvisols (4.18%) and Leptosols (1.93%) are of a limited spreading, while the areas of the Solonetz and Solonchaks (0.54%), Alisols (0.24%), and Gleysosl (0.10%), are at their lowest.

The Kastanozems' spreading is connected with loess, and semi-arid climate that has penetrated inside the country along the valley of the Danube River. The Chernozems are characteristic of the Moesian platform in North Bulgaria having subhumid – dry climate, but along with the Vertisols are also found in the valleys of South Bulgaria. The Luvisols and Planosols occupy the hilly and low-mountainous territories of the Alpine system, while the Cambisols characterize the Rhodopes massif and the remaining hilly and mountainous territories of the country. The Alisols are developed onto chloritic and amphibolic shales in the conditions of subhumid climate under Oriental beech and periwinkle as a shrub stratum. The Podzols and Podzoluvisol are of a limited spreading in the high mountainous, while typical representatives of the Andosols are not still found in the territory of the country (BOYADGIEV 1997).

### 2.4.2 Soil pollution

The main resources of Bulgaria are agricultural. The country also has a wealth of metallic and non-metallic minerals, mainly iron ore and coal. Approximately 20 percent of Bulgaria's agricultural, forest and urban lands are degraded or polluted. Natural causes such as erosion and acidification account for nearly 80 percent of the areas affected. The most serious environmental problems in Bulgaria are localized in specific areas, where point sources or groups of sources of pollution cause hazards to the health of the local population. Pollution in that area is mostly due to heavy industry (ferrous and non-ferrous metallurgy, chemical and cement factories) and is as severe as in the most polluted areas of Central Europe.

The diagnosis of trace element soil contamination requires knowledge of the original contents of these elements in soil, in other words, the pedogeochemical background content. This may be sought either by analysing the corresponding horizons of non-contaminated soils of the same type or by analysing the deep horizons of surface-contaminated soils. From available data about background content of trace elements in Bulgarian soil it seems that in most cases these concentrations are higher than mean concentration in other country. This is demonstrated by data in Table 2.3.



for the soils at early stage of weathering and profile development, where the pedogenic processes have not considerably changed the chemical and mineralogical composition of soil parent materials.

In soils located in the vicinity of point sources of pollutants like Cu-Zn-Pb smelters, the content of the trace elements is determined essentially by the deposition of air-transported particles containing these elements and the distance of the site from the source of pollution (ATANASSOV and ANGELOVA 1995; DIMITROV 1998). The concentration of the trace elements in surface soil horizons in case of pollutants deposition may prevail few times the naturally occurring background contents (HINOV and FAITONDJIEV 1977).

In Southern Bulgaria there are two big sources of heavy metals in Plovdiv and Pirdop. The Lead and Zinc smelter near Plovdiv is opened in 1963 and since then there have been continuously emitting dust in the atmosphere air containing Pb, Zn, Cd, Cu and some other heavy and toxic elements. It is estimated by DANCHEVA et al. (1990) that this emission is about 460 ton per year. Due to the air transportation the soils in the vicinity of the smelter are polluted.

The other source of heavy metals is MDK – Pirdop plant near Pirdop town. The smelter was opened in 1959 and its yearly capacity to produce blister copper is 120 000 tons. Besides the copper the plant also produces 1600 metric tons sulphuric acid per day and some amounts of Au, Ag and other chemical elements. Since the time of opening the MDK-Pirdop plant has been continuously emitting dust and gases, waste waters and solid materials into the surrounding environment. It is estimated that annually the Cu-Smelter has been emitting into the atmosphere approximately 17 tons of Cu, 1.2 tons of As, 1.4 tons of Pb, 1.3 tons of Cd, 100 tons dust (containing pollutants) and about 11 000 tons of SO<sub>2</sub> (as S). The toxic substances are carried away by the wind to different distances but the main part of them falls down in the vicinity of the Cu-smelter in soils, surface waters, and vegetation thus affecting the human population.