7 Summary

The soils are considered as a main and most important natural resource for Bulgaria, which are used in agriculture, forestry and many other branches of national economy. But the quality of the soils in same locations and their multifunctionality are threaten with the impact of a great number of point and diffuse sources of inorganic and organic pollutants. These sources of pollutants are connected with industrial activities during last 40 years.

Approximately 20 percent of Bulgaria's agricultural, forest and urban lands are degraded or polluted. The most serious environmental problems are localized in specific areas, where point sources of pollution cause hazards to the health of the local population. Pollution in those areas is mostly due to heavy industry (ferrous and non-ferrous metallurgy, chemical and cement factories) as well as to agriculture (fertilizers, pesticides, etc.), which is developed in those regions. As a result of these anthropogenic emissions into the environment, their toxicity, make the heavy metals and priority organic pollutants the ecotoxicological relevant problem in terrestrial ecosystems.

In southern Bulgaria is situated one of the main agricultural region – the Thracian Plain. In this region also are localized several point sources of heavy metals. Bulgarian soils are from accumulative type with retention of heavy metals during pedogenesis. Due to the developmend of powerful adsorbent of clay minerals, and also to high content of organic matter, which offers ideal adsorbent with a high sorption potential for different kind of pollutants. And due to the multiplicity of sources of emission, mainly anthopogenic, resulting of significant contamination in soils, as well near to the source as in background territories, reflecting via atmospheric deposition.

Important criteria for assessment the degree of contamination of soils, situated near to the point sources are the background values of inorganic and organic pollutants. But in case of polluted soils the values are difficult to be determined, because of the absence of the methods to distinguish the natural and anthropogenic contents of the chemical substances in soil horizons. This investigation was carried out as an attempt to find out a method for determination the background contents of some inorganic substances, which is not influenced by the degree of pollution in soils. For this purpose the total content of Cd, Cu, Ni, Pb, and Zn had been determined in whole soil samples and in particle-size fractions extracted from

main soil horizons of five representative soil profiles, situated in polluted and unpolluted sites in South Bulgaria.

The investigated soils are distinguished in two groups: polluted P1, P2, P3 (arable lands) and non-polluted P4, P5 (forest soils). Determined concentrations of studied elements in soil surface of P1, P2 and P3, which are in the impact zone of point sources of heavy metals, are for Cd: 2–32 mg/kg; Cu: 136-180 mg/kg; Ni: 34-54 mg/kg; Pb: 33-1370 mg/kg; Zn: 65-1890 mg/kg (Figure 7.1). The determined values varying in wide ranges and for elements (Cu, Pb and Zn) prevail the maximum permissible concentrations (MPC) according Bulgarian state standards, showing significant level of pollution from near Cu-Pb-Zn plants. Generally, the depth distribution profiles of studied metals show a similar course in all investigated soils: a significant accumulation in the upper approximately 30 cm of the soil profiles (plough layer) followed by a strong decrease below this layer and no metal migration into deeper horizons can be observed. The total amount of the elements in subsurface soil horizons is approximately as high, as variation of background values of these elements in the soils of Bulgaria.

Unlike arable soils, forest ecosystems are particularly affected by atmospheric input of heavy metals due to the filter effect of the canopy. The determined concentrations of investigated elements in forest soils are for Cd: <1mg/kg; Cu: 10-34 mg/kg; Ni: 15-80 mg/kg; Pb: 41-42 mg/kg; Zn: 70-153 mg/kg (Figure 7.1) and they are near to background values for Bulgarian soils. The main role in distribution of the trace elements in these soils plays the processes of leaching. There are no evidences for significant differentiation in the content of Cd, Cu, Ni, Zn and Pb between soil horizons and soil forming materials in this soils. This is result of absence of contamination and deep weathering in the soil-forming rocks.

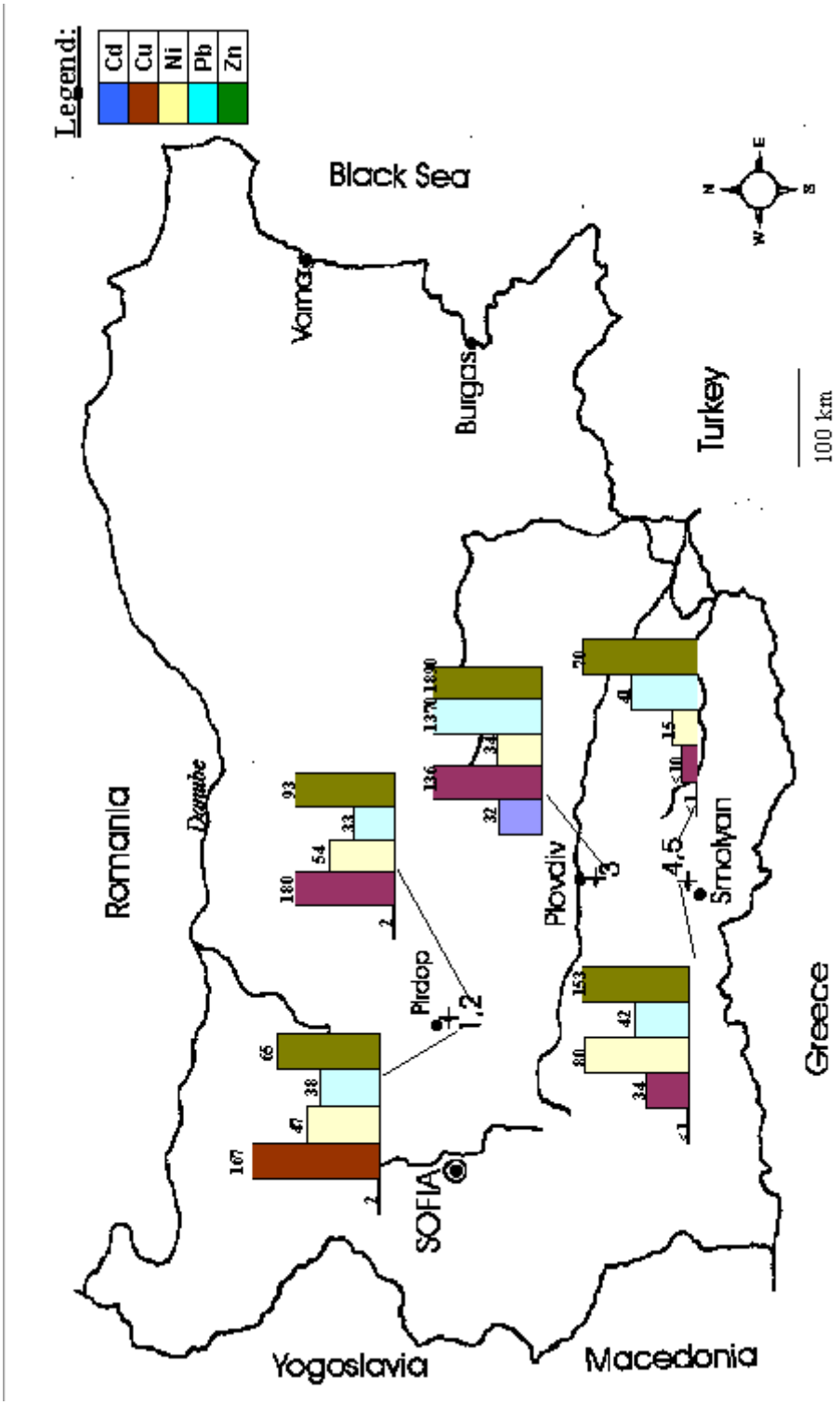

Fig. 7.1: Determined concentration of studied heavy metals (mg/kg) in soil surface of investigated profiles

In studied soils was observed clear trend for concentration of the analysed elements in clay fraction (particles <0.002 mm) in comparison to the whole soil. The content of investigated elements in sand fraction (particles 2.0 – 0.2 mm) separated from soil horizons is close to the mean background content of these elements in Bulgarian soils and in terrigenous soil forming rocks. This conclusion is valid for soils, located in impacted territories as well as for soils from unpolluted or background areas. Statistical procedure for finding similarities between content of studied elements in sand fraction extracted from A- and C-horizon of investigated soils was applied. The result show that with level of significance of 90%, sand fraction extracted from A-horizon brings information about geogenic/background content of investigated metals in soils, independently whether the soils are polluted or not polluted.

Determined total concentration of investigated element in studied soils were used as a base for calculation of the critical load for lead and cadmium (metals from first priority) according to Protocol of heavy metals signed in 1998 (GREGOR et al. 1999). The critical load is an indicator for sensibility in regions where the high input of trace metals is of ecological concern and where legislation should limit this type of pollution. Exceeding of critical load will occur in areas with high total loads of heavy metals. Exceeding can occur far from sources of pollution via air transported pollutants. For calculation of critical loads on a regional scale for arable and forest soil, were chosen simple model with aggregated descriptions of processes in whole-considered compartment. The critical load is the acceptable total load of anthropogenic heavy metal inputs (deposition, fertilizers, other anthropogenic sources). It corresponds to the sum of tolerable outputs from the system (harvest, leaching) minus the natural inputs (weathering release).

Environmental soil quality criteria constitute the basis of critical load calculation. Therefore the selection of critical limits is a step of major importance in deriving a critical load. With respect to heavy metals, environmental quality objectives based on total content in relatively unpolluted soils. Most often these are total metal concentration in the soil solid phase, protecting soil organisms. The problem with the concentration in solid phase is that they mostly lack an ecotoxicological basis. After regarding all-important pathways the most sensitive way was chosen for establishing the critical concentration in the soil solution (Critical Limits). But environmental quality criteria for metal concentrations in soil solution are lacking. Therefore the total metal contents in soil is used with using the trans-

formation functions incorporating relevant variables of soil characteristics (pH, organic matter, clay etc.) and transformed into bio-available concentrations or concentrations in the soil solution.

Calculated critical loads for lead and cadmium on a regional scale for both types of land use vary as follows:

- Cadmium: 1.0 – 3.12 $mg.m^{-2}.yr^{-1}$ for arable lands and 4.89 – 5.80 $mg.m^{-2}.yr^{-1}$ for forest soils.
- Lead: 7.0 – 10.39 $mg.m^{-2}.yr^{-1}$ for arable lands and 15.7 – 18.4 $mg.m^{-2}.yr^{-1}$ for forest soils.

Critical loads for Cd and Pb vary depending mainly on land use type. The values of calculated loads for both elements increased from arable to forest soil. The reason is that forest ecosystems had bigger filtering capability and also precipitation rate in studied region is high, that helps for deposition of pollutants on the forest floor.

Calculated critical load for cadmium is higher than those calculated for German soils (FEDERAL SOIL PROTECTION LAW 1998). It can be concluded that the calculated values for cadmium and lead give a good initial indication of the spatial variability of ecosystem sensitivity to heavy metal pollution in Bulgaria.

The other aim of this study was to determine the concentrations of priority organic pollutants in investigated soils and to obtain the basic data for content of this component as well in arable as in forest soils. The concentrations of ΣPAH ranges from 31.01 µg/kg to 56.44 µg/kg d. w. for arable lands, and for forest soil these concentrations are between 22.09 µg/kg and 28.66 µg/kg d.w (Figure 7.2). These concentrations are quite low and they do not show the contamination with these compounds.

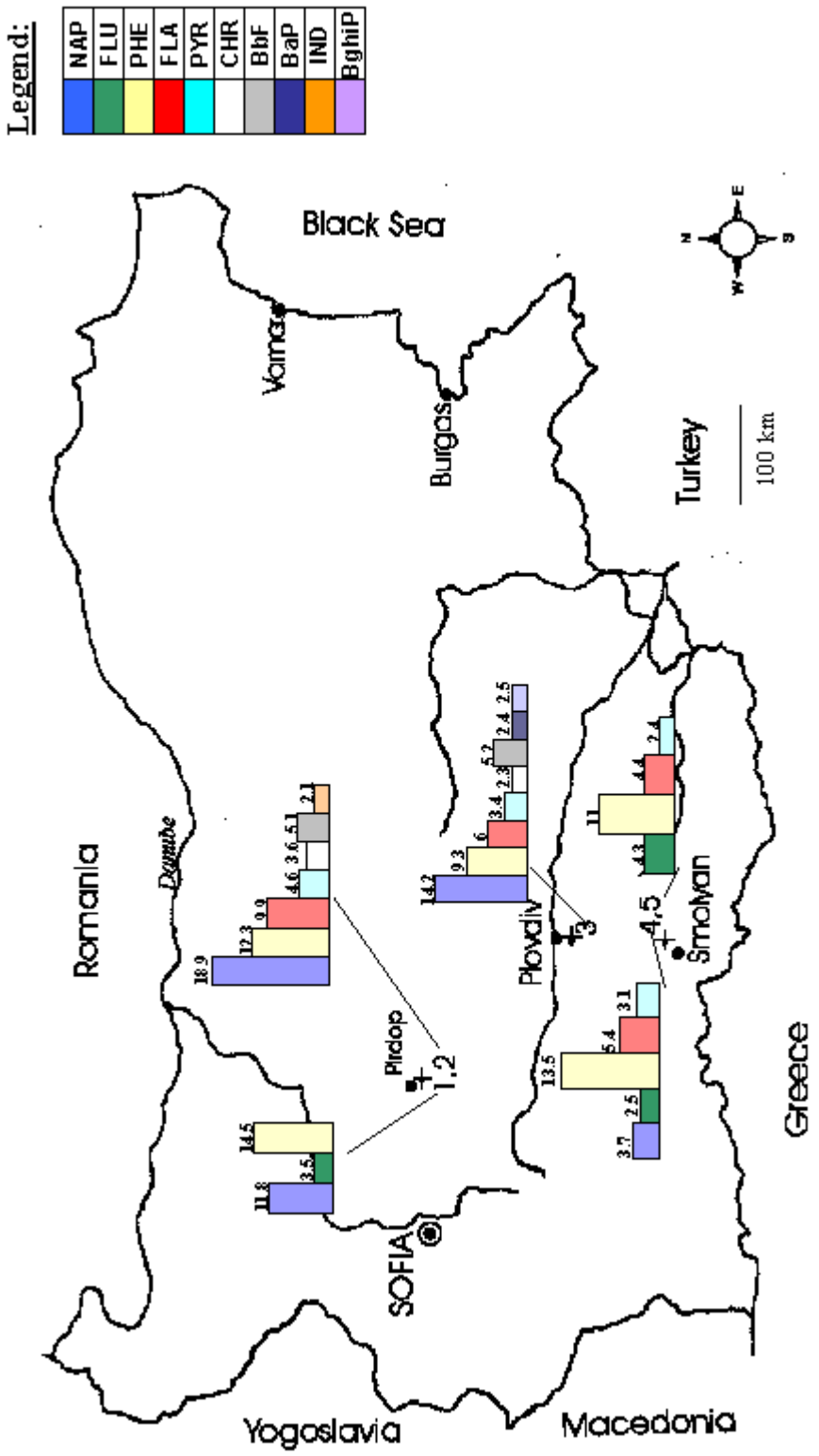

Fig. 7.2: Determined concentration of individual PAH compounds (µg/kg) in soil surface of investigated profiles

From individual compounds predominate PAH consisting of 2 to 4 benzene rings like naphtalenes, phenanthrenes, fluoranthenes, and to a lesser degree, pyrenes and crysenes. The PAH patterns at the different sites investigated depend on the number and kind of PAH sources. The dominant PAH typical for motor vehicle emission (benzo[b]fluoranthene, benzo[g,h,i]perylene) are detected only in arable soils (P1, P2, and P3). In forest ecosystems some PAH compounds can be produced biologically, like phenanthrene, which results from reduction of abietic and pimaric acid which occur e.g., in *Pinus* species. The content of individual PAH components in all studied sites is near to estimated natural background levels of 1-10 µg/kg d.w.

Unlike PAHs, the determined concentration of DDX-compound vary in a wide ranges from 11.24 µg/kg to 950.43 µg/kg d.w. (Figure 7.3). The Σ DDX concentration in the most contaminated soil (P2 = 950.43 ng/g d.w.) was at least a factor of 30 higher than other samples. Ratios of p,p'-DDT/p,p'-DDE is indicative of aged (microbially degraded) DDT and a value much greater than one indicates fresh application. The ratios in the present study were quite variable ranging from 0.12 to 1.10. The highest ratio occur in the site (P2) - area of Pirdop = 1.10. Fresh application of DDT - technical mixture can be a reason for this high content which exceed the precautionary values for Bulgarian soils. The concentrations of other DDT metabolites are quite low, they do not show contamination or fresh application of DDT mixture and they are mainly result from continued slow processes of DDT microbial degradation.

The obtained results of this investigation prove that due to the complexity of problems a large investigations for distribution of heavy metals and organic pollutant in Bulgarian soil are necessary. Obtained values for heavy metals and organic pollutants are derived only for restricted number of soils and in no case represent the true picture for all soils of Bulgaria. Because of that the results can be considered as preliminary and they can serve only for orientation about matter.

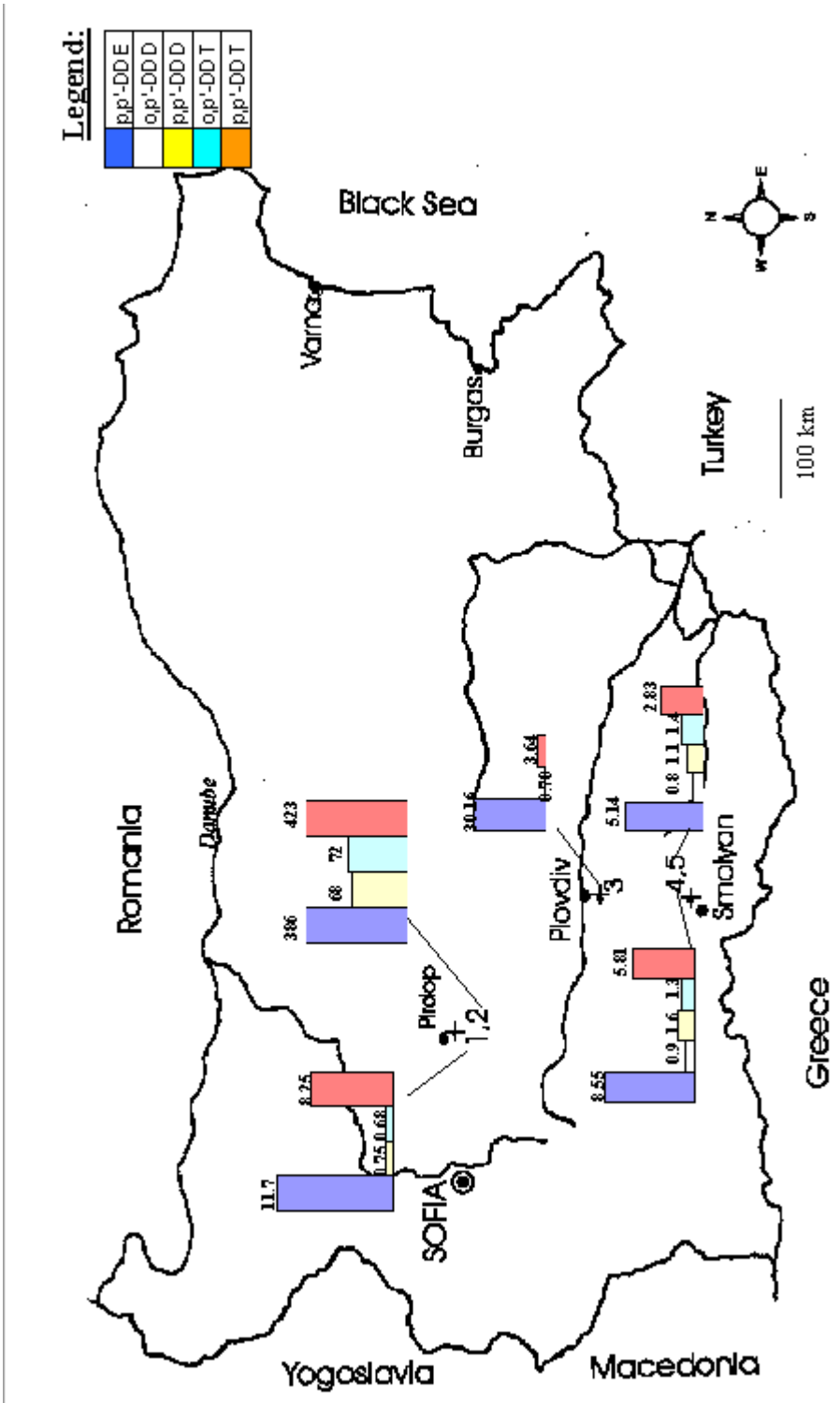

Fig. 7.3: **Determined concentration DDX-compounds (µg/kg d.w.) in soil surface of investigated profiles**