

5 Results and discussion

5.1 Distribution of heavy metals in soil horizons

The distribution of heavy metals in soil horizons is a result of many factors, including the intensity of weathering and soil-forming processes, the initial content of investigated element in parent rocks and the deposition intensity of pollutants on the soil surface. On the other hand, the total content of the metal studied in soil horizons is controlled by their geochemical mobility and behavior during surface weathering and soil forming. In this investigation was studied the depth distribution of the total amount of Cd, Cu, Ni, Pb, and Zn in arable soils situated near to sources of pollution and forest soils from background territories.

5.1.1 Distribution of heavy metals in arable soils, damaged by metal pollution

For arable soils there are two major routes for input of trace elements: aerial (e.g., aerosols, particulate matter, resuspended and airborne dusts, etc.), and land (fertilizers, pesticides, solid wastes, other soil amendments, etc.). Profiles 1 and 2 were located in the vicinity of Cu-smelter-Pirdop, and profile 3 – near Pb-Zn smelter near Plovdiv. These soils are regularly ploughed and the surface soil is well – mixed and as a result heavy metal concentration and soil properties are uniform throughout this plough layer. The depth distribution of investigated elements in Profile 1, 2 and 3 is shown in Figure 5.1, 5.2, and 5.3. All investigated soils indicate that the major part of the contamination is restricted to the upper 20 or 30 cm.

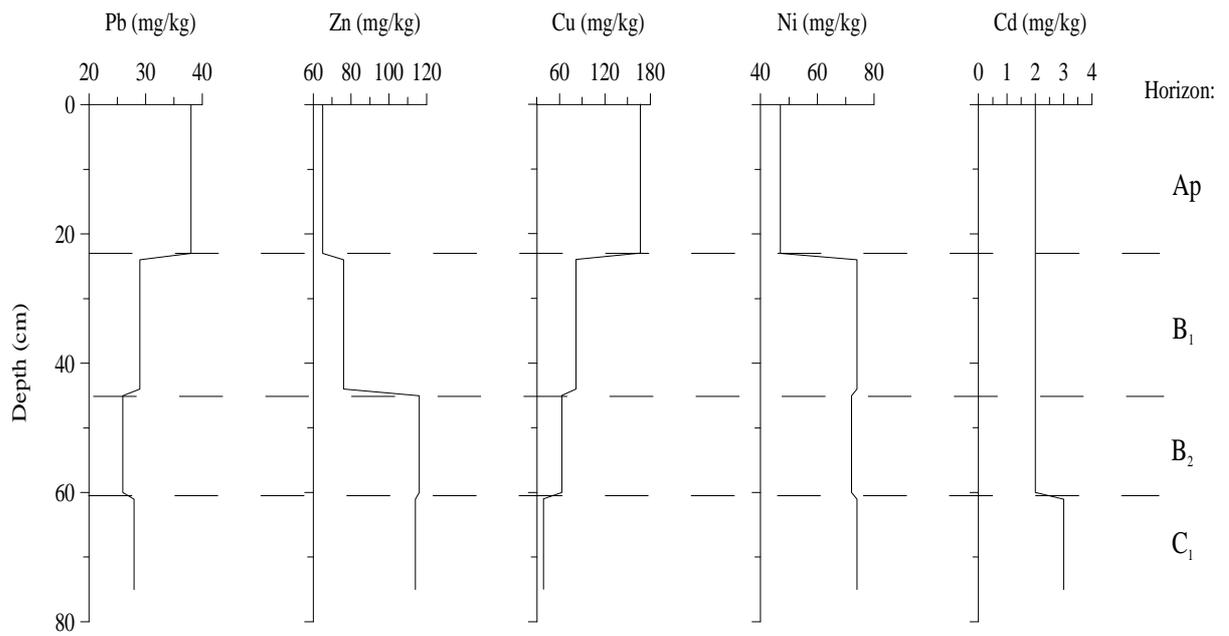


Fig. 5.1: Depth distribution of studied heavy metals in Profile 1

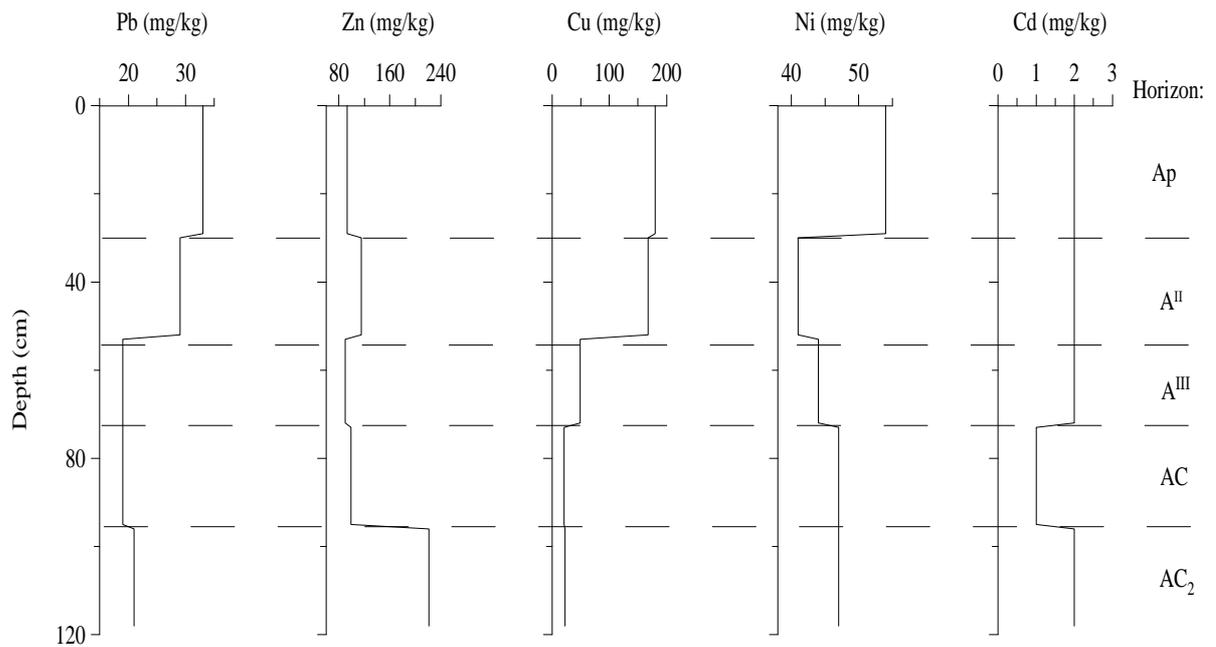


Fig. 5.2: Depth distribution of studied heavy metals in Profile 2

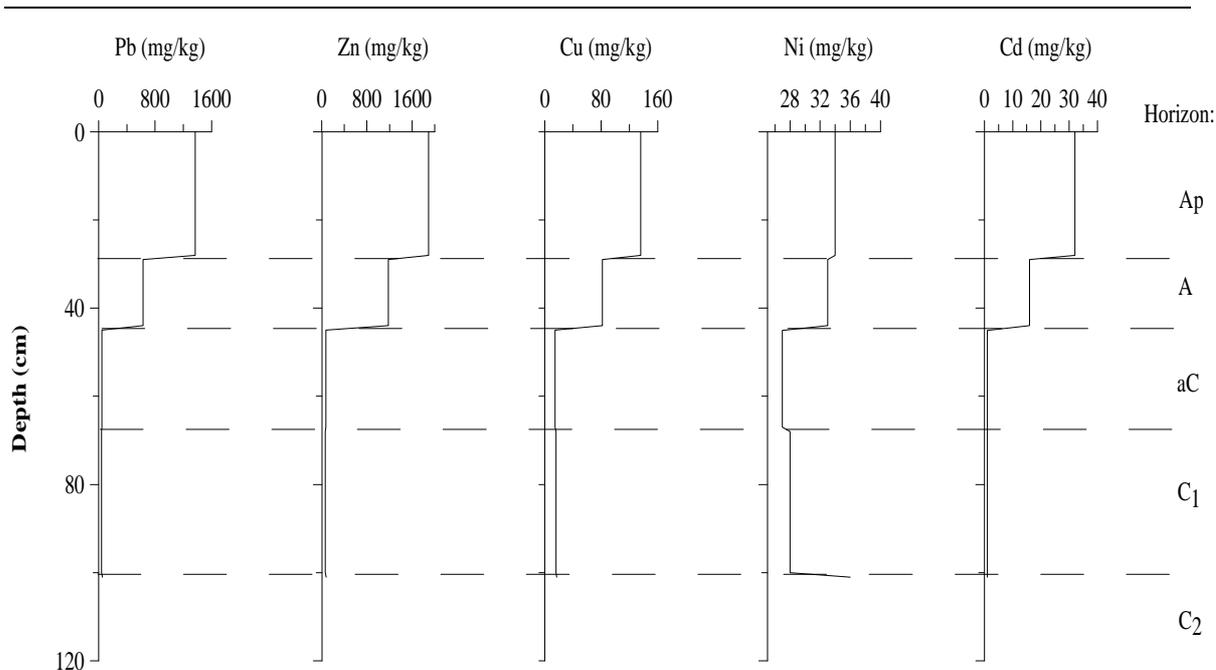


Fig. 5.3: Depth distribution of studied heavy metals in Profile 3

LEAD

This element is concentrated mainly in surface soil horizons of all profiles. The total content of Pb in the upper soil horizons is 38 mg/kg for Profile 1, 33 mg/kg for Profile 2, and 1370 mg/kg for Profile 3. The lead content in Profile 3 greatly exceeds the concentrations in other two profiles. The 90p values of lead in Bulgarian soils from background territories are estimated to 26 mg/kg (ATANASSOV et al. 2000). So the concentration of lead in the upper soil layer of Profile 3, significantly exceeds the background values for this element in Bulgarian soils. Such high content indicates process of contamination, as a result of flue dust addition from smelter. KUIKIN et al. (2001) estimated that the mean content of lead in soil-parent material is 21.0 mg/kg, and the ratio $Pb\ soil / Pb\ rocks = 1.2$ shows that lead tends to accumulate in the soil horizons.

ZIMDAHL and SKOGERBOE (1977) demonstrated that lead accumulation in the surface horizon was associated with high organic matter content, partly the result of reactions involving insoluble organic matter. They found that the majority of lead immobilised by soil was associated with organic matter and fixation by organic matter was more important than precipitation or sorption by hydrous oxides. Organic matter and clay were also found to be the dominant constituents contributing to lead retention (SOLDATINI et al. 1976; RIFFALDI et al. 1976). However it can be inferred that increasing organic matter content in top soils

might reduce the mobility in contaminated soils, because lead in soil was not solubilized by soluble organic substances (LI and SHUMAN 1996). The lead concentration beneath 40 cm is low and fairly uniform throughout each profile (Figures: 5.1, 5.2, and 5.3).

ZINC

The total concentration of zinc in the topsoil for profile 1 and 2 is 65 mg/kg and 93 mg/kg respectively. For profile 3 - 1890 mg/kg, which content also exceed like with lead the mean value of this element for Bulgarian soils (80 mg/kg) (ATANASSOV et al. 2000). The mean concentration of zinc in main soil-forming rocks is estimated of 45.0 mg/kg (KUIKIN et al. 2001), and the ratio Zn soil / Zn rocks gives value 1.5. In this case soils as a whole are relatively enriched with zinc in the degree higher than the lead. This high content is also result of the dust additions, and concentration decreased with depth increased. For profiles 1 and 2 were determined high concentration of these element in subsoil horizon. This indicates that some zinc from the topsoil had migrated downward under natural field conditions due to low pH measured in this soils and water flow through soil profiles. It seems that zinc as a result of soil forming processes tend to migrate from upper to lower soil horizons and accumulate in B- or Bt horizons.

COPPER

All investigated profiles show high total content of copper in A-horizons. The measured values are 167, 180, and 136 mg/kg, respectively for Profile 1, 2, and 3. According ATANASSOV et al. (2000) the mean content for Bulgarian soils is 34 mg/kg, and the mean content of copper for main soil-forming rocks in Bulgaria is 20.0 mg/kg. The estimated ratio background content of copper against mean content in soil-forming materials is 1.7. During surface weathering and soil formation copper tends, like lead and zinc to accumulate in soil horizons. This is an effect of various factors between them, copper concentration in surface soils reflects the bioaccumulation of the metal and also recent anthropogenic sources. Although Cu is one of the least mobile heavy metals in soil, this metal is abundant in soil solutions of all types of soil. The depth of these impacts reaches to 40-50 cm.

NICKEL

The measured total content in studied profiles is 47, 54 and 34 mg/kg for profile 1, 2 and 3, respectively. The mean concentration of nickel in the main soil-forming rocks of Bulgaria

is 17.0 mg.kg^{-1} (KUIKIN et al. 2001). The ratio Ni soil / Ni rocks is 1.9. Like Zn, Cu, and Pb, during soil formation nickel enriched in the upper soil horizon. The concentration of this element do not show contamination of soils. In surface soil horizons Ni appears to occur mainly in organically bound forms, a part of which may be easily soluble chelates (BLOOMFIELD 1981). Because of this Ni may move from soil surface and accumulate in soil horizons directly under soil surface (Figure 5.1).

CADMIUM

Determined concentration of Cd for profile 3 is 32 mg/kg. This concentration is several times higher than mean values for Bulgarian soil (0.3 mg/kg) or MPC for Bulgarian soils (2 mg/kg). The mean value for soil-forming materials is 2.3 mg/kg. Cadmium tends to accumulate in soil surface horizons for profile 3 (horizons Ap and A^{II} – with depth to 44 cm). The distribution curves for Cd in other profiles are monotonous and they do not show differences. The high cadmium concentration can be considered anthropogenic contamination. Generally speaking cadmium is immobile in contaminated soil profiles (ADRIANO 1986). Previous studies indicated that cadmium accumulated in the surface layers of soil profiles contaminated by smelting operations and concentrations were close to background level at depth of about 30 to 40 cm (KOBAYASHI 1979; JOHN et al. 1972). ADRIANO (1986) pointed out that most cadmium is organically complexed in the upper horizon rich in organic matter. Similarly, ANDERSSON (1977) observed higher accumulations in the upper part of soil profiles, paralleling the humus distribution. The appearance of cadmium below a depth of 30 cm (profile 1 and 2) could be caused by a small transport in the soil profile by soil solution, possibly aided by soluble organic complexes (LI and SHUMAN 1996). Cadmium may be retained in this strongly adsorptive horizon after reaching it as a result of cycling through vegetation or from applications of Cd-containing fertilizers and manures, or from wet deposition from the atmosphere (ALLOWAY 1995).

From Figure 5.1 and 5.2 it can be concluded that the curves of distribution of investigated elements for profiles 1 and 2 are the same for all investigated elements. Only the concentrations of copper for these soils prevail the maximum permissible concentration, which is a result of pollution from situated near by Cu-smelter. Even that this two profiles are highly enriched with copper, movement of which will be mainly in the solution phase within the soil and with the soil lost as a result of erosion. The amount of copper lost by leaching is

very small. The curves of distribution shows that there do not occur movement of copper down the soil profile.

All investigated elements have the same distribution curves for profile 3 (Figure 5.3). This profile received dust containing Pb, Zn, Cd from situated near by smelter, and from regular application of Cu – containing fungicides. Intensively heavy metal accumulation occurred only in the top soil. Below the plough layer the concentration of elements decreases rapidly and no metal migration into deeper horizons can be observed. The presence of calcareous materials in all soil horizons and the alkaline pH decrease the solubility of the heavy metal compounds and restrict the migration of these substances in the lower soil horizons. The total amount of Pb, Zn, Cd and Cu in subsurface soil horizons is approximately as high as variation of background values of these elements in the soil in Bulgaria. The heavy metals (especially Cd, Pb, and Zn) content on the upper soil layers is dependent primary on the distance from the smelter. It was not so evident in the case of Cu, probably due to the smaller content of this pollutant in the dust particles.

5.1.2 Distribution of heavy metals in forest soils, situated in background areas

Unlike agro-ecosystems, there is only one input pathway in established forest ecosystems, and that is atmospheric input. Forest ecosystems are particularly affected by inputs due to the filter effect of the canopy. In forest ecosystems heavy metals accumulate in the forest floor and the humic mineral soil horizons. Figure 5.4 and 5.5 represents depth distribution of Cd, Cu, Ni, Pb, and Zn in profile 4 and 5.

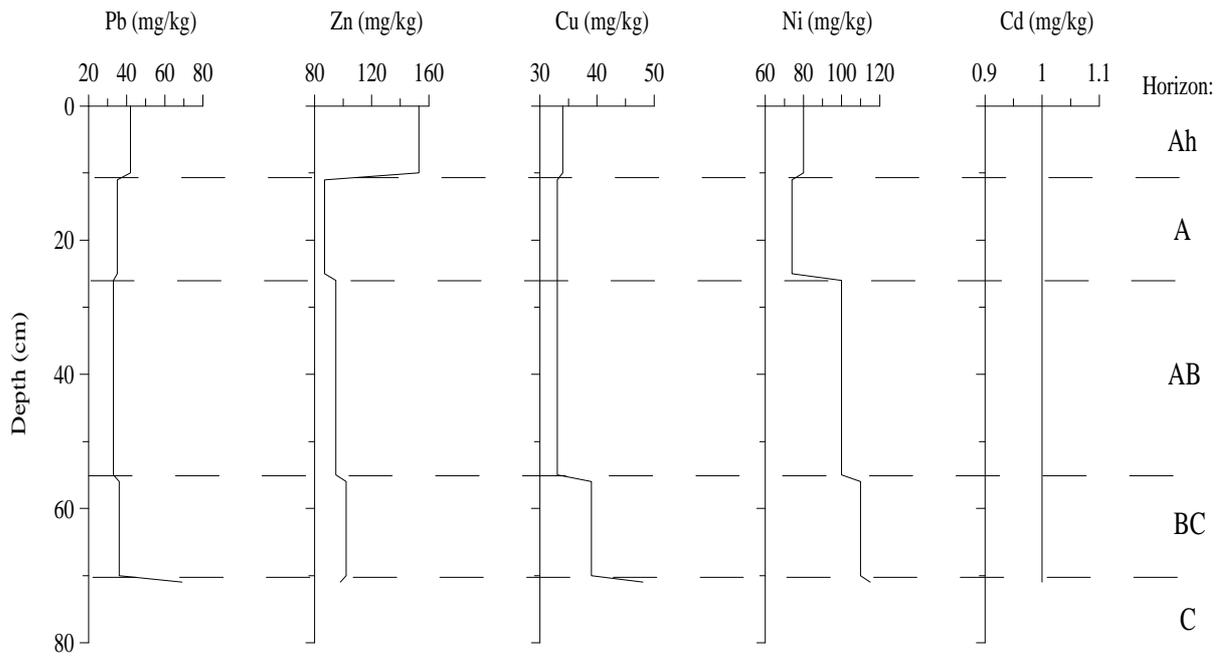


Fig. 5.4: Depth distribution of studied heavy metals in Profile 4

Forest soils however, will be largely undisturbed, they may be subjected to some minor forms of disturbance from grazing, cutting or harvesting of grass. Therefore the distribution curves for trace elements do not show big differences in different horizons (Figures: 5.4 and 5.5), and distribution of metals is monotonously.

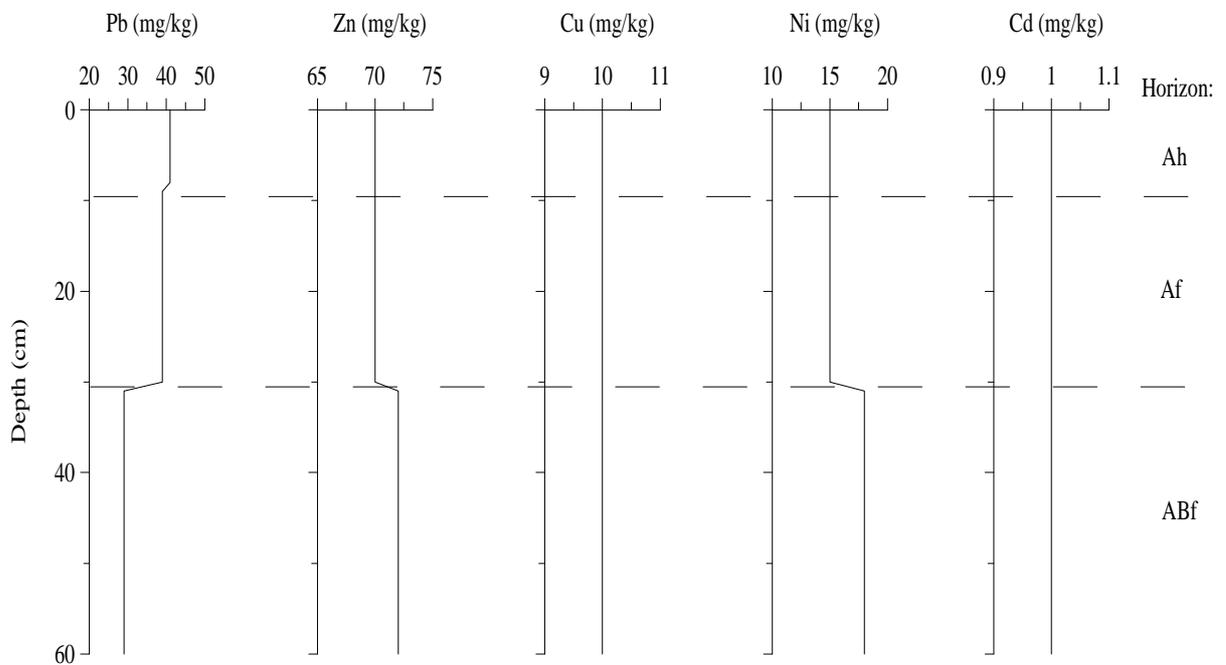


Fig. 5.5: Depth distribution of studied heavy metals in Profile 5

LEAD

The content of lead in upper soil layer is 42 mg/kg - profile 4 and 41 mg/kg - profile 5. Measured total content of trace elements is higher than accepted from ATANASOV et al. (2000) mean values for Bulgarian soils (26 mg.kg⁻¹). The high concentration of lead may be related with long – distance transport from the Pb-Zn smelter near Plovdiv and trans-boundary air transported pollutants. Other source of lead is natural content of soils which is strongly related to the composition of the bedrock. According DAVIS (1989), the average crystal rock contains approximately 16 mg Pb/kg and the lead content increases with silica content. But this content is much higher in some sedimentary rocks, such shales and mudstones and can reach 23-25 mg/kg. According KUIKIN et al. (2001), the background values for lead in crystal rocks in Bulgaria vary between 5 and 30 mg/kg, depending on the mineralogical composition. As a rule, the content of Pb is higher in acid magmatic rocks (up to 30.0 mg/kg) and lower in ultrabasic metamorphic rocks (not more than 5 mg/kg). In comparison with other investigated metals the mobility of Pb is smaller. These elements tend to accumulate with organic matter and with clay minerals. The same results have been reported in the investigations of KABATA-PENDIAS and PENDIAS (1984) and from QUERALT and PLANA (1993).

ZINC

The distribution curves of zinc are similar as of lead. Profile 4 is characterized with high content of zinc in topsoil (153 mg/kg), which concentration sharply decreases in subsoil. It can be assumed that this high content comes from air transported pollution. Profile 4 is characterised with high content of organic matter in upper horizon (8.15%) and bound zinc in stable organo-chelatic complexes. The solubilization of Zn minerals during weathering produces mobile Zn²⁺, especially in acid, oxidizing environments. Zinc is however, also easily adsorbed by mineral and organic components and thus, in most soils its accumulation in the surface horizons is observed. MC BRIDE (1994) stated that nucleation of zinc hydroxide on clay surface may produce the strongly pH – dependent retention in soils. The adsorption of Zn²⁺ can be reduced at lower pH (pH<7) by competing cations and this results in easy mobilisation and leaching of zinc from soils. At higher pH values, while an increase of organic compounds in soil solution becomes more evident, Zn–organic complexes may also account for the solubility of this metal.

NICKEL

In the two investigated profiles 4 and 5, the content of nickel in soil horizons vary between 15 and 80 mg/kg and the content of this element in the parent rocks vary between 20 and 100 mg/kg (Figures: 5.4 and 5.5). The background value for nickel in Bulgarian soils is estimated of 46 mg/kg (ATANASSOV et al. 2000). In the case of investigated soils the content of nickel in the soil profile 4 is higher and in profile 5 it is lower than the average background values in Bulgarian soils. On the other hand, the content in parent rocks corresponds to the concentration of this element in basic magmatic rocks (KUIKIN et al. 2001). Nickel tend to migrate from upper soil horizons and accumulate in soil parent materials. The degree of this migration can be calculated using ratio:

$$\frac{\text{Ni content in horizon A}}{\text{Ni content in horizon C}}$$

In the scale of whole country this ratio is approximately 0.5 (ATANASSOV et al. 2000). For investigated soil this ratio is respectively 0.6 and 0.7. This supports the conclusion that under surface weathering and soil formation Ni like Fe in acid condition increases his mobility and migrates from upper to deeper soil horizon.

COPPER AND CADMIUM

The profiles 4 and 5 contain different amount of copper in soil horizons. For profile 4 the concentration of copper is approximately 35 mg/kg, and 10 mg/kg for profile 5. Recently estimated from Atanassov et al. (2000) background values in Bulgarian soils are 34 mg/kg. In the case of investigated soils the amount of copper found in soil horizons of profile 4 is close to the background values and for profile 5 it is lower than these values. As a whole, there is no differentiation in concentration of copper and cadmium between soil horizons.

The main role in distribution of trace elements in forest soils plays the processes of leaching. Generally speaking the metals demonstrate two distinct patterns of release. In the first pattern soluble organic acids, predominantly humic substances, play a critical role. These are released in great quantities when the organic matter in the topsoil is mineralized. The organic acids are transported through the A-horizon with percolating soil water. Lead and copper are known to form stable complexes with dissolved organic acids and are transported through the soil in a complexed form (KEILEN 1978). A high biological activity in

the mor layer favours the formation of dissolved organic acids and hence, the release of these metals from the soil. Most of the copper and lead released from the A-horizon is accordingly accumulated in the upper B-horizon of Cambisols (BERGVIST 1986).

The second pattern is associated with soil acidity. A gradual release of metals from the mineral soil and an increase in soil solution concentration of metals through the B-horizon are characteristic features of Zn, Cd, and Ni (BERGVIST 1986). These metals are very susceptible to changes in soil acidity.

5.2 Distribution of Cd, Cu, Ni, Pb, and Zn in particle - size fraction extracted from polluted and unpolluted soil profiles

The main sources of heavy metals in the soil are the parent materials from which the soils were derived but the influence of parent materials on the total content and forms of the metals in soils is modified to varying degrees by pedogenetic processes. Ordinarily Cd, Cu, Ni, Pb, and Zn are considered as trace elements in rocks and soils. For soils at early stages of weathering and profile development the content of these elements in soil horizons is inherited from the parent materials. For soils near to the source of pollution the content of elements is due of additional deposition from different sources of pollution.

The diagnosis of metal pollution of soils 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 soil of the same type or by analysing the deep horizons of surface contaminated soils (BAIZE 1994). Using background concentration of trace elements is suitable because they show local peculiarity of different soils. Background concentration for soil situated near to sources of pollution was difficult for determination. The coarse < 2 mm fraction of the C - horizon can be used for mapping background element levels and regional variations. According REIMANN et al. (1998) using this concentration is not very propriety because same elements are leached from vertical processes in soil profile.

Some investigations ascertain on the relations between the mineralogical composition of soil/parent materials and the content of trace elements. MIRCHEV (1995) shows that the concentrations of Zn, Cu, Cr, Ni, Co and Pb, founded in particle-size fraction 1 - 0.1mm,

extracted from soil horizons and parent materials of five Bulgarian soils depend of the mineralogical composition of this fraction. In soils with low rate of weathering like Chernozem and Smolnitza, the content of above-mentioned elements in sand fraction has been similar both for soil horizons and for parent materials. For more weathered soils like Cinnamonic and Grey forest soil these elements tend to reduce their concentrations in A-horizons in comparison with the contents found in C- horizons.

According the concept of LABO (1995), the background values of the heavy metals in soil have two main components: geogenic basic content which encompasses the substance composition of parent rocks or soil forming primary minerals and “ubiquitous/diffuse” content, which is due to the distribution of substances as a consequence of diffuse entry into the soil.

The coarser particle-size fractions, like coarse, medium and fine sand fractions usually contain only primary minerals and can be considered as indicative for original autogenous minerals, presented in soil parent materials. It can be expected, that the air-transported pollutants will not influence the content of the trace elements in coarse soil fraction. On this base, the chemical composition and the content of trace elements in sand fractions, extracted from soil horizons can be indicative for geogenic basic content of these elements in soils.

Up to now no studies have been carried out on heavy metal distribution among the particle-sized fraction of polluted vs. unpolluted soils. It is expected, that this study will show the relative contribution of different particle-sized fractions to the total amount of the trace element in the soil and verify whether the metal content in different particle-sized fractions, extracted from soil horizons and parent materials contain information about geogenic or basic (background) contents of these elements in the soil.

In this study was examined the distribution as in whole soil (see chapter 5.1) as in soil size separate fraction (e.g. sand and clay fraction). The distribution of Cd, Cu, Ni, Pb, and Zn in the sand (particles 2.0-0.2 mm) and clay (particles <0.002 mm) separates is presented in Figures 5.6; 5.7; 5.8; 5.9, and 5.10.

The results show that the investigated metals tend to accumulate in clay-sized separate, especially in clay fraction extracted from A- horizons of the studied profiles. This is equally significant for polluted profiles (1, 2, 3) as well as for the profiles from the background areas (4 and 5). The degree of accumulation can be calculated by using the ratio:

$$\frac{\text{Content of Metal in clay fraction}}{\text{Content of Metal in whole soil}}$$

The results of this comparison are presented in Table 5.1. The metals like Cu and Zn their content increase in fine clay fraction between 1.5 up to 9.5 – 10.5 times in comparison with the content in whole soil. The processes of accumulation in clay fraction are not so intensive for Ni and Pb, and for Cd. It seems, that the content of this metal in whole soil and in clay fraction in most cases is the same. There is no clear dependence between degree of accumulation of the investigated metals in clay-sized separate and the content of organic matter. In some profiles like profile 4 and 5, the degree of accumulation of Cu is higher in the clay fraction, extracted from A-horizon, but in other profiles (profile 2) the degree of enrichment of clay fraction with Cu is more significant for the horizons without big amount of organic matter (Table 5.1).

Tab. 5.1: Degree of accumulation of Cd, Cu, Ni, Pb, and Zn in clay-sized separate (particles < 0.002 mm) in studied profiles

Soil Profile	Horizons, cm	Ratio: $\frac{\text{Content of Metal in clay fraction}}{\text{Content of Metal in whole soil}}$				
		Cd	Cu	Ni	Pb	Zn
1	A _p 0-23	1	1.5	1.7	1.2	2.9
	B ₁ 23-44	2	1.8	1.5	1.6	2.6
	B ₂ 44-60	-	-	-	-	-
	C ₁ 60-75	-	-	-	-	-
2	A _p 0-29	1	1.9	1.1	1.4	2.8
	A ^{II} 29-52	1	1.8	2.1	1.4	3.5
	A ^{III} 52-72	1.5	1.8	1.5	2.0	2.6
	AC 72-95	1.5	4.7	1.4	1.9	2.4
	AC ₂ 95-118	1.0	4.8	1.6	2.1	1.3
4	A _h 0-10	1	2.4	1.2	1.8	1.9
	A 10-25	1.5	2.3	1.3	2.2	8.9
	AB 25-55	2.0	2.0	1.3	1.7	3.1
	BC 55-70	2.0	2.0	1.2	1.4	3.2
	C 70-↓	-	-	-	-	-
5	A _h 0-8	1	9.5	2.2	2.5	9.8
	A _f 8-30	1	8.6	2.3	2.5	10.5
	AB _f 30-60	1	5.4	2.2	1.9	1.4
	C _f 60-↓	-	-	-	-	-

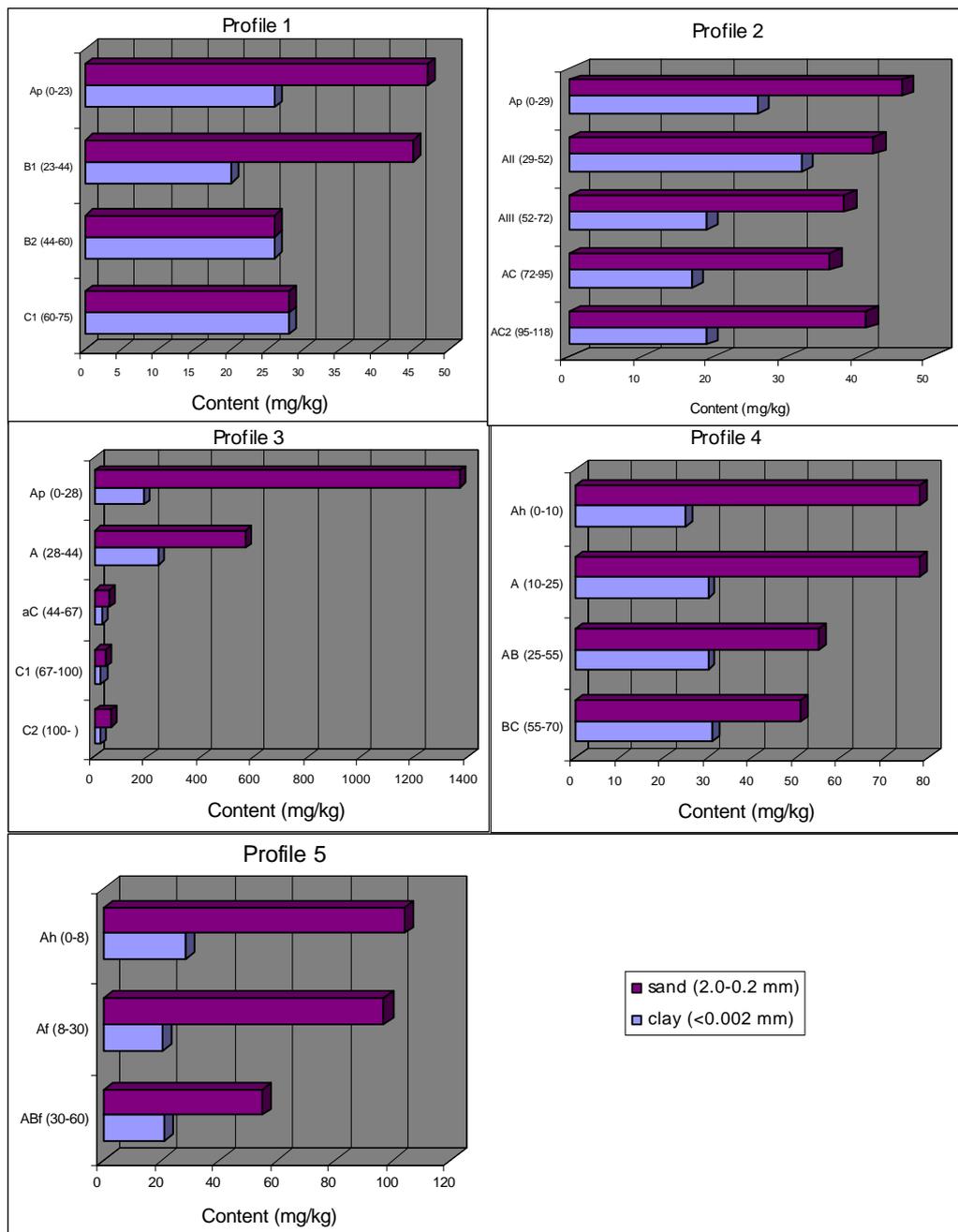


Fig. 5.6: Distribution of Pb in sand (2.0-0.2 mm) and clay (<0.002 mm) fraction in main soil horizons of investigated profiles

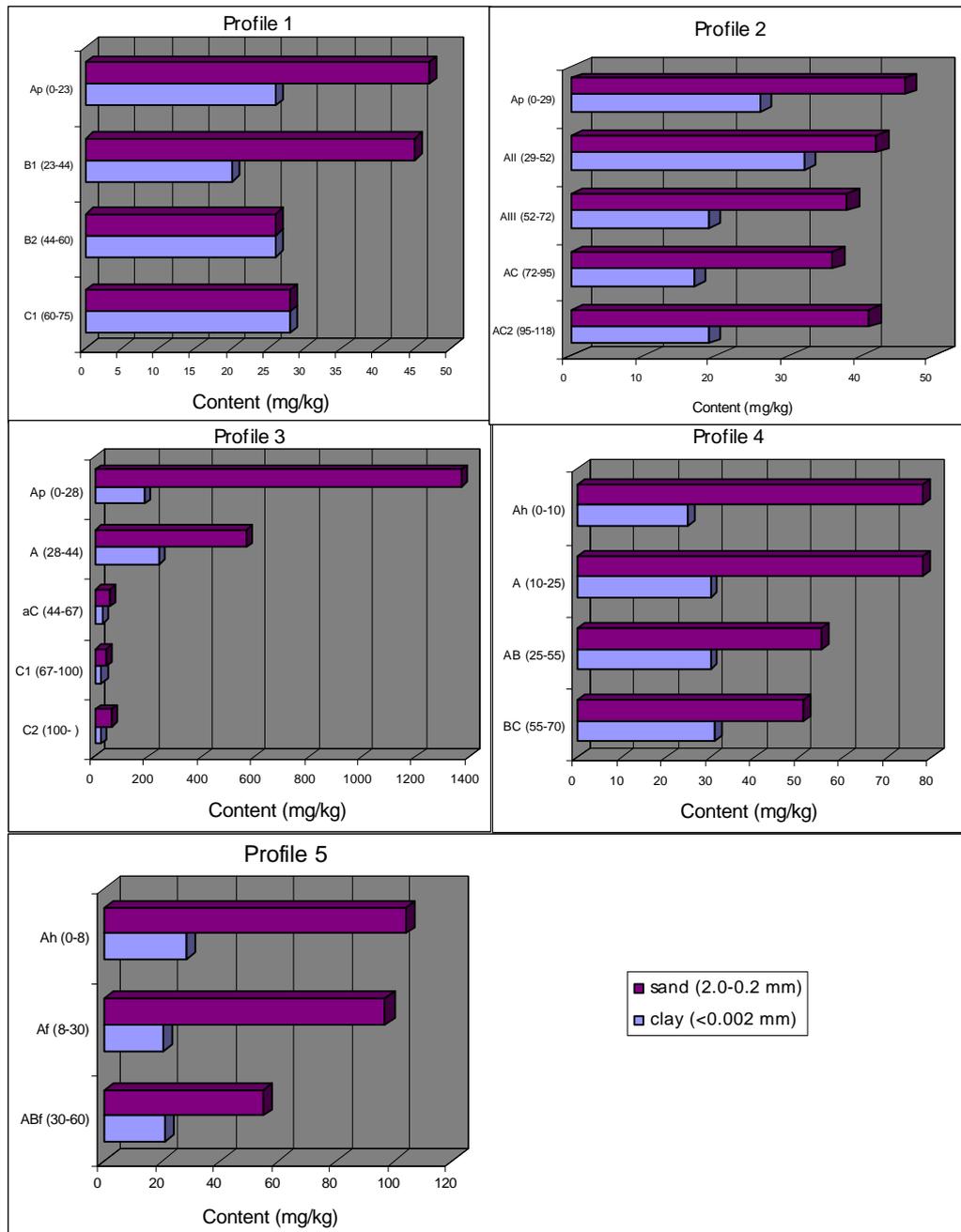


Fig. 5.7: Distribution of Zn in sand (2.0-0.2 mm) and clay (<0.002 mm) fraction in main soil horizons of investigated profiles

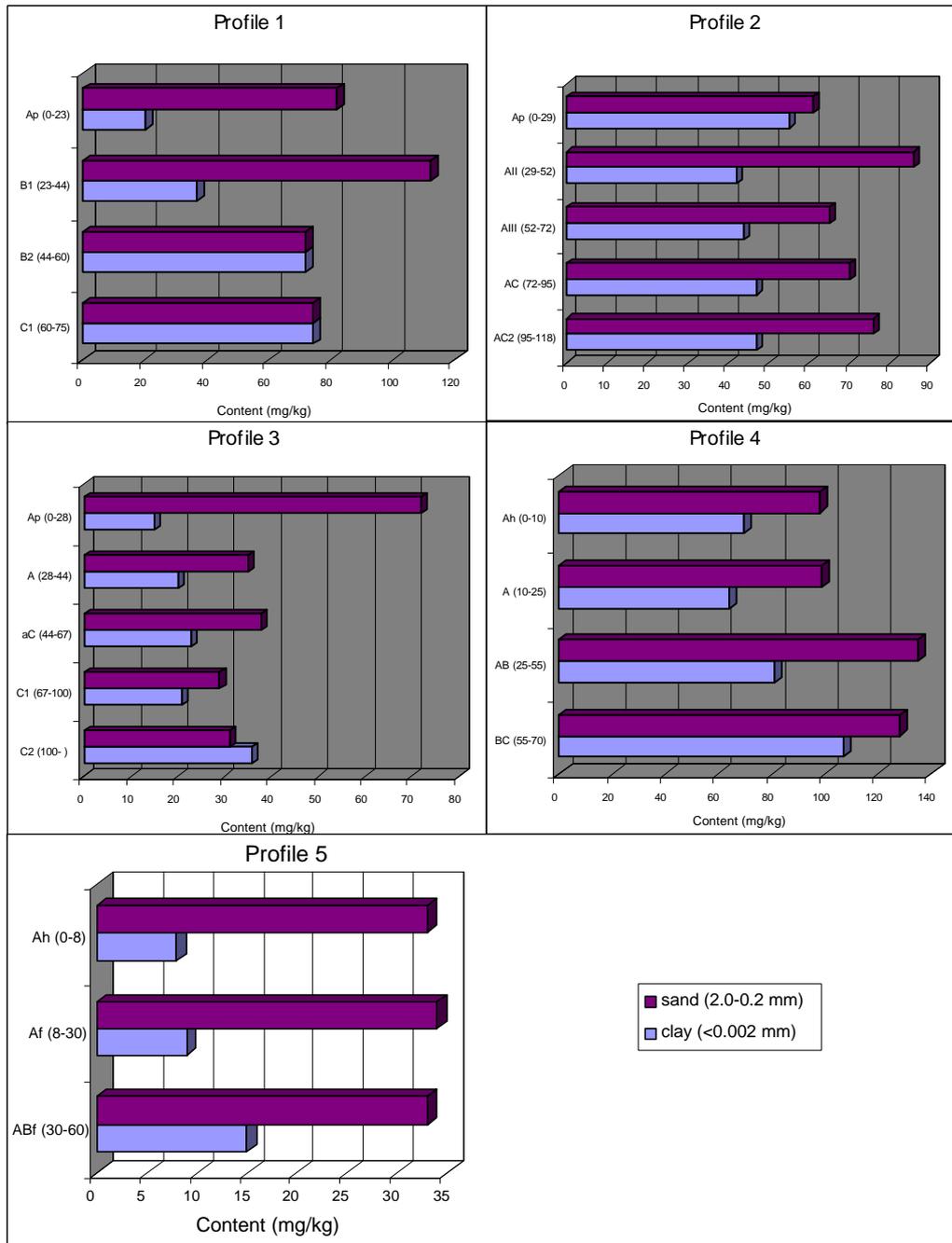


Fig. 5.8: Distribution of Ni in sand (2.0-0.2 mm) and clay (<0.002 mm) fraction in main soil horizons of investigated profiles

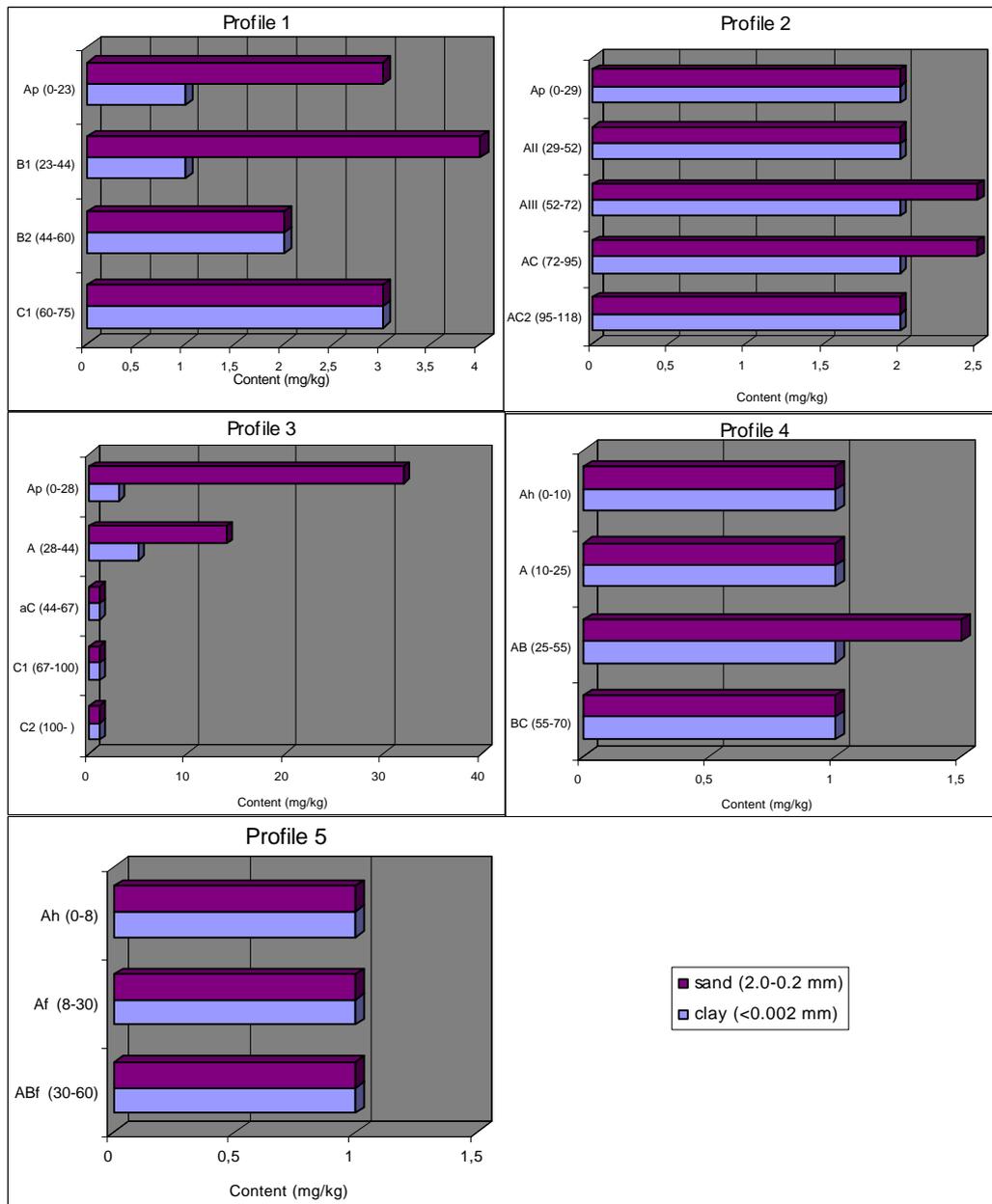


Fig. 5.9: Distribution of Cd in sand (2.0-0.2 mm) and clay (<0.002 mm) fraction in main soil horizons of investigated profiles

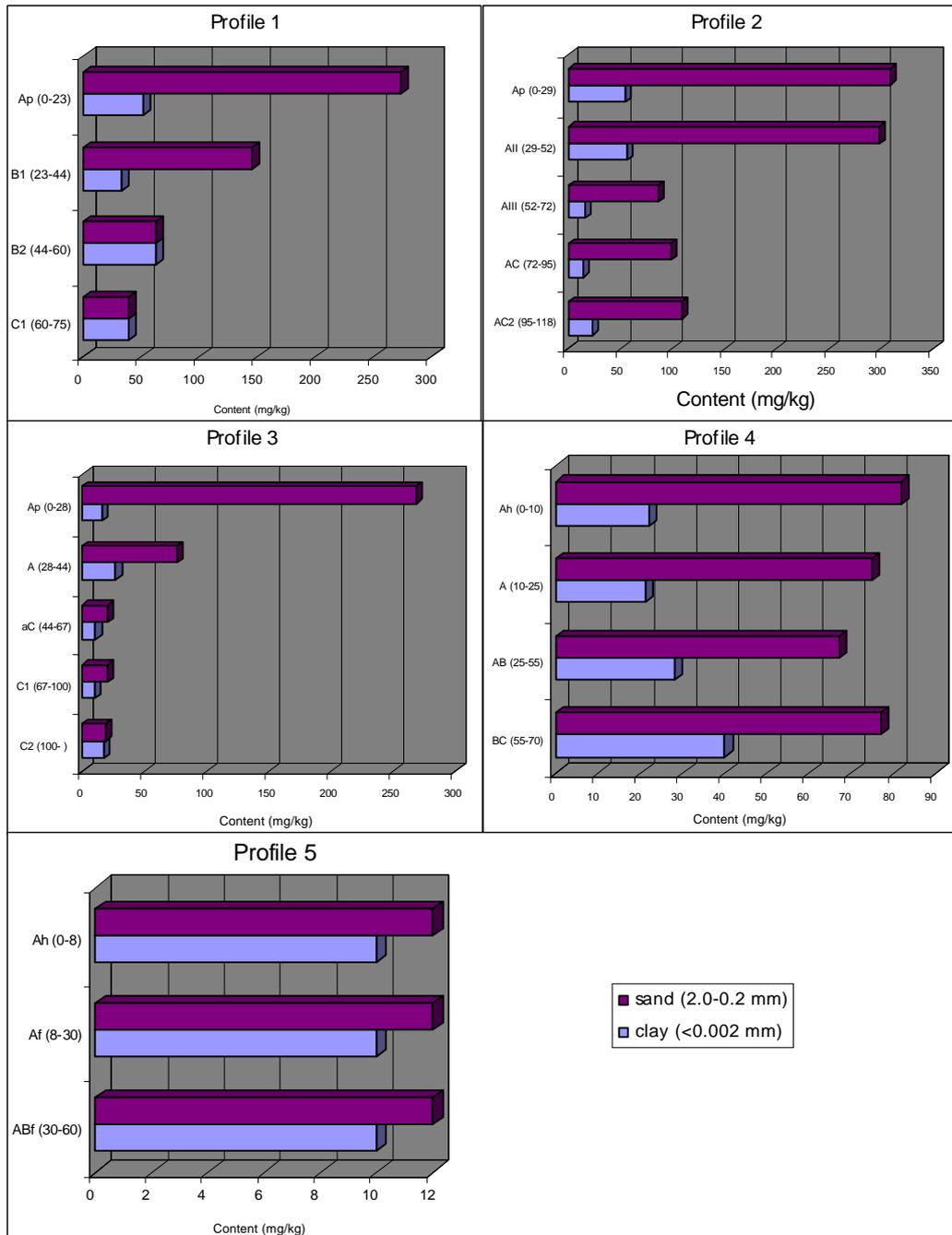


Fig. 5.10: Distribution of Cu in sand (2.0-0.2 mm) and clay (<0.002 mm) fraction in main soil horizons of investigated profiles

As a whole, the investigated elements tend to accumulate in fine sized fraction regardless whether the soil is situated in polluted or in background area. This is because of the increased adsorption of the above mentioned heavy metals by organic matter and clay particles in fine-sized separates. On the other hand, the anthropogenic heavy metals occur principally as airborne particles with size less than 50 μm (LIVET 1988) and after deposition on the soil surface they tend to accumulate in the fine-sized soil separated (size fraction $<0.002\text{mm}$). The coarser soil separates remain unaffected by pollutants.

From Fig. 5.6 – 5.10 it seems that in most cases content of Cd, Cu, Ni, Pb, and Zn in sand fraction is lower than in clay fraction. This is a result from higher specific surface of clay particles, which allows them to adsorb more metals, and also of relatively enrichment of clay fraction with organic matter. These increase additionally adsorption capacity of clay fraction in relation with investigated metals.

Sand fraction is constructed mainly from primary minerals, which are inherit from parent rocks. They have small specific surface and as a rule they do not adsorb additionally other elements – in this case Cd, Cu, Ni, Pb, and Zn. It can be expected that chemical content of this fraction is determined mainly from inherit primary minerals. In studied case it can be expected that concentration of investigated elements in sand fraction reflect geogenic content, typical for parent rocks.

Through determining the content of these metals in the sand fraction of the soil (particle 2.0-0.2 mm) it is possible to reveal values which could be considered as geogenic/background, regardless of whether the soil is polluted or non-polluted. The particles with size of 2-0.2 mm carry the fingerprint of the natural concentrations of the above-discussed elements and it can be used for description of the geogenic/background concentrations of heavy metals in the soil.

In Table 5.2 it is made comparison between determined contents of studied elements in sand fraction, separate from master soil horizons of investigated soils and 90p content of these elements in Bulgarian soils.

Tab. 5.2: Comparison of the contents of Cd, Cu, Ni, Pb, and Zn in sand separates (particles 2.0 – 0.2 mm) extracted from five soil profiles and 90p values of these elements in Bulgarian soils (ATANASSOV et al. 2000)

Soil Profile	Horizons, cm	Content, mg/kg				
		Cd	Cu	Ni	Pb	Zn
1	A _p 0-23	1	51	20	26	29
	B ₁ 23-44	1	33	37	20	35
	B ₂ 44-60	2	39	70	20	116
	C ₁ 60-75	3	39	70	-	-
2	A _p 0-29	2	55	55	26	95
	A ^{II} 29-52	2	56	42	32	89
	A ^{III} 52-72	2	16	44	19	100
	AC 72-95	2	15	47	17	92
	AC ₂ 95-118	2	14	47	19	98
3	A _p 0-28	3	16	15	188	204
	A 28-44	5	27	20	238	389
	AC 44-67	<1	11	23	31	44
	C ₁ 67-100	<1	10	21	26	35
	C ₂ 100-↓	<1	7	18	24	34
4	A _h 0-10	<1	22	69	25	69
	A 10-25	<1	21	74	30	69
	AB 25-55	<1	28	81	30	75
	BC 55-70	<1	40	107	31	94
	C 70-↓	-	-	-	-	-
5	A _h 0-8	<1	<10	8	28	47
	A _f 8-30	<1	<10	9	20	51
	AB _f 30-60	<1	<10	15	21	73
	C _f 60-↓	-	-	-	-	-
Background values as 90p values for soils in Bulgaria		0.4	34	46	26	88
Mean geogenic contents for clastic rocks		2.3	28	22	24	60

The presented data show, that there exists close relationship between concentration of Cd and Pb in fraction 2.0-0.2 mm and 90p, background concentration of these elements, estimated for Bulgarian soils. In most cases, determined contents for Cu and Ni in sand fraction are equal with those for background soils. Exception made only cases with horizon A for profiles 1 and 2, where is observed higher Cu content. It can be suggest, that the sand fraction were not good cleaned in time of extraction. Similar effect can be seen for Pb content in sand fraction of profile 3.

The distribution of Cd in particle-sized separates obviously is not the same as for Cu, Ni, Pb and Zn. It seems, the amount of Cd is not influenced by the size of soil particles or organic matter accumulation, and the distribution of these elements remain uniform to soil horizons and particle-sized separates.

As a quantitative measure for the accumulation of heavy metals in sand fraction in the top-soil (A-horizon) was compared with the sand fraction of lowermost sampled horizon (C-horizon). The existence of similarity was tested with nonparametric Wilcoxon matched-pairs test. The significant level was set at $p < 0.10$. After applying statistical procedure were found out that with significance of 90% that concentration of Cd, Cu, Ni, Pb and Zn in sand fraction extracted from A- horizon of different soils represents the content of this elements in parent rocks for studied soil types.

The concentration of Cd, Cu, Ni, Pb, and Zn in sand fraction extracted from A-horizon of polluted and unpolluted soils can be used for diagnosis of soil pollution because it reflect the original content of this elements in soils, in other words, the pedogeochemical background content.

5.3 Determination of priority organic compounds in investigated soils

With agreement with European standards Ministry of Environment and Water of Bulgaria (1997) identified as “priority pollutants”: 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, γ -HCH). The knowledge about atmospheric deposition and soil contamination levels of POPs in Bulgaria (MÜLLER et al. 1998, ATANASSOV et al. 1999) is much more limited than for heavy metals.

The interest on the background contents of the organic substances in soil, which can cause contamination arise during last few years due mainly to the possibilities these values to be used as a scientific basis for setting soil quality standards.

5.3.1 Polyaromatic hydrocarbons (PAH)

The total concentrations $\Sigma 16$ PAHs are small at all studied sites (Table 5.3). Determined concentrations of different compounds are generally quite low as well as in arable lands as in forest areas. For three arable soils, which are included in agricultural lands the concentrations of Σ PAH ranges from 31.01 $\mu\text{g}/\text{kg}$ to 56.44 $\mu\text{g}/\text{kg}$ d. w. For studied forest soil concentration of Σ PAH varies from 22.09 $\mu\text{g}/\text{kg}$ (P5) to 28.66 $\mu\text{g}/\text{kg}$ d. w. (P4). Natural background concentrations estimated by EDWARDS (1983), resulting from plant synthesis and natural fires, is in range 1-10 $\mu\text{g}/\text{kg}$ for individual PAHs. The concentration of all determined individual components is close to this natural level and when it is occurring exceed of this level, then this is result from traffic and industrial emissions. Typical soil Σ PAH concentration derives from samples from rural areas is estimated at about 100 $\mu\text{g}/\text{kg}$ d. w. (TRAPIDO 1999). This concentrations is characteristic for the areas where no anthropogenic pollution sources occur and all studied soils had Σ PAH concentrations less than those value and also measured values were lower than the target value set by Dutch government for unpolluted soil (20-50 $\mu\text{g}/\text{kg}$ dry weight, VAN BRUMMELEN et al. 1996).

Tab. 5.3: Concentration of determined PAH in investigated soils

Compounds	Concentration, ($\mu\text{g}/\text{kg}$ d.w.)				
	P1	P2	P3	P4	P5
Naphthalene	11.80	18.85	14.20	3.65	n.d.
Fluorene	3.51	n.d.	n.d.	2.47	4.33
Phenanthrene	14.51	12.30	9.30	13.74	10.99
Fluoranthene	n.d.	9.93	5.98	5.71	4.37
Pyrene	n.d.	4.61	3.42	3.09	2.40
Chrysene/Triphenylene	n.d.	3.58	2.29	n.d.	n.d.
Benzo[b]fluoranthene	n.d.	5.14	5.24	n.d.	n.d.
Benzo[a]pyrene	n.d.	n.d.	2.38	n.d.	n.d.
Indeno[123-cd]pyrene	n.d.	2.03	n.d.	n.d.	n.d.
Benzo[ghi]perylene	n.d.	n.d.	2.45	n.d.	n.d.
S PAHs	31.01	56.44	45.26	28.66	22.09

n.d. – not detected

PAH PROFILES

From individual compounds predominate PAH consisting of 2 to 4 benzene rings like naphthalenes, phenanthrenes, fluoranthenes, and to a lesser degree, pyrenes and crysenes. These components tend to be strongly adsorbed to the soil. Strong sorption coupled with very low water solubility and very low vapour pressures make leaching and volatilisation insignificant pathways of PAH dissipation. The PAH patterns in different investigated sites depend of the number and kind of PAH sources (Figure 5.11). The A-horizon of the forest soil can be only affected due to the atmospheric deposition of PAH. Comparison between arable and forest soil is carried out to identify the possible sources of PAH. As shown in Figure 5.11, the dominant PAH typical for motor vehicle emission (benzo[b]fluoranthene, benzo[g,h,i]perylene) are detected in P1, P2, and P3, and these component are not detected in forest soils. The determined values of benzo[b]fluoranthene for P2 and P3 are 5.14 $\mu\text{g}/\text{kg}$ and 5.24 $\mu\text{g}/\text{kg}$ d. w. respectively, and 2.45 $\mu\text{g}/\text{kg}$ benzo[g,h,i]perylene for P3. For forest soils only air transported particles are the main source of PAHs, and the concentration of these components correlates significantly with the corresponding levels in air. Substantial amounts of PAH are transferred to forest soils via vegetative litterfall, because the compounds adsorb from air onto broad-leaf and needle surface. According to WICKSTRÖM and TOLONEN (1987) some of the PAH compounds may be produced biologically. LAFLAMME and HITES (1978) detected the phenanthrene homologues retene (1-methyl-7-iso-propylphenanthrene) and pimanthrene (1,7-dimethyl-phenanthrene) in non-contaminated remote soils and sediments and assumed that these compounds result from the reduction of abietic and pimaric acid which occur e.g., in *Pinus* species. Studied sites P4 and P5 are located in coniferous forests and detected higher phenanthrene concentration in comparison with arable soils is probably result from abietic acid reduction (fig. 5.11).

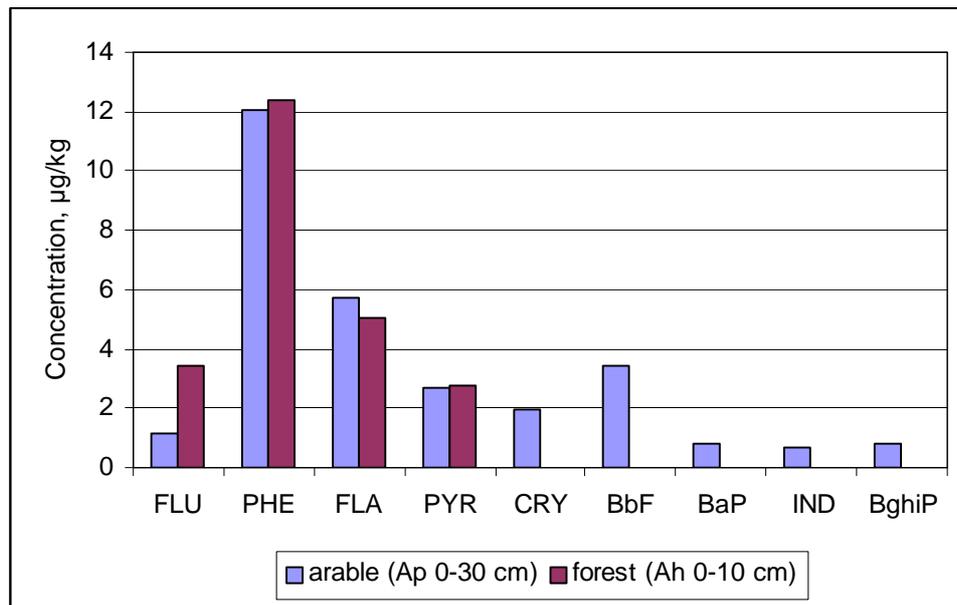


Fig. 5.11: Comparison between PAH distribution patterns of the A-horizon in arable and forest soils

Comparison between determined concentration of individual PAH compounds in studied soils with previous studies of Plovdiv and Sofia regions (MÜLLER et al. 1998), background values estimated from ATANASSOV et al. (1999) and with background concentration for forest soil - Speewald (BÄULKE 1994) is present in Figure 5.12. From presented results it becomes evident that in all studied soils the concentration of individual PAH components are near to estimated natural values for each compound and lower than proposed background concentration.

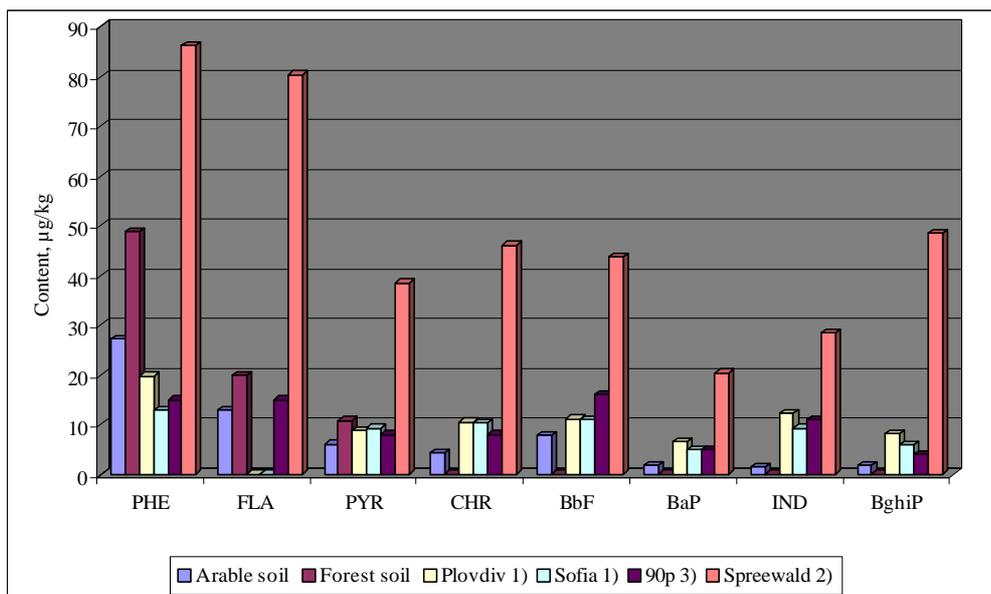


Fig. 5.12: Content of individual PAH in soil surface of studied soils (arable and forest), compared with those from previous study (MÜLLER et al. 1998), background values (90p) (ATANASSOV et al. 1999), and determined concentration in Spreewald (BÄULKE 1994).

POLYCHLORINATED BIPHENYLS (PCBS)

In all samples PCB values are uniform and are below limits of detection, only 5- and 6-chlorinated congeners were close to limit of determination. The reason for these relatively lower concentrations of PCBs may be less release of these compounds into the environment, a shorter accumulation time, enhanced photo-oxidation, biodegradation, and volatilization or enhanced leaching and release from soils. Another possible explanation is the stronger sorption of PAHs to OM than of PCBs resulting in a reduced availability for degradation, leaching, or volatilization. CHIOU et al. (1998) attributed this to the higher affinity of PAHs for aromatic structures in soil organic matter by π - π interaction or an enhanced sorption because of the planar molecular structure. This all can be reasons for this low content of PCB in analysed soils.

5.3.2 Organochlorine pesticides

From priority organochlorine pesticides in all studied samples were detected only DDX-compounds. Concentration of Σ DDX varies in wide limit form 11.24 $\mu\text{g/kg}$ d.w. (P5) to 950.43 $\mu\text{g/kg}$ d.w. (P2) (Table 5.4). Studied forest soils have been exposed only to aerial application of DDT, and the Σ DDX concentrations in these soils ranges from 11.24 to 18.12 $\mu\text{g/kg}$ d. w. The Σ DDX content in the most contaminated soil (P2) was at least a factor of 30 higher than other samples. Site P2 is arable land in which the major vegetation is wheat and crops. It have been previously reported that organochlorine pesticides persist much longer in soils with high organic matter content than soils with low organic matter content (EDWARDS 1983). The organic matter content in P2 is 4.05%, which is higher compared with other studied arable lands. This can be reason for higher content of DDX compounds, but the detected values prevail purposed precautionary values for Bulgarian soils (ATANASSOV et al. 1999). Other reason is that this values are due to fresh application of commercial DDT, which is actually made from mixture of DDT, DDE and DDD, that is evident from detected high values of DDT metabolites (see Table 5.4). and from ratio: p,p'-DDT/p,p'-DDE. In general, a small value of the p,p'-DDT/p,p'-DDE ratio is indicative of aged (microbially degraded) DDT (DIAMON and OWEN 1996) and a value much greater than one indicates fresh application, however, there is a large variability with soil type. Ratios of p,p'-DDT/p,p'-DDE in the present study were quite variable ranging from 0.12 to 1.10. The highest ratio occur in the P2 - area of Pirdop = 1.10.

Tab. 5.4: Concentrations of DDX compounds in studied soils

Site	p,p'-DDE ($\mu\text{g/kg}$)	o,p'-DDD ($\mu\text{g/kg}$)	p,p'-DDD ($\mu\text{g/kg}$)	o,p'-DDT ($\mu\text{g/kg}$)	p,p'-DDT ($\mu\text{g/kg}$)	Σ DDX ($\mu\text{g/kg}$)	DDT/DDE ratio
P1	11.70	n.d.	0.75	0.68	8.25	21.38	0.71
P2	386.34	n.d.	68.32	72.17	423.60	950.43	1.10
P3	30.16	n.d.	n.d.	0.78	3.64	34.58	0.12
P4	8.55	0.93	1.55	1.28	5.81	18.12	0.68
P5	5.14	0.76	1.07	1.44	2.83	11.24	0.55

n.d. – not detected

DDT - METABOLITES

The main analogues of DDT degradation found in the environment and in analysed soils, are: o,p'- and p,p'-DDT; o,p'- DDD[1,1-dichloro-2-(o-chlorophenyl)-2-(p-chlorophenyl) ethane] and p,p'-DDD[1,1-dichloro-2-bis-(p-chlorophenyl) ethane]; and o,p'-DDE [1,1-dichloro-2-(o-chlorophenyl)-2-(p-chlorophenyl) ethylene] and p,p'-DDE [1,1-dichloro-2,2-bis-(p-chlorophenyl) ethylene] (see appendix Fig. A2).

In soil, DDT is microbially transformed to the stable and toxic metabolites DDE and DDD (Figure 5.13). Microbial degradation of DDT, DDD, and DDE is generally slow, resulting in environmental persistence of these compounds. The rate of transformation depends on several factors including soil type, temperature, moisture and organic carbon content (HITCH and DAY 1992; BOUL et al. 1994). Results of a long-term study of forest soils indicate that DDT persist with a half-life of 20-30 years. (DIMOND and OWEN 1996). Under certain conditions, however, DDT may degrade to DDD with a half-life of a few days. Regardless, because o,p'-DDT and o,p'-DDD are chiral molecules, their degradation by biological processes and their transport across biological membranes are expected to be enantioselective, that is, one enantiomer will degrade faster than the other or be preferentially transported (Table 5.4). The principal products of dechlorination of DDT - two isomers in reducing environments are o,p'-DDD and p,p'-DDD, respectively (YOU et al., 1996). Reductive dechlorination of o,p'- and p,p'-DDD can ultimately produce small yields of o,p'-DDA [o-chlorophenyl p-chlorophenyl acetic acid] and p,p'-DDA [bis (p-chlorophenyl) acetic acid] as well as several other minor products. o,p'-DDE and p,p'-DDE are produced by dehydrochlorination of the respective DDT under aerobic conditions; they are the principal DDT analogues found in soils (see appendix Fig. A2) after weathering and also are important sediment pollutants.

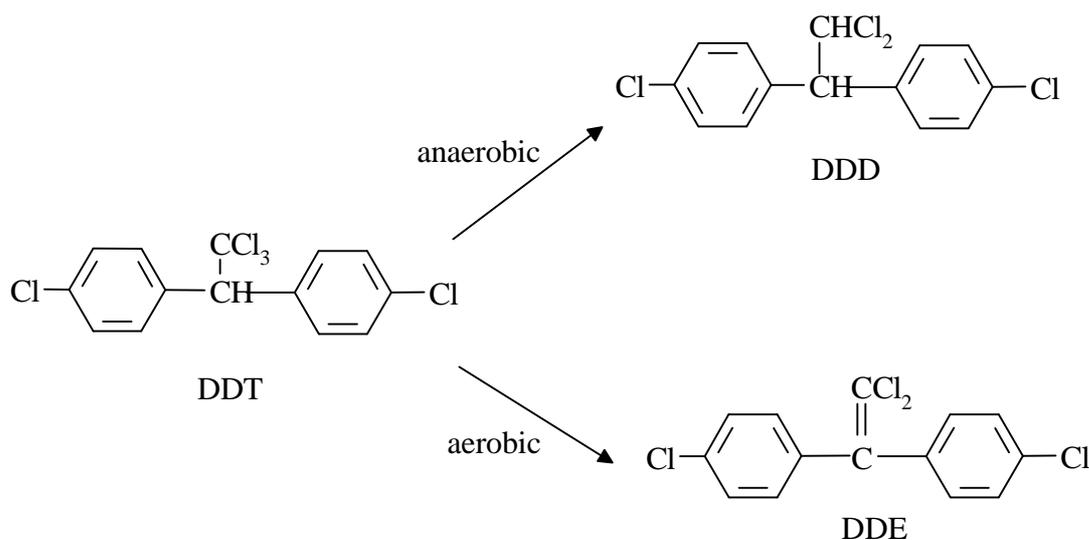


Fig. 5.13: Example of anaerobic and aerobic products resulting from the biological transformation of DDT

In all recent samples (without P2) the p,p'-DDE was the predominant residue (Table 5.4), with the remainder being mainly p,p'-DDD with low level of o,p'-DDT. In studied forest soils were detected concentrations of each of DDT-metabolites, even than this soils are exposed only to air-transported pollution. Slow degradation in this soils may be attributed to unplowed conditions resulting of lower soil porosity which is less ideal for microbial activity.

Although the use of organochlorine pesticides ceased in Bulgaria in 1970, the results indicate that even after a period of 30 years, residues still persist in samples of top soil. It is evident that volatilisation and degradation of all the pesticides examined do occur in soil although the process may be slow.

5.4 Statistical analysis

In order to determine existence of linear similarities between the variables (soil parameters, chemical and heavy metal content) of the data record of the investigated soil samples the statistical procedure of applying Spearman correlation (see Chapter 4.4) was consulted.

In Table 5.5 are presented estimated simple correlation coefficient between all variables. From listed coefficients it is evident, that even when it is applied non-parametrical methods for quantitative description of widely varying values as in studied case (comparison between all studied soils-polluted and non polluted) it can not be find dependencies between variables. It was made attempt to compare five different soils with different heavy metal concentrations in soil surface, which may results from varying chemical composition of different geogenic layers, pedogenic redistribution, and anthropogenic inputs, etc. Only content of Fe₂O₃ and heavy metals show significant correlation. As heavy metals are strongly sorbed to Fe₂O₃ (ADRIANO 1986), they may accumulate in surface horizons. Generally, the content of Fe₂O₃ correlate significantly with elements, Cu, Ni, Mn. Near soil surface the content of Pb and Zn is independent of the Fe-oxides content ($r_{SZn}=-0.50$; $r_{SPb}=-0.90$) and reflects a change in the input of heavy metals into soil - probably caused by increased emissions due to industry. Organic matter and clay, which together with Fe₂O₃ are the main adsorber of heavy metals in soil do not show significant correlation.

Tab. 5.5: Correlation matrix of data from soil surface of studied sites (p<1%)

	pH	OM	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	Na ₂ O	K ₂ O	Cd	Cu	Ni	Pb	Zn	ΣDDX	ΣPAH
pH	1.00													
OM	-0.70	1.00												
SiO ₂	-0.30	0.00	1.00											
Al ₂ O ₃	-0.70	0.20	0.80	1.00										
Fe ₂ O ₃	-0.60	0.10	0.90	0.90	1.00									
Na ₂ O	0.50	-0.40	-0.60	-0.40	-0.70	1.00								
K ₂ O	-0.70	0.20	0.80	1.00	0.90	-0.40	1.00							
Cd	0.53	-0.95	-0.11	-0.11	-0.11	0.53	-0.11	1.00						
Cu	-0.10	-0.60	0.60	0.60	0.70	-0.20	0.60	0.63	1.00					
Ni	-0.20	0.00	0.50	0.20	0.60	-0.90	0.20	-0.16	0.40	1.00				
Pb	0.70	-0.20	-0.80	-1.00	-0.90	0.40	-1.00	0.11	-0.60	-0.20	1.00			
Zn	0.30	-0.30	-0.70	-0.70	-0.50	0.10	-0.70	0.32	-0.10	0.20	0.70	1.00		
ΣDDX	0.00	-0.70	0.20	0.30	0.40	0.00	0.30	0.79	0.90	0.30	-0.30	0.30	1.00	
ΣPAH	0.00	-0.70	0.20	0.30	0.40	0.00	0.30	0.79	0.90	0.30	-0.30	0.30	1.00	1.00