Chapter 7

Soil Contamination in Forest and Industrial Regions of Bulgaria

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Additional information is available at the end of the chapter

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Abstract

Based on systematic data from 1988 to 2015, the main sources of soil contamination in forest and industrial areas of Bulgaria were presented. The processes of soil acidification and eutrophication as well as accumulation of heavy metals in forest and industrial soils were analysed. The content of heavy metals in soils, pasture grasses and medicinal plants from two National Parks—Central Balkan and Pirin, as well as from two Natural Parks—Bulgarka and Strandzha was also reported. Data on heavy metals accumulation in leaves of tree species in some industrial areas of the country were presented as well. Soil and plant contamination with heavy metals were estimated according to the applied criteria of ICP Forests.

Keywords: air pollution, atmospheric depositions, forest soils, heavy metals, medicinal plants, foliar analysis, protected area

1. Introduction

Soil and air pollution turned to be a serious ecological problem during the last decades. Significant elevation of pollutant concentrations was established in many European countries [1–4]. The alteration of the chemical composition of ecosystems near emission sources is among the main environmental impacts of industry. Industrial sources make a significant contribution to environmental pollution of soil and plants with the emitted heavy metals [5, 6]. Irrespective of their sources in the soil, accumulation of heavy metals can degrade soil quality and reduce crop yield and the quality of agricultural products and thus negatively impact the health of human, animals and the ecosystem [7].

Forest ecosystems present one of the main parts of biosphere. They affect the composition and the quality of atmosphere and also shape climate conditions both on regional and on global scales [8, 9]. The forest stands were endangered from the harmful effect of air and soil pollutants [10–13]. Global change involves simultaneous and rapid alterations in several key environmental parameters that control the dynamics of forests [14]. Climate change and air pollution affect forests by changes in soil processes, tree growth, species composition and distribution, increased plant susceptibility to biotic and abiotic stress factors, increased fire danger, decreased water resources and recreation value [9, 15, 16]. The physical and ecological conditions of forest ecosystems have been influenced mainly by the deposition of atmospheric pollutants and by changing climatic conditions with a series of warm and dry periods. Apart from the weather conditions, heavy metals were shown to be one of the primary causes of tree damages. The knowledge of the heavy metal accumulation in soil, the origin of these metals and their possible interactions with soil properties are priority objectives in the environmental monitoring [17, 18]. The surface soil layer is of particular interest in the forest ecosystem monitoring due to its role as a stable adsorbent of the deposited atmospheric substances. The behaviour of heavy metals in soils and their impact on the living organisms have been described in details in the literature. The main effects of their increased concentration are connected with inhibited microbial activity, delayed litter decomposition processes, changes in nutrient availability and increased accumulation from the plants [19–24].

The movement of air masses from urban and industrial regions results in frequent episodes of high levels of ozone in forests. Being a major phytotoxic atmospheric pollutant in most European countries, ozone is a significant cause of reduction in growth of tree vegetation [25–27]. It has been shown that the indirect forcing of climate change through ozone effects on the land carbon exchange could be an important factor and can induce a positive feedback for global warming [28]. High concentrations of ozone occur not only in areas with large sources of pollution but also in suburban and rural sites, located away from major sources of emissions [29, 30]. Elevated concentrations of ambient ozone are also of great concern for our country because ozone is turned to be the most important air pollutant in both relatively clear forest areas in Bulgaria [31–33]. At the suburban and remote mountain sites forest trees were subject to the impact of elevated ozone concentrations at especially the beginning of the vegetation period when the growth process is intensive [33].

The major contributor to forest degradation was also sulphur dioxide, a gaseous substance with direct and powerful phytotoxic and acidifying effects. Nitric oxides affect woody plants directly by entering through the stomata and indirectly through soil acidification and environmental eutrophication. Drought stress predisposes trees to the negative effect of pollutants [25, 34].

National parks and other protected areas despite their special management regimes are subjected to air pollution. Air pollution impact was reported by the National Parks Conservation Association of the USA. The analyses showed that national parks have significant air pollution problems and 36 of them at times experienced "moderate" or worse ozone pollution [35]. Air pollution affects European Protected Areas as well. Moderate-to-high ozone levels were measured inside Spanish national parks and protected areas [36]. Air pollution represents a serious hazard for the ecosystems in national parks in the Czech Republic, Slovakia and other countries [37, 38].

Despite considerable research on the mechanisms of damage, it still remains a challenge to distinguish pollution injury from natural stress injury in the field [39]. Little research has been done in regard to the tolerance of trees to metal pollution, due to the size and longevity of most species. Information is still needed on the precise limits of tolerance of individual plant species, particularly trees, to metals.

2. Air pollution

2.1. Emissions of certain air pollutants and tendencies

The main sources of emission of air pollutants on the territory of Bulgaria (sulphur dioxide, nitrogen oxides, particulate matter) are the thermal power stations (TPS), operating on solid fuels and fuel oil, road transport and household sources [40]. In 2013, the annual emissions of sulphur dioxide were 193.97 kt/year. The thermal power stations were the main sources of sulphur dioxide—72% (see **Figure 1**). The annual emission of nitrogen oxides was 123.54 kt. The thermal power stations and road transport had the biggest share—62% of the total amount, equally divided between the two sectors (**Figure 2**).

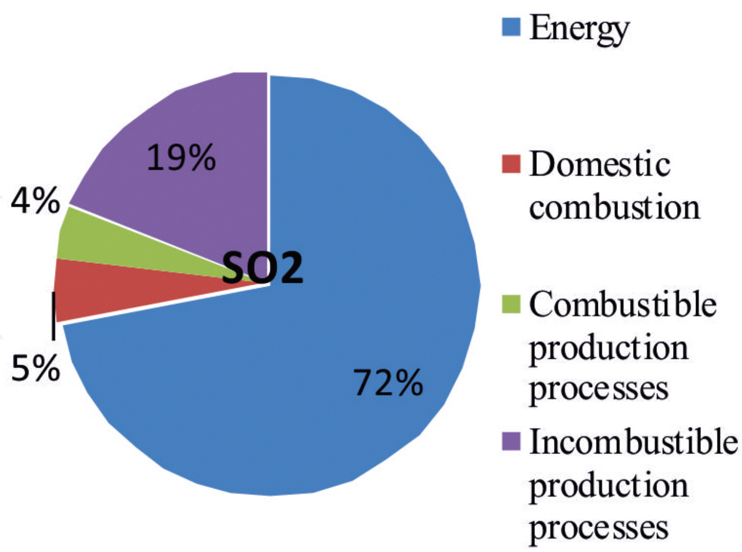

Figure 1. Main sources of sulphur dioxide in Bulgaria, 2013.

One of the pollutants, causing the most serious problems regarding air quality in the major Bulgarian cities, is particulate matter (PM10). The total amount of PM10 in 2013 was 42.44 kt.

The main source of particulate matter emissions is domestic heating—59% of PM10 (see **Figure 3**) and 82% of PM2, 5.

The emissions of the main pollutants tend to decrease for the period 2009–2013. This trend is most clearly observed for sulphur dioxide, resulting from the construction of desulphurization installations to the major thermal power stations (TPS), operating on coal. The increased emissions in 2011 were the result of burned larger quantities lignite coal throughout the year (see **Figure 4**).

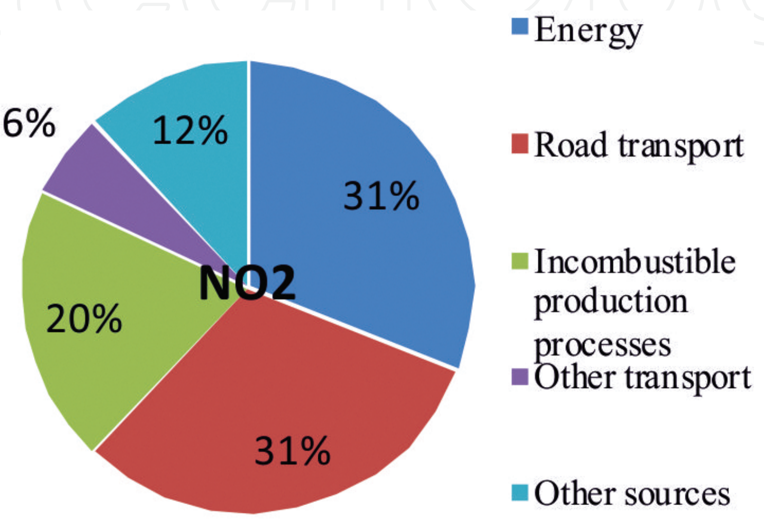

Figure 2. Main sources of nitrogen dioxide in Bulgaria, 2013.

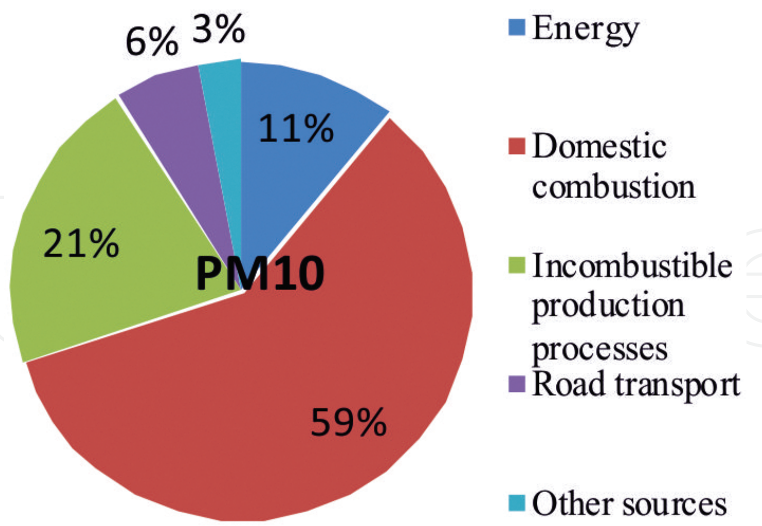

Figure 3. Distribution of particulate matter emissions by sources.

The share of the emission sources changed over the years—in 2009, sulphur dioxide from the TPS was 93.9% of the total amount, reported in Bulgaria; the main source of nitrogen oxides was the road transport—49% of the total emissions in the country.

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The condition of the air in Bulgaria is controlled by the National Air Quality Monitoring System. Three of the air quality monitoring units equipped with automatic measuring stations (AMS), monitor the air condition in forest territories. These are the stations for intensive monitoring (IM), located in the regions of Yundola, Vitinya and Staro Oryahovo. The observations are carried out in relation to the implementation of the International Cooperative Programme "Forests". The aim is to trace the transfer of pollutants and their impact on the different components of the forest ecosystems. The concentrations of the following pollutants are measured—sulphur dioxide, nitrogen oxide, nitrogen dioxide and ozone. The ML®9850 sulphur dioxide analyser is an ultraviolet fluorescence spectrophotometer for continuously measuring of SO_2 concentrations. The ML®9841A nitrogen oxides analyser works on the basis of gas-phase chemiluminescence detection to perform continuous analysis of nitric oxide (NO), total oxides of nitrogen (NO_x), and nitrogen dioxide (NO_2). Non-dispersive ultraviolet photometer serves as the basis for the ML®9812 Ozone Analyser. The atmospheric depositions in the open and under the forest canopies are also measured—quantity, acidity, concentration of acidic and basic ions and heavy metals [41].

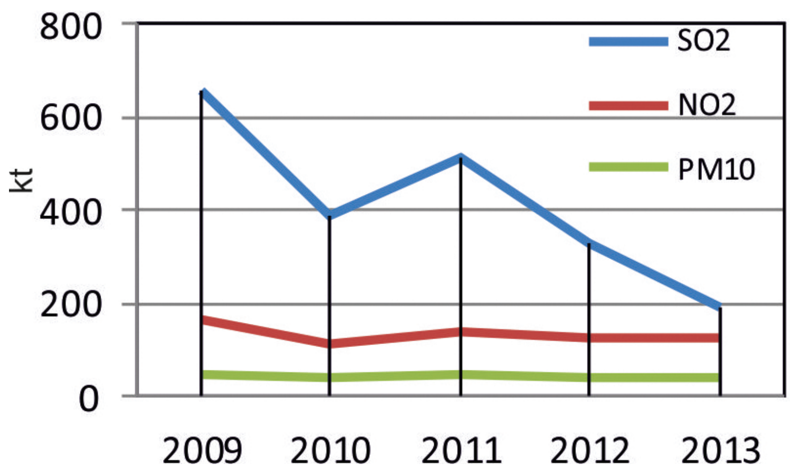

Figure 4. Tendencies in emissions of sulphur dioxide, nitrogen dioxide and PM10 (2009–2013).

2.2. Atmospheric pollutants in the intensive monitoring stations

The average annual concentrations of sulphur dioxide varied from 3.97 to 17.4 µg m^{-3} for the region of St. Oryahovo, from 3.62 to 18.5 µg m^{-3} for Vitinya and from 2.09 to 12.9 µg m^{-3} in Yundola (see **Figure 5**). The highest values for St. Oryahovo and Vitinya stations were determined in 2008 and for Yundola in 2009. In the period 2008–2011, there was a significant decrease of the annual concentrations from 4.5 to 6 times, followed by a gradual increase until 2015.

The trends regarding the average annual values of sulphur dioxide were almost the same for the three stations, regardless of the considerable distance between them, which indicates that nearly identical regional values occurred as a result of the transfer. The measured concentrations did not exceed the limit value (LV) for vegetation protection [42].

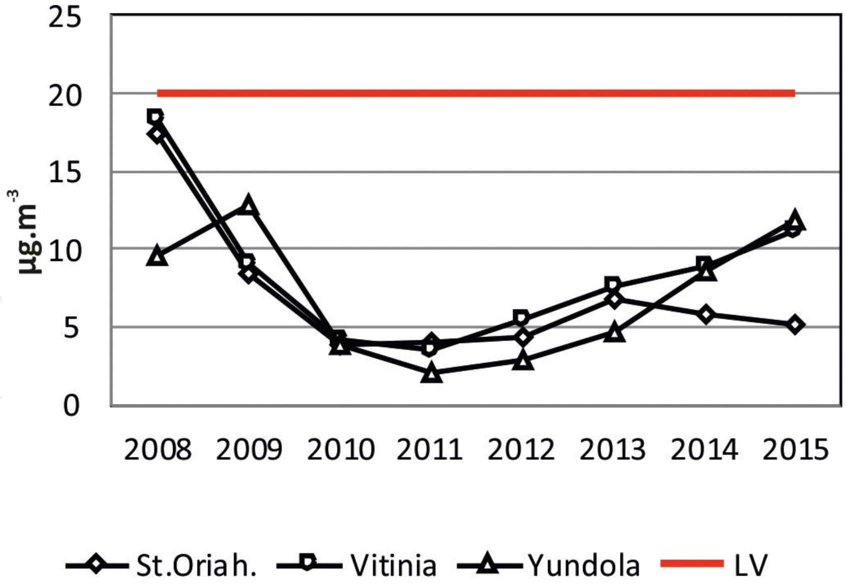

Figure 5. Average annual concentrations of sulphur dioxide (LV–limit value).

The annual mean values for nitrogen oxides varied in a wider range—from 5.03 to 20.6 μg m^{-3} for the region of St. Oryahovo, from 7.87 to 51.6 μg m^{-3} for Vitinya and from 3.37 to 19.8 μg m^{-3} for Yundola (see **Figure 6**). Higher values were measured during the first 2 years of the period 2008–2015; the lowest values were registered in 2011 for St. Oryahovo and Vitinya, and in 2014, for Yundola.

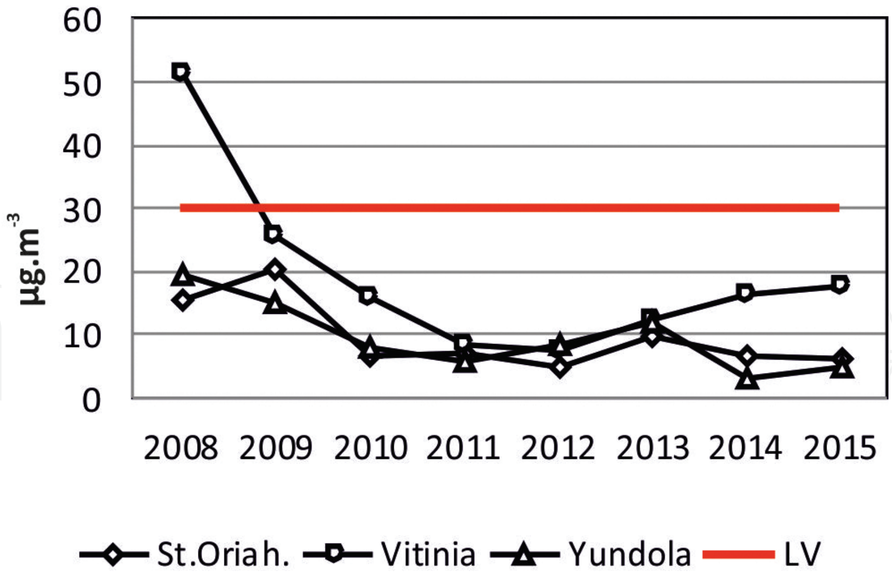

Figure 6. Average annual concentrations of nitrogen oxides (LV–limit value).

During the period 2008–2011, the tendency was similar to that of sulphur dioxide and was characterized by decreased concentrations; after that period, the values continued to decrease with insignificant fluctuations for St. Oryahovo and Yundola. Regarding the region of Vitinya, the values gradually increased till 2015. The measured concentrations exceeded the LV for vegetation protection only in 2008 for the region of Vitinya [42].

The AOT40 index (index of accumulated ozone exposure over a threshold of 40 ppb (80 μg m^{-3}), calculated for the period from May to July, was used to assess the ozone impact on forest ecosystems. The data, presented on **Figure 7**, indicate that ozone is almost constant stress factor for the forests in the region of Yundola, where the target value for protection of vegetation was exceeded for the prevailing part of the period 2008–2015, with a maximum value in 2015—about 2 times above the target value [42].

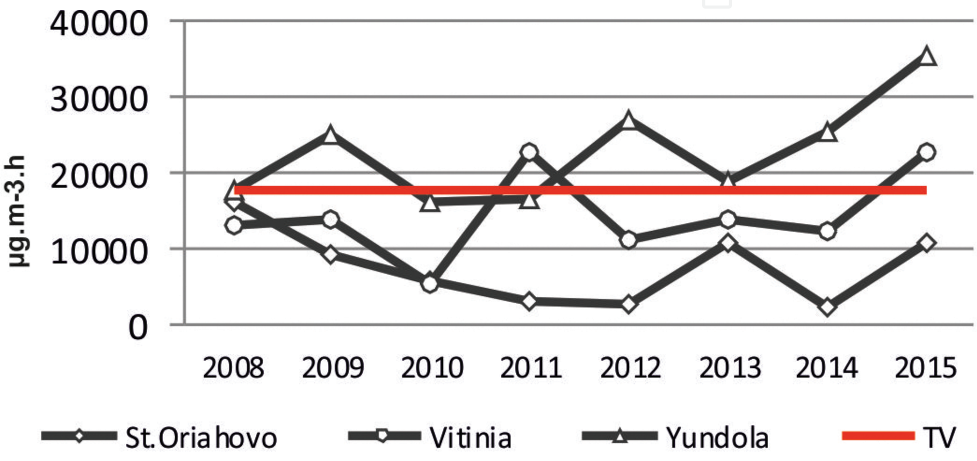

Figure 7. Index of accumulated ozone exposure over a threshold of 40 ppb (80 μg m^{-3}) (AOT40). TV—target value for protection of vegetation.

No exceedances of AOT40 were registered for the region of St. Oryahovo; for the region of Vitinya, the AOT40 was exceeded in two years—2011 and 2015 [42].

2.3. Atmospheric pollutants in industrial regions

The study was made in Devnya region—a big industrial zone in the Eastern Bulgaria. Forest vegetation consisted of 20-year-old plantations of *Celtis australis* L. and *Fraxinus americana* L. grown at 500 m from the sources of intensive air pollution and near a highroad with heavy traffic. Even-aged control stands were grown as plantations in relatively unpolluted region about 15,000 m far from the chemical plants. The air pollutants, emitted from Devnya industrial region, included sulphur dioxide, nitrogen oxides, CO, HF, NH_3, Cl_2, HCl, CaO, $CaCO_3$, high levels of silicon, solid and liquid aerosols, organic compounds, particulate matter of dust and soot, Al and heavy metals. The great part of nitrogen oxides and sulphur dioxide are dissolved as nitric and sulphuric acids, which causes acid rains on the region. The monitoring of air pollution in the industrial region was made continuously by automatic station.

Monitoring data for sulphur dioxide during 2004 showed a wide variation of 1-h means between 1.3 and 210 μg m^{-3}. There were many short time events of high sulphur dioxide concentrations mainly during the winter period. The maximal 24-h values of sulphur dioxide were between 10.5 and 39.3 μg m^{-3}. Within the six-month growth period of trees (April—September), the month values for sulphur dioxide were between 4.8 and 17 μg m^{-3} (**Figure 8**).

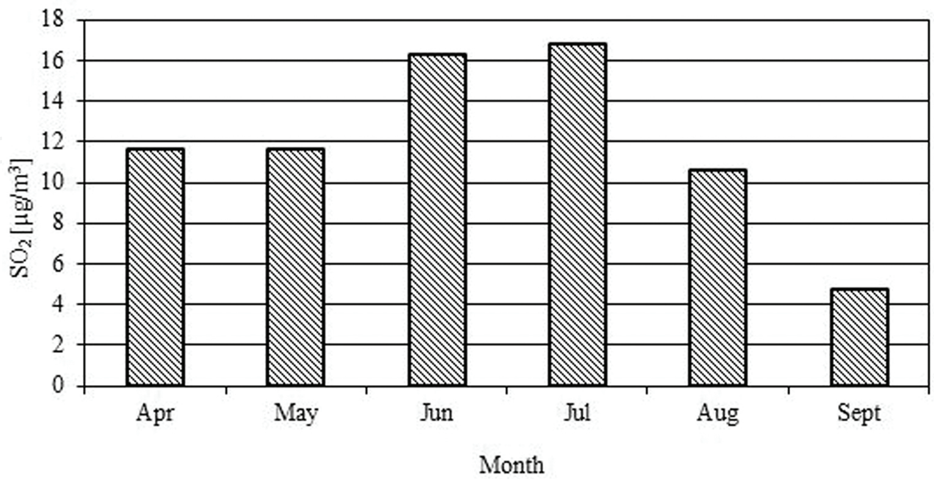

Figure 8. Month values for SO_2 in Devnya industrial region during the growing period of 2004.

Maximal 24-h means of NO_2 for 2004 were between 10 and 30 ppb. The all of 4-h means for NO_2 were below 80 μg m^{-3} for the entire period of monitoring. Month average concentration of nitrogen dioxide during the growth period of 2004 varied between 20.5 and 55 μg m^{-3} (**Figure 9**).

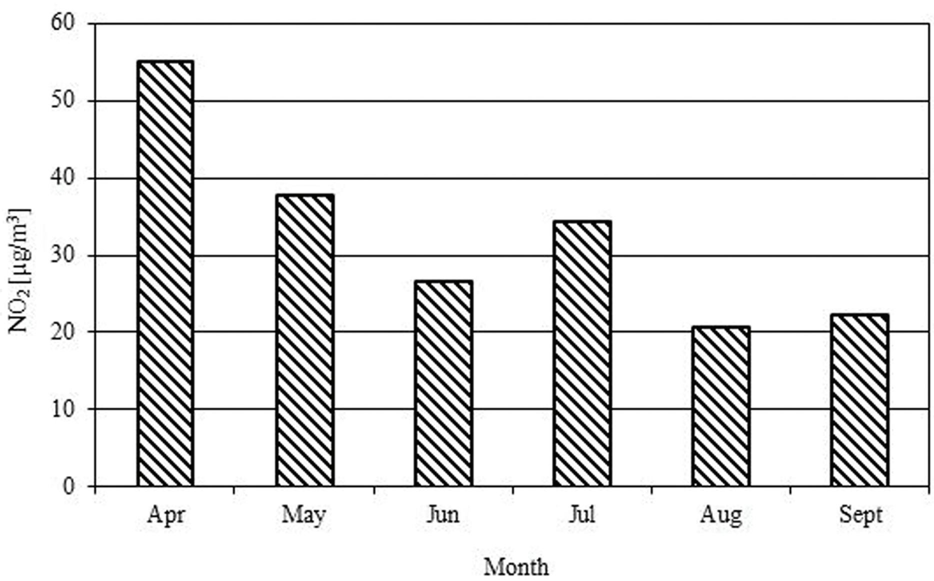

Figure 9. Month values for NO_2 in Devnya industrial region during the growing period of 2004.

The maximal 24-h means of ozone concentrations within six-month growth period of 2004 varied between 55 and 83 μg m^{-3}. The highest values of the maximal 24-h means for ozone concentrations were observed in July and August (**Figure 10**).

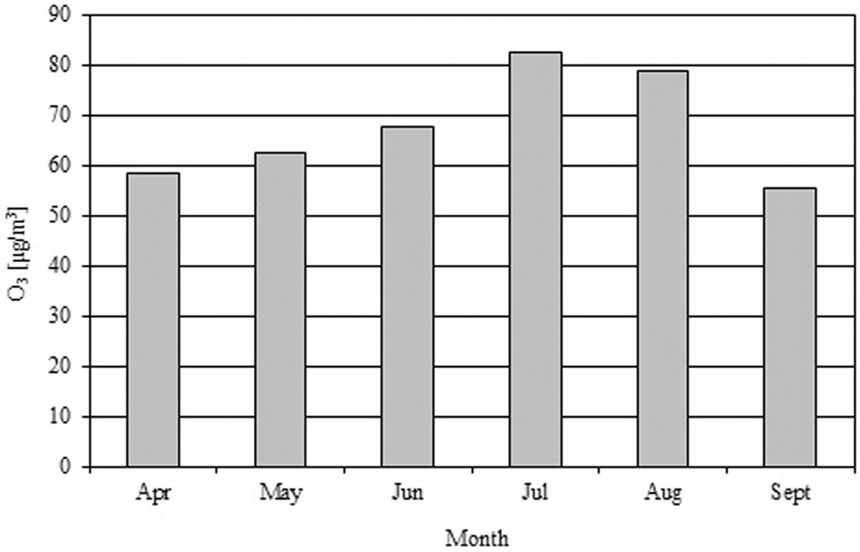

Figure 10. Maximal 24-h means of ozone concentrations in Devnya industrial region during the growing period of 2004.

The average and maximal 1-h concentrations of ozone were 52.2 and 103.5 μg m^{-3}, respectively. Over the growing season of 2004, the daily means of ozone concentrations were only during a few days below 50 μg m^{-3}. The target value of the index AOT40 for protection of vegetation [42] was permanently exceeded during the 5-year period of monitoring (**Figure 11**). In 2003, the index AOT40 was 3 times above the target value.

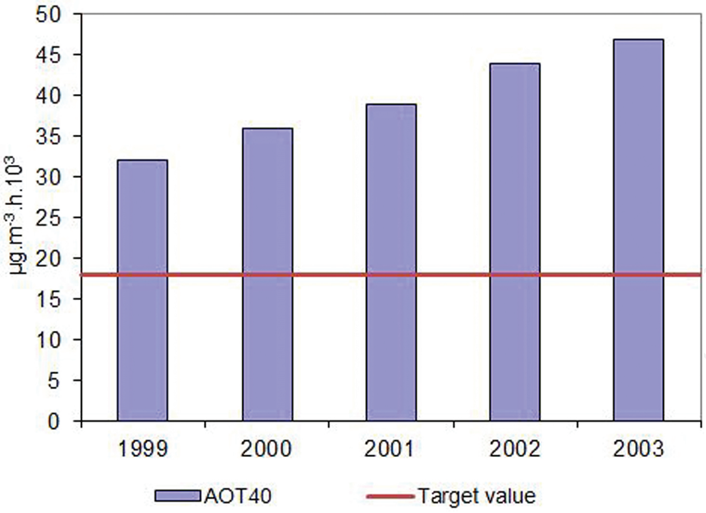

Figure 11. Index of accumulated ozone exposure over a threshold of 40ppb (80 μg m^{-3}) (AOT40) during the five-year period (1999–2003).

On the basis of the data processing for the concentrations of SO_2, NOx and O_3 in the air in Devnya region, we can draw the conclusion that the most remarkable air pollution is with ozone. Therefore, a negative effect on the forest ecosystems during the growth period should be expected mainly for the ozone. This pollutant is turned to be the most important ecological risk factor for woody plant in the region during the period of their high physiological activity. In regions with low NOx concentration, ozone formation is dependent entirely on NOx (NOx sensitive regions) [43]. In contrast to the threshold value for accumulated ozone dose (10,000 μg m^{-3}) concerned the six-month growing period of trees, some studies showed that a possible effect of ozone occurs only at very high AOT40 (>70,000 μg m^{-3}) [44].

2.4. Atmospheric depositions in the intensive monitoring stations

The amount of depositions for the period 2008–2015 is presented on **Figure 12**, which shows significant variation over the years. The average acidity of depositions for the respective period varied from pH 5.06 to pH 6.75 for the region of St. Oryahovo, from pH 5.05 to pH 5.5 for Vitinya and from 5.42 to 5.89 for the region of Yundola (see **Figure 13**).

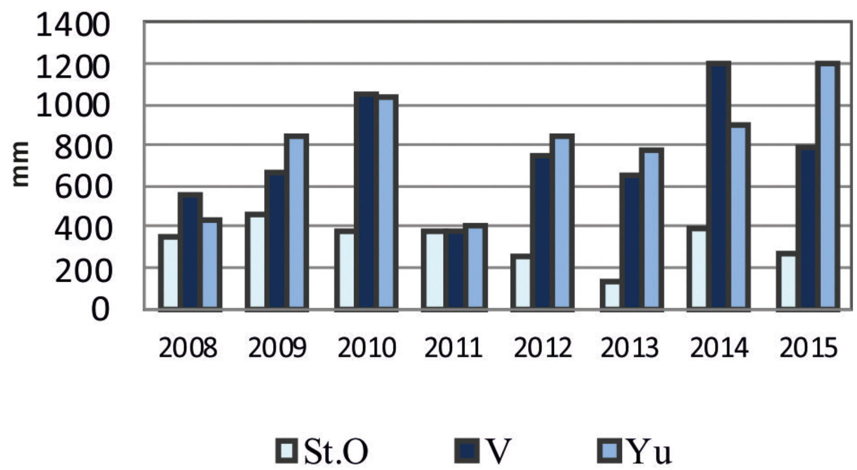

Figure 12. Amount of atmospheric depositions in the open. St. O—stationar Staro Oriahovo, V—stationar Vitinia, Yu—stationar Yundola.

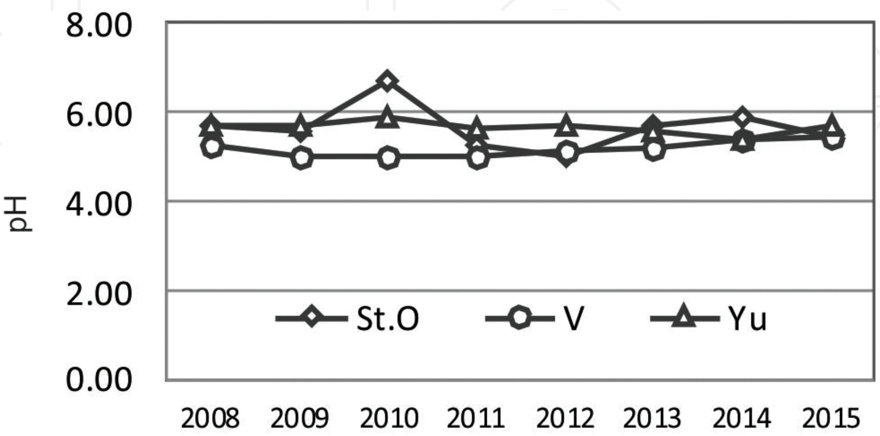

Figure 13. Acidity of atmospheric depositions in the open. St. O—stationar Staro Oriahovo, V—stationar Vitinia, Yu—stationar Yundola.

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From the presented data, it can be concluded that during the respective period, the depositions in the region of Vitinya were within the scope of "acid rain"—pH < 5.5. Regarding the other two regions, the acidic depositions were observed only in certain years—2011, 2012 and 2015 for St. Oryahovo, and in 2014, for Yundola.

The amount of sulphate sulphur varied within the range from 0.35 to 4.3 kg ha^{-1} annually for the region of St. Oryahovo, from 1.91 kg to 7.78 kg ha^{-1} annually for Vitinya and from 1.57 to 10.53 kg ha^{-1} annually for Yundola (see **Figure 14**).

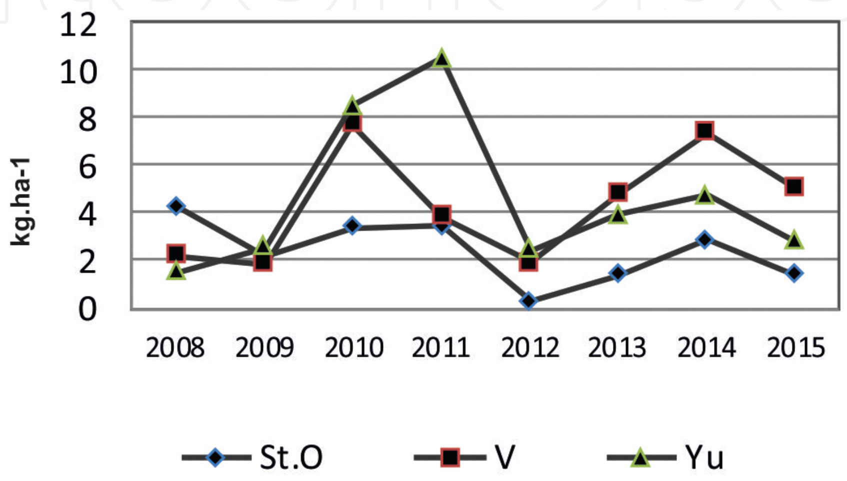

Figure 14. Intake of sulphate sulphur with the deposition in the open. St.O—stationar Staro Oriahovo, V—stationar Vitinia, Yu—stationar Yundola.

The relatively low concentration of sulphur dioxide in the region of Yundola did not correlate with the high sulphur levels in the depositions. The amount of nitrogen depositions in the region of Yundola was also higher—from 3.01 to 10.46 kg ha^{-1} annually (see **Figure 15**).

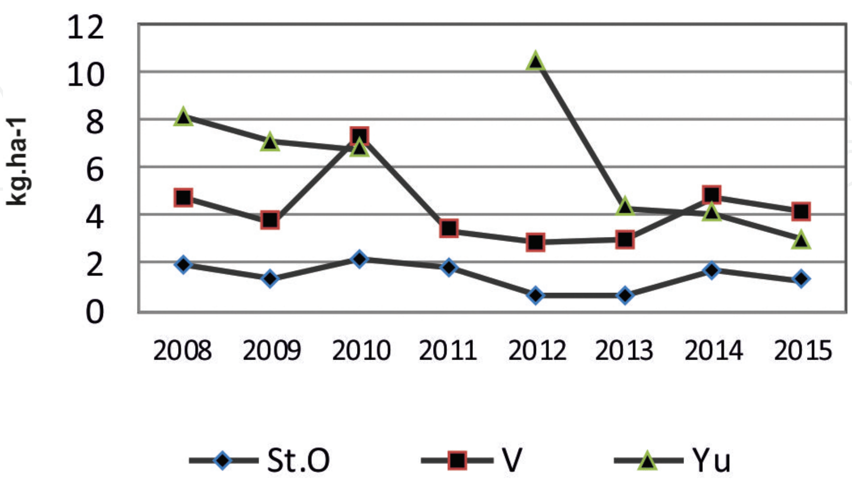

Figure 15. Intake of nitrogen (ammonium and nitrate) with the depositions in the open. St.O—stationar Staro Oriahovo, V—stationar Vitinia, Yu—stationar Yundola.

3. Pollution of soils, observed by the forest ecosystem monitoring network

The International Co-operative Programme on Assessment and Monitoring of Air Pollution Effects on Forests operating under the UNECE Convention on Long-range Transboundary Air Pollution (CLRTAP), level I, has been implemented in Bulgaria since 1986, and level II—since 1998. The "Manual on methods and criteria for harmonized sampling, assessment, monitoring and analysis of the effects of air pollution on forests" (1986–2010), adopted by the Programme, is implemented in order to study the acid status, eutrophication and heavy metal content in soils. A significant part of the obtained results has been published [45–49]. The results, obtained for soils of a total of 104 soil profiles, were summarized for a 20-year period—from 1986 until 2008 [50].

The results for Cambisols and Luvisols from the regions of western Balkan Mountains, Sredna Gora, Rhodope Mountains and Strandzha, obtained for the period 2009–2015, are presented in this book. Data on 62 level I soil profiles from the national forest ecosystem monitoring network were summarized.

3.1. Soil acidification

The implementation of the forest ecosystem monitoring in Bulgaria began in 1986—a period when soil acidification in some parts of Europe had already been proven [51–56].

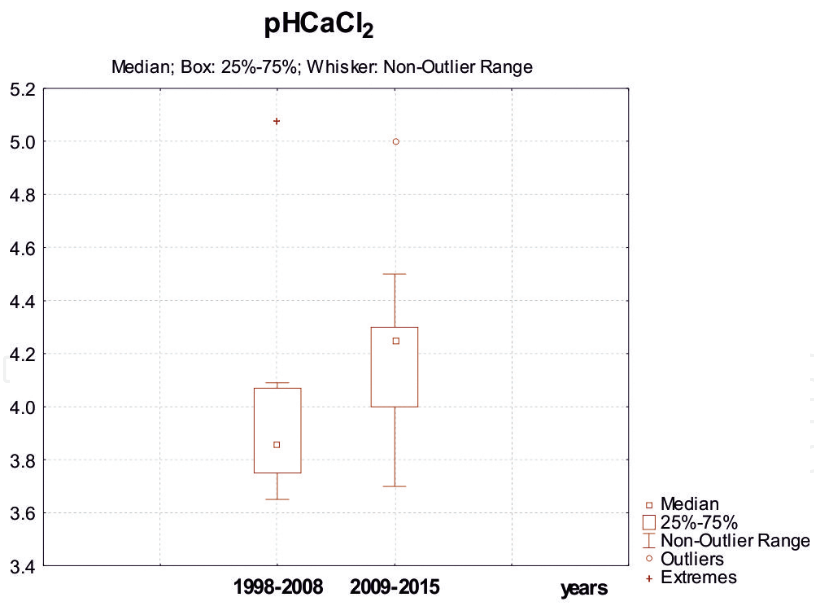

Figure 16. $pHCaCl_2$ in Cambisols for the periods 1998–2008 and 2009–2015.

The lack of basic information about time series data, obtained from permanent sample plots in the past, did not allow to record the impacts of regional and/or global transfer of acid atmospheric depositions on soils, as well as the subsequent restoration processes due to the measures undertaken. On the basis of the information, obtained for a 20-year period, it was proven that soil acidity is stable over time and did not change for the period from 1986 to 2008 [50].

The trends of stability in soil acidity continued for the period 2009–2015. The absence of statistically significant differences between the values of pH$CaCl_2$ for the periods from 1998 to 2008 and from 2009 to 2015 for Cambisols and Luvisols is presented on **Figures 16** and **17**.

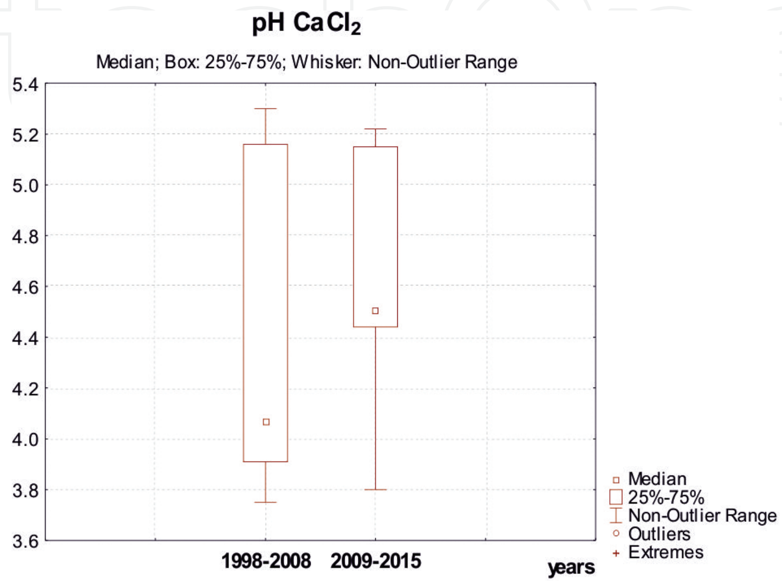

Figure 17. pH$CaCl_2$ in Luvisols for the periods 1998–2008 and 2009–2015.

The average pH value of Cambisols was 4.28 and 4.78 of Luvisols, respectively. The buffer range, assessed using Ulrich's concept [57], did not change and remained in the "mostly low" category. It was mainly due to proton exchange with base cations.

The analysis of the available information allows to conclude that there no impact of acid atmospheric depositions on pH of the monitored Cambisols and Luvisols for the period 1986–2015.

3.2. Soil eutrophication

The ratio organic C/N organic layer: organic C/N mineral layer in forest soils has been accepted as the indicator for changes occurring in nitrogen cycle due to increased amounts of nitrogen depositions. It is considered that regarding soils in forest ecosystems in Europe, the values of this ratio, which are below the critical minimum (1.0), occur in areas with increased deposition of nitrogen-containing components. Exceptions are determined in the northern parts of the continent due to causes of natural origin—harsh climatic conditions, delayed decomposition and accumulation of organic matter [22]. The changes, occurring in soils under the impact of nitrogen depositions, are towards eutrophication [58, 59]. According to ICP Forest data (2011), 61% of the soils on the continent are sensitive to this process. Under the impact of eutrophication, nitrogen in soils shifts from a state of shortage to saturation—a process, most clearly expressed in northern and Central Europe [60].

No decrease of this ratio under the critical level, due to increased nitrogen depositions, was registered for soils in Bulgaria during the period 1998–2008 [50] (see **Table 1**).

Layer/period	Mean	SD	min	max
	[org. C/total N (litter)]/[org. C/total N (surface soil layer)]			
	1998–2008			
OL/0–10 cm	2.52	0.33	1.87	2.80
OF/0–10 cm	2.08	1.18	0.43	5.52
	2009–2015			
OL/0–10 cm	3.74	2.04	1.39	6.63
OFH/0–10 cm	1.70	2.04	0.80	2.38

Table 1. Ratio org. C/total N in litter (mull—OL and OF and moder—OL and OFH) compared to the ratio org. C/total N in 0–10 cm soil layer.

The results, obtained during the next evaluation period (2009–2015), confirmed this trend. The minimum values, specified in **Table 1**—0.43 for the period 1998–2008 and 0.80 for the period 2009–2015, were determined in spruce stands from the Rhodope Mountains at an altitude of 1400–1600 m (in the regions of Shiroka polyana locality and Progled village). The stands are located on flat terrains with northern exposure, where the accumulation of organic matter occurs. Under the influence of the cold mountain climate, the decomposition of the organic matter is delayed. Since there are other sample plots in these areas, the results of which are not below the critical limit, it can be assumed that the determined low ratios are the result of naturally occurring processes.

3.3. Heavy metal content in soils in forest ecosystems

It is considered that heavy metal content in litter represents the sum of their background concentration plus the contribution of atmospheric depositions [61]. The amounts of heavy metals in litter and soils in forest ecosystems in Bulgaria have been a subject to monitoring since 1986. The lack of previous information does not allow determining the impacts of regional and/or global transfer of pollutants. The assessment of data, collected in the period 1986–2008, reveals that in most of the cases the heavy metal content in litter was higher compared to the surface soil layer. The conducted analysis proved that litter, formed on more acidic and scarce in some element soils, contains higher concentrations than the surface soil layer of the respective soil profile. This is most clearly expressed for Cu and Mn. The results, obtained for copper, are presented on **Figures 18** and **19** [50].

It has been determined that the high soil acidity creates a large amount of easily accessible for the plants forms of heavy metals, which is one of the main ways to enrich the litter. In such cases, the high concentrations of heavy metals in litter should be considered as a function of soil acidity and not as a contamination with aerosol origin.

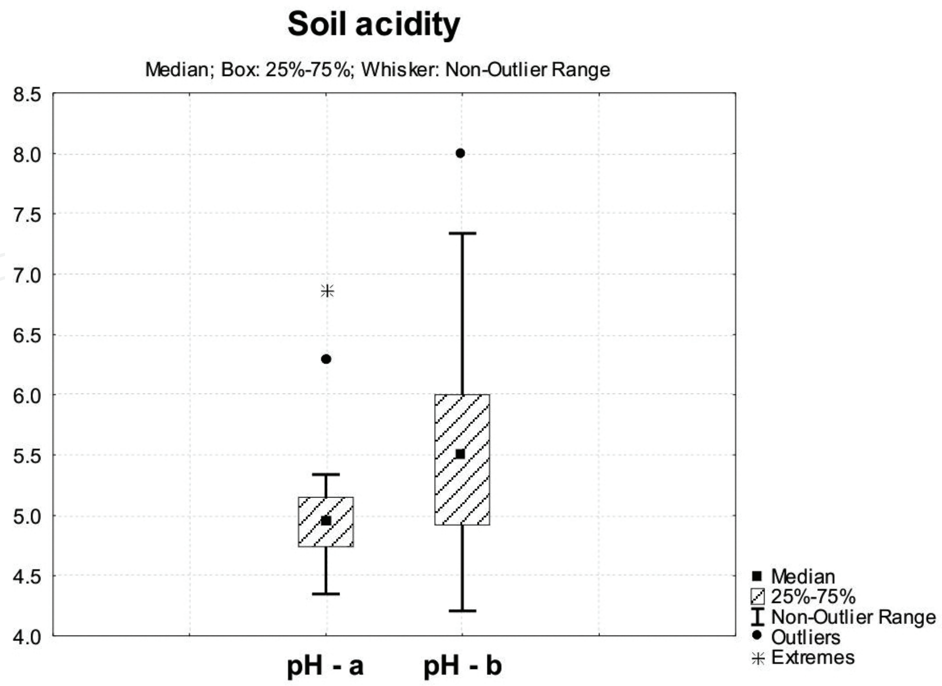

Figure 18. Reaction of soil solution. pH-a—reaction of soils where the Cu content in litter is higher than the content in the surface soil layer; pH-b—reaction of soils where the Cu content in litter is lower than the content in the surface soil layer.

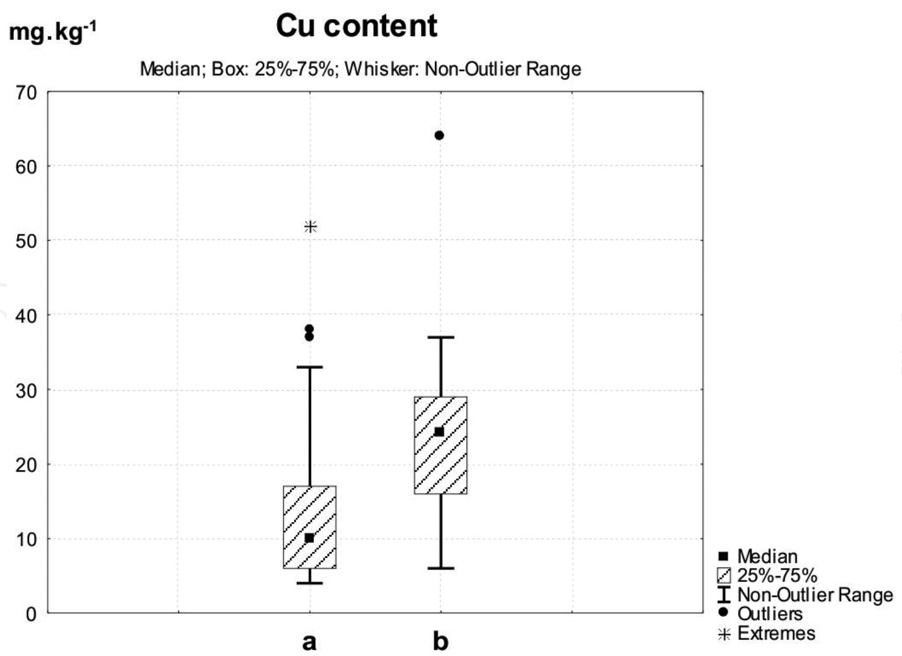

Figure 19. Copper content in soils with moder type of litter. (a)—copper content in soils where the concentration of copper in litter is higher than the concentration in the surface soil layer; (b)—copper content in soils where the concentration of copper in litter is lower than the concentration in the surface soil layer.

The content of Cu, Pb and Zn in soils from the regions of western Balkan Mountains, Sredna Gora, Rhodope Mountains and Strandzha remained relatively constant for the period 1986–2008 [50]. That tendency remained over time due to the absence of statistically proven differences in the content of Cu, Pb and Zn in Cambisols and in Luvisols for the periods 1998–2008 and 2009–2015 (see **Figures 20–25**).

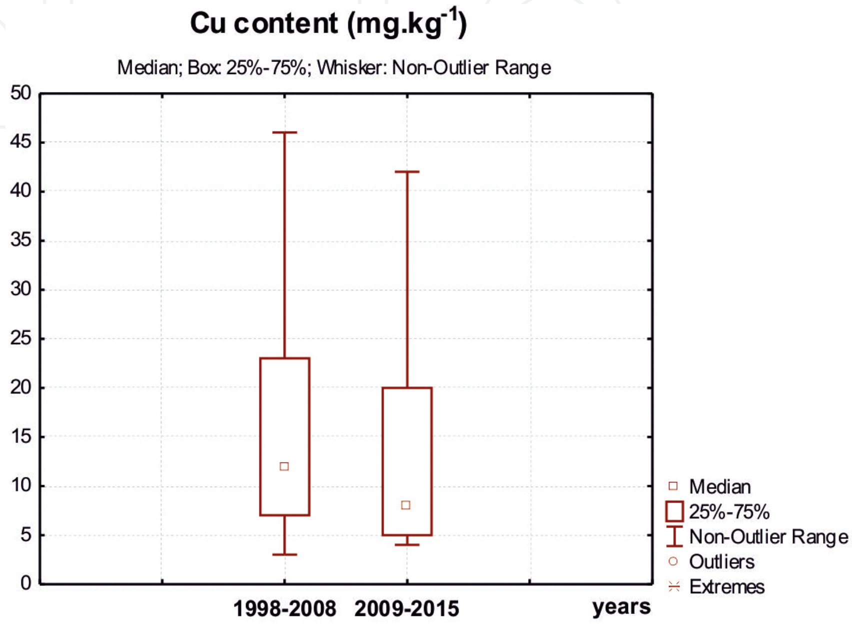

Figure 20. Cu content in Cambisols in the periods 1998–2008 and 2009–2015.

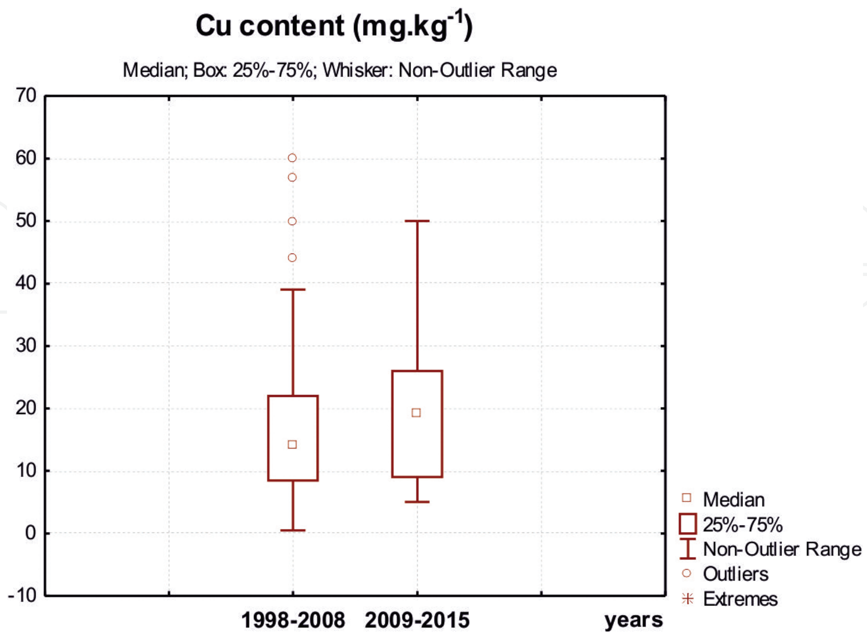

Figure 21. Cu content in Luvisols in the periods 1998–2008 and 2009–2015.

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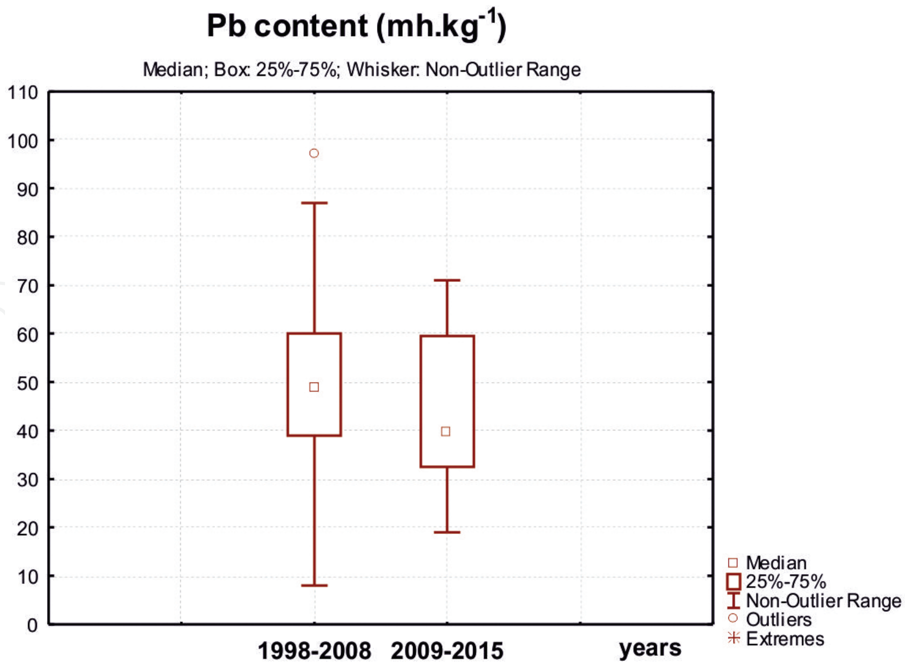

Figure 22. Pb content in Cambisols in the periods 1998–2008 and 2009–2015.

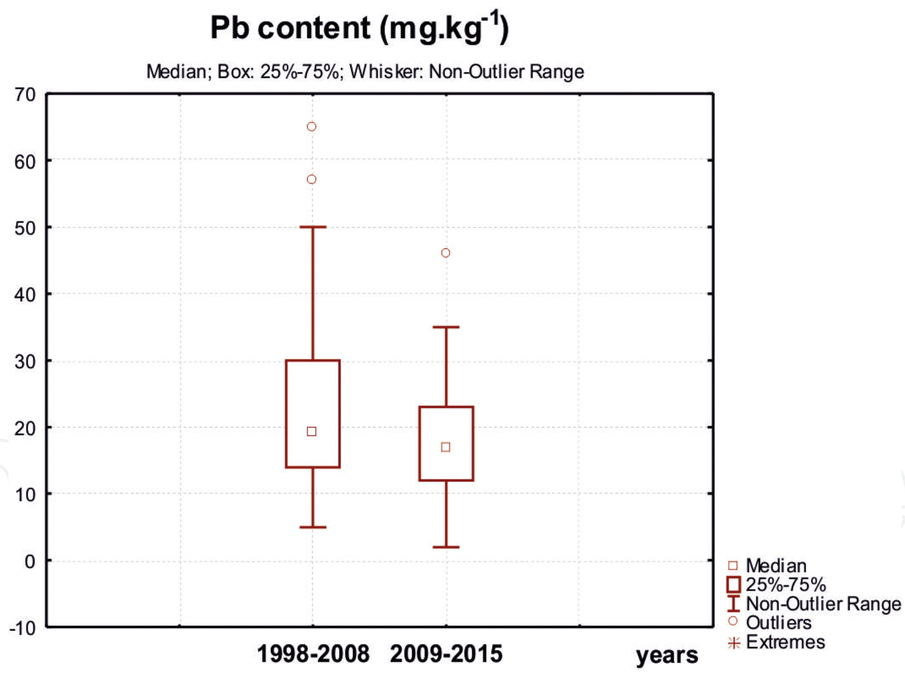

Figure 23. Pb content in Luvisols in the periods 1998–2008 and 2009–2015.

Pollution was determined in some areas, located near industrial enterprises. Pollution of Regosols, based on an example of the copper producing plant near the town of Pirdop, which affects mainly the surface soil layer and litter due to active absorption of copper from plants in acidic environment (pH H_2O = 4.34) is presented on **Figure 26**.

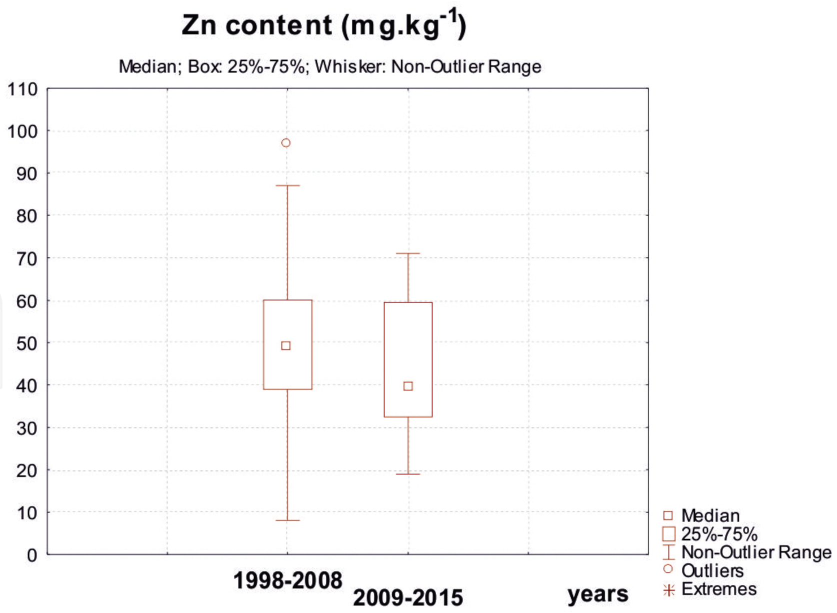

Figure 24. Zn content in Cambisols in the periods 1998–2008 and 2009–2015.

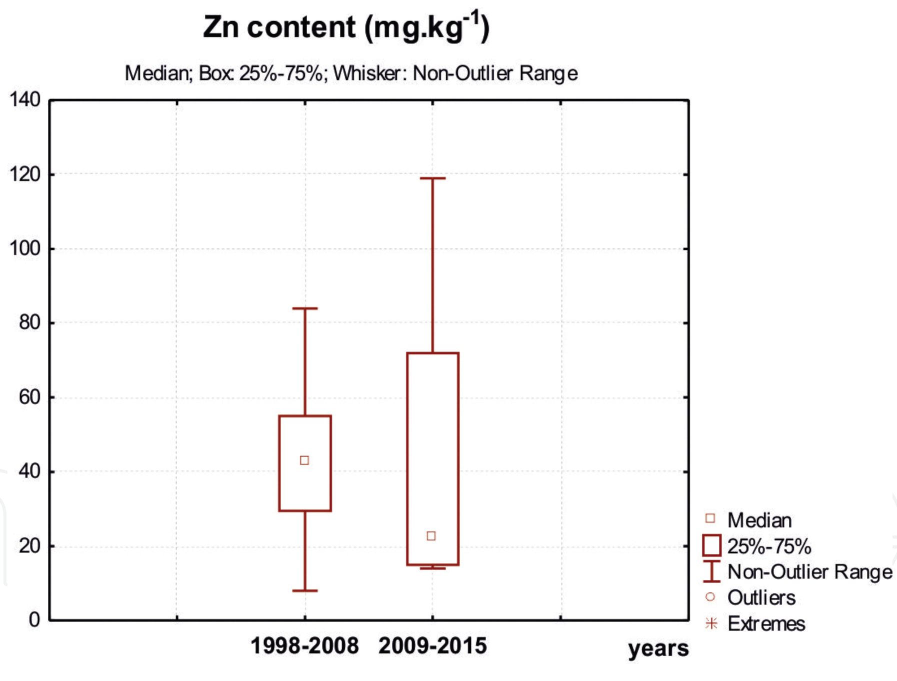

Figure 25. Zn content in Luvisols in the periods 1998–2008 and 2009–2015.

Due to the lack of norms for evaluation of soil pollution with heavy metals in forest ecosystems in Bulgaria, the accumulation rate (AR) has been accepted as the criterion for its confirmation. It is calculated as the ratio between the concentration of a certain metal in the surface soil layer (0–10 cm) and the layer 60–80 or 20–40 cm, depending on the soil depth. According to some authors [62, 63] when AR >1.50, the soil is polluted and the main pollution source is the atmospheric depositions. Regarding the soils from agricultural lands in Bulgaria, these rates were differentially calculated by types of metals back in 1978 [64] and the AR values are close to 1.5.

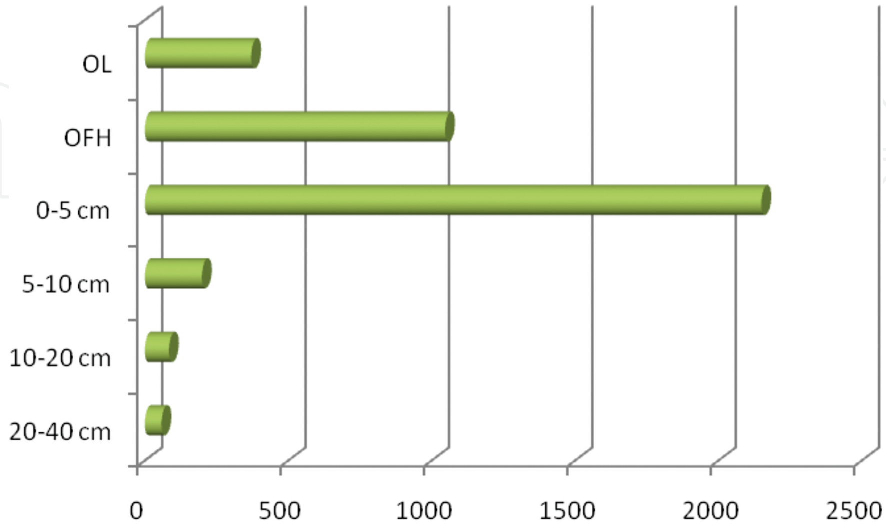

Figure 26. Cu content in Regosols (mg kg^{-1}). OL—unaltered dead remains of plants; OFH—fragmented partly decomposed and well-decomposed organic matter.

The forest ecosystem soils are characterized by biogenic-accumulative processes, which are part of the forest soil-forming process. Under its influence, the rates increase regardless of the presence or absence of exchangeable acidity [50] and repeatedly exceed the value of 1.50. These processes should be taken into consideration when assessing heavy metal content in soils and should not be considered as pollution. Average and maximum values of AR were determined for the soils from the regions of western Balkan Mountain, Sredna Gora, Rhodope Mountain and Strandzha, calculated on the basis of data, collected in the period from 1986 to 2015, from sites located away from industrial emission sources.

The maximum accumulation rates as the result of the natural heavy metal content in surface soil layers are presented in **Table 2**.

Soil unit	**pH_{H2O}**	**Mn**	**Zn**	**Cu**	**Pb**
				AR	
Luvisols	>6.0	3.42	1.30	2.63	4.00
	<6.0	4.16	1.59	3.18	5.46
Cambisols	<6.0	3.28	3.73	6.36	4.04

Table 2. Ratio org. C/total N in litter (mull—OL and OF, and moder—OL and OFH) compared to the ratio org. C/total N in 0–10 cm soil layer.

Higher values should be determined in order to prove pollution.

3.4. Nutrient and heavy metal content in Devnya industrial zone

Soil in the territory of Devnia industrial region is of the type Haplic kastanozems, with pH 7.3 and well supplied with basic nutrients. The humus content varied between 2.00 and 3.56%, total nitrogen was in the range of 0.135–0.344% [65]. The mean values of nutrients and heavy metals determined in surface soil layers in the open and under the plantations with *Frainus americana* and *Celtis australis* for 10-year period (1996–2005) are reported in **Table 3**.

Element	In the open		*Fr. americana* L.		*Celtis australis* L.	
	Polluted area	Control	Polluted area	Control	Polluted area	Control
P (mg/100 g)	114.0	58.0	81.2	40	143.2	75.6
K (mg/100 g)	800.3	698.6	595.6	405.8	984.3	807.8
Ca (mg/100 g)	3984.7	848.3	4450.6	596.5	4000.5	1103.2
Mg (mg/100 g)	421.6	318.3	400.5	255.8	469.8	350.8
Cu (mg/kg)	74.6	26.9	78.6	17.5	44.3	18.8
Zn (mg/kg)	65.8	34.3	51.2	30.8	80.0	39.6
Pb (mg/kg)	40.0	19.6	38.5	17.2	41.3	24.1

Table 3. Ten year (1996–2005) mean values of nutrients and heavy metals in soil in the open and under plantations of *Fraxinus americana* L. and *Celtis australis* L. in Devnya industrial region: Polluted area and Control—at 500 and 15,000 m from the point source of pollution, respectively.

The data showed a higher content of all analysed elements in the polluted area. In the open, at 500 m to the emission sources, the level of Ca (4.7 times more than the control) and P (2 times above the control) was particularly increased, while the content of K and Mg increased with 15 and 32%, respectively. The surface soil layers of the industrial area contained 2.8 times more copper, 2 times more lead and 1.9 times more zinc than the remote area. Remarkable accumulation of calcium was found under the plantations with Fraxinus *americana*—7, 5 times more than under the control plantation, while under the plantations with *Celtis australis,* this accumulation was 3.6 times more than the control. The accumulations of the other macroelements in the surface soil under the two plantations were approximately the same. This accumulation is due to dust and aerosol deposition entering the soil from industrial production and transport. This is especially true for calcium, phosphorus and copper. Potassium, phosphorus and magnesium had higher values under the plantation with *Celtis australis*. The mean concentrations of heavy metal in the polluted soil ranged from 44.3 to 78.6 mg/kg for Cu, from 51.2 to 80 mg/kg for Zn and from 38.5 to 41.3 mg/kg for Pb. The highest content of copper was established in the soil under *Fr. americana* and of zinc—under *C. australis*. The lead content in the polluted soil was almost the same in the open and under of the two plantations. Most elements in the polluted zone, with the exception of calcium and copper, were accumulated in largest quantities in the soil under the plantation with *C. australis*. This can be used in the selection of species for afforestation in such areas. As the metals have a different mobility, they are transported from roots to shoots in different manner. Zn is more mobile than Cu and Pb

[66], and the accumulation of Zn in the aboveground parts of the trees could be expected to be more intensive. The observed levels of Zn and Pb in the studied soil were within the range of the maximum tolerable levels. The soil content of Cu in the open and under the plantation with *Fr. americana* slightly exceeded the maximum tolerable level [17]. Results showed that under the impact of the local industrial emissions the soils in Devnya region were contaminated with heavy metals.

3.5. Nutrient and heavy metal content in leaves of tree species in Devnya industrial region

According to the data for the leaf chemical composition of *Frainus americana* L. and *Celtis australis* L., grown in Devnya industrial zone, there were well-pronounced differences between polluted and control trees in relation to leaf nutrient concentrations (**Table 4**).

Element	***Fraxinus americana* L.**			***Celtis australis* L.**		
	Polluted leaves	**Control**	**Ratio polluted versus control**	**Polluted leaves**	**Control**	**Ratio polluted versus control**
N (%)	0.94 ± 0.08	0.73 ± 0.06	1.288	0.66 ± 0.13	0.87 ± 0.09	0.759
P (mg/gDW)	1.34 ± 0.11	2.98 ± 0.17	0.450	1.05 ± 0.17	1.15 ± 0.26	0.942
K (mg/gDW)	12.82 ± 0.17	19.95 ± 0.44	0.643	12.87 ± 0.34	22.32 ± 0.81	0.577
Ca (mg/gDW)	30.07 ± 0.48	22.00 ± 0.22	1.367	87.3 ± 0.54	54.15 ± 1.13	1.612
Mg (mg/gDW)	3.45 ± 0.22	3.72 ± 0.17	0.928	4.33 ± 0.27	3.52 ± 0.19	1.230
Cd (mg/100 gDW)	0.143 ± 0.05	0.140 ± 0.05	1.021	0.380 ± 0.07	0.242 ± 0.06	1.570
Cu (mg/100 gDW)	1.383 ± 0.17	1.333 ± 0.17	1.038	2.067 ± 0.33	0.917 ± 0.33	2.254
Fe (mg/100 gDW)	13.183 ± 0.17	11.867 ± 1.26	1.111	19.850 ± 0.79	15.650 ± 0.61	1.268
Mn (mg/100 gDW)	9.433 ± 0.24	4.833 ± 0.17	1.952	8.133 ± 0.39	5.167 ± 0.17	1.574
Zn (mg/100 gDW)	2.317 ± 0.17	1.083 ± 0.24	2.139	1.283 ± 0.52	1.175 ± 0.18	1.092
Pb (mg/100 gDW)	2.283 ± 0.81	0.950 ± 0.36	2.403	4.650 ± 0.55	2.917 ± 0.17	1.594

Table 4. Nutrients and metals content (M ± SD, N = 3) in the leaves of *Fraxinus americana* L. and *Celtis australis* L. growing in the polluted and control area and ratio polluted versus control.

A misbalance was observed in some nutrients in the damaged trees. Total nitrogen increases in damaged *Fr. americana* trees and decreases in polluted leaves of *C. australis*. The higher total nitrogen content in damaged leaves mainly was due to the presence of nitrogen oxides in polluted air masses, coming from the emission sources in this area. Trees take up nitrogen from the soil and air. The highest level of total nitrogen was found in the damaged leaves of *Fr. americana*, while the damaged leaves of *C. australis* had relatively poor nitrogen supply. Total phosphorus showed a severe decrease in damaged leaves of *Fr. americana*. In two of the tree species, polluted leaves had extremely lowered content of potassium. Decreased levels of total phosphorus and potassium may cause alteration in nutrient uptake because of their less efficient retranslocation in polluted stands [67]. Due to the high level of calcium in the soil, the leaves in both control and damaged trees had a great amount of calcium. A more pronounced tendency for calcium and magnesium accumulation in polluted region was found in the leaves of *C. australis*, despite of the antagonistic effect of calcium on magnesium uptake. Among the elements, the greatest accumulation was established for calcium (from 3.5 to 7 times higher than the control) and phosphorus (on average 2 times over the control). The higher magnesium level in damaged leaves of *C. australis* could be explained with an increased exchange of magnesium in polluted soils. The lower nutrients content in polluted leaves, especially of potassium and phosphorus, was due to the inhibition of total functional activity in damaged trees. The decreased concentration of potassium, known to play an important role in water regime regulation, might be regarded as an indicator for a water misbalance in polluted leaves [68]. Some specificity was found in the accumulation of separate micronutrients and heavy metals among the species. The most pronounced difference between damaged and control trees were found in copper, manganese, zinc and lead concentrations. Remarkable copper accumulation was observed in the leaves of *C. australis*. Severe manganese accumulation was found in polluted leaves both of *Fr. americana* and *C. australis*. According to some authors, manganese toxicity might be a significant constraint for the health of forests on disturbed soils [69]. The accumulation of zinc was higher in polluted leaves of *Fr. americana*. Cadmium was accumulated mostly in the leaves of afflicted *C. australis* trees and exceeded the levels of toxicity [22]. The greater amount of soluble manganese is favourable to iron availability. In polluted stands, iron was accumulated extremely by *Fr. americana* and moderately by the leaves of *C. australis*. Complex changes in chemical composition, disturbed balance of nutrient elements and increase in the content of heavy metals accompanied decline processes [68]. An uptake of heavy metals by plants occurs together with nutrients through the roots or directly through leaves. The entry of elements through the leaves is more significant for the pollution ones. The slightly alkaline reaction of soil in Devnya region does not create a large amount of easily accessible for the plants forms of heavy metals. Therefore, the accumulation of heavy metals in the leaves might be mainly due to the deposition of air pollutants. Zinc, being an essential element to the plant metalloenzymes, is translocated extensively and its uptake is dependent on metal concentration in extractable fraction in soil as well [70, 71]. The response of vegetation to pollutants depends on the degree of pollutant loading. At low pollutant loads, vegetation can act as a sink for pollutants, and no or minimal physiological alteration occurs [39]. In our study, such role may play *C. australis*. The content of copper, cadmium and especially lead in the leaves of *C. australis* exceeded the excessive values for tree vegetation and can be regarded as damaging [17]. Although the heavy metals are mostly below the critical levels of decreased growth, they may threaten tree vegetation in the region. Hence, the area studied was with slight to moderate heavy metal contamination. The accumulation levels obtained are air and soil orientated [72, 73]. The examined species accumulated mainly lead, copper, zinc and manganese.

In conclusion, each of these pollutants can be suggested as an indicator for the influence of industrial emission on the soil of the region. Changes in foliar element concentrations, however, can take place long before pollution-mediated plant injuries, and foliar element content is commonly used as biomonitor to investigate the distribution of air pollution.

4. Pollution of soils in protected areas

The content of heavy metals and other pollutants in soils from the territories of national and nature parks in the country is poorly studied. With the exception of soils from Strandzha Nature Park, their territories are not subject to monitoring within the national forest ecosystem monitoring network. Due to the large mapping areas, steep terrains and difficult access, some authors apply the landscape ecological approach, which allows to specify relatively homogeneous landscape units in relation to selected criteria [74–77]. They are accepted as a representative sample and serve for conducting different scientific studies, including assessment of soil pollution.

Central Balkan National Park was established in 1991 in order to protect self-regulating ecosystems and is characterized by exceptional biodiversity, communities and habitats of rare and endangered species. The park occupies the highest part of the Balkan Mountains and has a total area of 72,021.07 ha, being the second largest national park in Bulgaria. Some authors reported pollution of soils and plants in pastures with copper, arsenic, lead and cadmium, as well as leaves of *Fagus silvatica* [78]. Natural soil enrichment with cadmium was determined in some areas [79, 80].

Analysis of the park landscape structure was performed in 2015 [81, 82], and 71 relatively homogenous territorial units in relation to the soil-forming rocks and terrain were established within the "forest" landscape category. Analysis of soils and plants was performed using a representative sample—"landscape formed on schists". The soil is Regosols with 20 cm soil depth. Soil material in the layer 10–20 cm showed enrichment of soil-forming rocks with copper, arsenic and cadmium (see **Table 5**). The amounts of Cu and Cd in the litter repeatedly exceeded the toxic levels determined for forests in Europe [22], 20 and 3.5 mg kg^{-1}, respectively.

Depth (cm)	pH (H_2O)	pH ($CaCl_2$)	Mn	Zn	Cu	Cd	As
					mg kg^{-1}		
OL	4.5	4.0	1620	108	346	3.58	4
OFH	5.3	4.8	2832	178	1242	9.93	21
0–10	5.2	4.7	3608	112	1100	0.521	61
10–20	5.3	4.5	3164	76	332	<0.10	12

Table 5. Content of heavy metals and arsenic in soils from the area of the Central Balkan National Park.

The content of heavy metals and arsenic in *Pinus sylvestris* needles was also analysed at the same site (**Table 6**).

Needle age	Pb	Cu	Mn	Zn	Cd
			μg g^{-1}		
Current year	2.7	15.7	459	36.8	0.49
Ranges ICP forests	3.94	2.28–7.7	172.05–912	32–77.5	0.05–0.45
1 year	4.9	22.1	1466	49.6	0.54
Ranges ICP forests	0.14–5.59	1.96–6.88	222.05–1331.95	31.5–96	0.06–0.50

Table 6. Content of heavy metals in *Pinus sylvestris* needles from the area of Central Balkan National Park.

Repeatedly increased copper content was determined in comparison with the established variation limits of these elements within the ICP Forests [41]. The exceedances of manganese and cadmium were relatively low.

Bulgarka Nature Park is adjacent to the Central Balkan National Park. The park is located on the northern slopes of the central part of the Balkan range, occupying a total area of 21,772.163 ha. Environmental pollution risk in landscapes formed by alpine pastures, due to the soil enrichment with heavy metals, was determined on the park territory [79]. The maximum measured values of lead in soils reached 497 mg kg^{-1} and of arsenic—112 mg kg^{-1}. These values were determined at the pasture of the Malusha locality. The following herbaceous plants were identified as strongly lead-accumulating plants: *Holcus lanatus* (29.29 mg kg^{-1}), *Thymus sp.* (42.32 mg kg^{-1}), *Viola tricolor* (9.81 mg kg^{-1}), etc. Arsenic-accumulating plants are *Viola dacica* (3.1 mg kg^{-1}), *Rubus idaeus* (2.9 mg kg^{-1}), *Fragaria vesca* (1.5 mg kg^{-1}), etc. [83].

The studies of heavy metal content in soils and plants of *Pirin National Park* are also very limited. The park was created in 1962 in order to preserve the natural character of the ecosystems and landscapes along with their plant and animal communities and habitats. The park territory, occupying 40,356.0 ha, has not been differentiated into appropriate landscape units yet. In order to study the soil pollution in 2015, the authors carried out a research on representative for the area soil units (see **Table 7**).

Soil unit	Horizon	Depth	pH	Pb	Cu	Mn	Zn	Cd
		cm	(H_2O)			mg kg^{-1}		
Umbrisols	A turf	0–8	5.7	58	16	549	82	1.35
	A	8–60	6.5	55	14	519	67	1.50
Cambisols	A_0	3–0	5.4	26	7	336	47	1.65
	A	0–33	5.0	41	12	252	56	0.90
	B	33–75	6.2	32	13	204	55	1.15
Rendzic Leptosols	A_0	5–0	5.8	27	10	63	68	1.55
	A	0–33	7.1	52	11	110	68	2.45

Table 7. Heavy metal content in soils from the territory of the Pirin National Park.

Only cadmium content can be assessed as excessive in accordance with the criteria on forest soils [22].

Strandzha Nature Park is the only park in the country with a developed national forest ecosystem monitoring network. The park was established in 1995, occupying an area of 116,054.21 ha, and is aimed at long-term preservation of the unique nature of the drainage basins of the Veleka and Rezovska rivers. The studies of heavy metal content for the period 1987–2008, carried out at 11 sample plots, indicated the absence of pollution or natural soil enrichment. The average values of Cu, Pb and Zn in *Luvisols* and *Alisols* for the period 2009–2015 (see **Table 8**) also confirmed this tendency.

Soil unit	Value	Cu	Pb	Zn
			mg kg^{-1}	
Luvisols	Mean	28	22	63
	SD	17	9	35
Alisols	Mean	27	28	49
	SD	7	12	4

Table 8. Heavy metal content in soils from the territory of the Strandzha Nature Park.

Single studies carried out in the Uzunbodzhak biosphere reserve, located on the territory of the Strandzha Nature Park, also confirmed the absence of soil pollution [84].

5. Conclusion

The content of Pb, Cu and Zn in *Cambisols* and *Luvisols* from the regions of the western Balkan Mountains, Sredna Gora, Rhodope Mountains and Strandzha, remained stable during the period 1986–2015. Soils were not affected by acidic atmospheric depositions. The high heavy metal content in litter should be evaluated in relation to the soil pH. When evaluating the pollution of soils with heavy metals, it is necessary to take into consideration the maximum coefficients of their natural accumulation in the surface soil layers. Higher values of these coefficients should be achieved in order to determine pollution. It is necessary to expand the studies of heavy metal content in soils in national and nature parks. Sometimes, environmental risks can occur due to natural enrichment of soils with certain toxic elements. It is recommended to perform soil mapping and, if necessary, to restrict harvesting of medicinal plants and pasture in particular areas.

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