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The Added Value of Urban Trees (*Tilia tomentosa* Moench, *Fraxinus excelsior* L. and *Pinus nigra* J.F. Arnold) in Terms of Air Pollutant Removal

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Abstract: The serious densification of human settlements necessitates an increase in the role and importance of green infrastructures in the overall functioning of urban ecosystems. Accordingly, the aim of the present study was to (1) assess the efficiency of air pollutant removal (potentially toxic elements) of three common ornamental trees (*Tilia tomentosa* Moench, *Fraxinus excelsior* L. and *Pinus nigra* J.F. Arnold) and (2) model the air quality regulatory services (removal of PM_{10}, $PM_{2.5}$ and NO_2). Three different approaches were applied—enrichment factor (EF) and metal accumulation factor (MAI) per tree species, as well as simulation modeling for the whole urban forest. The MAI values of the three studied species were found to be very similar, in the range of 22.35 to 23.08, which suggests that these species could be a good choice for planting in urban areas with worsened air quality. The highest EF values were observed for U (3–18), followed by As (1.6–2.56) and Sr (0.87–2.46). The potential of urban forests in countering air pollution was highlighted by three simulated scenarios for PM_{10}, $PM_{2.5}$ and NO_2 removal. The highest removal efficiency was calculated for evergreen species, followed by the mixed composition of deciduous (90%) and evergreen trees (10%), and the scenario with wholly deciduous trees had the lowest one. The contribution of nature-based solutions in meeting air quality standards and enhancing resilience in urban areas was clearly demonstrated. The functional complementarity of the different functional tree groups (coniferous, evergreen and deciduous broad-leaved species) was proven to be crucial for the support of both functional stabilities of the phytocenosis under diverse climatic conditions and during the change of seasonal cycles in the vegetation.

Keywords: PM_{10}; $PM_{2.5}$; NO_2; heavy metals; enrichment factor; metal accumulation index; ecosystem services

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1. Introduction

Humanity is a part of nature and depends on it not only for its own existence, but also for providing its needs, resources for the economy, for its development and its well-being. Ecosystems (natural and anthropogenic) provide food, materials, raw materials, water and other resources without which our life is impossible [1,2]. Far more important and invaluable, however, are all the intangible benefits that ecosystems provide us—air, water and soil purification; climate regulation; biodiversity conservation and even spiritual satisfaction, inspiration and recreation in nature [3]. In fact, the term "ecosystem services" includes all those direct or indirect benefits that nature provides to humanity. In addition to the in-depth understanding of human dependence on natural processes at different spatial and temporal scales, there is also the need to assess the monetary value of these ecosystem services according to economic and management criteria and indicators [4–6].

A city is a complex ecological system that consists of social, economic and natural factors. The quality of life in an urbanized environment is a function of the combined impact of both abiotic and biotic factors (air, soil, water, microclimate, biodiversity, vegetation, etc.). Urbanization leads to the continuous change of ecosystems and landscapes towards increasingly affected air, water, soil, plant and animal communities [7–9]. Air pollution is considered a primary threat to human health in Europe due to the permanent inhalation of gases and fine particles, even at low levels [10]. For this reason, the regulating services of green infrastructures are regarded to be crucial for human well-being [11]. In this group, the priorities are urban air quality improvement [12,13], microclimate regulation and urban heat island mitigation [14], as well as precipitation runoff limitation [15].

Green systems in cities are based on the inclusion of the natural environment into the highly urbanized urban structure. An appropriate green system can play an effective role in purifying the air, improving the microclimate, suppressing noise, beautifying the surrounding space and improving the comfort of living in general [11]. There are many other ecosystem services that could synergize for sustainable urban development; hence, green infrastructures need a proper species composition, especially in terms of ornamental trees, for their successful implementation.

The serious densification of settlement territories with an increase in the density and intensity of construction necessitates an increase in the role and importance of green systems in the overall functioning of the urban ecosystem. The construction and management of green infrastructure in settlements should be carried out on the basis of in-depth studies on the mechanisms of interaction between the urban environment and vegetation, which in turn requires an assessment of the species-specific tolerance and adaptation abilities of individual plant species [16], and thus their ability to serve as biomonitors and as "green filters" of the urban environment [17,18]. Numerous studies have discussed the potential of green systems to improve air quality, even as a physical barrier between air pollution and people [19]. Tremper et al. [20,21] planted an ivy green screen around a playground in a primary school in Enfield, UK. The reduction in the daily PM_{10} concentrations on the playground side of the screen reached 38%, while for the hourly PM10 level it was 41% [20]. Daily NO_2 concentrations after the plants' growth decreased by 15 μg m^{-3} (21.8%), and the reduction in hourly NO_2 concentrations was found to be up to 18.3 μg m^{-3} (22.5%) [21]. This study clearly demonstrated the effectiveness of green barriers in reducing air pollution, especially during daytime hours, when both emissions and exposure are highest. Another study from England [22] measured and compared different pollutants' concentrations in front of and behind vegetation of three types—only shrubs, trees and shrubs and only trees. At a local level, the authors revealed that the shrub scenario offered better improvement in air quality, at both away-road and close-road sites (up to 63% reduction in black carbon level), followed by the combination of shrubs + trees. However, the capacity of urban forests to provide regulatory services is often limited to small green spaces. When regarding a city's scale, the effect of vegetation is significantly lower. Notably, Baró [23] showed that only 0.47% of the carbon emissions and 0.52% of the NO_2 emissions in Barcelona (Spain) could be absorbed by urban vegetation. However, there are some options to enhance this regulatory service if the selection of plant species with higher retention potential, spatial scale, urban heterogeneity, and the target air pollutants are taken into account [19].

Such problems could be solved by the implementation of a nature-based solution aiming to improve the urban green infrastructure. This could be done by studying trees' tolerance to air pollution and then performing a revision and revaluation of the adaptation ability of the new planted ornamental trees to the worsened urban conditions [24]. The second step should be related to the selection of tree species, among the possible ones, with a higher removal capacity towards air pollutants, and thus with a greater potential for providing such ecosystem services. Accordingly, the aim of the present study was to (1) assess the efficiency of air pollutant removal (potentially toxic elements) of three common ornamental trees (*Tilia tomentosa* Moench, *Fraxinus excelsior* L. and *Pinus nigra* J.F. Arnold) and (2) model the air quality regulatory services (removal of PM_{10}, $PM_{2.5}$ and NO_2) of the urban forest.

2. Materials and Methods

2.1. Study Area

The city of Plovdiv, Bulgaria (42°8′9.9492″ N; 24°44′31.8048″ E), one of the most polluted cities in Europe for more than 15 years [25], was chosen as the study area. The urban conditions in this city are quite harmful for plants' well-being. The main factors contributing to the worsened air quality have been considered to be domestic heating (during the cold period) and motor traffic [26].

For proper identification of the local air quality, we chose four monitoring plots that should reflect different types of anthropogenic impacts (Figure 1). They were situated in the NE, SE, SW and NW directions from the city center, aiming to include areas with different traffic intensities and domestic heating loads (Table 1). Plot 1 was located in the central part, NE direction, adjacent to a busy road junction with heavy traffic and a high level of traffic emissions. Plot 2 was also located in the central part, SE direction, but the area is subject to moderate motor traffic and a medium level of domestic heating. Plot 3 was located in the west suburb, SW direction, near a busy road junction with very heavy railroad and vehicle traffic. Plot 4 was also located in the west suburb, NW direction, but within a big forest, excluding traffic and buildings, so we planned to use it as a conditional control for the urban environment [24,27].

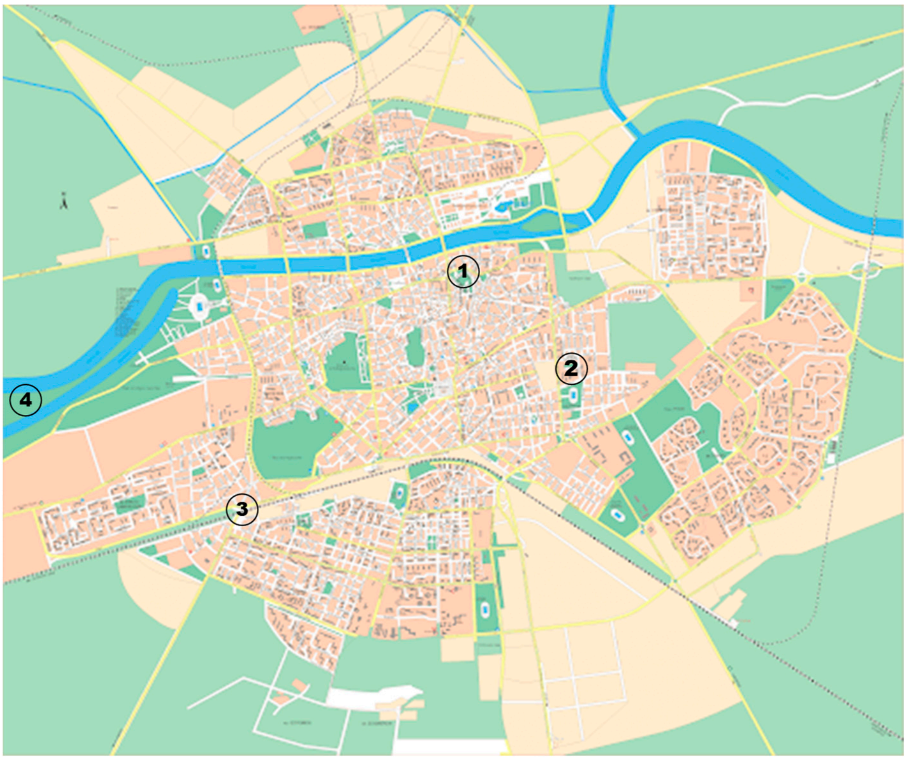

Figure 1. Map of the city of Plovdiv (Bulgaria) and locations of the four monitoring plots.

Table 1. Urbanization intensity evaluated on the basis of built-up area and traffic volume.

Motor Traffic (Car Number per 10 min)	Built-Up Area (%)	Urbanization Intensity	Experimental Plot
0–10	0–10	Low	Plot 4
10–50	10–40	Medium	Plot 2
50–150	40–70	High	Plot 1
>150	>70	Very high	Plot 3

Traffic load was assessed on the basis of the number of cars (or motorcycles) in a period of ten minutes at 8 a.m. on a working day [27]. The percentage of built-up area within a 1 km^2 area was quantified in ArcGis version 11 software using the city general layout plan (Municipality of Plovdiv). As these two features can be quantified in any urban environment, regardless of geographical, cultural and historical variation, they represent an adequate proxy of urbanization intensity [27].

2.2. Experimental Design

During the spring of 2015, 8-year-old seedling material was purchased from a certified nursery and planted at the abovementioned monitoring plots (Figure 2), with 3 individuals per species per plot as a group planting [28]. Periodic observations were made on their development, physiology and health status between 2015 and 2020, and some results from this 6-year period were published in previous studies [16,24,27].

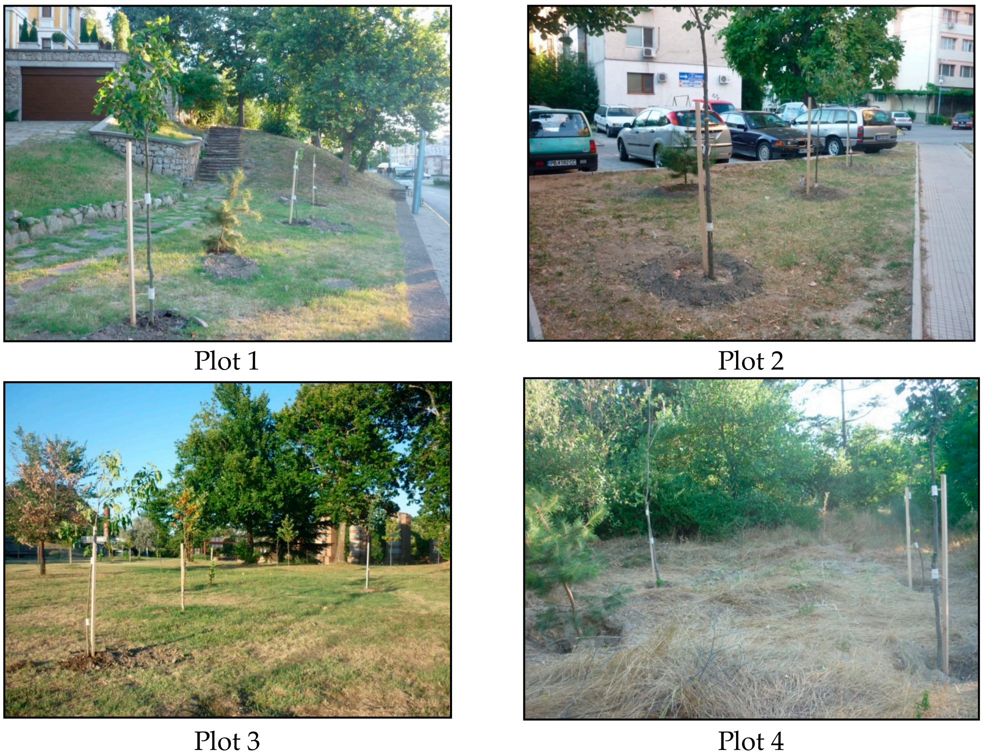

Figure 2. Photos of experimental plots two years after planting.

Leaf sampling was performed in August when the leaves were fully developed. The Expert Tree Pruner with a telescopic handle of 1.5–2.5 m (Draper Tools, Draper Tools Ltd., Hampshire, UK) was used to cut off some branches from the crown. On average, 80–100 fully expanded leaves (needles) per tree were taken, and a representative homogenous sample was prepared for analyses. All the samples were stored in clean, labeled polyethylene bags to avoid contamination during transport [17].

2.3. Chemical Analyses

About 1 g of dried and ground leaves was digested with 5 mL of nitric acid (Merck, Merck KGaA, Darmstadt, Germany) for 24 h at room temperature. After that, the samples were treated for 5 min at maximum power (600 W) in closed cuvettes in a microwave digestion system (Microwave Digestion System CEM MDS 81D, CEM Corporation, Matthews, NC, USA). After cooling at room temperature for 1 h, the cuvettes were opened and 2 mL HNO_3 and 3 mL 30% H_2O_2 were added and allowed to react for another 1 h. The cuvettes were then sealed and placed again for 10 min at 600 W for complete decomposition of the organic matter. The resulting filtrate was diluted with double distilled water to a volume of 50 mL.

The contents of 12 potentially toxic elements (As, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Sr, U, V and Zn) were determined by inductively coupled plasma mass spectrometry (ICP-MS) using an Agilent 7700 ICP-MS (Agilent Technologies Inc., Waldbronn, Germany) instrument (2009), DF 1000. All samples, blanks and standards were diluted with international standardizing agents— final concentrations of 50 ppb Ge and 5 ppb Rh in the solutions. Multy VI (MERCK) calibration standards were prepared immediately prior to the analyses from 1 to 1000 ppb in 0.05 vol% HNO_3. A single standard of 100 ppt Hg was also used in the calibration. Quality control was ensured with a plant standard (NCS DC73348) [29]. The data for each zone are the arithmetic mean of three samples, and the data for each individual sample are the arithmetic mean of three analytical measurements.

2.4. Calculations of Air Pollutant Removal Efficiency

To assess the air pollutant removal efficiency, three different approaches were applied—enrichment factor and metal accumulation factor per tree species, as well as a modeling method for the whole urban forest.

2.4.1. Enrichment Factor (EF)

The enrichment factor (EF) was calculated in order to assess the accumulation of potentially toxic elements in the tree leaves/needles [24]. We used the formula of Mingorance et al. [30]:

$$EF = \frac{C_{urban}}{C_{control}}$$

where C_{urban} and $C_{control}$ are the contents of each element in the plant biomass sampled from the urban (Plots 1–3) and rural/control environments (Plot 4), respectively. We used the following scale for the *EF* to assess the environmental pollution level: (1) EF $\leq$ 1.2—no pollution; (2) 1.2 < EF $\leq$ 2.2—low pollution; (3) 2.2 < EF $\leq$ 3.3—medium pollution; (4) 3.3 < EF $\leq$ 4.3—heavy pollution; (5) EF > 4.3—very heavy pollution [31].

2.4.2. Metal Accumulation Index (MAI)

The metal accumulation index (MAI) [32] gives an option to evaluate the ability of different tree species to accumulate HMs from the ambient air. The MAI values were calculated using the following equation:

$$MAI = \left(\frac{1}{N}\right)\sum_{j=1}^{N} I_j$$

where N is the total number of HMs analyzed, and I_j = x/δx is the sub-index for variable j, obtained by dividing the mean value (x) of each metal by its standard deviation (δx).

2.4.3. Simulation Model

The mitigating role of urban vegetation for PM_{10}, $PM_{2.5}$ and NO_2 was estimated by considering the minimum (period without domestic heating, 1 April–30 September) and maximum (period with domestic heating, 1 Ocotber–31 March) concentration values (C) recorded in the Municipality of Plovdiv during the same period (Table 2). These were based on pollutants' yearly time series, obtained by two automatic monitoring stations of air quality in the city. One of them is focused mainly on traffic-related pollution, while the other aims to assess domestic-related pollution. Detailed measurement data have been obtained by the municipal program of air quality management in the city of Plovdiv from 2018 to 2023 [33] and have been averaged into Table 2.

Table 2. Pollutant level in the ambient air (data from automatic measurement system).

Pollutant	Average Concentration per Year (Sum of All Emitters)	Average Concentration during the Period 1 Ocotber–31 March	Average Concentration during the Period 1 April–30 September	Emitter	Annual Emissions per Emitter	Annual Concentration per Emitter
PM_{10}	48 μg/m^3	65.67 μg/m^3	31.17 μg/m^3	Domestic heating	245 t/y	34.4 μg/m^3
				Traffic	23 t/y	3.3 μg/m^3
				Industry	2 t/y	0.3 μg/m^3
				Background	-	10 μg/m^3
$PM_{2.5}$	34.2 μg/m^3	45.73	22.67 μg/m^3	Domestic heating	172.1 t/y	26.2 μg/m^3
				Traffic	16.3 t/y	2.5 μg/m^3
				Industry	1 t/y	0.2 μg/m^3
				Background	-	5.2 μg/m^3
NO_2	30 μg/m^3	38.67	21.33 μg/m^3	Domestic heating	65.1 t/y	2.4 μg/m^3
				Traffic	342.9 t/y	12.3 μg/m^3
				Industry	144.6 t/y	5.3 μg/m^3
				Background	-	10 μg/m^3

The mitigating role of urban vegetation for three air pollutants was estimated following Nowak [34], as described in Manes et al. [35]. This method is implemented in the present study using the following equation:

$$Q = F \times L \times T \times 0.5 \times LAI_i$$

where the following variables are used:

Q—the amount of pollutant in the air, removed by trees in a certain period of time;
F—the flow of the pollutant;
L—the total green coverage of the area;
T (in seconds)—the vegetative period of urban trees, which was considered equal to 244 days (8 months, May—November) for deciduous and 365 days for evergreen species;
0.5—the rate of resuspension of particles that return to the atmosphere [36];
LAI_i —a variable used to indicate the removal of 1 m^2 of soil covered by plants from a functional group (for trees, LAI_i = 4).

For the purposes of physiological modeling, the woody vegetation was divided into two functional groups [11,37]: (1) broad-leaved deciduous trees and (2) evergreen trees (broad-leaved and conifers), allowing an assessment of the ecosystem services in the autumn–winter and spring—summer periods separately. Thus, three different scenarios were generated for ecosystem service simulation modeling purposes: vegetation covers consisting of only evergreen trees (broad-leaved and conifers) (Scenario 1), only broad-leaved deciduous trees (Scenario 2) and a current species composition (dendroflora) (Scenario 3). This approach has the advantage of providing a methodological framework to serve in the formulation of strategies for the development and sustainable management of a green system, as well as to increase its added value in the context of an increased capacity to purify air from pollutants.

The above equation was used for estimating the pollutant removal by simulating as if all the trees belonged to one single functional group. In the three scenarios, one for each group, the total area covered by tree vegetation within the Municipality of Plovdiv was attributed to each one of them. For this simulation, an average between the maximum and minimum deposition values of each pollutant (t ha^{-1}) was considered. Estimates were carried out on a seasonal basis, with and without domestic heating. The data on the area of the green system and the species composition (ratio of deciduous/coniferous species) were according to the Program for the Development, Maintenance and Protection of the Green System of the City of Plovdiv [37]. The data are as follows: 10,187.6 ha total city area, 381.5 ha total green coverage of trees, 90% deciduous trees and 10% coniferous species.

2.5. Statistical Evaluation

The raw data obtained were processed using the SPSS 21 software package. The relationships between the analyzed variables were assessed through Pearson's correlation coefficients. Cluster analysis (complete linkage, Pearson r-distance) was applied for assessing elements' relationships as well as for evaluating accumulation patterns by plant species ($p < 0.05$).

3. Results

3.1. Leaf Concentrations of Potentially Toxic Elements

The concentrations of the studied potentially toxic elements (mainly heavy metals) in the leaves of urban trees are presented in Table 3. Generally, the concentrations of the potentially toxic elements in urban tree leaves were higher at Site 3 and Site 1 (with some exceptions in Tilia), subjected to more intensive traffic, than at Site 2 with a moderate anthropogenic load. The lowest values were measured in samples from Site 4 (with some exceptions in Tilia), subjected to a low anthropogenic impact (very low traffic and low level of air pollution); thus, we used them as a "conditional control" of the urban environment. When comparing the plant species, they showed similar bioaccumulations of As, Cr, U and Zn. Tilia tomentosa was found to be a good accumulator of Fe, Mn, Ni, Pb and Sr; Fraxinus excelsior was a good accumulator of Cu and Sr and Pinus nigra was a good accumulator of Cd, Mn and Pb. The intensity of urban pressure on trees was very well expressed as all three species accumulated high contents of Pb, Sr, U, V and Zn at Site 3 (very heavy railroad and vehicle traffic, resulting in a very high level of air pollution).

Table 3. Concentrations of potentially toxic elements in urban tree leaves, mg/kg (SD)

Species	Site	As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Sr	U	V	Zn
Tilia tomentosa	1	0.51 (0.03)	0.05 (0.002)	0.76 (0.016)	5.5 (0.26)	151 (7.7)	55 (2.09)	1.03 (0.04)	2 (0.09)	68 (2.7)	0.01 (0.001)	0.21 (0.01)	14 (0.52)
	2	0.43 (0.024)	0.04 (0.002)	0.46 (0.032)	5.8 (0.18)	148 (5.18)	47 (1.79)	1.04 (0.07)	1.5 (0.06)	106 (4.2)	0.01 (0.001)	0.19 (0.01)	18 (0.7)
	3	0.35 (0.018)	0.08 (0.003)	0.53 (0.212)	4.5 (0.19)	155 (6.67)	65 (2.28)	0.78 (0.05)	4.8 (0.17)	123 (4.6)	4.01 (0.148)	0.24 (0.01)	16 (0.51)
	4	0.23 (0.01)	0.09 (0.005)	0.36 (0.019)	5.2 (0.22)	99 (5.15)	54 (2.05)	0.81 (0.05)	2.8 (0.11)	83 (3.6)	0.27 (0.001)	0.23 (0.01)	13 (0.53)
	Av	0.51 (0.03)	0.05 (0.002)	0.76 (0.016)	5.5 (0.26)	151 (7.7)	55 (2.09)	1.03 (0.04)	2.0 (0.09)	68 (2.7)	0.01 (0.001)	0.21 (0.01)	14 (0.52)
Fraxinus excelsior	1	0.38 (0.019)	0.04 (0.003)	0.55 (0.011)	4.5 (0.16)	122 (5.49)	36 (1.13)	0.53 (0.02)	1.3 (0.06)	47 (2.3)	0.02 (0.001)	0.16 (0.01)	14 (0.5)
	2	1.07 (0.055)	0.02 (0.001)	0.35 (0.01)	8.4 (0.29)	105 (3.78)	20 (0.8)	0.52 (0.03)	0.8 (0.03)	76 (3.3)	0.01 (0.001)	0.11 (0.01)	18 (0.68)
	3	0.22 (0.016)	0.06 (0.003)	0.27 (0.011)	29.4 (1.12)	106 (4.66)	31 (1.12)	0.71 (0.04)	2 (0.07)	98 (4.4)	0.64 (0.022)	0.14 (0.01)	15 (0.51)
	4	0.18 (0.011)	0.03 (0.003)	0.21 (0.009)	11.8 (0.44)	60 (2.94)	21 (0.74)	0.45 (0.02)	1 (0.05)	90 (3.9)	0.06 (0.003)	0.08 (0.01)	14 (0.5)
	Av	0.46 (0.024)	0.038 (0.003)	0.345 (0.01)	13.53 (0.5)	98 (4.22)	27 (0.95)	0.55 (0.03)	1.28 (0.05)	78 (3.48)	0.18 (0.007)	0.12 (0.01)	15 (0.55)
Pinus nigra	1	0.16 (0.01)	0.15 (0.007)	0.49 (0.017)	3.0 (0.13)	185 (7.96)	19 (0.87)	0.5 (0.03)	4.4 (0.18)	7.0 (0.59)	0.03 (0.001)	0.29 (0.02)	25 (0.88)
	2	0.17 (0.009)	0.06 (0.003)	0.4 (0.02)	2.0 (0.01)	125 (5.38)	10 (0.43)	0.25 (0.01)	1.3 (0.05)	4.0 (0.44)	0.02 (0.001)	0.13 (0.01)	17 (0.71)
	3	0.18 (0.011)	0.1 (0.005)	0.62 (0.027)	2.7 (0.16)	151 (4.98)	8.0 (0.34)	0.31 (0.02)	4.7 (0.18)	42 (2.02)	3.5 (0.13)	0.31 (0.01)	27 (1.7)
	4	0.09 (0.006)	0.07 (0.005)	0.34 (0.014)	1.5 (0.06)	143 (5.43)	7.0 (0.35)	0.29 (0.02)	4.1 (0.17)	6.0 (0.46)	0.05 (0.002)	0.24 (0.01)	13 (0.44)
	Av	0.15 (0.01)	0.095 (0.005)	0.46 (0.02)	2.3 (0.09)	151 (5.94)	11.0 (0.49)	0.34 (0.02)	3.63 (0.13)	14.75 (0.88)	0.9 (0.03)	0.24 (0.01)	21 (0.93)

Av—average value per studied urban area (Plovdiv, Bulgaria).

Mathematical processing of the data showed 14 positive and 2 negative correlations ($p < 0.05$) (Table 4). The most significant positive correlations were those for V and Pb (r = 0.89), Cd (r = 0.82), Fe (r = 0.79) and Cr (r = 0.76) and between Cd and Pb (r = 0.84), Mn and Ni (r = 0.89). Negative relationships existed between Cu and Fe (r = −0.75) as well as between Cu and V (r = −0.64) ($p < 0.05$). Only for the element As no correlation was found.

Table 4. Values of the correlation coefficient ($p < 0.05$).

	V	Cr	Mn	Fe	Ni	Cu	Zn	As	Sr	Cd	Pb	U
V	1.00											
Cr	0.76	1.00										
Mn	0.06	−0.03	1.00									
Fe	0.79	0.49	0.06	1.00								
Ni	0.03	−0.00	0.89	0.12	1.00							
Cu	−0.64	−0.49	−0.03	−0.75	−0.00	1.00						
Zn	0.53	0.64	−0.43	0.50	−0.30	−0.23	1.00					
As	−0.38	−0.19	0.18	−0.21	0.29	0.04	−0.08	1.00				
Sr	−0.28	−0.12	0.67	−0.50	0.70	0.43	−0.37	0.34	1.00			
Cd	0.82	0.60	−0.09	0.67	−0.17	−0.44	0.59	−0.55	−0.40	1.00		
Pb	0.89	0.53	−0.01	0.66	−0.14	−0.44	0.44	−0.52	−0.31	0.84	1.00	
U	0.43	0.68	0.03	−0.16	−0.08	−0.09	0.24	−0.14	0.29	0.28	0.33	1.00

Significant correlations are marked in red.

The cluster dendrogram shows the separation of two main groups (Figure 3). A general trend could be deduced for the elements Pb, Cr, V, Fe, Cd, Zn and U, which were separated into a separate cluster. Mathematical processing showed that there is a dependence between them and there are elements of synergism in their action, evidence of which is the positive correlation (Table 4) and their falling into the same groups in the cluster analysis. These results give us reason to assume that in the area of our study, the specified elements have a common origin, namely as waste products from road transport. These include emissions from spent fuel, braking systems and tire wear: Fe is released from car braking systems, Pb and Cd from exhaust gases and V from various alloys [38,39]. It was of interest to us to make a comparison between the values of the investigated heavy metals and toxic elements in the leaf samples of Pinus nigra, Tilia tomentosa and Fraxinus excelsior. Greater proximity was confirmed between the two broad-leaved species, and the coniferous species showed specific differences (Figure 4).

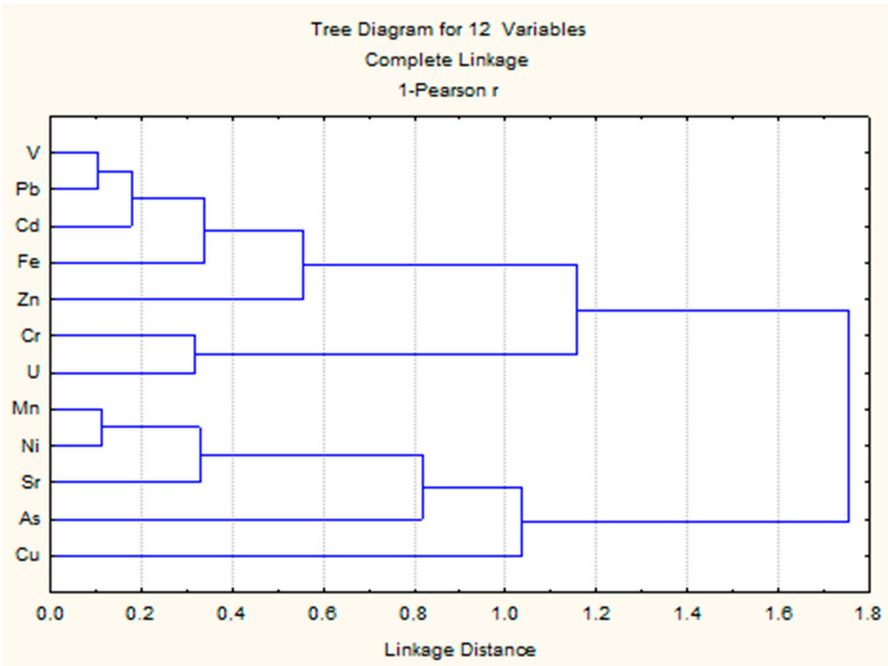

Figure 3. Cluster analysis of the investigated toxic elements in the leaf samples.

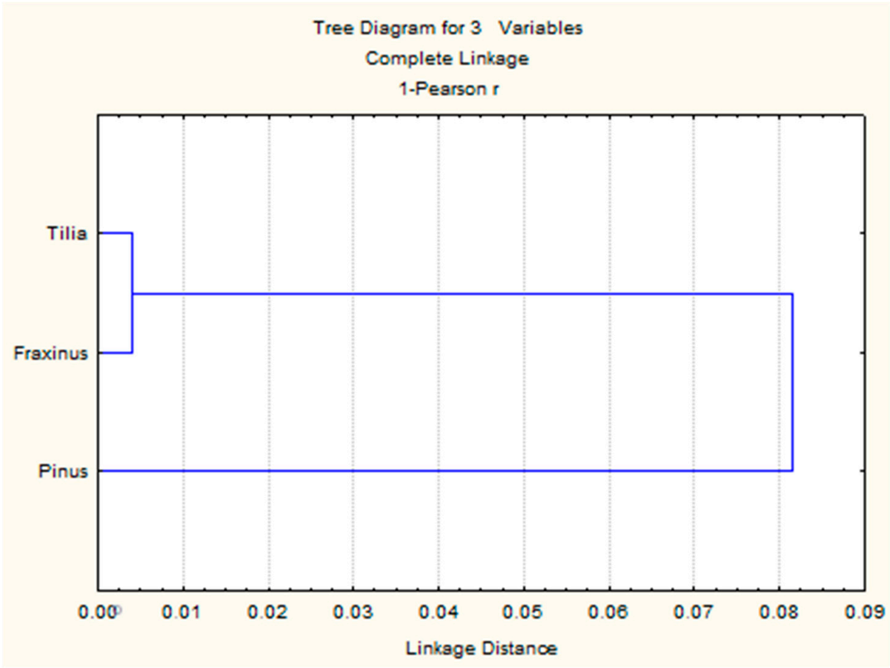

Figure 4. Cluster analysis of similarity between studied tree species based on content of potentially toxic elements in leaves.

3.2. Calculating Efficiency of Air Pollutant Removal (Potentially Toxic Elements)

The values of the enrichment factor (EF) are shown in Table 5. It can reflect the ability of plants to uptake a single HM. The average EF of U was the highest, in the range from 3 to 18, while the rest of the elements varied between 0.72 (Cd) and 2.56 (As).

Table 5. Enrichment factor values of potentially toxic elements in urban tree leaves.

Species	As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Sr	U	V	Zn
T. tomentosa	1.65	0.72	1.47	1.01	1.39	1.02	1.14	0.99	1.15	4	0.96	1.15
F. excelsior	2.56	1.27	1.64	1.15	1.63	1.29	1.22	1.28	0.87	3	1.5	1.07
P. nigra	1.67	1.36	1.35	1.53	1.06	1.57	1.17	0.89	2.46	18	1	1.62

Tree leaves accumulate different elements simultaneously. Using the data obtained in the present study, we calculated the accumulation index to assess the overall performance of the trees in terms of metal accumulation (MAI). The MAI values found were as follows: *Tilia tomentosa* = 22.37, *F. excelsior* = 23.08 and *P. nigra* = 22.35. The obtained MAI values in the present study are higher than those reported previously by Hu et al. [40], Alahabadi et al. [41] and Liu et al. [32], which suggests that these species could be a good choice for planting in urban areas with worsened air quality.

3.3. Modeling Efficiency of Air Pollutant Removal (PM_{10}, $PM_{2.5}$ and NO_2)

The calculated annual and seasonal quantities of pollutants removed from the composition of atmospheric air on an annual basis, according to the two simulated scenarios and the real distribution of the dendroflora of the city of Plovdiv, are presented in Figure 5. According to the observations made, deciduous trees were active in the period from May to November (6 months without domestic heating and 2 months with emissions from heating), and in this period, if all urban forest is represented by such species, they could accumulate up to 301.1 t of PM_{10}, 228.6 t of $PM_{2.5}$ and 215.1 t of NO_2. The real values, calculated on the basis of actual urban forest (90% deciduous, active for 8 months, and 10% evergreen species, active in the whole year), are significantly higher—377.4 t of PM_{10}, 272.5 t of $PM_{2.5}$

and 254.1 t of NO_2 ($p < 0.05$). The obtained results clearly indicate the role of the green system as a filter of ambient air in settlements.

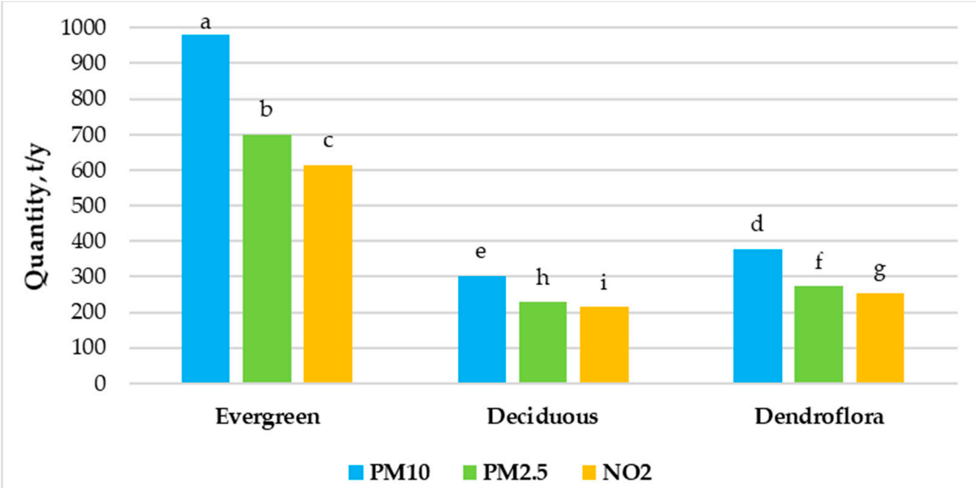

Figure 5. Simulation model of the removed amounts of pollutants from the atmospheric air in the city of Plovdiv according to the three scenarios. Different letters indicate significant differences.

It is noteworthy that with the configuration of only evergreen trees, the obtained effect of purifying the atmosphere from the specified pollutants is three times greater compared to the configuration of only deciduous trees ($p < 0.05$), which also shows the lowest degree of removal of pollutants. The actual dendroflora configuration is slightly better able to provide this ecosystem service—25% more PM_{10}, 19% more $PM_{2.5}$ and 18% more NO_2 removal ($p < 0.05$), highlighting the importance of the green system's species composition to maintain its functional stability.

4. Discussion

Data concerning the EF values (Table 3) pointed out that from the three studied ornamental trees, *Tilia tomentosa* had the lowest pollutant removal efficiency, as an EF value of more than 1.2 for potentially toxic elements was found only for four of them (U—4.0, As—1.65, Cr—1.49, Fe—1.37). *Fraxinus excelsior* was found to be a better accumulator of As (2.56), Cr (1.64), Fe (1.63), V (1.5), Mn (1.29), Pb (1.28) and Cd 91.27), while *Pinus nigra* tended to accumulate U (18), Sr (2.46), As (1.67), Zn (1.62), Mn (1.57), Cu (1.53), Cd (1.36) and Cr (1.35). Similar EF values for Cu, Pb, Zn and Mn in *Tilia* leaves have been reported by Serbula et al. [42] in rural areas of Serbia, while data from an industrial site in the city of Bor were twice higher. When regarding the Serbian data for *Pinus* needles, the EF values of these elements ranged from 0.6 (Mn) to 4 (Pb). A study from Spain (Huelva) has reported some EF values for pine needles (*Pinus pinea*), collected from three heavily industry-influenced locations, ranging from 4 up to 16 [30].

The MAI values obtained for Plovdiv's tree leaves are notably higher (up to 6–7-fold) when compared to some other studies [32,40,41]. For example, the MAI values found by Hu et al. [40] in the city of Yanan (China) were 2.56 (*Sophora japonica*), 2.33 (*Picea asperata*) and 2.16 (*Fraxinus chinensis*), while the MAI value calculated for *Sophora japonica* from Beijing (China) was 9.0 [32]. Data from Yazd city (Iran) [41] were also in the range between 3.31 (*Fraxinus excelsior*) and 6.66 (*Pinus moldarica*). Roy et al. [43] found that *Ficus bengalensis* had higher MAI values from the 10 species studied, with the MAI from the industrial site = 5.15 and the MAI from the commercial site = 6.09, indicating its higher accumulation capacity. These differences between results from the abovementioned studies could be explained by the influence of various factors such as differences in local atmospheric chemistry and meteorology properties, sampling altitude, sampling time, plant characteristics, etc., which affect the removal capacity of air pollutants from urban plants [44,45]. The number of analyzed elements was also different—12 elements in our study and generally lower numbers (4–7) of elements in the others. According to the above MAI values, all studied species have sufficient accumulation properties, and as they can grow in contaminated environments, they can be used as bioindicators or biomonitors for potentially toxic element contamination in the urban environment. Thus, the present study confirms the other authors' recommendations [41] that these plants should be used more frequently as barriers between contaminated and vulnerable areas, such as parks, schools, hospitals and residential areas.

Particulate matter is a dominant air pollutant in urban areas, and both fractions (PM_{10} and $PM_{2.5}$) have negative effects on public health [46]. Many studies have demonstrated the significant contribution of urban forests in improving air quality [17,34]. One of the main parameters affecting this regulatory ecosystem service is the physiology of the main tree functional groups (evergreen broadleaves, deciduous broadleaves and conifers), as well as their abundance and spatial distribution within cities [35,47]. A spatial analysis integrating dynamic green system modeling and geostatistics was applied to estimate the seasonal and annual amounts of pollutants removed by the two functional groups of trees. The main emitter of PM in the city of Plovdiv was considered to be domestic heating; hence, the simulations were set to distinguish the accumulation provided by deciduous and evergreen species between the cold and warm seasons. A similar approach has been proven to be appropriate and effective in other urbanized areas from different continents [34,47–51]. Temporal dynamics are more often associated with tree phenology and ecophysiology, accounting for the specific functional response to both seasonal dynamics of climate factors [51] and interannual climate variability. The dynamics in space are instead related to the complex interactions between the spatial distribution of the functional groups of trees on the urbanized territory and the seasonal dynamics in the amount of emitted pollutants [35]. Fusaro et al. [52] studied the PM_{10} removal by trees in the Municipality of Rome, Italy, and revealed that, with a total of 293.83 t/y (0.019 t/ha), evergreen trees were also found to be more effective. This removal quantity is similar to our data (301.1 t/y), but the effectiveness of urban trees in Plovdiv for PM_{10} removal was calculated to be 0.0296 t/ha. The higher values obtained in our study could be a consequence of different PM_{10} levels in the air, the biological properties of the plant species, local peculiarities, etc. The functional complementarity of the different functional tree groups (coniferous, evergreen and deciduous broad-leaved species) will support the functional stability of the phytocenosis under diverse climatic conditions and during the change of seasonal cycles in the vegetation. The observed synergism, as a consequence of the specific seasonal phenological and ecophysiological dynamics of the three tree groups, proves the need for biodiversity conservation, especially in urbanized ecosystems and in the context of global climate change.

It should be noted that there are some limitations to these estimates, but nevertheless, the results obtained are useful in terms of evaluating the magnitude of air pollutant removal by urban trees, as well as quantifying their added value to human health and well-being. Limitations of such studies include the following: (i) uncertainties related to tree cover estimation and/or leaf area volume; (ii) the formulas used to model particulate matter removal at a local and/or national level; (iii) the limited number of pollutant monitoring stations which provide pollutant concentration data; (iv) the negative effects (disservices) of urban forest not being accounted for (VOC emissions, pollens, reduced wind speed, etc.).

5. Conclusions

Trees are important for reducing urban pollution, and street trees play the leading role. Using detailed data provided a more accurate insight into the role of three widespread trees in air pollution mitigation. When comparing the plant species, we revealed a similar bioaccumulation of As, Cr, U and Zn. *Tilia tomentosa* was found to be a good accumulator of Fe, Mn, Ni, Pb and Sr; *Fraxinus excelsior* for Cu and Sr and *Pinus nigra* for Cd, Mn and Pb. Greater proximity was confirmed between the two broad-leaved species, and the coniferous species showed specific differences. The highest EF values were observed for U (3–18), followed by As (1.6–2.56) and Sr (0.87–2.46). The MAI values of the three studied species were found to be very similar, in the range of 22.35 to 23.08, which suggests that these species could be a good choice for planting in urban areas with worsened air quality.

The potential of the urban forest in countering air pollution was highlighted by three simulated scenarios for PM_{10}, $PM_{2.5}$ and NO_2 removal. The highest removal efficiency was calculated for evergreen species, followed by the mixed composition of deciduous (90%) and evergreen trees (10%), and the scenario with only deciduous trees had the lowest one. The contribution of nature-based solutions in meeting air quality standards and enhancing resilience in urban areas was clearly demonstrated. The functional complementarity of the different functional tree groups (coniferous, evergreen and deciduous broad-leaved species) was proven to be crucial for the support of both functional stabilities of the phytocenosis under diverse climatic conditions and during the change of seasonal cycles in the vegetation.

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