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ACCUMULATION OF PARTICULATE MATTER, PAHs AND HEAVY METALS IN CANOPY OF SMALL-LEAVED LIME

AKUMULACJA MIKROPYŁÓW, WWA I METALI CIĘŻKICH W KORONIE LIPY DROBNOLISTNEJ

Key words: dust, environmental contamination, urban trees, *Tilia cordata* L.
Słowa kluczowe: pyły, zanieczyszczenie środowiska, drzewa miejskie, *Tilia cordata* L.

Rośliny odgrywają kluczową rolę w codziennym życiu, przede wszystkim jako jedyne źródło tlenu, ale również jako narzędzie oczyszczania powietrza z groźnych zanieczyszczeń. Celem niniejszych badań była ocena zdolności lipy drobnolistnej (Tilia cordata Mill.) w kierunku gromadzenia mikropyłów, wielopierścieniowych węglowodorów aromatycznych (WWA) oraz metali ciężkich w całej koronie drzewa. Próby liści zebrane zostały pod koniec dwóch kolejnych sezonów wegetacyjnych (2009, 2010) z lip rosnących przy ul. Rodowicza „Anody” w Warszawie i przeanalizowane na zawartość mikropyłów, 16 WWA i 13 metali ciężkich. Na korony drzew założono siatki w celu zebrania wszystkich liści po ich naturalnym opadnięciu. Liście ważono, liczono oraz mierzono ich powierzchnię przeliczając uzyskane wartości na całą koronę.

Uzyskane wyniki potwierdziły zdolność lipy drobnolistnej do gromadzenia zanieczyszczeń powietrza na powierzchni i w tkankach liści. Całe ulistnienie przeciętnej korony lipy zgromadziło w sumie 4.81 g mikropyłów, 4.38 mg WWA oraz 1.27 g metali ciężkich.

1. INTRODUCTION

Recent decades have made people more aware of various issues regarding their health. Numerous studies reported that the number of diseases that can be related to envi-

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ronmental pollution is steadily increasing, amongst which those attributed to urban air contamination have a considerable share [Pope et al. 1995, Seaton et al. 1995, Nicolai 2002].

Particulate matter – suspended in the air mixture of liquid and solid substances from various anthropogenic and natural sources consisting of, among others, heavy metals (HM) and polycyclic aromatic hydrocarbons (PAH) [Maher et al. 2008, Jouraeva et al. 2002] are considered as most responsible for human health risks and reduced life expectancy in European countries [EEA, 2007].

Due to extensive studies, heavy metals are known to pose various health risks including lung disease, central nervous system and brain disorders, foetus handicap, hearing impairment, kidney damage, cancer [Järup 2003, Maher et al. 2008, Shi et al. 2011]. Similarly, PAHs are also cause of numerous health problems as many of them have carcinogenic and mutagenic properties [Bakker et al. 2000].

Vegetation has been discovered to be able to intercept particulate matter both on epicuticular wax surface and inside wax layer covering the leaves, referred to as ‘surface PM’ and ‘in-wax PM’ respectively, through which it can remove the particles from the atmosphere [Dzierżanowski et al. 2011]. Both these categories contain particles of various fractions, which have diverse effect on human health, with the smallest being the most dangerous [Dockery et al. 1993]. Research on chemical composition of leaves of different species indicated presence of various heavy metals arising from primary soil composition or soil pollution, but even up to 30 % of their amount may originate from aerial deposition on leaf surface, e.g. from resuspended soil particles or, what is more important, from anthoropogenic sources [Mingorance and Rossini Oliva 2006]. Contrary to this, for PAHs the prevailing path of uptake is the air-to-leaf one, because their highly hydrophobic character and therefore weak water-solubility limit the soil-to-root uptake [Alkorta and Garbisu 2001]. Deposition on the leaves depends on numerous factors regarding volatility of the compounds, which appear in the atmosphere in gaseous and particle-bound form, and leaf physiological features [Howsam et al. 2000, Jouraeva et al. 2002, Wang et al. 2008].

The purpose of this work was to determine the overall retention of particulate matter, heavy metals and polycyclic aromatic hydrocarbons in the canopy of small-leaved lime (*Tilia cordata* Mill.).

2. MATERIALS AND METHODS

The sampling area was two rows of small-leaved lime trees growing at WULS-SGGW campus along Rodowicza “Anody” street. Leaf samples collected in two consecutive years 2009 and 2010 were analyzed for particulate matter (PM) accumulation, as well as polycyclic aromatic hydrocarbons (PAHs) and heavy metals (HMs) content. Each sample consisted of leaves gathered from different parts of the canopy with regard to height, crown exposure towards street traffic and position of leaf within the crown to make it representative for the tree. PM of three size fractions were determined on leaf surface and in wax layer using the method described by Dzierżanowski et al. [2011]. Leaf samples were first rinsed with water in order to wash off surface PM and then with chloroform in order to dissolve the epicuticular wax layer and wash off in-wax PM. Amounts of particles were calculated per unit of leaf area, which was determined for each sample using digital camera based image analysis software (Skye Instruments Ltd., UK). In other samples, concentrations of 16 polycyclic aromatic hydrocarbons were measured using GC/MS or HPLC and 13 heavy metals with ICP-AES methods.

After vegetation season of the year 2010, two photographs of each tree were taken in N-S and E-W orientations. These were used for image based measurements of each tree with ImageJ software [http://rsbweb.nih.gov/ij/]. Tree height, canopy height and canopy width were measured, as well as other dimensions which were used for manual canopy volume calculations.

At the end of both growing seasons polyethylene nets were put over tree canopies to collect all leaves. The whole foliage of each canopy was air dried and weighed. For each tree 5 % (by weight) leaves were selected and leaf count was conducted. Afterwards, samples of 125 leaves each were taken to measure the area of every leaf. On this basis overall foliage area and number of leaves were calculated.

All PM, PAH and HM amounts were calculated to cm^2 of leaf area, g of leaves, one average leaf, m^3 of canopy volume and whole canopy in order to give a detailed information about environmental cleaning value of a single lime tree.

3. RESULTS AND DISCUSSION

Calculations performed on the basis of the whole foliage collection at the end of the growing season are presented in table 1. These values give an insight into properties of small-leaved lime canopies and enable to picture their ability to cleanse urban air via particulate matter, HM and PAHs accumulation.

Table 1. Parameters characterising leaves and canopy of small-leaved lime

Tabela 1. Parametry charakteryzujące liście i koronę lipy drobnolistnej

	Unit leaf area, cm^2	Leaf DW, g	One average leaf	Unit canopy volume, m^3	Whole canopy
Leaf DW, g	0.01	x	0.24	244.66	2481.41
Number of leaves	x	4.25	x	1030.47	10546.33
Leaf area, cm^2	x	121.25	28.53	29013.03	300874.83

Note: Values present the ratio between the parameters listed in first column and the first row of the table.

The area of one single leaf, as well as leaf area per gram of dry weight are comparable with the findings of Jouraeva et al. [2002], who investigated leaves of *Tilia × euchlora* and *Pyrus calleryana*. These authors drew a conclusion that PAHs and heavy metals deposition cannot be attributed to the size of a leaf, but rather to other properties, e.g. its surface or wax layer characteristics.

The quantities of particulate matter obtained in the analyses of this study are presented in table 2, expressed per leaf area, leaf dry weight, one average leaf, crown volume and single tree basis (μg·cm^{-2}, μg·g^{-1} DW, μg·leaf^{-1}, mg·m^{-3}, g·tree^{-1}, respectively).

Table 2. Mean amounts of PM of different categories and size fractions in small-leaved lime leaves with respect to canopy parameters

Tabela 2. Średnia zawartość mikropyłów z podziałem na kategorie i frakcje w liściach lipy drobnolistnej w odniesieniu do parametrów korony

PM category	μg·cm^{-2}	μg·g^{-1} DW	μg·leaf^{-1}	mg·m^{-3}*	g·tree^{-1}**
Surface 10–100 μm	6.43	780.11	183.54	186.67	1.94
Surface 2.5–10 μm	0.61	74.22	17.46	17.76	0.18
Surface 0.2–2.5 μm	0.48	58.08	13.67	13.90	0.14
In-wax 10–100 μm	6.99	848.13	199.55	202.94	2.10
In-wax 2.5–10 μm	0.96	116.28	27.36	27.82	0.29
In-wax 0.2–2.5 μm	0.49	59.88	14.09	14.33	0.15
Total	15.97	1936.70	455.66	463.41	4.81

Notes: * Canopy volume.
** An average small-leaved lime tree in the experiment.

The greatest share of the total PM were large particles (10–100 μm diameter). In all three size fractions more PM were bound in wax layer. These data are in contrast to previous study [Dzierżanowski et al. 2011], where eight species were reported to accumulate higher amounts of surface large PM, while for other fractions the differences were less evident. However, it is suggested that the possibility of trapping particles in waxes depends greatly on the structural and chemical characteristics of wax [Jouraeva et al. 2002], which should be examined in this case. In a study conducted by Dzierżanowski et al. [2011] total PM amounts for small-leaved lime were higher (more than 20 μg·cm^{-2}), even though they took into consideration only the two larger fractions. The reason for this might be, that the experimental trees used in the present study grew at a larger distance to the street, thus were less exposed to traffic pollution.

Results of PAHs analyses are presented in table 3, expressed per similar units as for PM. Three groups of PAHs based on partitioning were distinguished:

1) low molecular weight (LMW PAHs) – existing mainly in the gaseous phase;
2) medium molecular weight (MMW PAHs) – partitioning between gaseous and particulate phases (environmental conditions' dependent);

3) high molecular weight (HMW PAHs) – existing predominantly in the particulate phase [Jouraeva et al. 2002].

Table 3. Mean amounts of PAHs in small-leaved lime leaves with respect to canopy parameters
Tabela 3. Średnia zawartość WWA w liściach lipy drobnolistnej w odniesieniu do parametrów korony

PAHs	ng·g^{-1} DW	ng·cm^{-2}	ng·leaf^{-1}	µg·m^{-3}*	µg·tree^{-1}**
LMW					
Naphtalene	1.59	0.01	0.38	0.38	3.95
Acenaphthylene	< 0.1	–	–	–	–
Acenaphthene	< 0.5	–	–	–	–
Fluorene	74.47	0.61	17.52	17.82	184.78
MMW					
Phenanthrene	818.26	6.75	192.52	195.79	2030.44
Anthracene	30.88	0.26	7.27	7.39	76.62
Fluoranthene	381.90	3.15	89.85	91.38	947.65
Pyrene	252.17	2.08	59.33	60.34	625.74
Benzo(a)anthracene	40.95	0.33	9.64	9.80	101.62
Chrysene	55.96	0.46	13.17	13.39	138.86
HMW					
Benzo(b)fluoranthene	28.50	0.24	6.70	6.82	70.71
Benzo(k)fluoranthene	13.79	0.11	3.25	3.30	34.23
Benzo(a)pyrene	15.73	0.13	3.70	3.76	39.03
Dibenzo(a.h)anthracene	2.07	0.03	0.49	0.50	5.15
Benzo(g.h.i)perylene	29.88	0.25	7.03	7.15	74.15
Indeno(1.2.3-cd)pyrene	21.16	0.18	4.98	5.06	52.51
Total	1765.72	14.56	415.44	422.50	4381.48

Notes: * Canopy volume.
** An average small-leaved lime tree in the experiment.

The MMW group had the largest share in the total amount of PAHs, with the highest concentration noted for phenantrene. On the contrary, the lowest amounts of PAHs were noted in the LMW group, which corresponds with the results obtained by other researchers [McLachlan and Horstmann 1998, Howsam et al. 2000, Jouraeva et al. 2002, De Nicola et al. 2008]. Lower concentrations of HMW PAHs as compared to MMW ones are pronounced by various researchers to be a result of climatic conditions, as HMW PAHs are mainly bound to particles which can be removed throughout the vegetation season by wind or rain, and also are subject to influence of temperature and sunlight [Kamens et al. 1990, Franzaring 1997; Jouraeva et al. 2002, Jouraeva et al. 2006].

The amounts of 13 heavy metals analysed in this work are presented in table 4, expressed per similar units as for PM and PAHs. For As, Co and Sb the concentrations in leaf tissues were below the level of detection. For Ba, Cd, Cu, Mn, Ni and Zn the values corresponded with the results obtained by Kosiba [2008] and stayed within the typical ranges found in literature for small-leaved lime and other deciduous species [Maisto et al. 2004; Baycu et al. 2006; Mingorance and Rossini Oliva 2006; Reimann et al. 2007; Cekstere and Osvalde 2009]. Slightly elevated were the concentrations of Cr and Fe, while Pb appeared in rather small amount.

Table 4. Mean amounts of heavy metals in small-leaved lime leaves with respect to canopy parameters

Tabela 4. Średnia zawartość metali ciężkich w liściach lipy drobnolistnej w odniesieniu do parametrów korony

Heavy metals	$\mu g \cdot g^{-1}$ DW	$\mu g \cdot cm^{-2}$	$\mu g \cdot leaf^{-1}$	$mg \cdot m^{-3}$*	$mg \cdot tree^{-1}$**
As – Arsenic	< 2	–	–	–	–
Ba – Barium	38.42	0.32	9.04	9.19	95.35
Cd – Cadmium	0.11	0.00	0.03	0.03	0.28
Co – Cobalt	< 0.3	–	–	–	–
Cr – Chromium	1.81	0.02	0.43	0.43	4.48
Cu – Copper	7.10	0.06	1.67	1.70	17.62
Fe – Iron	209.77	1.73	49.36	50.19	520.54
Mn – Manganese	49.20	0.41	11.58	11.77	122.07
Ni – Nickel	1.21	0.01	0.29	0.29	3.00
Pb – Lead	0.66	0.01	0.16	0.16	1.64
Sb – Antimony	< 2	–	–	–	–
Sr – Strontium	172.09	1.42	40.49	41.18	427.03
Zn – Zinc	33.05	0.27	7.78	7.91	82.01
Total	513.21	4.23	120.75	122.80	1273.47

Notes: * Canopy volume.
** An average small-leaved lime tree in the experiment.

Kosiba [2008] proved strong influence of the quality of pollution dependent on point-emission sources on metal content in leaves, others also pointed out traffic intensity and distance dependence [Baycu et al. 2006, Mingorance and Rossini Oliva 2006], as well as seasonal accumulation trends [Aničić et al. 2011].

4. SUMMARY

Small-leaved lime shows ability to accumulate pollutants, such as particulate matter, polycyclic aromatic hydrocarbons and heavy metals on leaves and therefore potential to enhance the quality of urban environment. Amounts of accumulated pollutants corresponded with results of previous research. Average small-leaved lime tree in this experiment retained 4.81 g PM, from which the most dangerous fine fraction (0.2–2.5 μm diameter size) amounted to 0.19 g. Whole foliage accumulated 4.38 mg of total PAHs, while HMW PAHs, amongst which one can find the most hazardous ones, amounted to 275.78 μg. Single tree intercepted also 1.27 g of different heavy metals, including lead, cadmium and copper, perceived as the most harmful to human health.

This study was supported by a grant from Norway through the Norwegian Financial Mechanism, # PNRF-193-AI-1/07 granted to S.W. Gawroński and A. Sæbø.

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