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HEAVY METALS IN MAPLE AND DANDELION LEAVES FROM DIFFERENT LAND-USE AREAS IN MOSCOW'S EASTERN DISTRICT

ABSTRACT. This article is based on extensive biogeochemical research conducted in Moscow's Eastern Administrative District, where motor-vehicle traffic and heavy industry have resulted in some of the highest levels of pollution in the city. For this study, 26 samples of maple leaves (*Acer platanoides*) and 49 samples of dandelion leaves (*Taraxacum officinale*) were collected on a regular grid at 500–700 m intervals. Concentrations of Fe, Mn, Mo, Cd, Pb, Zn, Cu, As and Sb in these plants were measured using atomic absorption spectrometry after washing, drying and $HNO_3 + H_2O_2$ digestion. Maples accumulated $Sb_{9,7}As_{4,6}Mo_{2,2}Fe_{2,0}Zn_{1,5}Pb_{1,4}Cu_{1,2}$, while dandelions accumulated $Mo_{12,7}Pb_{4,9}Cd_{4,4}Fe_{4,3}As_{3,9}Sb_{2,7}Cu_{1,4}$ — normalized to concentrations in background samples from an unpolluted site west from Moscow. The plants' geochemical specialization was detected and compared in the following land-use areas: industrial, traffic, recreational, agricultural, and high-, mid-, and low-rise residential development. For maples, the highest concentration factor levels were found in industrial areas, with accumulations of $Sb_{19}As_{2,4}Mo_{1,7}Zn_{1,7}Fe_{1,5}Cu_{1,4}Pb_{1,4}$. These levels were 2–5 times lower for maples in other land-use areas. Dandelions and maples do not accumulate Mn because of antagonism between Zn, Mo and Mn in soils. Copper is not concentrated by herbaceous species because of antagonism between Mo and Cu. Differences in geochemical specialization were shown using the Sb/Mo ratio: in dandelions this was 5 times lower than in background samples, while in maples it was 4.5 times higher. A Z_v ratio was used to evaluate the intensity of biogeochemical transformation in urban plants. The highest Z_v ratios were found in plants near industrial zones and large roads.

KEY WORDS: heavy metals and metalloids, urban plants, dandelion, maple, Moscow, ecogeochemistry.

INTRODUCTION

Cities are often sites of concentrated pollution resulting from dense population and industrial production. In Russia, as in many countries worldwide, the ecological situation in urban areas is near critical [Bityukova et al., 2011]. Cities consume 75% of the world's resources while occupying only 2% of the land. More than half the world's population — 3.6 billion people — now live in urban areas, and by 2025 this population is projected to reach 58%, or 4.6 billion people [World Urbanization Prospects, 2011]. In Russia, 73% of the population — 103 million people — live in 1,060 cities and 2,070 townships [Ekologiya..., 2004].

Pollutants accumulate in various parts of the urban landscape, including soil, atmospheric dust, snow cover, water, plants and animals. In studying urban pollution, heavy metals and metalloids (HM) are particularly important. Plants can be used to monitor urban pollution, as they accumulate HM through their leaves and roots [Deu & Kreeb, 1993; Bargagli, 1998]. Leaves absorb elements more selectively than roots [Kvesitadze et al., 2005]. Urban biomonitoring is often conducted with maple leaves [Smith, 1973; Lepneva & Obukhov, 1987; Piczak et al., 2003; Kosiba, 2009; Tomašević et al., 2011] and dandelion leaves [Kuleff & Djingova, 1984; Lepneva & Obukhov, 1987; Djingova & Kuleff, 1999; Marr et al., 1999; Czarnowska, Milewska, 2000; Winter et al., 2000; Keane et al., 2001; Krolak, 2003; Shishlova & Khristoforova, 2009; Hussain & Khan, 2010; Klinskaya & Khristoforova, 2011; Gjorgieva et al., 2011; Malizia et al., 2012].

Research on HM accumulation focuses mainly on Mn, Fe, Pb, Cu, Zn, Cd and As, with only a few studies that include Sb and Mo [Kuleff & Djingova, 1984; Winter et al., 2000; Kosiba, 2009]. Antimony, the companion element of arsenic, has unknown biological functions and some researchers consider it potentially toxic to living organisms. It is also classified as a priority pollutant by the European Union and the United States Environmental Protection Agency, and is on the list of hazardous compounds banned as a result of the Basel Convention [Bargagli, 1998; Shtangeeva et al., 2011; Bech et al., 2012]. Yet some scientists are unsure about the ecotoxicity of antimony [Filella et al., 2009], or even claim that its mutagenic, carcinogenic and teratogenic risks are not highly significant [Leonard & Gerber, 1996]. Molybdenum, on the other hand, is an essential element [Bargagli, 1998; Alloway, 2013] despite its relatively low physiological necessity for plants [Kabata-Pendias, 2011]. Human use of these elements is increasing, as evident in their accelerated rates of production [Kasimov & Vlasov, 2014].

Among the major industrial centers in Russia, Moscow is one of the most polluted [Ekogeokhimiya..., 1995]. Its Eastern Administrative District (EAD) is known as the main industrial area, with dozens of enterprises located on its territory. Comprehensive geochemical investigation in the EAD began during the 1980s under E.M. Nikiforova and other scientists from the Landscape Geochemistry and Soil Geography Department at Lomonosov Moscow State University [Nikiforova & Lazukova, 1991]. This research continued under E.M. Nikiforova, N.E. Kosheleva and N.S. Kasimov. Over more than 20 years, these scientists have assembled substantial data on the migration and accumulation of HM in different landscape components and functional areas [Kosheleva et al, 2005; Nikiforova et al., 2010; Kasimov et al., 2012].

Biogeochemical assessment of HM pollution was conducted in the district between 1989 and 1991 [Nikiforova & Lazukova, 1995]. This included investigating the accumulation of Fe, Mn, Zn, Cu, Pb, Cd, Ni, Co and Cr in unwashed samples of poplar and linden (both leaves and branches), mowed grasses (*Elymus repens*, *Deschampsia cespitosa*, *Agrostis vulgaris* reed and ground) and dandelions, as well as samples of cabbage, fennel, corn, carrots, barley and oats in home gardens. This study determined that poplar leaves accumulate HM more intensively than linden leaves. Plants in industrial zones showed the highest levels of contamination. Along railways, poplar leaves accumulated Fe, Mn, Zn, Pb, while herbaceous species accumulated Rb, Cr, Cs and Pb. In residential areas, the most concentrated metals were Zn, Pb, Ni, Cr, Cs and Rb [Nikiforova & Lazukova, 1995]. There were high levels of contamination in the EAD among crops such as dill (Zn, Cr, Ni, Cu), cabbage (Zn, Cs), corn (Cr, Zn, Pb), potatoes (Zn) and grain (Ni). Fieldwork conducted in 2005 revealed spatial and temporal trends in lead accumulation by plants in the district [Nikiforova et al., 2010].

The present study focuses primarily on biogeochemical characteristics found in washed samples of maple and dandelion leaves, determining the rate of geochemical transformation for plants in comparison with background samples, and identifying spatial differences in the accumulation of Mn, Fe, Pb, Cu, Zn, Cd, Mo, Sb and As.

MATERIAL AND METHODS

Study area and sampling. This study was carried out in the southern EAD over the first ten days of July 2010. The main source of anthropogenic impact in Moscow is motor-vehicle transportation. In the EAD there are also a range of industrial operations, which include energy processing, metalwork, mechanical engineering, chemical production, textile manufacturing, building-material production, and incineration (Fig. 1).

For the current study, levels of HM were detected in leaves of woody (maple, *Acer platanoides*) and herbaceous (dandelion, *Taraxacum officinale*) plants. Samples of 5–7 maples and 15–20 dandelions were taken at different locations and a mixed-sample of each species was prepared. Seven types of land use were studied (Fig. 1): industrial & non-residential, traffic, recreational, agricultural and residential development with high- (over 9 floors), mid- (6–9 floors) and low-rise (1–5 floors) buildings [Kasimov et al., 2012]. In all, 26 sites with maples and 49 sites with dandelions were sampled. Plant material was collected on a regular grid with at 500–700 m intervals. At each site, maple leaves were taken from a height of 2 m above ground at different quarters of the tree crown after more than 5 days without rain, as recommended [Bargagli, 1998]. Approximately 125 g of plant material was taken at each location. The same types of plants were sampled near the town of Zvenigorod, 40 km west of Moscow, to serve as a background sample. This location of background sites was chosen to minimize impact from Moscow according to the main west wind direction.

Fig. 1. Sampling sites in areas with different types of land use in the southern part of Moscow's Eastern Administrative District. Figure based on published work [Kasimov et al., 2012b; Bolshoi Atlas Moskvy, 2012] and data collected through the present study

Laboratory technique and analysis. Maple leaf petioles were separated from leaf blades in the laboratory. The blades and dandelion leaves were then rinsed with distilled water to remove deposited dust from their surface. Rinsed leaves were air-dried for 5 hours, and then the samples were dried in an oven at 75 °C for 5 hours.

Plant material was digested in Teflon autoclaves using extra-pure nitric acid and hydrogen peroxide (4:1). It was then heated in stages at the following temperatures: 160 °C for 1 hour, 200 °C for 2 hours, and 180 °C for 1 hour. This material was cooled and diluted to 25 ml with deionized water.

Detection and measurement of Fe, Mn, Mo, Cd, Pb, Zn, Cu, As and Sb was carried out using flame atomic absorption spectrometry (novAA-400, Analytik-Jena AG, Germany and AA-240Z, Varian Inc., USA) in the Ecogeochemical Research and Educational Center at Lomonosov Moscow State University.

RESULTS AND DISCUSSION

Levels of heavy metals and metalloids in maple and dandelion leaves. For maples, mean concentrations of Fe, Pb, Cu, Mo, Sb and As in background samples were lower than their average concentrations in terrestrial plants (Table 1). Mn, Zn and Cd concentrations, on the other hand, were higher in background samples than average for terrestrial plants. A somewhat different situation was encountered in dandelions: mean concentrations of Fe, Mn, Pb, Cu, Mo, Sb and As were lower in background samples, while Cd was slightly higher and Zn was substantially higher than average concentrations in terrestrial plants [Perel'man & Kasimov, 1999].

On the other hand, levels of all elements except Mn and Cd in maples, and Mn and Zn in dandelions, were higher in the EAD than outside Moscow. This was due to antagonism between Mn, Zn, Mo and other elements in soils, as well as increasing soil alkalinity [Nikiforova et al., 2010; Kabata-Pendias, 2011]. P.V. Elpatievsky found similar results among urban oaks. He also found that maximum concentrations of Mn were reached just before leaf fall among urban oaks, and in midsummer among non-urban oaks [Elpatievsky, 1993]. That is because plants on non-polluted areas accumulate Mn faster than on polluted territories. Thus, lower concentrations of Mn for urban versus non-urban maples in the present study may be due to sampling leaves at midsummer. Copper is not concentrated by herbaceous species because of antagonism between Mo and Cu, i.e. the physiological barrier to Mo uptake by plants is much less effective than that to Cu uptake [Kabata-Pendias, 2011].

Concentrations of heavy metals and metalloids in urban maple leaves are highly variable for different land uses (Table 1). The highest average concentrations of Fe, Pb, Mo, Sb and As in plant material were found in industrial areas: 756, 2.8, 0.034, 0.103 and 0.01 mg per kg of dry weight, respectively. The highest average concentrations of Fe, Pb and Sb were found in dandelions at industrial sites: 417, 1.5 and 0.024 mg per kg of dry weight, respectively. The main industrial sources of Fe are emissions from metalwork and mechanical engineering; for Pb they are energy processing, metalwork, mechanical engineering, textile manufacturing, chemical production, and incineration; for Mo they are energy processing, metalwork and mechanical engineering; for Sb they are metalwork, mechanical engineering, chemical production, textile manufacturing, building-material production, and incineration; for As they are energy processing, metalwork, chemical production, and incineration [Ekologiya..., 2004; Bezuglaya & Smirnova, 2008].

There were high levels of Sb among maples in transportation areas, averaging 0.089 mg per kg of dry weight. Average levels of Mn, Zn, Cu and Cd in maples were highest near roads: 569, 67, 7.8 and 0.2 mg per kg, respectively. Concentrations of these

Table 1. Heavy metals and metalloids concentrations (mg/kg dry weight) in maple and dandelion leaves from different land-use areas in the EAD, compared with samples from the Moscow region and average composition for these plants

Territory (*n*)	Maple leaves, *Acer platanoides*								
	Fe	Mn	Pb	Zn	Cu	Cd	Mo	Sb	As
Industrial & non-residential area (3)	756 (182–1286)	405 (113–696)	2.8 (0.8–5.2)	65 (56–72)	7.0 (6.3–7.7)	0.12 (0.06–0.20)	0.034 (0.026–0.050)	0.103 (0.007–0.232)	0.010 (0.004–0.02)
Traffic area (3)	165 (88–293)	569 (274–779)	1.3 (1.2–1.5)	67 (56–74)	7.8 (7.3–8.3)	0.20 (0.09–0.38)	0.011 (0.007–0.013)	0.089 (0.049–0.168)	0.003 (0.002–0.004)
High-rise buildings (2)	176 (174–178)	152 (147–158)	0.66 (0.33–0.98)	49 (47–51)	7.7 (7.3–8.1)	0.11 (0.06–0.15)	0.007 (0.005–0.009)	0.067 (0.054–0.079)	0.010 (0.008–0.011)
Mid-rise buildings (4)	112 (71–140)	566 (395–906)	1.2 (1.0–1.5)	58 (40–78)	6.0 (3.6–8.4)	0.14 (0.08–0.17)	0.013 (0.006–0.021)	0.036 (0.010–0.074)	0.003 (0.001–0.006)
Low-rise buildings (8)	194 (85–345)	498 (138–641)	1.1 (0.3–1.6)	63 (35–83)	6.2 (4.5–8.6)	0.11 (0.06–0.16)	0.009 (0.002–0.028)	0.028 (0.005–0.065)	0.004 (0.001–0.007)
Recreational area (6)	122 (77–213)	548 (165–1077)	1.2 (0.7–1.4)	56 (19–85)	7.3 (6.3–8.8)	0.22 (0.06–0.64)	0.013 (0.002–0.028)	0.014 (0.001–0.036)	0.005 (0.002–0.010)
EAD (26)	225 (71–1286)	491 (113–1077)	1.3 (0.3–5.2)	60 (19–85)	6.8 (3.6–8.8)	0.15 (0.06–0.64)	0.014 (0.002–0.05)	0.045 (0.001–0.23)	0.005 (0.001–0.015)
Control samples from Moscow region (5)	110 (94–135)	826 (204–1060)	0.93 (0.62–1.32)	40 (29–54)	5.7 (5.3–6.8)	0.26 (0.05–0.43)	0.006 (0.001–0.024)	0.005 (0.001–0.011)	0.001 (0.001–0.002)
Territory	**Dandelion leaves, *Taraxacum officinale***								
	Fe	**Mn**	**Pb**	**Zn**	**Cu**	**Cd**	**Mo**	**Sb**	**As**
Industrial & non-residential area (7)	417 (147–853)	122 (74–215)	1.5 (0.60–3.3)	32 (21–62)	6.6 (6.1–7.2)	0.21 (0.09–0.42)	0.39 (0.25–0.58)	0.024 (0.003–0.066)	0.008 (0.002–0.018)
Traffic area (7)	255 (66–510)	153 (102–247)	0.89 (0.71–1.2)	34 (19–58)	6.3 (5.9–6.8)	0.67 (0.12–2.7)	0.49 (0.07–1.8)	0.018 (0.005–0.044)	0.003 (0.001–0.005)
Agricultural area (5)	113 (35–262)	251 (120–326)	0.45 (0.14–0.65)	51 (7.8–109)	8.6 (6.5–15)	1.7 (0.37–2.9)	0.57 (0.06–1.6)	0.007 (0.001–0.021)	0.002 (0.001–0.004)
High-rise buildings (6)	156 (78–188)	167 (113–248)	0.68 (0.12–0.95)	54 (20–152)	6.3 (4.5–7.1)	0.45 (0.22–0.67)	0.32 (0.022–0.51)	0.005 (0.001–0.013)	0.003 (0.001–0.008)
Mid-rise buildings (6)	197 (134–251)	144 (126–158)	0.77 (0.16–1.3)	39 (20–81)	6.0 (3.5–6.9)	0.80 (0.25–3.1)	0.49 (0.35–0.85)	0.021 (0.004–0.047)	0.011 (0.003–0.038)
Low-rise buildings (11)	169 (27–358)	136 (75–215)	0.62 (0.044–1.7)	50 (16–148)	6.3 (5.8–6.8)	0.46 (0.052–1.0)	0.30 (0.05–1.0)	0.011 (0.002–0.040)	0.005 (0.002–0.009)
Recreational area (7)	196 (117–471)	163 (99–260)	0.74 (0.45–1.1)	42 (29–71)	6.5 (5.7–7.1)	1.2 (0.19–3.4)	0.57 (0.40–0.86)	0.021 (0.003–0.054)	0.009 (0.001–0.023)
EAD (49)	215 (27–853)	157 (74–326)	0.81 (0.044–3.3)	43 (7.8–152)	6.6 (3.5–15)	0.72 (0.052–3.4)	0.43 (0.022–1.8)	0.015 (0.001–0.066)	0.006 (0.001–0.038)
Control samples (5)	50 (18–171)	177 (150–204)	0.17 (0.10–0.24)	46 (30–63)	4.6 (3.3–5.4)	0.16 (0.10–0.22)	0.034 (0.028–0.043)	0.006 (0.002–0.011)	0.002 (0.001–0.004)
Parameter	**Terrestrial plants**								
	Fe	**Mn**	**Pb**	**Zn**	**Cu**	**Cd**	**Mo**	**Sb**	**As**
Average composition of terrestrial plants[a]	150	350	1.5	6.3	10	0.15	0.8	0.04	1.5

[a]Perel'man & Kasimov, 1999.

elements were high among dandelions in transportation areas, but lower than in industrial and agricultural areas. As reported by Lough et al. [2005], Thorpe & Harrison [2008] and Limbeck & Puls [2011], the main sources of Mn in transportation emissions are wearing of brake pads and resuspension of soil particles; for Zn and Sb they are motor oil emissions and wearing of tires and brake pads; for Cu they are exhaust and motor oil emissions as well as wearing of tires and brake pads; for Cd they are wearing of tires.

Only dandelions were sampled at agricultural sites, where their mean concentrations of Mn, Cu, Cd and Mo were higher than in other land-use areas. Highest average levels of Zn were found in dandelions around high-rise buildings, while for Mo they occurred in recreational areas. However, the same concentrations of Zn and Mo were found in agricultural areas. Their presence in agricultural fields was due to the use of phosphate fertilizers [Yanin, 1999].

Table 2 compares maple-leaf composition in the EAD with maple-leaf composition in other cities. Concentrations of Mn were higher than in other cities, while levels of Cu were lower. Fe and Pb levels were lower than in other cities except Waibrzych and Wrociaw, Poland. For Zn and Cd, concentrations were slightly higher or almost even with other cities. There is relatively little information on Mo, As and Sb concentrations in urban maple leaves, which prevented us from identifying significant differences between their presence in the EAD and in other cities. For herbaceous species (Table 2), concentrations of Mn in dandelions from the EAD were higher than in other cities, while concentrations of Cu and Pb were lower. Levels of Cd, Fe and Zn were either higher or lower in the EAD than in other cities. It should be noted that, as with maples, there is insufficient information about Mo, As and Sb levels in urban dandelions.

Urban versus non-urban concentrations of pollutants can be compared using the enrichment factors (*EF*) ratio: $EF = C/C_b$, where C is the element concentration in an urban plant, and C_b is the concentration of the same element in the reference (background) plant. The depletion factor (DF) is the reverse index of EF: DF = 1/EF. The depletion factor can only be used when EF < 1.

Fig. 2. Shows levels of EF and DF for chemical elements in maple and dandelion leaves in areas with different types of land use. The mean EF of chemical elements in EAD maples was (hereafter, the subscript number shows the EF value) $Sb_{9,7}As_{4,6}Mo_{2,2}Fe_{2,0}Zn_{1,5}Pb_{1,4}Cu_{1,2}$, while in dandelions it was $Mo_{12,7}Pb_{4,9}Cd_{4,4}Fe_{4,3}As_{3,9}Sb_{2,7}Cu_{1,4}$.

The main feature of maples found in each land-use area was strong Sb accumulation. Moreover, high EF values were calculated for As in all land use areas. Industrial areas had the highest levels of the following elements: $Sb_{22}As_{9,2}Fe_{6,8}Mo_{5,4}Pb_{3,1}$. These pollutants are contained in emissions from energy processing, metalwork, mechanical engineering, chemical production and incineration plant located in the EAD [Bezuglaya & Smirnova, 2008]. These elements — as along with Cu and Zn — are also emitted by automobiles, which is why maple leaves in traffic areas contain high concentrations: $Sb_{19}As_{2,4}Mo_{1,7}Zn_{1,7}Fe_{1,5}Cu_{1,4}Pb_{1,4}$. Residential buildings of different heights correspond with different elements at maximum CF: Sb, As and Cu for high-rise developments, Mo for mid-rise, and Fe for low-rise. This may be a result of different lengths of time in which soil has been accessible to contamination. For example, the most-polluted soils are found in areas with old low-rise development, whereas the least-contaminated soils are in newer developments where high-rise buildings predominate [Nikiforova et al., 2011].

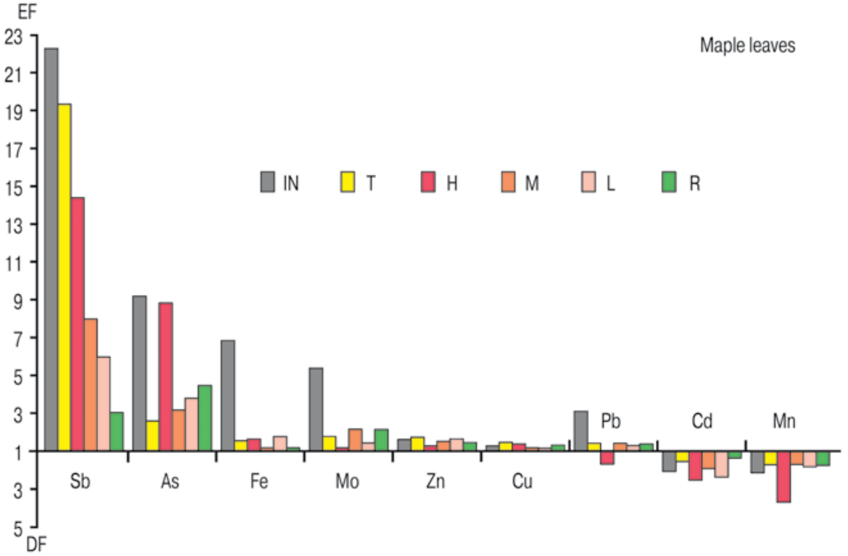
The main difference between dandelions and maples is strong Mo accumulation in all types of land-use areas by herbaceous plants. Moreover, Cd had high EF values in all land-use areas except industrial. Cu concentrations in herbaceous plants from all areas in the EAD are slightly higher than

Table 2. Heavy metals and metalloids concentrations (mg/kg dry weight) in maple leaves from the EAD compared with concentrations in maple leaves from other cities

Territory, season, pollution source, washed/unwashed, sample preparation, analysis technique, number of samples *n*	Mn	Fe	Cu	Pb	Zn	Cd	Mo	As	Sb	Reference
Maple leaves Acer platanoides										
EAD, industry and traffic, summer, washed, $HNO_3 + H_2O_2$ digestion, AAS, $n = 26$	491 (113–1077)	225 (71–1286)	6.8 (3.6–8.8)	1.3 (0.3–5.2)	60 (19–85)	0.15 (0.06–0.64)	0.01 (0.002–0.05)	0.005 (0.001–0.015)	0.04 (0.001–0.23)	Our data
Parks and Botanical Garden, Belgrade, Serbia, summer, traffic, unwashed, $HNO_3 + H_2O_2$ digestion, ICP-MS, $n = 15$	296	640	22	7.4	35	0.09	–	0.55	–	Tomašević et al., 2011
–//– washed	303	357	9.8	5.3	32	0.217	–	0.46	–	–//–
Poland (different voivodeships), summer, industry and traffic, washed, ashing + HNO_3, AAS, $n = 45$	120 (23–853)	264 (25–2975)	8.5 (1.6–24)	9.3 (0.30–34)	57 (14–165)	0.85 (0.01–3.0)	1.6 (0.21–4.1)	–	–	Kosiba, 2009
Waibrzych and Wrociaw, SW Poland, summer, traffic, washed, $HNO_3 + H_2O_2$ digestion, ICP-AES, $n = 3$	174	170	7.5	0.67	52	0.17	–	–	–	Piczak et al., 2003
–//– autumn	319	278	8.6	6.1	84	3.0	–	–	–	–//–
Territory of Lomonosov Moscow State University, Moscow, summer, traffic, ashing, AAS	–	–	7,5	2,7	7,5	0,3	–	–	–	Lepneva, Obukhov, 1987
New Haven, Connecticut, USA, autumn, traffic, unwashed, ashing + HNO_3, AAS, $n = 32$	414 (69–1799)	512 (186–1349)	9 (0.5–31)	146 (45–485)	142 (28–429)	1.1 (0.5–2.0)	–	–	–	Smith, 1973
Dandelion leaves Taraxacum officinale										
EAD, industry and traffic, summer, washed, $HNO_3 + H_2O_2$ digestion, AAS, $n = 49$	157 (74–326)	210 (4–853)	6.6 (3.5–15)	0.8 (0.05–3.3)	43 (8–152)	0.72 (0.05–3.4)	0.43 (0.02–1.8)	0.01 (0.001–0.04)	0.02 (0.001–0.07)	Our data
Wislinka, Northern Poland, autumn, phosphogypsum stack, unwashed, $HNO_3 + H_2SO_4$ digestion, ICP-OES, $n = 3$	–	421	38	174	69	–	–	–	–	Boryio et al., 2013
Rome, Italy, spring, traffic, washed, HNO digestion 3, ICP-AES, $n = 15$	64	–	30	8	102	–	–	–	–	Malizia et al., 2012
–//– summer	49	–	36	15	113	–	–	–	–	–//–
–//– autumn	37	–	33	8	77	–	–	–	–	–//–
Veles, Macedonia, lead and smelting plant, summer, washed, $HNO_3 + H_2O_2$ digestion, ICP-AES	~59	–	~10	~45	~135	7.2	–	–	–	Gjorgieva et al., 2011

Cont.

Territory, season, pollution source, washed/unwashed, sample preparation, analysis technique, number of samples *n*	Mn	Fe	Cu	Pb	Zn	Cd	Mo	As	Sb	Reference
Birobidzhan, Russia, traffic	–	–	–	7.6	0.9	0.35	–	–	–	Klinskaya, Khristoforova, 2011
Khabarovsk, Russia, traffic	–	–	–	4.9	–	0.3	–	–	–	–//–
Vladivostok, Russia, traffic	–	–	–	14	3.4	1.4	–	–	–	–//–
Cengio, Savona, Italy, waste dump of a chemical factory, washed, HNO_3 digestion, ICP-MS	50	146	13	0.9	143	0.2	–	0.1	–	Massa et al., 2010
Peshawar, Pakistan, washed, ashing + HNO_3, AAS	2.7	32	1.4	5	–	–	–	–	–	Hussain, Khan, 2010
Ussuriysk, summer, traffic, metalwork, unwashed, $HNO_3 + H_2SO_4$ digestion, AAS, n = 4	77	394	19	11	50	0.35	–	–	–	Shishlova, Khristoforova, 2009
Poland (South and East), spring, metallurgy, washed, $HNO_3 + H_2O_2$ digestion, AAS, *n* = 35	–	–	44	24	161	1.2	–	–	–	Krolak, 2003
Cincinnati, Ohio, USA, autumn, traffic, washed, ashing + HCl + HNO_3, ICP-AES, *n* = 6	83 (30–114)	1569 (155–3916)	22 (9–58)	19 (1–45)	97 (51–180)	1.6 (0.6–3.1)	–	–	–	Keane et al., 2001
Zittau, Germany, spring, traffic, washed, $HNO_3 + H_2O_2$ digestion, ICP-OES, *n* = 57	29	116	14	1.1	46	0.21	1.7	0.47	–	Winter et al., 2000
Warsaw suburbs, Poland, spring, traffic, washed, ashing + HCl, AAS, *n* = 16	28	410	15	9	86	1.1	–	–	–	Czarnowska, Milewska, 2000
Montreal, Canada, old industrial areas, washed, HNO_3 digestion, AAS, ICP-AES, *n* = 4	26	–	9	7	95	1.0	–	–	–	Marr et al., 1999
Sofia, Bulgaria, spring-autumn, traffic, washed, HNO_3 + HCl digestion, ICP-AES, *n* = 14	21	–	12	1.5	56	0.45	–	–	–	Djingova, Kuleff, 1999
Territory of Lomonosov Moscow State University, Moscow, summer, traffic, ashing, AAS	–	–	3.6	4.1	13.5	2.8	–	–	–	Lepneva, Obukhov, 1987
Sofia, Bulgaria, summer, traffic, washed, NAA	–	–	–	–	69	0.93	–	1.7	0.19	Kuleff, Djingova, 1984
Unpolluted territories of Europe	56	260	14	1.8	44	0.23	–	0.16	–	Bargagli, 1998
Unpolluted territories of Europe and the USA	15–200	60–500	5–20	0.3–6	30–100	0.2–0.8	0.6–2.9	0.1–0.4	–	Djingova et al., 2004



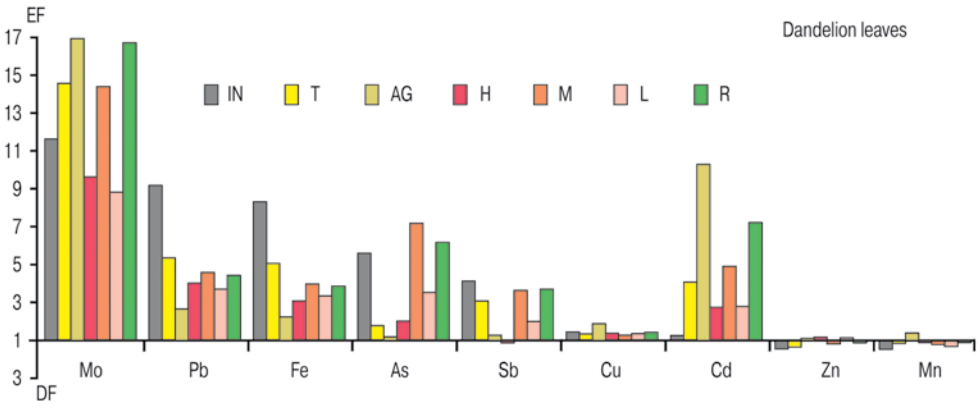


Fig. 2. Levels of EF and DF for chemical elements in the EAD maple and dandelion leaves. Types of land use:

IN — industrial and non-residential, T — traffic, AG — agricultural, H — high-rise buildings, M — mid-rise buildings, L — low-rise buildings, R — recreational

in background dandelions, while Zn and Mn are slightly lower. The highest EF levels in industrial areas were found in Pb, Fe, As and Sb. In traffic areas, the highest were in Pb, Fe and Sb. In agricultural areas they were in Pb and Fe. Recreational areas as well as low-rise and mid-rise developments showed high EF levels in dandelions for each element except Cu, Mn and Zn. Concentrations of all elements in dandelions around high-rise buildings were lower than in other areas. There were higher EF levels in dandelions than in woody plants. This can be explained by the fact that dandelions take nutrients and microelements from the soil's surface layer, which is the most polluted, whereas maples draw from deeper layers [Nikiforova et al., 2011].

The ratio of toxic to essential elements. An element is essential if it participates in the metabolism of a living organism and cannot be substituted by another element in performing biochemical roles. For terrestrial plants, the elements Cu, Fe, Mn, Mo and Zn are essential, while Cd, As, Sb and Pb are toxic or nonessential [Bargagli, 1998]. Mechanisms of the various interactions between HM in plants and soils are not-well understood [Kabata-Pendias, 2011].

Key functions of urban plants can be represented using Fe/Mn and Pb/Mn ratios. The Fe/Mn ratio shows the intensity of photosynthesis, while Pb/Mn represents the consumption of anthropogenic and biophilic elements [Arzhanova & Elpatievsky, 1990; Novikova & Kosheleva 2007; Kasimov et al., 2011].

Table 3. Ratios of chemical elements in maple and dandelion leaves from the EAD in relation to background plants

Ratios	IN		T		AG	H		M		L		R		EAD	
	1	2	1	2	1	1	2	1	2	1	2	1	2	1	2
Fe/Mn	12.0	13.9	5.9	2.2	1.6	3.3	8.7	4.8	1.5	4.3	2.9	4.2	1.7	4.8	3.4
Pb/Mn	13.3	6.3	6.2	2.0	1.9	4.3	3.9	5.7	1.9	4.8	2.0	4.8	1.9	5.5	2.4
Zn/Mn	1.0	3.3	0.9	2.4	0.8	1.2	6.6	1.0	2.1	1.4	2.6	1.0	2.1	1.1	2.5
Cu/Mn	2.1	2.5	1.6	2.0	1.3	1.5	7.3	1.6	1.5	1.8	1.8	1.6	1.9	1.6	2.0
Cd/Mn	1.8	0.9	4.7	1.1	7.2	2.9	2.2	6.0	0.8	3.6	0.7	7.8	1.3	4.9	1.0
As/Mn	8.0	18.8	2.1	3.4	0.8	2.1	47.7	8.8	4.6	4.5	6.3	6.7	6.7	4.4	7.8
Sb/Mn	6.0	45.3	3.5	28.1	0.9	1.0	78.1	4.5	11.5	2.5	9.9	4.0	4.4	3.0	16.4
Mo/Mn	16.8	10.9	16.9	2.5	11.9	10.1	6.0	17.7	3.0	11.3	2.3	18.1	3.1	14.3	3.7
Fe/Pb	0.9	2.2	0.9	1.1	0.8	0.8	2.3	0.8	0.8	0.9	1.5	0.9	0.9	0.9	1.4
Zn/Pb	0.1	0.5	0.1	1.2	0.4	0.3	1.7	0.2	1.1	0.3	1.3	0.2	1.1	0.2	1.0
Cu/Pb	0.2	0.4	0.3	1.0	0.7	0.3	1.9	0.3	0.8	0.4	0.9	0.3	1.0	0.3	0.8
Cd/Pb	0.1	0.2	0.8	0.6	3.8	0.7	0.6	1.1	0.4	0.7	0.3	1.6	0.7	0.9	0.4
As/Pb	0.6	3.0	0.3	1.7	0.4	0.5	12.4	1.6	2.4	1.0	3.1	1.4	3.5	0.8	3.2
Sb/Pb	0.4	7.2	0.6	13.7	0.5	0.2	20.3	0.8	5.9	0.5	4.9	0.8	2.3	0.5	6.7
Mo/Pb	1.3	1.7	2.7	1.2	6.3	2.4	1.5	3.1	1.5	2.4	1.2	3.8	1.6	2.6	1.5
Cu/Zn	2.1	0.8	1.8	0.8	1.7	1.2	1.1	1.5	0.7	1.2	0.7	1.6	0.9	1.5	0.8
Cd/Zn	1.8	0.3	5.5	0.5	9.2	2.3	0.3	5.8	0.4	2.5	0.3	7.9	0.6	4.7	0.4
As/Zn	8.0	5.7	2.4	1.4	1.0	1.7	7.3	8.5	2.2	3.2	2.5	6.7	3.2	4.2	3.1
Sb/Zn	5.9	13.9	4.1	11.6	1.1	0.8	11.9	4.3	5.5	1.8	3.9	4.0	2.1	2.8	6.5
Mo/Zn	16.7	3.4	19.6	1.0	15.2	8.2	0.9	17.0	1.4	8.0	0.9	18.1	1.5	13.5	1.5
Cd/Cu	0.9	0.4	3.0	0.6	5.4	2.0	0.3	3.7	0.5	2.0	0.4	5.0	0.7	3.1	0.5
As/Cu	3.8	7.5	1.3	1.7	0.6	1.5	6.5	5.5	3.0	2.6	3.5	4.3	3.5	2.8	3.9
Sb/Cu	2.8	18.1	2.2	14.1	0.7	0.7	10.7	2.8	7.4	1.4	5.5	2.6	2.3	1.9	8.1
Mo/Cu	8.0	4.4	10.6	1.2	9.0	6.9	0.8	11.0	1.9	6.4	1.3	11.6	1.6	8.9	1.8
As/Cd	4.4	19.8	0.4	3.0	0.1	0.7	21.8	1.5	5.9	1.3	9.4	0.9	5.2	0.9	8.0
Sb/Cd	3.3	47.7	0.7	24.9	0.1	0.3	35.6	0.7	14.7	0.7	14.7	0.5	3.5	0.6	16.9
Mo/Cd	9.2	11.5	3.6	2.2	1.6	3.5	2.7	2.9	3.8	3.2	3.5	2.3	2.4	2.9	3.8
Sb/As	0.7	2.4	1.7	8.2	1.1	0.5	1.6	0.5	2.5	0.5	1.6	0.6	0.7	0.7	2.1
Mo/As	2.1	0.6	8.1	0.7	15.2	4.8	0.1	2.0	0.6	2.5	0.4	2.7	0.5	3.2	0.5
Sb/Mo	0.4	4.1	0.2	11.3	0.1	0.1	13.1	0.3	3.8	0.2	4.3	0.2	1.4	0.2	4.5
Пt/Пe	32.8	56.6	9.4	18.5	0.8	1.4	109.7	45.2	8.2	6.8	7.8	36.1	5.9	14.8	16.2

Notes. Types of land use areas: IN — industrial and non-residential, T — traffic, AG — agricultural, H — high-rise buildings, M — mid-rise buildings, L — low-rise buildings, R — recreational. Species: 1 — dandelion, 2 — maple. Пt — amount of toxic elements (Cd·As·Pb·Sb), Пe — amount of essential elements (Mn · Cu · Mo · Zn). Ratios marked yellow if values ⩾ 2.0 and green if values ⩽ 0.5.

Average Fe/Mn ratios in EAD maple and dandelion leaves relative to background plants were up to 3.4 and 4.8, respectively; Pb/Mn ratios were up to 2.4 and 5.5, respectively. This is due to the contravention of photosynthesis processes, when accumulation rates of essential elements, which play role in plant growth, decrease and accumulation rates of toxic elements increase (Table 3). The highest Fe/Mn (13.9 and 12.0) and Pb/Mn (6.3 and 13.3) ratios in maples and dandelions were found in industrial areas. Among maples, slightly lower values appeared in areas with high-rise buildings (Fe/Mn of 8.7, Pb/Mn of 3.9). For dandelions, Fe/Mn and Pb/Mn ratios were slightly lower in traffic areas (5.9 and 6.2, respectively) where they were exposed directly to motor-vehicle emissions.

The ratios Zn/Mn and Mo/Mn can be used to compare photosynthesis processes and plant growth. For maple leaves in the EAD, Zn/Mn was 2.6 times higher than in background samples, while in dandelions it was 1.1 times higher. This ratio varied from 2.5 for maples in mid-rise developments to 8.2 for those in industrial areas, and 36.5 for those in high-rise developments. Among dandelions, it varied from 0.8 in agricultural areas to 1.4 in low-rise developments (Table 3). Variation in Mo/Mn ratios was greater than in Zn/Mn ratios. The lowest Mo/Mn ratio in maples (2.3) occurred in low-rise developments, while the highest (10.9) was in industrial areas; the average Mo/Mn ratio for EAD maples was 3.7. Variation was greater among Mo/Mn ratios for dandelions: the lowest (10.1) occurred in high-rise developments, and the highest (18.1) was in recreational areas; the average Mo/Mn ratio for EAD dandelions was 14.3.

Differences in biogeochemical specialization among herbaceous and woody plants can be shown using the Sb/Mo ratio. In the EAD, it was 4.5 times higher for maples, and about 5 times lower for dandelions, than at the background site (Table 3). The Sb/Mo ratio for dandelions was lower than 1 at all sites. The highest values of Sb/Mo were in maples near high-rise buildings and traffic areas (13.1 and 11.3, respectively), while the lowest levels were in dandelions around high-rise buildings and in agricultural areas (0.1).

To determine the integral ratio of toxic to essential elements, the following index is suggested: (Cd·As·Sb·Pb)/(Cu·Mn·Mo·Zn). For maple leaves from the EAD, this index was 16.2 times higher than for those from the background site; for dandelions it was 14.8 times higher. Except in mid-rise developments and recreational areas, integral index levels for maples were higher than for dandelions. This indicates higher accumulation of toxic elements by maples than dandelions.

Spatial distribution of pollutants. Total-pollution indexes can be used to calculate the level of toxic chemicals in plants. There are several related approaches to pollution assessment. The C_d index was introduced by L. Hekanson to determine levels of pollution in bottom sediments. It is calculated using the equation $C_d = \sum_{i=1}^{n} EF_i$, where EF_i is the enrichment factor of *i*-pollutant in sediments, and n is the total number of pollutants. If $C_d < n$, the level of pollution is low; if $n \leqslant C_d < 2n$, the level is medium; if $2n \geqslant C_d < 3n$, the level is high; and if $C_d \geqslant 3n$, the level is very high [Hekanson, 1980]. The Z_c total-pollution index, introduced by Yu. Saet, is calculated using the equation $Z_c = \sum_{i=1}^{n} EF_i - (n-1)$, ΣEF_i — (n — 1), where EF_i is the enrichment factor of *i*-pollutant in soils or snow dust, and n is the total number of pollutants with $EF > 1.5$ [Geochemistry..., 1990]. The grades of this index for plants have not yet been developed, which is why some scientists use grades for soils instead [Kasimov et al., 2012a]. If $Z_c < 16$, the level of pollution is low; if $16 \leqslant Z_c < 32$, the level is medium; if $32 \leqslant Z_c < 64$, the level is high; if $64 \leqslant Z_c < 128$, the level is very high; and if $Z_c \geqslant 128$, the level is extremely high.

Plants respond to environmental pollution not only with accumulation, but also with depletion of some chemical elements due to changes in the intensity of biological processes [Bargagli, 1998; Kabata-Pendias, 2011]. As a result, O. Sorokina [2013] proposed the biogeochemical transformation equation Z_V for poplar leaves and larch needles in Ulaanbaatar City: $Z_V = \sum_{i=1}^{n1} EF_i + \sum_{j=1}^{n2} DF_j - (n_1 + n_2 - 1)$, where EF_i is the enrichment factor of i-element in plants, n_1 is the total number of elements with $CF > 1$, DF_j is the depletion factor of j-element in plants, and n_2 is the total number of elements in which $DF > 1$. The Z_V index shows disruption of normal correlations for elements in different parts of a plant according to its phylogenetic and ontogenetic specialization. This index also provides a quantitative representation of imbalances among element ratios due to anthropogenic pressure. O. Sorokina suggested that if $Z_V < 15$, the level of biogeochemical transformation is low; if $15 \leqslant Z_V < 20$, the level of biogeochemical transformation is medium; if $20 \leqslant Z_V < 25$, the level of biogeochemical transformation is higher than medium; and if $Z_V \geqslant 25$, the level of biogeochemical transformation is 2 times higher than medium. But Z_V levels may differ in various plant species. Fig. 3 shows the number of sites in the EAD with different levels of Z_V in maple and dandelion leaves. Figure analysis was used to identify new gradations of Z_V for these species (Table 4).

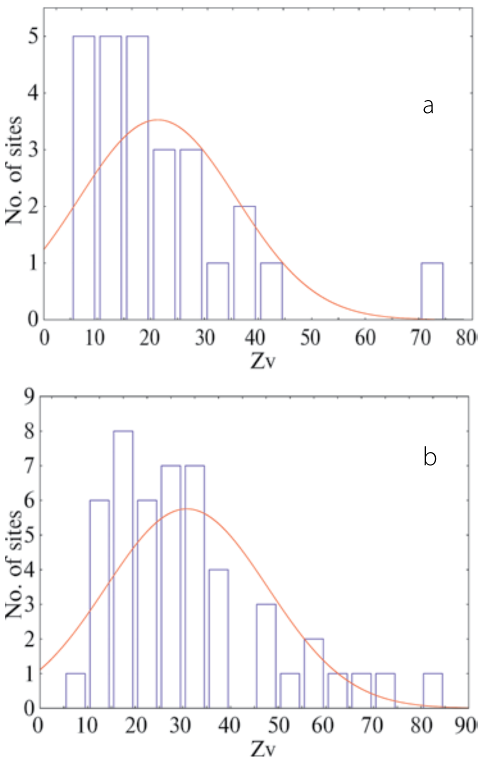


Fig. 3. Number of sites with different levels of biogeochemical transformation factor Z_V in maple (a) and dandelion (b) leaves

Table 4. Gradations of Z_V for maple and dandelion leaves from the EAD and corresponding levels of biogeochemical transformation

Values of Z_V in leaves		Biogeochemical transformation
maple	dandelion	
<15	<15	Very low
	15–25	Low
15–25	25–35	Medium
25–35	35–45	High
35–45	45–55	Very high
>45	>55	Extremely high

Fig. 4. shows the spatial distribution of Z_V in EAD maple and dandelion leaves. In recreational areas and low-rise developments there were low and medium levels of biogeochemical transformation in maple leaves. This indicates low-intensity anthropogenic impacts on plants in these areas.

High biogeochemical transformation of maple leaves was found in recreational areas as well as mid- and high-rise developments near industrial sites, major roads and railways (Fig. 4). A similar situation was found in old residential areas with low-rise buildings in the southeast EAD (sites 18 and 19). There were very high Z_V levels in maple leaves from the following areas: along Entuziastov Rd., around the high-rise buildings near Veshnyakovskaya Rd., and at the Sokolinaya Gora industrial zone in the northwest EAD. Sokolinaya Gora showed particularly intense anthropogenic impact, resulting in extremely high rates of biogeochemical transformation in maple leaves.

In most recreational areas and high-rise developments, along with some mid-rise and low-rise developments, there were

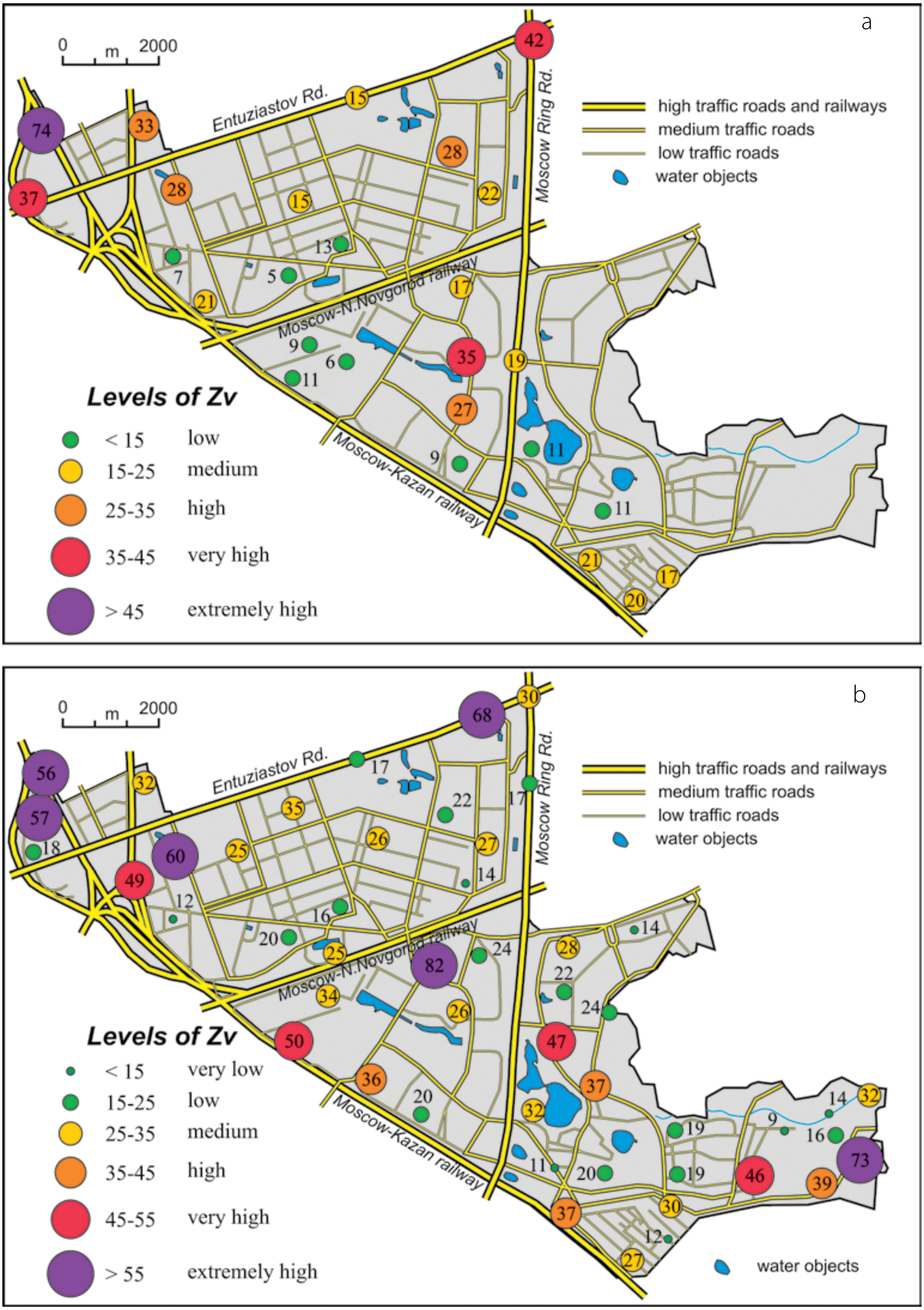


Fig. 4. Spatial distribution of biogeochemical transformation factor Z_V of maple (a) and dandelion (b) leaves in the EAD

very low and low levels of biogeochemical transformation in dandelion leaves. Medium and high Z_V levels were found in low-rise developments, some agricultural areas, recreational zones, medium-rise developments and high-rise developments. Extremely high and very high biogeochemical transformation in dandelion leaves appeared at industrial sites near Entuziastov Rd. and the railway.

CONCLUSION

In the EAD, dandelions accumulate $Mo_{12,7}Pb_{4,9}Cd_{4,4}Fe_{4,3}As_{3,9}Sb_{2,7}$ $Cu_{1,4}$, while maples accumulate $Sb_{9,7}As_{4,6}Mo_{2,2}Fe_{2,0}Zn_{1,5}Pb_{1,4}Cu_{1,2}$ — normalized to concentrations in background samples from an unpolluted site west from Moscow.

High Sb accumulation was a key feature among maples in each land-use area. The main difference between dandelions and maples was strong Mo accumulation in all land-use areas by herbaceous plants. Another difference between herbaceous and woody plants was higher EF levels in dandelions. This can be explained by the fact that dandelions take nutrients and microelements from the surface layer of soil, which is normally more polluted than deeper layers. Dandelions and maples do not accumulate Mn due to antagonism between Zn, Mo and Mn in soils. Copper is not concentrated by herbaceous species because of antagonism between Mo and Cu.

The highest Fe/Mn and Pb/Mn ratios were found in industrial areas for both species. The ratios Zn/Mn and Mo/Mn may also be useful for considering photosynthesis processes and plant growth. Differences in the biogeochemical specialization of herbaceous and woody plants can be shown using Sb/Mo ratios. These ratios were 4.5 times higher for urban maples and about 5 times lower for urban dandelions in the EAD than for corresponding background samples. Ratios for integral estimation of toxic and essential elements were calculated using the following index: (Cd·As·Sb·Pb)/(Cu·Mn·Mo·Zn). In all areas except mid-rise developments and recreational zones, integral index values were higher for maples than for dandelions.

A Z_v ratio was used to show the biogeochemical transformation intensity of urban plants. High and very high biogeochemical transformation for maple leaves was found in recreational areas, around mid- and high-rise buildings, near industrial sites, and along large roads and railways. There were extremely high and very high rates of biogeochemical transformation among dandelion leaves in the industrial area near Entuziastov Rd. and near the railway.

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