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ORIGINAL PAPER

Impact of simulated acid rains on leakage of mineral elements from foliage of conifers and monocotyledons – adaptability matters

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Abstract

The concept of the research is based on the effects of acid rains on the foliage of plants. The study was carried out on 12 coniferous tree (thuya, fir, larch, juniper, Scots pine, black pine, common spruce, silver spruce, cypress, yew tree, oriental thuya, Douglas fir) and 8 monocotyledonous plants (maize, wheat, barley, oats, rye, ryegrass, fescue, ditch reed). Samples of needles and leaves were collected from 20 species during the growth season from spring to summer at different sites of Poznan agglomeration. The needles and leaves were treated with 6 simulated acid rains (SAR) of pH 3.0, 3.5, 4.0, 4.5, 5.0, and 5.5 and kept for 72 h at 22°C. The filtrates were tested for Ca, Mg, K, Na, Zn and Fe. The data showed that the concentrations of leaked elements were closely related to the pH of SAR and also depended on the species. The most deleterious simulated acid rains for all tested plants were within the range pH = 3.0 - 4.0. Mineral leakage of coniferous needles as well as monocotyledonous leaves fitted mostly *exponential* and *linear* models, with exception of Na, which was described by the *quadratic* course. On the basis of the photosynthetic maintenance index PMI = Mg/(Zn+Fe), 67% of coniferous tree (CT) represented very low photosynthetic maintenance, contrary to monocotyledons (MP) with 75% corresponding to low photosynthetic maintenance. The high share of MP in this range is the finding which clearly points to the potential adaptability of the latter species to highly anthropogenic ecosystems. Urban greens should not be planted predominantly with conifers, although some may develop slight (grand fir, cypress, oriental thuya, Douglas fir) to high adaptability (Thuya occidentalis, juniper, yew tree) to urban conditions. Nearly all monocotyledons, particularly ryegrass, fescue, wheat, barley, oats and rye may be growing within anthropogenic zones, having strong adaptability features.

Keywords: simulated acid rain, mineral leakage, conifers, monocotyledons, photosynthetic maintenance index, species adaptability, urban green covers

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INTRODUCTION

Acid rains (ARs) with high acidity, i.e. low pH, are described extensively in numerous scientific reports. According to Debnath et al. (2021), acid rains are considered as rainwaters with hydrogen ion concentrations higher than 2.5 eq^{-1} and the pH value lower than 5.6. The factors responsible for the emergence of acid rains are various, but often linked to emissions of sulfur dioxide and nitrogen oxides (Lu et al. 2011, Mao et al. 2014, Li et al. 2021). These compounds undergo chemical reactions with water, resulting in the formation of sulfuric acid as well as nitric acid rains (Zhang et al. 2007). Such low pH and the resulting processes may create environmental concerns due to deleterious effects on specific ecosystems (Wang et al. 2014, Burns et al. 2016, Debnath et al. 2020). Their impacts on plant foliage have been a matter of detailed investigations (Debnath, Ahammed 2020).

Plants are an essential component of terrestrial ecosystems and are affected by acid rain pollution (Liu et al. 2018), exhibiting growth inhibition, necrotic spots, premature defoliation or premature aging, destructing chloroplast ultrastucture, blocking the synthesis of chlorophyll and decreasing photosynthesis and disturbing cation homeostasis (Macaulay, Enahoro 2015, Du et al. 2017). In addition, acid rain accelerate the leaching of nutrients (Ca, Mg, K, and Na) from leaves which leads to the abnormal or restricted growth (Wang et al. 2014). The plant aerial parts are the first to be affected by acid rain, which directly suppresses their light-harvest functions by eroding surface waxes and cuticles, inhibiting wax biosynthesis, and leaching base cations from mesophyll cells to accumulate intracellular H^+ and other harmful ions (Neves et al. 2009, Shu et al. 2019). Additionally, AR has been proven to increase the concentration of reactive oxygen species (ROS) in foliage, such as hydrogen peroxide (H_2O_2), singlet oxygen ($1O_2$), superoxide anions (O_2•–), and hydroxyl radicals (•OH) (Neves et al. 2009), causing elevated lipid peroxidation (Gill, Tuteja 2010), as well as changes in foliage enzyme activities (Ren et al. 2018) and chlorophyll fluorescence characteristics (Sun et al. 2016).

Soil is the final recipient of acid rain in terrestrial ecosystems, and thus the underground parts of the ecosystem are probably more sensitive to acid rain than the aboveground ones (Wei et al. 2017). Acid rain indirectly causes severe damage to plant roots by triggering soil acidification, changing cation adsorption and solution chemistry in soils (Qiu et al. 2015), and affecting nitrogen metabolism related genes and proteins (Liu et al. 2013), which further influence amino acid biosynthesis and disturb the balance of carbon and nitrogen metabolism.

In response to acid rain stress, plants have developed complex sensing and signaling mechanisms for regulating the ion homeostasis. Reports of Dai et al. (2013) and Qiu et al. (2015) showed that AR is able to mobilize base cations, decompose organic compound, and lose mineral structure in the soil.

The negatively charged sulphate and nitrate ions in the AR can act as "counterions", which allow cations to be leached from the soil. Through a series of chemical reactions, cations such as K^+, Na^+, Ca^{2+}, and Mg^{2+} are leached out and become unavailable to plants as nutrients (Ling et al. 2010, Liu et al. 2014). Previous studies have indicated that acid rain affects plant growth both indirectly by inducing nutrient leaching and increasing availability of toxic heavy metals (Singh, Agrawal 2007) and directly by damaging the foliage (de Vries et al. 2015). The direct injury of acid rain to plant foliage includes physiological (reduction in photosynthetic rate, variation in stomatal conductance and decrease in chlorophyll content) and morphological alternations (reduction in thickness of cuticle and occurrence of necrotic spots), (Du et al. 2017).

Industrial activity has been threatening the environment for decades (Menz, Seip 2004, Kohno 2017) and this has resulted among others in the dramatic damage of forest covers in the south-west part of Poland (Jabłoński et al. 2019). Data for the period 2021 - 2022 reported by the Polish Chief Inspectorate for Environmental Protection (GIOŚ, 2023) and including 22 air monitoring stations with 2058 daily rain samples show that about 35% of pH values were 5.6 (limit for acid rains). Various green covers, e.g. city parks, perennial grasses, allotment gardens, agricultural fields within urban agglomerations, build up complex urban ecosystems. All these green covers will exhibit specific responses to acid rains (AR) of different severity, depending on their sensitivity or resistance (adaptation) to such stressful factors.

This work reports the potential leakage of Ca, Mg, K, Na, Zn, and Fe as a response of the foliage from 12 coniferous tree species and 8 monocotyledonous plants species to simulated acid rains (SAR). The results will provide a scientific and decision making tool for developing acid rains adaptation strategies and maintaining sustainable plant growth in increasingly urbanized areas worldwide. Indices are suggested for a ground and specific evaluation of potential plant susceptibility to deleterious acid rain effects.

MATERIALS AND METHODS

Study area

The investigated area is located within Poznan agglomeration (Figures 1, 2) covering 261.9 km^2 with a population of 535 802 inhabitants. With reference to the whole area, the factors that could generate sulfur and nitrogen oxides as well as other volatile compounds are in decreasing order 1) individual house heating systems (91%), 2) public and private car traffic (6%), 3) industrial installations and power generators (2%) and finally 4) fields and paved roads (1%).

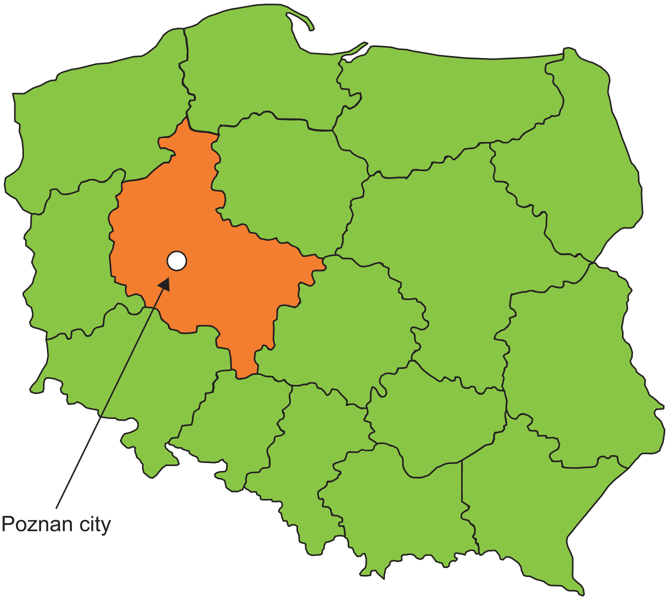

Fig. 1. Location of Poznan city in Wielkopolska Region and in Poland

Fig. 2. Poznan city with sampling zones: 1 – Cytadela Park (*ca* 100 ha), 2 – Szelagowski Park (*ca* 12 ha), 3 – Ecological site "Wilczy Mlyn" (*ca* 78 ha), 4 – Fort V area (*ca* 15 ha), 5 – Forest nearby the Warta river (*ca* 140 ha)

Experimental conditions and simulated acid rains (SAR) treatments

Green and well-developed needles and leaves (*ca* 20 g) were collected from early May 2016 to mid-July 2016. The plant material was obtained at the full vegetation period from 12 coniferous tree (CT) species (*Thuja occidentalis, Abies alba, Larix decidua, Juniperus comumis, Pinus sylvestris, Pinus nigra, Picea abies, Picea ssp., Chamaecyparis ssp, Taxus baccata, Platycladus orientalis, Pseudotsuga menziesii*) and from 8 monocotyledonous plant (MP) species (*Zea mais, Triticum aestivum, Hordeum sativum, Avena sativa, Secale cereal, Lolium perenne, Festuca pratensis, Phragmites australis*). For the coniferous trees (CT), the needles were gathered at 1.5 to 2.0 height from the soil surface. In order to reduce alterations and particularly moisture losses, needles and leaves were inserted into PE bags (Figure 3*a*), sealed tightly and kept in ice boxes at 10°C for 4-5 h before starting the tests with various waters simulating acid rains (AR).

Fig. 3*a*. Conifer needles (left) and monocotyledon leaves (right)

Prior to starting leaching tests, fresh needles and leaves were minced and triplicated portions of 1.00 ± 0.005 g were weighed into test tubes for mineralisation in 5 cm^3 of concentrated HNO_3 (MARS5, CEM Corporation, USA). After cooling, the digests were filtered into 10 cm^3 test tubes, which were further filled up with deionized water (DW). Calcium, Mg, K, Zn, Mn and Fe were determined by atomic absorption spectrometry (AAS; Varian SpectrAA 250 plus, Varian Inc., Palo Alto, Calif., USA). The precision test was based on the average relative standard of deviation (RSD, %), which varied from 0.50 to 1.0% for the determined elements. Mineral elements assayed by this method represented the total concentrations in the fresh needles and leaves biomass.

Preparation of simulated acid rain (SAR) solutions

The concept of contact/leaching solutions is to create a slight mimic of acid rain (AR), whose chemical composition, besides CO_2, in most cases consists of SO_x and N_xO_y compounds. The pH of AR ranges from about 3.0 to 5.5, although values as low as pH 3.0 have been reported (Dai et al. 2013). To reflect the composition of local AR, we first prepared a stock solution from diluted H_2SO_4 (H_2SO_4:H_2O as 1:1) and HNO_3 (HNO_3:H_2O as 1:1) at a ratio of 70:30 (v/v), respectively by chemical equivalents. The SAR solutions at pH 3.0, 3.5, 4.0, 4.5, 5.0, and 5.5 were prepared by diluting the above stock solution with deionized water (DW, pH = 6.55) and monitoring the expected pH with a pH-meter (Multifunctional device Elmetron CX701). A SAR of pH 5.5 was prepared as a control. The total amount of SAR was 1000 mm based the annual average precipitations in Poznan (520 mm).

Experimental design

Five (5) g of the collected fresh needles and leaves of each plant species were weighed (duplicated) and next promptly rinsed with deionized water (DW). Then, they were inserted into 100 ml PE containers and 25 ml of the SAR solutions were added. Needles and leaves should be immersed completely in SAR solutions (Figure 3*b*).

Fig. 3*b*. Needles and leaves immersed in the SAR solutions and treatments (sealed containers) subjected to incubation process.

All treatments (needles and leaves and respective SAR solutions) of the coniferous trees as well as monocotyledonous plants were incubated at 22°C within a growth chamber for 72 hours. After the contact time, the leachates were filtered through Whatman filters and analyzed first for pH (Multifunctional device Elmetron CX701) and next for Ca, Mg, K, Na, Zn, Mn and Fe by atomic absorption spectrometry (AAS; Varian SpectrAA 250 plus, Varian Inc., Palo Alto, Calif., USA). In the precision test, the average RSD (%) for all elements varied from 0.75 to 1.85%.

Statistical evaluation

Statistical analysis of data was performed by using Statistica 10.0© Package (StatSoft) and Excel© sheet. Descriptive statistics have been applied for enabling an easy follow up of the developed concept in terms of data in tables as well as graphical visibility.

RESULTS

Coniferous trees and monocotyledonous plants are considered worldwide as species with low or slight requirements in terms of soils quality and mineral elements (ME) concentrations. These characteristics both under natural and man-made (anthropogenic) ecosystems could be viewed as inducing some specific phyto-adaptability or phyto-resistance to adverse abiotic factors, among others acidity generated from low pH of atmospheric rainfalls. For the purpose of the current research, the latter ones are expressed as simulated acid rains (SAR) which may induce the leakage of mineral elements from the foliage of 12 coniferous trees (CT) species and 8 monocotyledonous plants (MP). If acid rains impact gradually the health and life of the tested plants, therefore we should expect some quantitative as well as qualitative "measurable" responses, reflected by the leakage dynamics. Some hypothised balance could be emerging between photosynthetic elements initiating and maintaining plant vegetative growth (Zn) and carbon dioxide assimilation (Mg, Fe) versus structural cell constituents (Ca) and assimilates controllers (K, basically).

Conifers and monocots variability for total Ca, Mg, K, Na, Zn and Fe content

The total concentrations of mineral elements (ME) listed in Table 1 and Table 2 display a great inter-species variation. For the coniferous trees (CT), calcium (Ca) concentrations range within a large scale, i.e. between 127.7 (Common spruce) and 1427.1 (Larch) mg kg^{-1}, expressed by a coefficient of variation (CV) of 38.8%. Magnesium (Mg), iron (Fe) and zinc (Zn) outline the highest CV values of 50.3, 60.2 and 63.8%, respectively, contrarily to sodium (CV = 15.1%) and potassium (CV = 23.5%). Observations made for CT revealed, that Larch recorded the highest concentrations for Ca and Mg; Common spruce as well as Larch for K; Common spruce for Zn, Silver spruce and Common spruce for Fe. In the case of sodium (Na), 75% of its concentrations exceeded 750 mg kg^{-1}, with the highest ones recorded for Black pine (803.3 mg kg^{-1}) and Cypress (851.8 mg kg^{-1}). The overall order based on mineral element contents follows: K > Na > Ca > Mg > Fe > Zn. Calcium within the order has discriminated two groups, i.e. K and Na (for transpiration and assimilates regulation) and Mg, Fe, Zn for potential photosynthetic activity and maintenance of these processes under abiotic impact.

Table 1

Total content of Ca, Mg, K, Na, Zn, and Fe in the fresh needles biomass of coniferous trees (CT)

Coniferous trees (CT)	Ca		Mg		K		Na		Zn		Fe	
	(mg kg^{-1}) fresh needles biomass											
	mean[a]	SD[b]	mean	SD	mean	SD	mean	SD	mean	SD	mean	SD
Thuya occidentalis – *Thuja occidentalis*	457.1	38.1	220.4	10.8	1168.1	410.0	535.6	85.8	2.36	0.48	7.99	0.27
Grand Fir – *Abies alba*	562.3	30.2	138.3	15.8	1114.7	86.1	497.4	5.0	4.01	0.16	30.30	3.23
Larch – *Larix decidua*	1427.1	815.5	755.1	329.6	1283.6	475.6	445.1	3.5	14.51	1.22	13.88	2.53
Juniper – *Juniperus communis*	323.3	0.4	94.0	1.1	725.4	206.1	758.2	79.8	1.93	0.06	1.55	0.05
Scots pine – *Pinus sylvestris*	470.7	1.7	225.0	33.1	1059.9	54.7	733.3	5.6	6.83	0.08	9.21	1.83
Black pine – *Pinus nigra*	279.8	68.2	184.2	25.5	1055.2	364.3	803.4	30.5	5.77	0.19	16.82	2.60
Common Spruce – *Picea abies*	127.7	27.0	174.4	32.2	1364.9	52.1	760.4	48.2	17.82	0.53	36.85	2.56
Silver spruce – *Picea ssp.*	338.6	3.4	125.8	6.0	734.1	68.0	788.1	54.8	4.77	0.17	46.18	8.56
Cypress – *Chamaecyparis ssp*	520.8	47.3	152.2	26.7	938.6	168.2	851.8	0.3	15.43	0.25	13.93	1.23
Yew tree – *Taxus baccata*	395.9	8.6	87.5	21.9	473.5	109.6	769.7	45.1	9.88	0.39	26.53	1.63
Oriental thuya – *Platycladus orientalis*	374.7	11.4	128.4	16.6	821.8	93.3	733.1	11.2	1.44	0.07	1.73	0.11
Douglas fir – *Pseudotsuga menziesii*	374.5	37.7	108.6	58.1	674.0	243.8	786.3	40.8	3.61	0.08	25.64	3.76
CV (%) for species[c]	38.8	-	50.3	-	23.5	-	15.1	-	63.8	-	60.2	-

[a] n=3, [b] Standard deviation, [c] coefficient of variation

Table 2

Total content of Ca, Mg, K, Na, Zn, and Fe in the fresh leaves biomass of monocotyledonous plants (MP)

Monocotyledonous plants (MP)	Ca		Mg		K		Na		Zn		Fe	
	(mg kg^{-1}) fresh leaves biomass											
	mean[a]	SD[b]	mean	SD	mean	SD	mean	SD	mean	SD	mean	SD
Maize – *Zea mais*	1093.6	20.7	921.9	190.8	2139.3	35.6	1065.8	76.4	7.81	3.08	6.28	1.54
Wheat – *Triticum aestivum*	378.0	75.5	117.0	26.0	1261.8	19.3	49.9	7.0	2.27	0.28	0.75	0.035
Barley – *Hordeum sativum*	955.7	71.1	296.1	9.7	1970.7	192.7	86.1	5.6	2.31	1.65	0.57	0.567
Oats – *Avena sativa*	868.8	47.9	229.1	79.8	2203.7	168.7	71.9	10.5	3.09	0.81	1.42	0.420
Rye – *Secale cereale*	453.1	17.8	194.5	18.3	1143.4	115.2	48.8	7.6	1.81	0.39	0.50	0.210
Ryegrass – *Lolium perenne*	4278.4	123.8	1171.7	138.4	1741.6	82.8	859.1	18.4	4.51	0.18	6.46	0.210
Festuca – *Festuca pratensis*	648.9	169.2	126.6	38.2	483.6	17.7	46.8	6.4	1.42	0.14	0.32	0.140
Ditch reed – *Phragmites australis*	939.4	25.4	229.5	168.6	1278.6	11.4	1063.2	57.9	1.14	0.32	0.53	0.035
CV (%) for species[c]	64.0	-	77.4	-	31.8	-	106.6	-	51.5	-	101.5	-

[a] n=3, [b] Standard deviation, [c] coefficient of variation

Monocotyledons display a totally different concentration patterns. In fact, the order based on mineral element contents was slightly similar to that observed for conifers and ranges accordingly: K > Ca > Mg > Na > Zn > Fe, with potassium still as first. Practically, two species (ryegrass and maize predominated for their highest contents as listed below:

Ca: Ryegrass (4278.4 mg kg^{-1}) and Maize (1093.6 mg kg^{-1});

Mg: Ryegrass (1171.7 mg kg^{-1}) and Maize (921.9 mg kg^{-1});

K: Oats (2203.7 mg kg^{-1}) and Maize (2139.3 mg kg^{-1});

Na: Maize (1063.2 mg kg^{-1}) and Ditch reed (1065.8 mg kg^{-1});

Zn: Maize (7.81 mg kg^{-1}) and Ryegrass (4.51 mg kg^{-1});

Fe: Ryegrass (6.46 mg kg^{-1}) and Maize (6.28 mg kg^{-1}).

The intra-species variability based on CV shows the following order: Na (CV = 106.6%) > Fe (101.5) > Mg (77.4) > Ca (64.0) > Zn (51.5) > K (31.8).

For the coniferous as well as monocotyledonous species, the total contents of K predominate over other mineral elements, but the observed intra-species variability was relatively low. Then, potassium may be playing a key adaptability role, since all investigated species "stabilized" its intracellular levels, irrespective of the ecosystems they grow. This characteristics outlines the possible high susceptibility (low K concentrations) versus low susceptibility (high K concentrations) to potential acids rains or similarly acting abiotic factors.

Simulated acid rains (SAR) versus potential mineral leakage

Mineral pools in green plant tissues may occur in two forms i) strongly bound with organic molecules forming then the reserve fractions and ii) and mobilisable, i.e. bio-active (directly involved into biochemical processes). The latter ones may be considered as a mobile phyto-fence activated under specific threatening conditions, like acid rains (AR). Data of mineral elements (ME) potentially leaked from coniferous needles and monocotyledonous leaves are reported in Table 3 and Table 4, respectively. These are mean values and standard deviation (SD), then coefficients of variation (CV, % = (SD/mean)*100) may be calculated for screening any intra-species variability (for conifers and monocotyledonous) in evaluating leakage characteristics as induced by the particular SAR (pH-SAR: 3.0, 3.5, 4.0, 4.5, 5.0, 5.5).

The concentrations of mineral elements (ME) leaked from conifers (CT) needles as well as monocotyledons (MP) leaves varied at large scales and depended on photosynthetic organs, SAR and also type of ME. In the case of the CT species (Table 3), it appears that larch leaked the most for Ca (212.2 mg kg^{-1}), Mg (124.8 mg kg^{-1}) and K (332.6, but equally high also for common spruce: 323.5 mg kg^{-1}). Next, Zn and Fe confirmed the predominance of common spruce, with 1.822 and 4.125 mg kg^{-1}, respectively. The intra-species variability within this group follows the order: Fe (67.9%) > Zn (57.7%) > Mg (45.2%) > Ca (38.8%) > K (26.0) > Na (23.3%). Another way to evaluate

Table 3

Amounts of Ca, Mg, K, Na, Zn, and Fe leaked from coniferous needles after contact with SAR for 72 h

Coniferous trees (CT)	Ca		Mg		K		Na		Zn		Fe	
	(mg kg^{-1}) fresh needles biomass											
	mean[a]	SD[b]	mean	SD	mean	SD	mean	SD	mean	SD	mean	SD
Thuya occidentalis – *Thuja occidentalis*	64.3	9.7	35.9	8.5	264.7	157.4	49.2	6.7	0.223	0.132	0.595	0.276
Grand Fir – Abies alba	64.0	13.1	23.8	4.1	189.3	17.0	44.3	9.7	0.310	0.086	1.558	0.519
Larch – *Larix decidua*	212.2	106.4	124.8	46.0	332.6	97.1	40.3	6.0	0.866	0.421	0.835	0.717
Juniper – *Juniperus communis*	41.4	5.1	16.0	3.3	149.6	40.8	92.4	7.5	0.077	0.066	0.118	0.056
Scots pine – *Pinus sylvestris*	50.6	6.0	40.7	5.9	206.9	26.5	88.9	1.5	0.547	0.067	0.511	0.183
Black pine – *Pinus nigra*	40.7	10.7	30.3	10.3	178.3	53.2	89.0	10.4	0.408	0.228	1.280	0.495
Common Spruce – *Picea abies*	19.6	8.9	37.3	6.3	323.5	33.5	88.8	9.4	1.822	0.405	4.125	1.205
Silver spruce – *Picea ssp.*	55.4	14.4	26.6	7.7	175.0	59.5	105.3	10.4	0.480	0.315	3.070	2.312
Cypress – *Chamaecyparis ssp*	58.7	11.1	22.7	4.4	159.1	43.9	114.0	6.1	0.774	0.279	0.788	0.551
Yew tree – *Taxus baccata*	42.1	6.0	16.8	7.5	105.1	39.6	90.9	9.7	0.375	0.169	0.959	0.169
Oriental thuya – *Platycladus orientalis*	64.2	16.2	24.9	7.2	211.5	30.5	88.3	4.2	0.130	0.062	0.141	0.132
Douglas fir – *Pseudotsuga menziesii*	70.2	11.6	26.9	7.3	153.8	26.3	111.9	9.8	0.434	0.112	1.998	1.018

[a] n=6 (pH-SAR: 3.0, 3.5, 4.0, 4.5, 5.0, 5.5), [b] Standard deviation

Table 4

Amounts of Ca, Mg, K, Na, Zn, and Fe leaked from monocotyledonous leaves after contact with SAR for 72 h

Monocotyledonous plants (MP)	Ca		Mg		K		Na		Zn		Fe	
	(mg kg^{-1}) fresh leaves biomass											
	mean[a]	SD[b]	mean	SD	mean	SD	mean	SD	mean	SD	mean	SD
Maize – *Zea mais*	119.2	25.2	166.0	44.5	402.6	34.7	99.97	6.84	1.115	0.563	1.010	0.402
Wheat – *Triticum aestivum*	68.0	8.1	29.5	3.32	314.2	55.2	12.90	1.53	0.453	0.090	0.134	0.052
Barley – *Hordeum sativum*	130.6	41.2	66.8	10.9	520.5	63.6	21.36	3.24	0.480	0.183	0.090	0.054
Oats – *Avena sativa*	109.8	30.8	43.1	9.5	519.8	117.6	17.31	1.68	0.622	0.212	0.225	0.155
Rye – *Secale cereale*	65.1	18.3	38.3	11.4	219.4	55.1	12.29	1.50	0.405	0.133	0.083	0.062
Ryegrass – *Lolium perenne*	367.9	36.3	173.7	21.3	270.4	26.5	102.07	16.81	0.407	0.107	0.644	0.262
Festuca – *Festuca pratensis*	74.3	14.5	27.6	4.00	112.7	18.2	11.78	1.39	0.287	0.140	0.120	0.036
Ditch reed – *Phragmites australis*	96.4	30.7	32.5	13.5	205.6	78.1	94.80	5.43	0.112	0.133	0.580	0.069

[a] n=6 (pH-SAR: 3.0, 3.5, 4.0, 4.5, 5.0, 5.5), [b] Standard deviation

the response of CT to simulated acid rains (SAR) is the use of mean values for discriminating species into those below and above the means, as follows:

Ca: 83% < 65.3 mg kg^{-1} < 17%;

Mg: 67% < 35.6 mg kg^{-1} < 33%;

K: 58% < 204.1 mg kg^{-1} < 42%;

Na: 25% < 83.6 mg kg^{-1} < 75%;

Zn: 75% < 0.54 mg kg^{-1} < 25%;

Fe: 67% < 1.33 mg kg^{-1} < 33%.

The finding is that most of the tested coniferous trees leaked relatively less (below the mean levels for all species), except for sodium (Na). This may be viewed as a strategic common phyto-mechanism regulating the flux of the bio-active pools of mineral elements (ME) for raising species adaptability under various ecosystems and also deleterious factors, like SAR.

Monocotyledonous plants (MP), Table 4 exhibited a distinct pattern in terms of the intra-species variation: Na (84.4%) > Fe (79.8%) > Mg (67.6%) > Ca (46.7%) > Zn (39.5%) > K (37.5%). Species – responded much more differently to Na and Fe leaking process as compared to mineral elements. We assume that more Fe was strategically accumulated by these plants at decidedly easily mobilisable various bio-active forms for supporting photosynthetic activity. Each species may be controlling accordingly its flux, then variability implies adaptability.

The use of mean values for discriminating MP species, as performed for the CT species resulted in the following patterns:

Ca: 75% < 128.9 mg kg^{-1} < 25%;

Mg: 75% < 72.2 mg kg^{-1} < 25%;

K: 63% < 320.7 mg kg^{-1} < 37%;

Na: 63% < 46.6 mg kg^{-1} < 37%;

Zn: 75% < 0.49 mg kg^{-1} < 25%;

Fe: 63% < 0.36 mg kg^{-1} < 37%.

The characteristics of leaking variability and hence adaptability deserve some insight, particularly for the orders, *conifers (CT):* Zn (57.7%) > Mg (45.2%) > Ca (38.8%) and *monocotyledonous (MP)*: Mg (67.6%) > Ca (46.7%) > Zn (39.5%). The patterns outlined for CT and MP are closely similar in somewhat order, implying that mechanisms for biological "management" of these elements remain of intrinsic common nature with Fe and K as mitigating counterbalance under SAR deleterious effects.

Individual mineral leakage dynamics versus SAR characteristics

The detailed evaluation of this process requires considering the whole SAR pH range graphically reported by the Figure 4 for Ca and Mg; Figure 5 in the case of K and Na and finally Figure 6 for Zn and Fe, respectively for coniferous trees (CT) and monocotyledonous plants (MP).

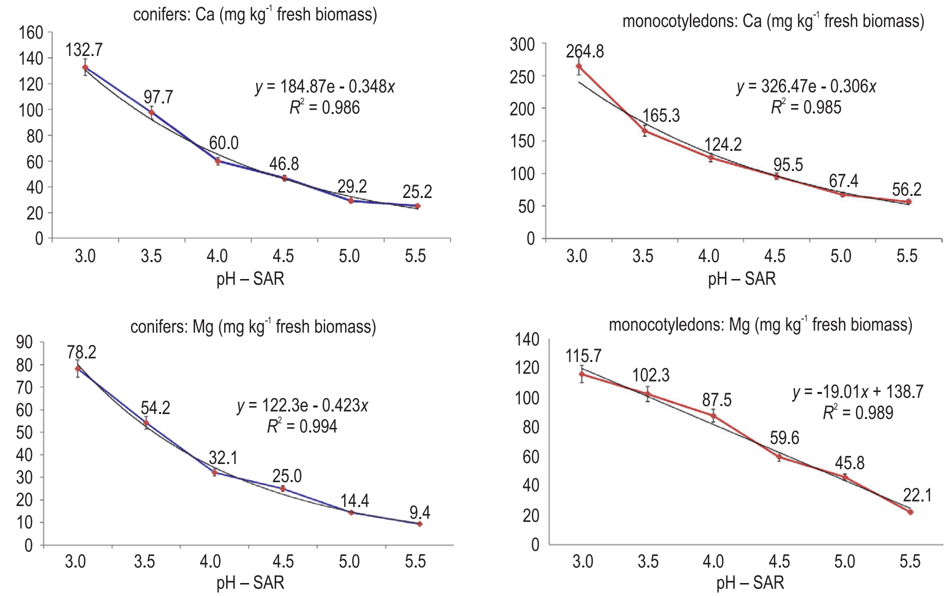

Fig. 4. Calcium (Ca) and magnesium (Mg) leaking from needles of coniferous trees and leaves of monocotyledonous plants after contact with SAR for 72 hours. Data are means of the whole conifers species (n=12) Vertical bars are standard deviations of the mean values

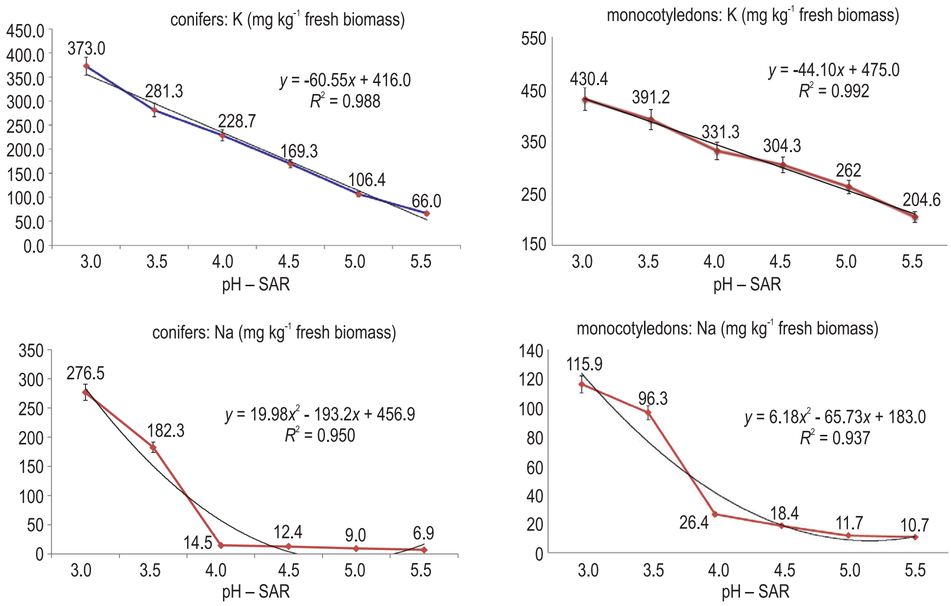

Fig. 5. Potassium (K) and sodium (Na) leaking from needles of coniferous trees and leaves of monocotyledonous plants after contact with SAR for 72 hours. Data are means of the whole conifers species (n=12). Vertical bars are standard deviations of the mean values

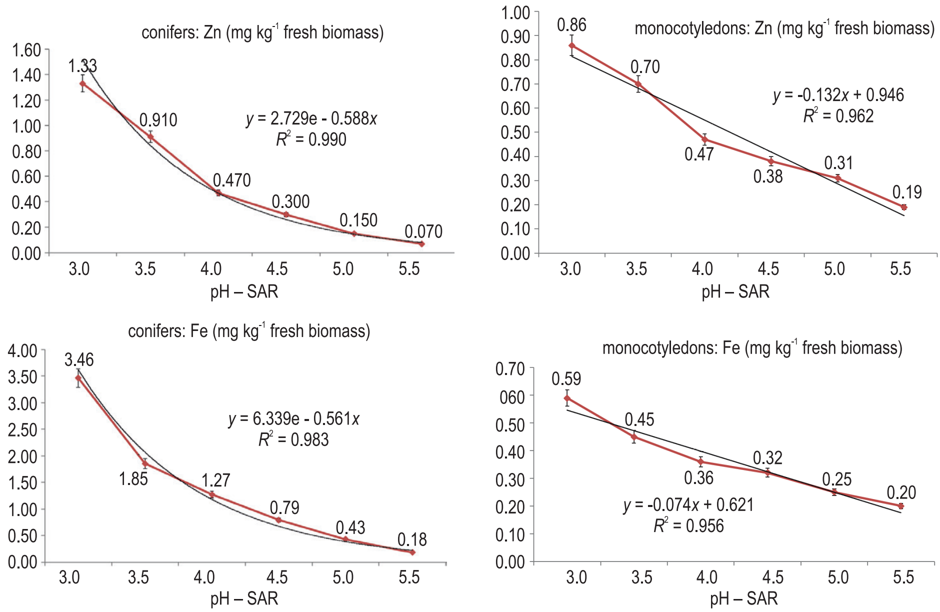

Fig. 6. Zinc (Zn) and iron (Fe) leaking from needles of coniferous trees and leaves of monocotyledonous plants after contact with SAR for 72 hours. Data are means of the whole conifers species (n=12). Vertical bars are standard deviations of the mean values

The deleterious effects of simulated acid rains (SAR), expressed as the concentrations of leaked Ca, Mg, K, Na, Zn and Fe have outlined three mathematical models reported as below:

1. **Exponential** model for:
   Ca – both conifers and monocotyledons,
   Mg – conifers,
   Zn – conifers,
   Fe – conifers.
2. **Linear** model for:
   Mg – monocotyledons,
   K – both conifers and monocotyledons,
   Zn – monocotyledons,
   Fe – monocotyledons.
3. **Quadratic** model for:
   Na – both conifers and monocotyledons.

The relationships for the pairs pH-SAR *versus* concentrations of mineral elements (ME) resulted in coefficients of determination (R^2) varying within the range 0.937 (Na monocotyledons) – 0.990 (Zn conifers). The main explanation of this process is that SAR were the key determinant for at least 90% of the leakage, irrespective of the species. For conifers (CT), the exponential models prevailed (except for K and Na), where the most pronounced mineral leakage occurred at SAR pH within the range 3.0 and 4.0. These simulated acid rains induced a linear leakage pattern which flattened gradually. It should be pointed out that the line slopes in reported cases were abrupt, indicating less resistance to SAR action. The models developed mostly by monocotyledonous plants (MP) were linear (except for Ca and Na). These species will support high as well as slightly SAR without disrupting the mineral element buffering capacity. This means that bio-active pools of Mg, K, Zn and Fe could have been the controlling and simultaneously driving force of this process.

The course (quadratic) outlined by Na leakage is specific as compared to other mineral elements. It leaked the most intensively within the range 3.0 and 4.0 and strictly stabilized at pH beyond (for conifers) contrarily to monocotyledons, where the course run gradually. This model is unique and biologically important for counteracting prompt acid based external abiotic factors, where hydrogen could be neutralized (buffered).

Some explanations may emerge from the geochemical characteristics discriminating conifers (CT) and monocotyledons (MP). The CT are generally characterized by low requirements towards soil mineral elements, hence their low concentrations in needles. Next, their deep rooting to soil bedrock and in most of cases acidification hardpans, reduce significantly any access to soil upper layers much more rich in these mineral elements. These features are practically reverse to soil ecosystems under monocotyledons, first shallow rooting and much more rich in mineral elements. This leads to the pronounced accumulation of ME raising then the bio-active pool, which in turn become mobilized with the emergence of SAR. We assume that this geo-ecological reason shapes the mineral nutritional activities increasing plant adaptation to various ecosystems, mostly man made.

Counteracting deleterious SAR effects – coniferous and monocotyledonous strategy

The response of both investigated species to harmful impact of simulated acid rains (SAR) is illustrated by the Figure 7. Two specific patterns may be observed, but similar in terms of the course line. The difference in pH of extracts recovered from needles (conifers) and leaves (monocotyledons) after contact with SAR for 72 h is higher than 1.0, with highest values recorded for monocotyledons. Next, the type of the lines imply that the response of the conifers was much more dynamic in alleviating the deleterious effects of SAR as compared to monocotyledons. Both species have exhibited two response strategies:

– For conifers the following ranges should be outlined:
  trees with needles extracts covering the pH range ≤ 5.30:
  Scots pine, black pine, common spruce, silver spruce;

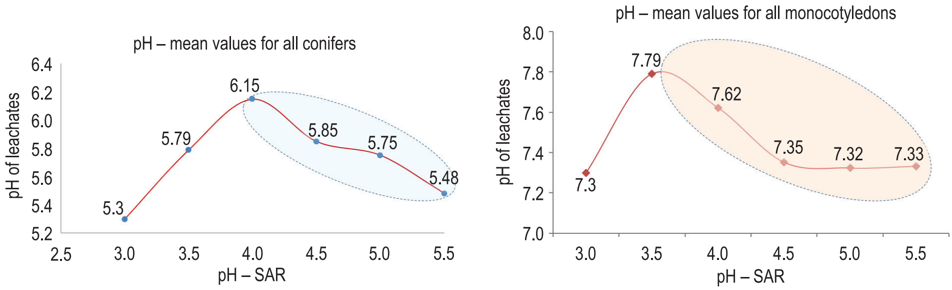

Fig. 7. Changes in pH of extracts from needles of conifers (CT) and leaves of monocotyledons (MP) after contact with SAR for 72 hours. Vertical bars are standard deviations of the mean values

trees with needles extracts covering the pH range 5.30 - 6.15:
Grand Fir, cypress, oriental thuya, Douglas Fir;
trees with needles extracts covering the pH range $\geq$ 6.15:
Thuya occidentalis, juniper, yew tree;

– For monocotyledons the ranges should be ordered as below:
plants with leaves extracts covering the pH range $\leq$7.30:
Maize, ditch reed;
plants with leaves extracts covering the pH range 7.30 - 7.79:
Wheat, barley, oats, rye, ryegrass, fescue.

The overall mechanisms that could be detected from these findings focus on the internal mineral-based acid buffering capacities developed by either coniferous trees (CT) or monocotyledonous plants (MP). The higher the concentrations of leaked mineral elements (ME), the more developed buffering capacities, the greatest the acidity mitigation process. The pH range of monocotyledonous extracts implies that their mineral-based adaptation strategy seems much more efficient with respect to conifers.

Magnesium, Zn and Fe as photosynthetic maintenance index (PMI) – SAR effect evaluation

The concept developed within this investigation was additionally verified by a photosynthetic maintenance index (PMI), (Tables 5 and 6) elaborated by the authors for the quantification of leakage process in terms of conifers and monocotyledons adaptability/recovery to adverse abiotic conditions, urban too. These elements (Mg, Zn, Fe) are fully involved in controlling and maintaining photosynthesis activity, particularly after various stressful impacts. Then, the ratios of their quantitative foliage concentrations could be indicative of photosynthetic recovery of both coniferous trees (CT) as well as monocotyledonous plants (MP), when impacted by various acid rains. For this purpose, we outlined five PMI ranges as follows:

Table 5

Mineral photosynthetic indices [Mg/(Zn+Fe)] for coniferous trees (CT)

Coniferous trees (CT)	Mg/(Zn+Fe)				
	min.	max.	mean[a]	SD[b]	CV (%)[c]
Thuya occidentalis – *Thuja occidentalis*	18.6	52.0	38.9	10.8	27.7
Grand Fir – *Abies alba*	8.8	22.1	15.9	4.7	29.4
Larch – *Larix decidua*	57.9	133.9	96.7	30.6	31.6
Juniper – *Juniperus communis*	31.9	564.3	189.1	197.0	104.2
Scots pine – *Pinus sylvestris*	30.5	52.3	45.6	6.4	14.1
Black pine – *Pinus nigra*	14.6	40.4	20.9	6.5	31.2
Common Spruce – *Picea abies*	3.8	8.9	5.9	1.6	27.7
Silver spruce – *Picea ssp.*	5.4	53.0	16.7	12.1	72.5
Cypress – *Chamaecyparis ssp*	9.7	133.9	47.1	35.7	75.7
Yew tree – *Taxus baccata*	5.2	113.0	63.4	34.9	55.1
Oriental thuya – *Platycladus orientalis*	61.4	169.9	103.0	36.2	35.1
Douglas fir – *Pseudotsuga menziesii*	8.1	28.2	14.7	4.7	31.7

[a] n=6 (pH-AR: 3.0, 3.5, 4.0, 4.5, 5.0, 5.5), [b] Standard deviation, [c] coefficient of variation

Table 6

Mineral photosynthetic indices [Mg/(Zn+Fe)] for monocotyledonous plants (MP)

Monocotyledonous plants (MP)	Mg/(Zn+Fe)				
	min.	max.	mean[a]	SD[b]	CV (%)[c]
Maize – *Zea mais*	39.4	99.6	75.0	15.0	20.0
Wheat – *Triticum aestivum*	38.8	70.6	52.8	7.9	15.0
Barley – *Hordeum sativum*	103.0	164.0	125.0	25.2	20.1
Oats – *Avena sativa*	41.6	70.5	52.9	7.2	13.5
Rye – *Secale cereale*	53.3	97.8	78.0	10.6	13.6
Ryegrass – *Lolium perenne*	106.8	337.3	205.7	84.4	41.0
Fescue – *Festuca pratensis*	44.1	85.8	68.5	12.7	18.6
Ditch reed – *Phragmites australis*	8.0	137.5	51.5	29.2	56.6

[a] n=6 (pH-AR: 3.0, 3.5, 4.0, 4.5, 5.0, 5.5), [b] Standard deviation, [c] coefficient of variation.

PMI < 50 – very low photosynthetic maintenance,
51 < PMI < 100 – low photosynthetic maintenance,
101 < PMI < 150 – intermediate photosynthetic maintenance,
151 < PMI < 200 – high photosynthetic maintenance,
PMI > 201 – very high photosynthetic maintenance.

This set of indices outlines a specific pattern for conifers (Table 5), where about 67% (based on mean values) of tree species represented the PMI < 50; two (larch and yew tree) the range 51 < PMI < 100; one (oriental thuya) for the range 101 < PMI < 150 and finally juniper exhibiting the highest photosynthetic recovery state (151< PMI < 200). Practically, one species i.e. juniper may be considered as of potential capacity for adaptation or recovery under acid rain constraints. Oriental thuya bears the intermediate photosynthetic maintenance position which could also be accounted to juniper. The markedly low and simultaneously most critical PMI indices are observed for common spruce (5.9); Douglas fir (14.7); silver spruce (16.7) and black pine (20.9), with the concentrations of leaked bio-active Mg appeared to be relatively low with respect to both Zn and Fe. Hence a potential shortage of Mg-chlorophyll molecules.

Data reported in Table 6 for monocotyledons (MP) outline different ranges, with no PMI < 50. Most of plants (75%) fitted the range 51 < PMI < 100; only barley (125.0) and ryegrass (205.7) represented the intermediate and very high photosynthetic maintenance, respectively, i.e., the ranges 101 < PMI < 150 and PMI > 201. Therefore, adaptation to heterogeneous zones, including highly anthropogenic should be a challenging strategy.

DISCUSSION

Urban green covers are in many cases heterogenous in terms of trees and plant species, which may develop various adaptability features to several anthropogenic factors. The same applies to conifers and monocotyledons being also exposed to abiotic stressors, simulated acid rains (SAR) among others. According to Akselsson et al. (2013**)**, weather conditions and geochemical characteristics are mostly one of the main determinants of plant adaptability to several ecosystems, predominantly related to pollutants and their unexpected effects (Menz, Seip 2004). This complexity contributes to a plethora of scientific methods and in most cases restricted to one or some plant species (Tomašević et al. 2011, Khavaninzadeh et al. 2014, Bouman et al. 2019).

The data revealed that all investigated 12 coniferous trees (CT) and 8 monocotyledonous plants (MP) have outlined various responses to all SAR of pH = 3.0, 3.5, 4.0, 4.5, 5.0, 5.5. This wide range was suited to cover the variety of rainfalls worldwide, from heavy industrial to urbanistic areas (Menz and Seip, 2004). Calcium has been widely reported as a plant cell builder and membrane stabilizer, hence controlling any mineral leakage out of cells. This structure fails in most cases when conifer and monocotyledons foliage is injured by acid rain, leading to potential leaching of alkaline elements, such as Ca, Mg, K, and Na, and microelements like Zn and Fe (Ju et al. 2017, Wu, Liang 2017). The pattern and course of the process were revealed by the pairs Ca *versus* Mg and K, for:

Conifers

$Mg_{(CT)} = 0.58*Ca_{(CT)} - 2.10$; $R^2 = 0.82$ (n=72);

$K_{(CT)} = -0.0037*Ca^2_{(CT)} + 2.39*Ca_{(CT)} + 79.55$; $R^2 = 0.45$ (n=72);

$Na_{(CT)} = 0.38*Ca^{1.12}_{(CT)}$; $R^2 = 0.43$ (n=72).

Monocotyledons

$Mg_{(MP)} = -0.0005*Ca^2_{(MP)} + 0.84*Ca_{(MP)} - 17.05$; $R^2 = 0.68$ (n=48);

$K_{(MP)} = -0.002*Ca^2_{(MP)} + 1.70*Ca_{(MP)} + 160.69$; $R^2 = 0.27$ (n=48);

$Na_{(MP)} = -0.0005*Ca^2_{(MP)} + 0.74*Ca_{(MP)} -29.66$; $R^2 = 0.42$ (n=48).

Biological characteristics of needles (CT) and leaves (MP) may be exhibiting specific responses to injuries induced by SAR, which could be eroding or disrupting their surfaces (cuticles). Calcium appears as the main tool (cell wall mineral fence) directly shaping and controlling the leakage of other minerals, such as Mg, K, Na along with Zn and Fe. This process is decidedly in line with the observations of Dong et al. (2017), implicating the non-linearity of direct effects of acid rain on the leaf photosynthetic rate of terrestrial plants.

Are calcium concentrations of coniferous needles monocotyledonous leaves a reliable parameter for tracing potential acid rains induced plant injury? The research by Bouman et al. (2019) on the N/Ca ratio implies that calcium appears to be the key mineral driving force, stabilizing and controlling leaf survival.

For conifers, Mg, K, and Na leakage from the needles is expressed by *linear*, *quadratic* and *power function* models, with Ca being much more the determinant of Mg leakage (R^2 = 0.82). This high relationship implies that the ecosystem adaptability of most of conifers will closely depend on Ca concentrations (reserve as well as bio-active pools at the cell walls) simultaneously with Mg fluxes (mobility) out of cell walls, as in the case of SAR impact. For a survival strategy, conifers are expected to accumulate more Ca in their needles and this process becomes a safety mechanism for controlling and retaining Mg in the cells.

A similar pattern, based on coefficients of determination (R^2) is observed for monocotyledons (MP), where the leakage process followed only *quadratic* models for Mg, K and Na. Calcium appeared to control less Mg fluxes (R^2=0.68) as compared to conifers; then for these species, an additional factor other than Ca was involved in the process.

The status of K and Na for both species deserves due attention. In fact, the relationships for the pairs Ca *versus* K and Na resulted in lower R^2 values 0.45 (for K) and 0.43 (for Na) in the case of conifers, but 0.27 (for K) and 0.42 (for Na) for monocotyledons, respectively. This implies that Ca was not controlling about 60% or even more of K and Na leakage. It means that these two mineral elements should not be accounted to as of a basic phyto-strategy in terms of environmental adaptability of green covers to deleterious factors which could initiate the leakage of vital photosynthetic elements, like Mg. Some trials for mimicking Ca, K, Mg, Na leaching from cabbage leaves, corn, peach and cotton leaves were also undertaken by using hydrous extraction (Russo, Karmarkar 1998), but diluted HCl for determining Ca, Mg, Zn and Mn in plant tissue extracts was also suggested as an efficient method (Sahrawat 1987). In their endeavor to discriminate some regional differentiation of foliar N/Ca in *Fagus americana* and *Fagus sylvatica*, Bouman et al. (2019) and Pinto et al. (2016) used leaf blades priorily dried at 70°C for three days and next digested in nitric acid for 8 h for Ca assessment. The effects obtained from the application of these methods are strictly parallel to those outlined in the current research.

Urban ecosystems in most worldwide agglomerations are being threatened by the emissions from house chimneys and post-combustion volatile residues, potentially inducing the emergence of acidic compounds. The concept of the current investigation focused, among others, on the application of SAR with pH ranging from 3.0 to 5.5. The post effect of this interaction resulted in pH of leachates varying from 5.3 to 6.15 for coniferous needles (CT) and 7.3 - 7.79 in the case of monocotyledonous plants (MP) as illustrated by the Figures 5 and Figure 6, respectively.

One of the basic explanations to the observed reactions should be the leakage of alkaline mineral elements, such as Ca, Mg, K and Na.

Briefly:

$$H^+\text{-SAR} \text{ ------> CT needles/MP leaves -------> } Ca^{2+}, Mg^{2+}, K^+, Na^+ + H^+\text{-SAR} \quad (1)$$

$$Ca^{2+}, Mg^{2+}, K^+, Na^+ + (H^+\text{-SAR} + H_2O) \text{ -------> } (Ca^{2+} + xOH^-, Mg^{2+} + xOH^-, K^+ + xOH^-, Na^+ + xOH^-) + H^+\text{-SAR} \quad (2)$$

where: H^+-SAR denotes the acidity (H^+) generated by SAR (simulated acid rains), xOH^- – hydrolysis product from the reactions of leaked alkaline elements with H_2O from SAR.

The inactivation of H^+-SAR, that is the intracellular mitigation process of harmful effect of H^+, depends directly on the concentrations of Ca^{2+}, Mg^{2+}, K^+, Na^+ leaked out from conifer needles as well as monocotyledonous leaves, and their further chemical hydrolysis. Therefore, coniferous trees (CT) and monocotyledonous plants (MP) may have responded accordingly to their needle/leaf concentrations of Ca, Mg, K, Na expressed as reserve and bio-active fractions. The latter ones prevailed quantitatively in MP as compared to CT (Tables 3 and 4). This biological stability (buffering capacity) is observed as highly efficient for the monocotyledonous plant (MP), whose leaves are naturally rich with Ca, Mg, K, Na as well as Zn and Fe, too. Contrarily to the conifers (CT), , the rooting zone of MP appears as the basic factor responsible for their potential and flexible adaptability to acid rains or similar anthropogenic stressors (Akselsson et al. 2013, Pinto et al. 2016, Callesen et al. 2019, Song et al. 2019).

The authors assume that species-based intracellular buffering mechanisms have been activated, then as a genetic or physiological feature. Classification of green covers on the basis of this process should be an efficient tool for targeted planting and maintenance of proper trees (like conifers) and plants (generally monocotyledons, grasses) in urbanistic zones or suborns. Urban green spaces are also the potential recipient of this solution, particularly regarding the choice of trees resistant to various deleterious environments (Song et al. 2019).

Mechanisms involved in the process of photosynthetic activity are numerous, but in most cases deal also with the concentrations of Mg, Fe in the green plant biomass. Next, the biological effects of Zn make it helpful to activate enzymes supporting the healing or recovery process after plant injuries (Kohno, 2017). Therefore, it seems useful to apply the photosynthetic maintenance index [PMI = Mg/(Zn+Fe)] elaborated for outlying the key role these minerals. On this basis, 67% of coniferous tree (CT) represented the PMI <50, that is very low photosynthetic maintenance as compared to monocotyledons (MP) with 75% of plants fitting the range 51 < PMI < 100 (low photosynthetic maintenance). The high share of MP in this range is a finding which decidedly points out at the potential flexibility of these species to adaptation to various ecosystems, highly anthropogenic among others. It means that rainfalls with significant acidity (below 5.0) will be inducing a complex adaptability process to both investigated species, but particularly conifers.

The basic finding of the current study is that urban green covers should not be in prevalence managed with conifers, as confirmed by the various indices. Next, some plants may develop slight (Grand fir, cypress, oriental thuya, Douglas fir) to good adaptability (Thuya occidentalis, juniper, yew tree). Nearly all monocotyledons may be growing within anthropogenic zones owing to marked adaptability traits, e.g. wheat, barley, oats, rye, ryegrass and fescue. This fact may be taken into consideration in the phytoremediation of air in cities.

CONCLUSIONS

The leakage process evaluated for coniferous needles (CT) and monocotyledonous leaves (MP) has shown strong intra-species variation. The intra-species variability within the CT group follows the order: Fe (67.9%) > Zn (57.7%) > Mg (45.2%) > Ca (38.8%) > K (26.0) > Na (23.3%), whereas for MP: Na (84.4%) > Fe (79.8%) > Mg (67.6%) > Ca (46.7%) > Zn (39.5%) > K (37.5%). The patterns outlined for CT and MP are closely similar in this order, implying that mechanisms for the biological "management" of these elements remain of an intrinsic common nature with Fe and K as mitigating the distorted balance due to SAR deleterious effects.

For conifers, Mg, K, and Na leakage from the needles is expressed by linear, quadratic and power function models, with Ca being a much greater determinant of Mg leakage (R^2 = 0.82). A similar pattern is observed for the monocotyledons, where the leakage process followed only *quadratic* models for Mg, K and Na. Calcium appeared to control less Mg fluxes (R^2=0.68) as compared to conifers.

The post effect of SAR resulted in pH of leachates varying from 5.3 to 6.15 for coniferous needles (CT) and 7.3 - 7.79 in the case of monocotyledonous plants (MP). This buffering capacity is observed as highly efficient for the monocotyledonous plant (MP), whose leaves are naturally rich in Ca, Mg, K, Na as well as Zn and Fe, contrarily to the conifers (CT).

On the basis of the photosynthetic maintenance index [PMI = Mg/(Zn+Fe)], 67% of coniferous tree (CT) represented very low photosynthetic maintenance as compared to monocotyledons (MP) with 75% of plants having low photosynthetic maintenance. The high share of MP in this range is a finding which decidedly points to the potential flexibility of these species to the adaptation to various ecosystems, highly anthropogenic among others.

Urban green covers should not be planted predominantly with conifers, as confirmed by the various indices. Some may develop slight (Grand fir, cypress, oriental thuya, Douglas fir) to good adaptability (Thuya occidentalis, juniper, yew tree). Nearly all monocotyledons may be growing within anthropogenic zones, owing to marked adaptability traits, e.g. wheat, barley, oats, rye, ryegrass and fescue.

Author contributions

J.D.: conceptualization, writing of original draft. M.W. and K.P-C: methodology, investigation. D.G. and J.N.: data curation. N.Y.: writing – review& editing. M.S.N.: formal analysis. All authors have read and agreed to the submitted version of the manuscript.

Conflicts of interest

The authors declare no conflict of interest.

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