# Influence of De-Icing Salt on K Supply and Street Trees Ecological Status in Riga, Latvia

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## Introduction

The street greenery as a very significant landscape's design element with important ecological value in Riga's central part is subjected to a multiple stresses, e.g. chemical injury. In urban area, safe driving conditions during winter season are of primary concern. The most common de-icing material used in Riga is sodium chloride (NaCl). The total area of streets and roads in Riga is 24.64 km$^2$ [1] and the average rate of NaCl application is about 10,000 t/year which leads to ca. 4.06 kg spread salt per m$^2$.

While $Na^+$ and $Cl^-$ in small amounts are thought to be beneficial for some plants or even essential for halophytes [2–4], in general these ions are toxic for plants. It was shown that high concentrations of $Na^+$ and $Cl^-$ in cells can inhibit membrane functions, induce ion deficiency, decrease chlorophyll concentration and the activity of several enzymes, producing disturbance of various metabolic processes, such as gas exchange and photosynthesis [5–10]. Plant injury can also be caused by salt-induced water stress [2]. One of the physiological mechanisms of salt toxicity in plants is closely related to unfavorable K/Na ratio. K as plant macronutrient has important functions as osmoregulation, maintenance of electrochemical equilibria, effects on protein conformation, regulation of enzyme activity etc. [3]. The most widespread tree species in the street greenery of Riga is *Tilia × vulgaris H.* In deciduous trees visual symptoms of $Na^+$ and $Cl^-$ damage usually appear as post-flushing dieback and foliage discoloration [5], burning of leaves [7], as well as chlorosis and necrosis of leaves [9, 11].

The first studies in Riga to assess the impact of chloride on Riga street trees were carried out in 1966/1967 by [12]. Our previous work on chestnut and lime in Riga

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showed a severe imbalance in the mineral nutrition of urban trees [13]. Investigation in 2004/2005 revealed high concentrations of $Na^+$ and $Cl^-$ in the street snow melt water, urban soil and *T.* × *vulgaris* leaves [10]. It is a topical problem as the street greenery currently covers 39% of the total street length in the centre of Riga and in general the status of trees could be characterized as damaged.

Our study was conducted to evaluate the toxic effect of soil and plant pollution level with sodium and chlorine on potassium supply and ecological condition of the street trees (*Tilia* × *vulgaris*) in Riga.

## Materials and Methods

Riga, the capital of the Republic of Latvia, is situated along the Baltic Sea at the southern part of the Gulf of Riga. The central part of the city is located on the right bank of the Daugava river. The climate is moderately warm and humid. Summers are relatively cloudy and cool. The average temperature in July is +16.9°C. Winters are relatively warm with frequent thaws, the average temperature in January is −4.7°C. The average amount of precipitation is 700–720 mm/year [1].

### *Sampling*

During the time period of March 2005 to August 2007, soil and leaf samples were collected from 14 sites (45 trees) in the central part of Riga, and from a control site (three lime trees) located in a park area – Viestura Garden (Fig. 1, Table 1). Soil samples were collected from the tree-rooting zone (road side) with a soil probe to a depth of 35 cm in March (the end of winter), June and July 2005, and June and August 2007.

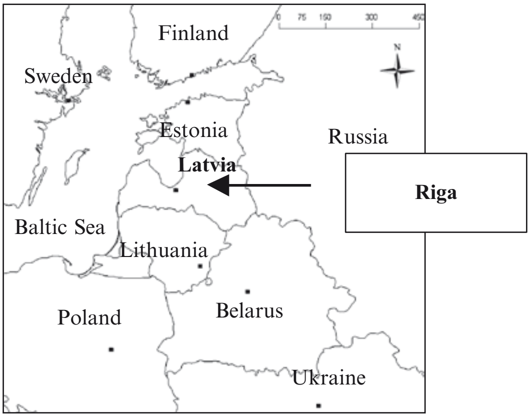

**Fig. 1** Location of Riga in Europe

**Table 1** Description of studied sites in Riga

| Site | Distance of tree's stems to street (m) | Status of trees in August 2005 and 2007 |
|---|---|---|
| 1 – Park (three trees) | >50 | 2005, 2007: Healthy[a] |
| 2 – Hanzas 1 (three trees) | ~2 | 2005: Damaged; 2007: damaged |
| 3 – Hanzas 2 (three trees) | ~2.15 | 2005: Medium damaged: 2007: medium damaged |
| 4 – Elizabetes (five trees) | ~0.7 | 2005: Three-damaged, two-healthy; 2007: one-dead in 2006, two-damaged, two-healthy |
| 5 – Kr.Valdemara (three trees) | ~0.7 | 2005: Damaged; 2007: medium damaged |
| 6 – Stabu 1 (three trees) | ~0.6 | 2005: Damaged; 2007: damaged |
| 7 – Stabu 2 (four trees) | ~0.6 | 2005: Three-damaged, one-healthy; 2007: three-damaged, one-healthy |
| 8 – Basteja 1 (three trees) | ~3.5 | 2005, 2007: Healthy |
| 9 – Basteja 2 (three trees) | 1.0–1.5 | 2005: Damaged; 2007: damaged; one tree dead in winter 2008 |
| 10 – Raina 1 (three trees) | ~7 | 2007: Healthy |
| 11 – Raina 2 (three trees) | ~7 | 2007: Healthy |
| 12 – Brivibas 1 (three trees) | ~1.5 | 2007: Medium damaged |
| 13 – Brivibas 2 (three trees) | ~7 | 2007: Healthy |
| 14 – Brivibas 3 (three trees) | ~1.5 | 2007: Medium damaged |
| 15 – Brivibas 4 (three trees) | ~7 | 2007: Healthy |

[a] Healthy: 0–15% crown necrosis; medium damaged: 20–70%; damaged: 75–100%.

For each soil sample three sub-samples were obtained and thoroughly mixed, to form one sample. Soil samples in the control site (Viestura Garden) were collected under the perimeter of the crown of trees and leaves from several branches of the crown.

Leaf samples were taken with telescopic scissors from leaves just reaching maturity and full size. For each sample 50 leaves were collected from different branches of trees along roadsides during the vegetation season of 2005 (June, July and August) and 2007 (June and August).

Along with leaf sampling bioindication research was done to diagnose the ecological status of *Tilia* × *vulgaris*. Leaf necrosis as percentage of damaged leaf area/ total leaf area was estimated in June and at the end of August. Intensity of crown necrosis in percent was estimated in August.

## *Laboratory Analysis*

***Sample preparation***. The soil samples were stored at +4°C, then dried at +35°C for 2 days and sieved <2 mm. Leaves were washed with distilled water, dried at +60°C and ground.

***Soil extraction and plant tissue ashing***. Na and K in the soil samples were extracted with 1 M HCl solution (soil-extractant mixture 1:5). $Cl^-$ content was determined in distilled water extract (soil-distilled water mixture 1:5). Leaf samples were dry-ashed in concentrated $HNO_3$ vapor and re-dissolved in HCl solution (HCl-distilled water mixture 3:100) to determine Na and K [14]. To determine $Cl^-$ leaf sampled were dry-ashed, then re-dissolved in distilled water.

***Chemical analysis***. $Na^+$ and K concentration in soil and plant samples was estimated by flame photometer *JENWAY PFPJ*. $Cl^-$ concentration in all samples was determined by $AgNO_3$ titration [14]. Analytical replication was three times.

## Results and Discussion

Results revealed that the use of de-icing material NaCl caused a considerably increased $Na^+$ and $Cl^-$ accumulation in the street greenery soil and lime leaves located close to the carriageway compared with the park (Figs. 2 and 3, Table 1).

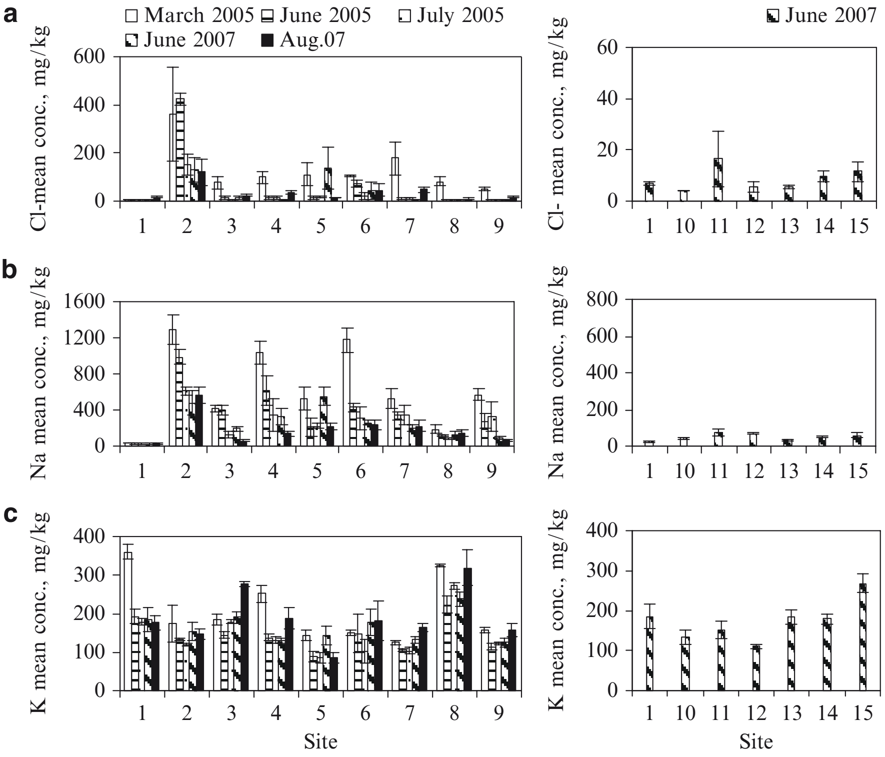

**Fig. 2** Mean concentrations from 3–5 samples ± SE of $Cl^-$ (**a**), Na (**b**) and K (**c**) (mg/kg) in soil samples from the central part of Riga (spring, summer 2005, 2007). Sites: 1 – park; 2 – Hanzas 1; 3 – Hanzas 2; 4 – Elizabetes; 5 – Kr.Valdemara; 6 – Stabu 1; 7 – Stabu 2; 8 – Basteja 1; 9 – Basteja 2; 10 – Raina 1; 11 – Raina 2; 12 – Brivibas 1; 13 – Brivibas 2; 14 – Brivibas 3; 15 – Brivibas 4

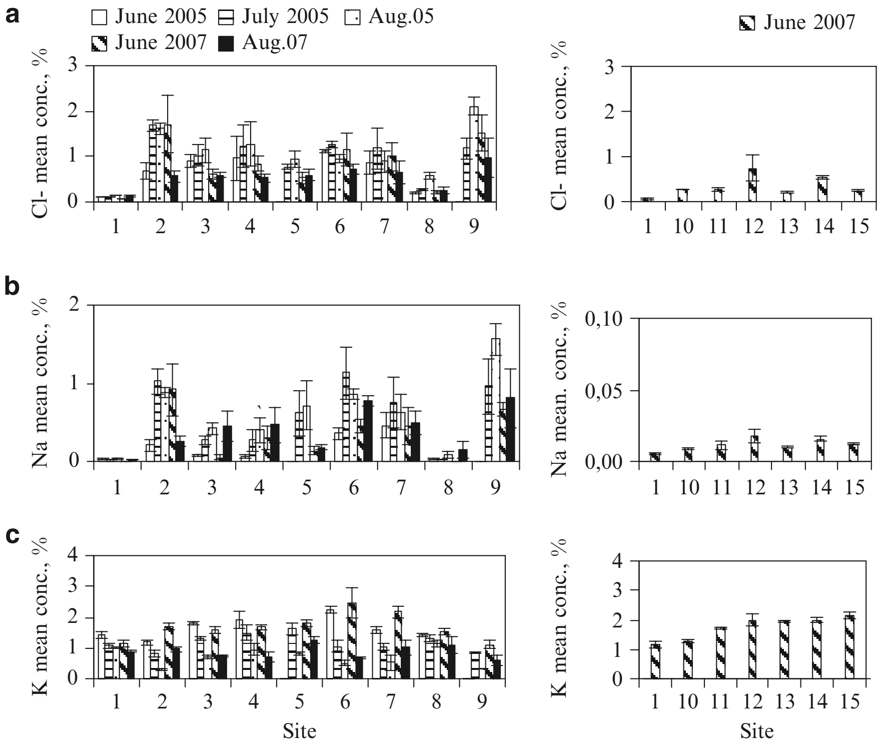

**Fig. 3** Mean concentrations from 3–5 samples ± SE of $Cl^-$ (**a**), Na (**b**) and K (**c**) (%) in leaf samples from the central part of Riga (spring, summer 2005, 2007). Sites: 1 – park; 2 – Hanzas 1; 3 – Hanzas 2; 4 – Elizabetes; 5 – Kr.Valdemara; 6 – Stabu 1; 7 -Stabu 2; 8 – Basteja 1; 9 -Basteja 2; 10 - Raina 1; 11 – Raina 2; 12 – Brivibas 1; 13 – Brivibas 2; 14 – Brivibas 3; 15 – Brivibas 4

Correlation coefficients and the level of statistical significance ($p < 0.05$) were found using SPSS 14.0 version. The coefficients were classified as follows: $r < 0.5$ week, $0.5 < r < 0.8$ medium close, and $r > 0.8$ close correlation.

Soil. The highest concentrations of Na and $Cl^-$ in soil samples of street greenery were found at the end of March 2005 - beginning of spring. Levels exceeding 1,000 mg/kg Na were found at sites 2 (max. 1,568.1 mg/kg), 4 and 6, which exceeded the background values by up to 51 times. A marked decrease in Na and especially $Cl^-$ concentrations occurred in spring and summer due to leaching from the root zone by precipitation and uptake by the plants. Compared to Na, the $Cl^-$ concentrations in 2005 and 2007 were considerably lower, ranging from 4.27 ± 0.08 mg/kg (Site 10) (similar to park results) to 359.5 ± 194.2 mg/kg (Site 2) or on average more than 60 times higher than in the park.

The obtained concentrations of $Cl^-$ in street soil samples collected in June 2005 and 2007 on average were not significantly different, while results of Na were significant higher in 2005 to compare with 2007. Such situation could be explained by the winter season of 2006/2007, which was warmer in comparison to 2004/2005 [15].

As a result, decreased amounts of de-icing salts were applied on streets and decreased accumulation of ions occurred in street soil. Besides, $Cl^-$ as anions are more leachable from the soil and a more rapid decrease compared to $Na^+$ occurred. $Cl^-$ usually follow the water and do not take part in chemical reactions, while $Na^+$ participate in chemical processes in the soil and are to a great extent retained in the upper part of the soil profile [16]. Thereby summer soil sampling results did not show the real situation with Na and $Cl^-$ pollution before the vegetation season had started.

A different situation was stated with K (Fig. 2). In the vast majority of sampling sites in 2005 the concentrations of K in the soil were lower compared to the park. It was consistent with other studies in urban areas where soil contained construction and demolition waste [13, 17]. The decrease of K concentrations was stated almost for all studied sites from March to July, mainly due to K uptake by plants. Better K status in soil samples was found in the vegetation season of 2007. In most of the studied street sites, the level of K was the same as in the park, or slightly elevated. It showed a tendency to increase from June to August, probably due to application of K containing fertilizers. In general, the concentrations of K in soil samples during 2005 and 2007 ranged from 85.10 ± 13.38 mg/kg (Site 5) to 318.90 ± 46.22 mg/kg (Site 8).

When comparing results from 2 years, the level of K in street soil samples was statistically significant higher in June 2007, in contrast to Na. Less amounts of Na in the street soil, which could displace K in the exchange sites in the soil, resulted in an improved K/Na ratio in 2007. In total, the K/Na ratio in the soil samples from the park ranged from 4.15 to 13.48. In the street soils, the K/Na ratio were 0.13–6.45 for healthy limes, for medium damaged limes up to 4.82, and for damaged trees 0.07–2.66. It means that the small K/Na ratio in street soil samples had additive harmful impact on the tree status.

**Plants**. In general, the concentrations of Na and $Cl^-$ in lime leaves increased during the summer of 2005 and 2007, showing opposite trends as those in the soil. The K content in lime leaves decreased (Fig. 3), thereby harmfully affected the tree status. The analysis of plant material showed that the soil salinity induced increased Na and $Cl^-$ concentrations in lime leaves in sites with higher soil salinity during 2005 and 2007. During the vegetation seasons, Na ranged from 0.01% in June to 1.93% in August, which was up to 48 times higher than values from the park. The $Cl^-$ concentrations in the leaves from the vast majority of street sites were significantly higher than those of the park site at all sampling times, as well as higher than the Na concentrations in lime leaves. The highest $Cl^-$ concentrations, found in Site 4 in July (3%) and August (2.90%), were more than 25 times above the background level. As the lime tree decayed in autumn, this concentration could be characterized as especially toxic to lime trees. In general, concentrations of $Cl^-$ in leaves higher than 2% were harmful to lime trees, causing tree decay.

The lowest concentrations of Na and $Cl^-$ in lime leaves were found in sites situated about 3.5 m from the carriageway (sites: 8, 10, 11, 13, 15), as well as sites 12 and 14. These limes were characterized as healthy.

There were no significant correlation between the element concentrations in soil and leaves, except the concentrations of Na in July 2005 ($r = 0.39$; $n = 30$). The results showed negative medium close correlation between the level of K in soil of

March 2005 and Na in leaves during summer 2005 ($r_{June} = -0.66$, n = 24; $r_{July} = -0.65$, n = 30; $r_{Aug.} = -0.66$, n = 30), which demonstrated the importance of soil chemical composition to plants just after winter.

As the external salt concentration rises, the concentration of $Na^+$ increases and that of $K^+$ decreases in the roots and leaves. It appears that $Na^+$ out-compete $K^+$ for specific binding sites on the $K^+$ transport proteins, causing $K^+$ deficiency [3]. Besides, $Na^+$ in the soil can replace not only $K^+$, but also $Ca^{2+}$, $Mg^{2+}$, $NH_4^+$ and other cations on the soil exchange complex. This could lead to nutrient deficiencies [2, 18] causing injury.

A wide dispersion of K concentrations and supply levels were stated in lime leaves during 2005 and 2007 (Fig. 3). The smallest K result (0.15%) was even up to 6.33 times lower compared with the minimum K concentration in lime leaves in the park. At the same time the highest concentrations of K (max. 3.40%) were also stated in lime leaves with necrosis, which mean that sufficient supply with K could not prevent the appearance of leaf necrosis. In Riga, K concentration in healthy lime leaves without necrosis ranged from 0.76% to 2.42%, which was in good agreement with results generalized by [19]. For normal plant growth, K concentration in plant tissues should be 0.5–1.2%. The decrease in K content in leaves during the vegetation season could be explained by K reutilization in plant [2], as well as an increase of Na content ($r_{Na,K\ aug.2005} = -0.76$, n = 30; $r_{Na,K\ aug.2007} = -0.43$; n = 29). As a result, the decrease of K/Na ratio from June to August was stated. The K/Na ratio for healthy lime leaves without necrosis in Riga's street greenery ranged from 2.92 to 237 (in park: 24.12–270.83), but for severe necrosis (>30% leaf necrosis) ranged even from 0.15 to 72.00. In general, the stated K/Na ratios diapasons in Riga were substantially wider compared with results reported by [9] in Opola for *Tilia cordata* L. (1.76–15.65). It can be concluded that sufficient K/Na ratio in lime leaves did not have a determinant role, if the stated leaf necrosis were caused by $Cl^-$ toxicity, or if the Na concentration in leaves reached toxic level.

The leaf chemical results revealed significant higher levels of Na and $Cl^-$ in August 2005 ($p > 0.05$) compared with results from August 2007, whereas the level of K was significant higher during the vegetation season of 2007. This fact could be the main reason for improved ecological status of street trees and decreased leaf necrosis in 2007 compared to 2005 (Table 2). The current research revealed significant close correlation between the intensity of the leaf necrosis and the concentration of Na and $Cl^-$ in leaves (maximum in August 2005, $r_{Na} = 0.92$; $r_{Cl} = 0.85$; n = 30), as well as negative correlation with concentrations of K in leaves (maximum in August 2007, r = –0.50).

The leaf necroses were observed in cases when the $Cl^-$ content in leaves reached at least 6,600 mg/kg of dry weight. These concentrations were lower in comparison with other investigations on leaf injury caused by $Cl^-$ toxicity [9, 12, 20]. These differences might be explained in the scope of factors such as the different tree species studied, methods used, a misbalanced supply of mineral nutrients, insufficient supply of water during the vegetation period, and too high concentrations of de-icing salt in the soil solution causing 'physiological drought' which promotes leaf necrosis development, as well as specific ion toxicity.

**Table 2** Intensity of lime leaf necrosis (%) in Riga, summer 2005, 2007

| | Range (mean ± SE) | | | |
|---|---|---|---|---|
| Site | June 2005 | August 2005 | June 2007 | August 2007 |
| 1 (n = 3) | 0 (0.0) | 0 (0.0) | 0 (0.0) | 0 (0.0) |
| 2 (n = 3) | 5 (5.0 ± 0.0) | 45–65 (56.7 ± 6.0) | 5 (5.0 ± 0.0) | 20–70 (36.7 ± 16.7) |
| 3 (n = 3) | 0–5 (3.3 ± 1.7) | 10–30 (18.3 ± 6.0) | 0–3 (1.0 ± 1.0) | 10–15 (11.7 ± 1.7) |
| 4 (n = 5; n = 4) | 0–30 (7.0 ± 5.8) | 0–85 (33.0 ± 14.7) | 0–5 (3.3 ± 1.81) | 0–70 (29.3 ± 16.1) |
| 5 (n = 3) | 0 (0.0) | 10–60 (36.7 ± 14.5) | 0–3 (1.0 ± 1.0) | 0–5 (1.7 ± 1.7) |
| 6 (n = 3) | 5 (5.0 ± 0.0) | 15–50 (28.3 ± 10.9) | 3 (3.0 ± 0.0) | 5–90 (43.3 ± 24.9) |
| 7 (n = 4) | 0–5 (3.6 ± 1.3) | 5–65 (38.8 ± 12.5) | 0–5 (2.8 ± 1.0) | 0–90 (30.0 ± 20.7) |
| 8 (n = 3) | 0 (0.0) | 0 (0.0) | 0 (0.0) | 0 (0.0) |
| 9 (n = 3) | 5 (5.0 ± 0.0) | 70–85 (78.3 ± 4.4) | 5–10 (6.8 ± 1.7) | 15–25 (18.3 ± 3.3) |
| 10–15 (n = 15) | 0 (0.0) | 0 (0.0) | 0 (0.0) | – |

The occurrence of the first toxic symptoms in the form of leaf necrosis caused by Na toxicity was detected when the Na content in most of the cases ranged from 0.14% to 0.26%. The obtained relationships between the Na content in the leaf samples and visual injury symptoms of the leaves are in good agreement with those reported by [7, 21].

## Conclusions

The results revealed that the ecological status of street trees in Riga could be characterized as seriously injured due to high concentrations of Na and $Cl^-$ in soil (maxNa 1,568.1 mg/kg; maxCl 744.9 mg/kg) and lime leaves (maxNa 1.93%; maxCl 3.00%). The concentrations exceeding 2.0% $Cl^-$ in lime leaves were revealed as extremely toxic for *Tilia* × *vulgaris*, leading to tree decay. The concentrations of Na and $Cl^-$ in lime leaves demonstrated a marked tendency to increase during summer, while the concentrations of K in leaves decreased (minimum 0.15%). The high variability in Na and K concentrations resulted in a wide range of K/Na ratios in Riga's greenery. Close correlations were found between the concentration of Na and $Cl^-$ in lime leaves and the extent of leaf necrosis, although unfavorable K/Na ratio has additive negative impact.

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