Impact of surface contamination on elemental composition of Sanguinea (Pall.) leaves

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Abstract. The leaves of *C. sanguinea* Pall. have the potential to accumulate dust on the surface. As the fine dust particles contain various chemical elements (ChEs), we studied the ChE composition in the leaves with different degrees of dust contamination to assess the impact on assay results. The samples of *C. sanguinea* leaves collected in the Kemerovo region (Russia) were divided into two groups based on the visual condition of plant material: clean leaves and dust contaminated leaves. The total ash assay revealed higher ash content, exceeding pharmacopoeial standards in the dust contaminated group. Dust contaminated leaf samples demonstrated significantly higher concentrations of many ChE: Si, Fe, Al, Na, Ti, Ni, Zr, Cr, V, Pb, La, Ga, Y, Sc and Yb comparing to non-contaminated plant material. The values of potentially hazardous ChEs were significantly lower than the maximum levels specified for medicinal raw materials in all studied samples.

1 Introduction

Crataegus sanguinea Pall. is the most prevalent medicinal species of hawthorn in Russian flora. Hawthorn flowers and fruits (*Crataegi flores*, *Crataegi fructus*) are included in the register of medicinal raw material (MRM) in the State Pharmacopeia of the Russian Federation (SP RF) [1]. However, leaves or leaves with flowers of hawthorn (*Crataegi folia*, *Crataegi folia cum flores*) are more common in the world medical practice [2-4, etc.]. Therefore, Russian researchers have initiated studies of hawthorn leaves, collected from domestic species, for potential addition to the list of MRM [5-7].

The usage of hawthorn leaves or flowers with leaves as an alternative to pharmacopoeial MRM seems promising as harvesting of hawthorn leaves is more effective in comparison to the harvesting of flowers. However, the studies on hawthorn leaves, especially on chemical element (ChE) composition remain limited due to the conventional use of other hawthorn MRM sources such as flowers and fruits and the

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predominant utilization of several species, widely distributed in the European part of Russia.

Furthermore, extensive accumulation of solid environment pollutants on pubescent leaf surface can limit the harvesting even in areas remoted from settlements. Since contamination of plant material with highly dispersed soil particles can take a great share in a significant increase of several ChE, including potentially hazardous to human ChE presented mostly in poorly soluble forms [8-10].

The total ash assay of plant material especially allows estimating the proportion of mineral impurities that reflects dustiness. The upper limit of total ash content for hawthorn flowers is 12% according to the SP PF [1], which likewise corresponds to a similar standard for hawthorn leaves in the SP RB [4]. The study aims to compare the ChE composition of *C. sanguinea* leaves with different degrees of dust contamination.

2 Materials and Methods

2.1 Object of study

The leaves of *Crataegus sanguinea* Pall. were collected in August, 2016 on the territory of the "Kedrovskiy" coal pit (Kemerovo city). The leaves were gathered from the middle part of the shoot. The samples were divided into groups: 1) clean leaves 2) leaves with obvious dust contamination. Each sample from different plants was analyzed severally. Plant material was air-dried and stored at room temperature.

Taxonomic identification was established by taxonomist R. A. Ufimov, PhD. Voucher specimens (LE 01020943, LE 01020944, LE 01020945, LE 01020946, LE 01020947) were deposited in the Herbarium of Vascular Plants of the Komarov Botanical Institute of the RAS, Saint-Petersburg. The Plant names are provided according to World Flora Online database [11].

2.2 Methods of study

Total ash assay was conducted according to requirements of the State Pharmacopoeia of the Russian Federation, Edition 14 [1]. The ChE composition was studied by atomic emission spectrometry after dry ashing. The As и Hg were assayed by atomic absorption spectrometry. Analyses were conducted in triplicate. The samples of birch leaf (LB-1) GSO 8923-2007 and *Elodea canadensis* Michx. (EC-1) were used as standards. The results of the ChE assay in the references were within their certified values. The data are given in terms of absolutely dry matter. The observation of epidermal trichomes was conducted with a binocular microscope MBS 10 [1].

2.3 Statistics

Statistical evaluation of experimental results was carried out with STATISTICA 6.1 software. The normality of all data was analyzed by Shapiro-Wilk's test. The homogeneity of dispersions was analyzed using Cochran's Q-test. All normally distributed data were analyzed using Student t-test, in other cases, Mann-Whitney U-test was applied. $p \leq 0.05$ were considered to be significant. Data on figures are presented as medians and 25^{th}-, 75^{th}-percentiles, and minimum and maximum values.

3 Results and discussion

The structural peculiarities of leaf surface are important for the dust holding capacity of plants [12-14]. In particular, simple unicellular trichomes and leaf teeth glands were observed on the epidermis of *C. sanguinea* specimens.

Total ash assay of clean leaves (C) revealed the values of 10.1-11.9%, which meet the requirements of the SP PF [1], while the ash content of dust contaminated samples (D) was 12.3-15.6%.

The amount of potentially hazardous ChE, did not exceed the Pharmacopoeial limits for MRM, (content in samples, mg / kg / maximum level, mg / kg): As <0.03 / 0.5 [1]; Cd 0.06-0.17 / 1.0 [1, 2]; Pb 0.7 - 1.9 / 6.0 [1] and 5.0 [2]; Hg<0,01 / 0,1 [1, 2].

However, significant differences in several ChE concentration were detected between compared groups of samples. (**Fig. 1**). Thus, ChE composition analysis of dust contaminated leaves revealed higher concentrations of Si, Fe, Al, Na, Ti, Ni, Zr, Cr, V, Pb, La, Ga, Y, Sc and Yb.

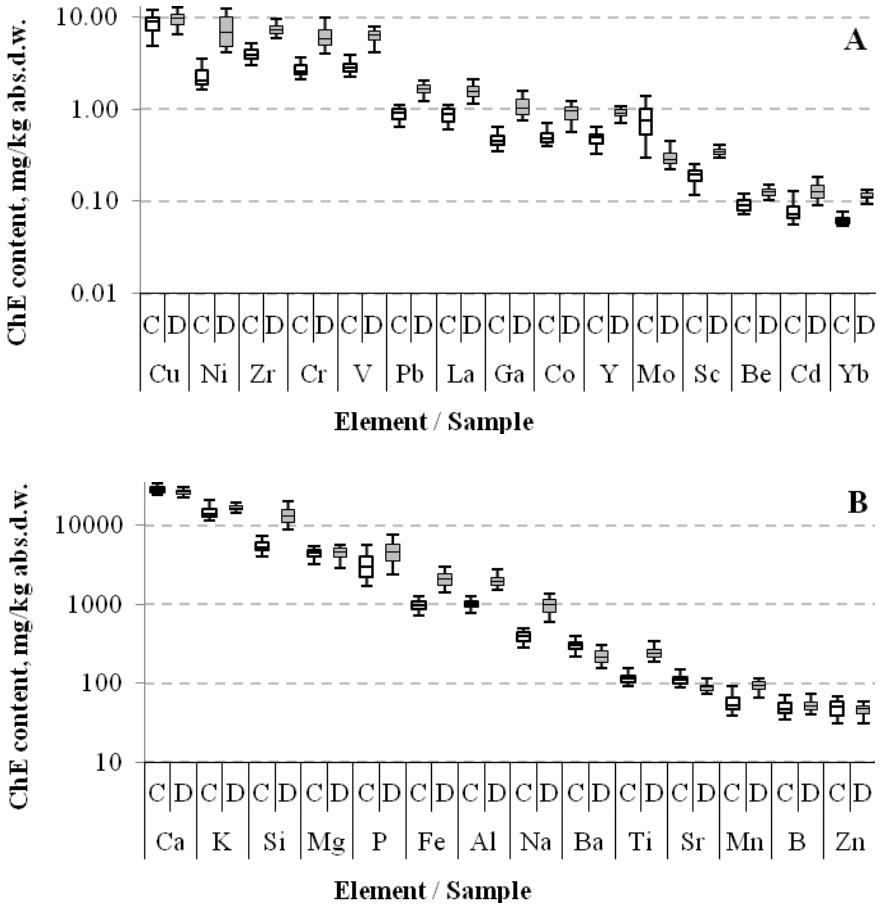

Fig. 1. Content of chemical elements in the conditionally clean (C) and dusty (D) leaves *Crataegus sanguinea* on the territory of the "Kedrovskiy" coal pit (Kemerovo city): A – ChE content 0,001–15 mg/kg; B – ChE content 10–50000 mg/kg.

The established list of chemical elements generally coincides with our data previosly obtained in the study of *Leonurus quinquelobatus* Gilib., *Artemisia sieversiana* Ehrh. ex Willd., *Urtica cannabina* L., *Populus tremula* L. [14].

C. Reimann et al. [13] also have reported that high values of Al and Fe can be taken as the first indicators of the possible influence of minerogenic dust on the observed ChE concentration in plant material. Considering that detecting a number of elements in some species (for example, Cr, Li, Sc and Th) is complicated, the best indicators of plant material dustiness are Al, Fe, Si, V, Y and Zr [15, 16].

The studies on ChE in leaves of *C. sanguinea* leaves appeared only in two publications introduced by Russian authors. With that, those investigations were devoted to a limited number of heavy metals. The ranges of Cd, Co, Cu, Mn and Zn content revealed during our studies were comparable with the results of other researchers [17, 18]. The observed content of Ni in non-contaminated leaves was close to the values presented in the literature [17]. However, the total Pb content was slightly higher than that found in the leaves of hawthorn plants in the Orenburg city [18].

4 Conclusion

The dust contamination of the leaf surface impacts Che composition (Si, Fe, Al, Na, Ti, Ni, Zr, Cr, V, Pb, La, Ga, Y, Sc and Yb) assay in the plant material, which is especially noticeable for pubescent leaves. At the same time, a significant part of the elements is contained not in plant tissues, but finely dispersed soil particles enriched with ChE and accumulated on their surface. The excess of the standardized limits of ChE (As, Hg, Cd, Pb) did not occur.

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