Determination of selected toxic elements in leaves of White Hawthorn grown in a remote area

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Abstract. One important plant of the Rosaceae family which is commonly used as phytopharmaceutical in Europe and North America is Hawthorn (*Crataegus monogyna*). The fruits, the leaves together with their extracts are applied in patients suffering mild cardiac disorders or nervosity. Since the leaves as well as the berries act as diuretics a sufficient micronutrient supply has to be guaranteed. On the other the quantities of toxic elements present in the plant parts should be at levels without harmful effects on human health. For this purpose Hawthorn leaves and flowers were collected in a remote area in 2011 and 2012 and analysed for their elemental composition. The metals uptaken from the soil were supposed to be in a similar range, thus the impact of airborne contamination by heavy metal translocation could be studied. The elements investigated were Ba, Cd, Co, Cr, Cu, Mn, Ni, Pb, Sr, and Zn. After harvesting the samples were dried, homogenized, digested and then analysed by ICP-AES. The contents of all elements are in the µg/g range. In the samples of 2012 higher concentrations were found for Co, Cu, Mn, Ni, and Zn, lower concentrations were registered for Ba, Pb, and Sr. The amounts of Cd and Cr were statistically insignificantly lower in 2012 than 2011.

Key words: Heavy metals, White Hawthorn, ICP-AES, airborne contamination

Introduction

Although metals are long known elements, their role in biological and environmental systems has not been studied for long. The possibility of studying more accurately their dose and effects in more recent times promoted metal related investigations. The investigation of toxic metals and those which cause environmental pollution started during the 1950s and 1960s. (Adriano, 2001) The dissemination of metals into the environment from industrial activities ensures that a significant part of the population is exposed to these contaminants. Vegetation represents a useful indicator of heavy metal contamination in environment not only via root uptake of metals, but also via precipitation from air, thus it can be used for monitoring pollution across both spatial and temporal scales. Whereas the composition of the mother rock does not change over time, the elemental soil composition depends from impact by contamination. Not only on-site, but even in remote areas, metal contamination can be found due to translocation processes.

Hawthorn (*Crataegus monogyna*), a member of to the Rosaceae family, is one commonly used phytopharmaceutical in European and North American. Hawthorn is a perennial plant growing in moderate, continental climate in the northern hemisphere in deciduous forests and underbrush. It is applied against mild cardiovascular diseases such as congestive heart failure, high blood pressure, hypoxia and hyperlipemia or nervosity (Baughman and Bradley 2003; Holubarsch et al. 2008). For therapeutic purposes mainly berries, flowers and leaves collected in spring time are used. The compounds of pharmaceutical relevance are present in the plant mainly in spring. The absence of these substances in autumn could influence the amount of metals uptaken and accumulated. Furthermore, even if the trees used for harvesting grow in a remote area non negligible quantities of toxic elements may be found in different parts of the plant, in dependency of the

collection time.

Thus, to study these parameters leaves of White Hawthorn were harvested at the same place in autumn 2011 and spring 2012 and analysed for their content of Ba, Cd, Co, Cr, Cu, Mn, Ni, Pb, Sr, and Zn. In addition this study should be provide data for a general elemental characterisation of White Hawthorn leaves, since this plant has been mainly analysed for its organic composition responsible for the antioxidant and antimicrobial activities (Kostic et al. 2012).
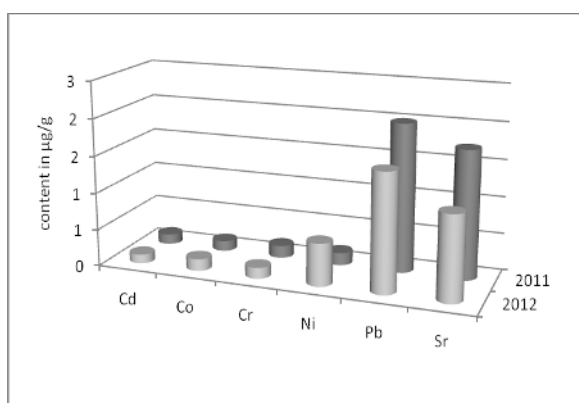
Materials and Methods

Chemicals

For the experimental work HNO_3 (p.a.) and a multi-element standard (ICP Multi-element Standard IV, Merck, Darmstadt, FRG) were used. All glassware was cleaned with nitric acid prior to use. Ultrapure water produced in-house was used for all dilutions and blanks.

Samples and sample preparation

All samples (White Hawthorn leaves) were collected from Hawthorn trees growing in Slunj, Croatia (N 45,07° - E 15,36°; A 280 m) in September 2011 and April 2012. Prior to use they were stored in a dry, dark and cool room. The samples were then dried and homogenised in a metal free mortar.

The resulting powder of the leaves (approx. 0.2 g) was digested with 50:50% v/v HNO_3 and 30% H_2O_2 in a MWS-2 Microwave System Speedware BERGHOF applying a three step procedure (110°C/15min – 170°C/15min – 140°C/15min). The clear digest solutions were filled up to 10 mL with ultrapure water.

Measurements

The ICP-AES determinations of the mineral content of the Hawthorn leaves were performed using a Prodigy High Dispersive ICP-AES spectrometer (Teledyne Leeman, Hudson, NH, USA) working in a simultaneous mode, equipped with a glass concentric nebuliser. All measurements were run in triplicate.

Results and Discussion

Analytical figures of merit

The precision of the method expressed in RSD ranged from 0.6 to 5%, the accuracy evaluated by determining the recoveries of the analytes by spiking experiments are from 84-115%.

Metals in White Hawthorn leaves

The metal determination of the White Hawthorn leaves showed that all elements could be detected. They were all found in quantities of µg/g dried matter (see fig. 1). Differences determined by collection time can be seen for all elements. In order to check the statistically significance of the differences a paired t-test was performed with all data sets. This revealed statistically significant differences for all metals studied except for Cd and Cr. In the samples of spring 2012 higher concentrations were found for Co, Cu, Mn, Ni, and Zn, whereas lower concentrations were registered for Ba, Pb, and Sr than in those from autumn 2012.
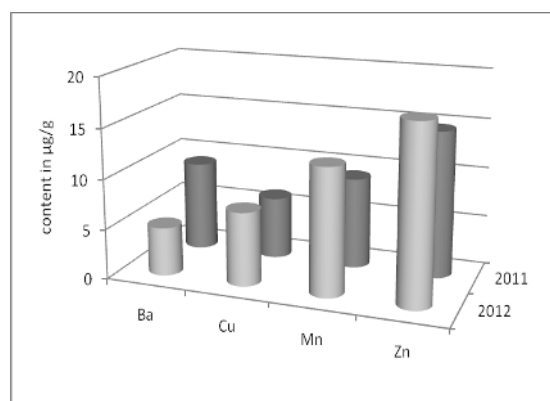

Fig. 1. Content of Ba, Cd, Co, Cr, Cu, Mn, Ni, Pb, Sr, and Zn in White Hawthorn leaves collected in 2011 and 2012.

Comparison with other leaves

Due to the lack of metal concentrations for Hawthorn leaves in literature the results reported on leaves from other trees were used for comparison. A study of poplar leaves (Portugal) obtained values of 2 to 3 µg/g for Pb, 0.1 to 0.2 µg/g for Cd, and 4 to 5 µg/g for Cu (Silva et al. 2005). These results are in the same order of magnitude as those of the presented study, namely 1.5 to 2 µg/g, 0.12 to 0.14 µg/g, and 6 to 7.5 µg/g for Pb, Cd, and Cu, respectively. Similar concentrations were also found in peppermint leaves used for preparation of infusions (Polish tea bags): for Pb, Cd, and Cu 2.41 µg/g, 0.09 µg/g, and 12 µg/g, resp. (Lozak et al. 2002). In general mint leaves contain higher amount of metals than White Hawthorn leaves as can be seen in table 1.

Table 1: Selected elements in leaves from White Hawthorn (WH) and mint (M; Lozak et al. 2002)

Element	WH [µg/g]	M [µg/g]
Ba	4.8 - 9.0	31.2
Co	0.13 - 0.16	0.10

Cr	0.15 - 0.17	0.94
Mn	9.0 - 13	188
Ni	0.17 - 0.57	2.99
Sr	1.2 - 1.7	2.40
Zn	15 - 18	51.0

Comparison with Hawthorn fruits

A Turkish research group (Özcan et al. 2005) analysed Hawthorn frutis for their physical and chemical properties. Cr, Ni, and Pb were found in the fruits in amount of about 1 µg/g.

Conclusion

Parts of perennial trees growing in remote areas present good samples for investigating environmental contamination and translocation processes. In this pilot study statistically significant differences in the elemental composition of White Hawthorn leaves collected in autumn 2011 and spring 2012 could be found for Co, Cu, Mn, Ni, and Zn (increase), and for Ba, Pb, and Sr (decrease). No statistically significant changes were registered for Cd and Cr. These differences may be caused by variations in the weather situation (amount of precipitation) and translocation processes. On the other hand the composition regarding organic compounds of pharmaceutical relevance changes from autumn to spring. Only the fresh plant parts contain the required concentration of phenolic compounds, flavonoids and anthocyanins.

Further research will be focused on longer time periods to be studied (5 - 10 years), trees from different areas and a correlation between elemental composition and amounts pharmaceutical active substances.

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