ELEMENT CONCENTRATIONS AND INTERELEMENT RELATIONS IN APPLE LEAVES, BLOSSOM LEAVES AND FRUITS AND ADJACENT SURFACE SOILS

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Abstract. Within this work, leaves, blossom leaves and fruits from apple trees together with respective topsoils were sampled at non-contaminated sites in the East of Austria, in order to find interelement relations within the same plant, as well with total contents and mobile fractions of adjacent surface soils. Aging of green leaves lowered total N, and increased Al, Si, Ca, Sr, Ba, Li and the Rare Earths vice-versa. Increased nutrient supply tended to increase the physiologically more important elements in the leaves, and decreased the Rare Earths. The composition of blossom leaves was largely independent from the corresponding leaves and fruits. In the fruits, only B and Mo correlated with some more elements in the blossom leaves, and vice-versa the nitrogen in the blossom leaves with Al, Fe, Na, and Rb in the fruits. There was no carry-over of Ce- and Eu- anomalies found in the adjacent soils. Presumable acid contents and harvesting period may lead to different leaf/fruit element proportions. Varieties of different expectable acid contents, period of harvest, and period of flowering, might show differences among interelement effects.

Keywords: Apple leaves, apple blossom leaves, apple fruits, trace elements, interelement relations

INTRODUCTION

In Austrian fruit farming, apples make 95% among pomaceous fruits, add the largest economic value, and are top for export. In 2017, Austrian apple consumption per capita amounted 14,1 kg, at 59% rate of self sufficiency (Grüner Bericht, 2018).

Element and trace element contents of apples depend on variety, rootstock, climatic conditions, and mobile soil fractions. It had been shown that element contents of cloudy varietal apple juices obtained from the same location and year may differ up to two-fold due to different varieties of origin (Sager and Gössinger, 2015a).

In spite of these possible differences, many encyclopedic compilations contain only simple data without any ranges nor references (Souci et al., 2000). But also, scientific papers about trace elements in apples do not necessarily contain indications aabout variety, rootstock, soil, and climatic conditions of fruit growth. In case, composition of fruits can be related to blossom leaves, leaves or topsoil, however, fruits could be predictable in advance, because these data are available months before harvest time. Therefore, a comprehensive study was launched to sample fruits, leaves, blossom leaves and adjacent topsoils of the same plants and the same year, to find possible relations and interactions.

Co and Mo concentrations in fruit and leaves as well as Cs and Rb to a lower extent, were affected by the vigour of the rootstocks, and in case of Si only in the leaves. Presumably because of different weather conditions, fruits from the second year contained less B, Cu and Na, as well as more Al, Fe, Cr and Mn. Only the leaves, but not the fruits, which were grown on M26, contained more Mn and Co but less Si, and leaves but not fruit grown on M7 contained more P and Cu. Both leaves and fruits grown on seedling tended towards more K. Alkaline earths, rare earths, Al, B, S and many trace elements did not show diff erences in their element contents in leaves and fruit among the rootstocks investigated. The ratio of elements in fruit and corresponding leaves was smallest for B, Sr, and Ca, and largest for Rb, Na, and B. It did not depend on total nitrogen in the leaves (Sager and Spornberger, 2015b).

Because roots penetrate into deeper soil layers, it is alsmost impossible to get samples from these respective soil horizons. Therefore in fruit farming, analysis of leaves is a wide-spread alternative to indicate the nutrient status of the respective trees (Mengel 1991). Leaf-composition data thus permit optimization of the fertilization regime to achieve high yields of high quality fruits. The most important period for nutrient uptake is probably after the end of flowering, when there is top nutrient need (Aichner and Stimpfl, 2002).

Analysis of leaves shows, to which extent the green plant can take mobile substances from the soil, irrespectively about discussions about plant available fractions. If levels in the leaves are too low, the soil might be too low also, or the respective mobilities in the soil are too low (Matteazzi, 2012).

Numerous data about apple fruits done by the author, have already been compiled as medians and ranges of concentrations (Sager, 2014a). Within this work, it will be tried to find relationships between element contents found in apple fruits, leaves, blossom leaves and adjacent soils, particularly in mobile soil fractions, to elucidate metabolic pathways within the tree. To cope with effects of variable climatic conditions, like humidity, temperature, and sunshine, only data obtained from the same yeare were considered. It will be bshown that the use of the entire dataset resulted in a rather low number of significant relations, because the individual variety seems to be of the largest influence. As much more varieties than locations were available, it was essential to classify the varieties within a few groups, such as expectable acid contents, flowering period, and harvest time. Because most locations contain many of these variety groups, a respective bias is avoided. Relations between leaves and fruits resp. blosssom leaves and fruits refer directly to the uptake of the plants, irrespective of discussions about the „plant-available“ soil fraction. Sampling of blossom leaves is more laborious than sampling of green leaves, but data are available about one months earlier, which enables the farmer to take possible actions of fertilization or detoxification before final fruit growing. Blossom leaves grow at about the same spot than the fruits, which overrules possible inhomogeneities inside the tree.

Spraying of Cu-contaning pesticides influences Cu and other trace element contents of the apple leaves, which has been already treated in detail (Sager and Spornberger, 2017). Leave samples used for this compilation, however, were obtained from non- Cu-sprayed items.

In particular, it is relevant to show, if the composition of green leaves or blossom leaves is more indicative for the fruits than the analysis of the 0-25 cm topsoil, which has been frequently recommended (Keppel et al., 1998), in spite of the fact that the trees are rooting mainly at much deeper layers.

MATERIAL AND METHODS

2.1 Locations

Samples were obtained from various locations in the East and South of Austria, both from intesive commercial agriculture, as well as from scattered fruit trees in meadows, shaped as standard trees, or as spindlebushes. This covers experimental stations, private orchards run by friends and relatives of the author, as well as commercial fruit farming (Table 1).

Table 1

Sampling locations and year of sampling

Region	Location		Tree shape	Soil type	blossoms	leaves	fruits
Wienerwald	Innermanzing	Meadow orchard	Standard tree	Stagnosol	2012	2012	2011/12
Wienerwald	Laaben	Meadow orchard	Standard tree	Cambisol	2012	2012	2012
Wienerwald	Klosterneuburg-Haschhof	Experimental fruit farming	Spindelbush	Cambisol	2011	2011/12	2011
Wienerwald	Klosterneuburg-Kierling	Experimental fruit farming	Standard tree	Cambisol	2011	2011/12	2011
Wien	Hirschstetten	Meadow orchard	Low standard tree	Regosol	2011/12	2011/12	2011/12
Wien	Jedlersdorf	Organic fruit farming	Spindelbush	Calcic chernozem	-	2012/13	2012/13
Wien	Stammersdorf	Experimental fruit farming	Low standard tree	Eutric cambisol	2014	2014	2014
Wr. Becken	Maria Lanzendorf	Private garden	Spindelbush	Calcic chernozem	2011/12	2011/12	2011/12
Wr. Becken	Unterwalters-dorf	Commercial fruit farming	Spindelbush	Gleyic chernozem	2012	2012	2012
Wr. Becken	Weigelsdorf	Commercial fruit farming	Spindelbush	Gleyic chernozem	2012	2012	2012
Wr. Becken	Gaisbach	Commercial fruit farming	Spindelbush	Chernozem	2012	2012	2012
Burgenland	Forchtenstein	Commercial fruit farming	Spindelbush	Chernozem	2012	2012	2012
Burgenland	Mattersburg	Commercial fruit farming	Spindelbush	Chernozem	2012	2012	2012
Pielachtal	Grünau	Meadow orchard	Standard tree	Cambisol	-	2012	2012
Pielachtal	Hofstetten	Meadow orchard	Standard tree	Cambisol	-	2012	2012
Graz	Haidegg	Experimental fruit farming	Spindelbush	Cambisol	2011	2011	-
Lavanttal	St. Andrä	Experimental fruit farming	Spindelbush	Cambisol	2011	2011	-

2.2 Soils

The soil samples were obtained by several corings down to 25 cm and 50 cm due to a standard procedure (ÖNORM L 1057), air-dried, and sieved minor 2mm. 0,16M acetic acid to get exchangeables plus weak-acid solubles, and subsequently

0,1M oxalate buffer pH 3 to get the pedogenic oxides (Fe-Al-Mn), were selected (Sager, 2014b; Sager, 2016). In addition, pressure digestion with $KClO_3/HNO_3/H_2O$ was carried out, which is equivalent to aqua regia, but permits improved detection limits for green plants because of higher permissible sample weight, as well as complete recovery of the non-metals B, S and I (Sager, 2011). Total digestion of soils was done in open PTFE-cups at a heating block with $HNO_3/HClO_4/HF$, and final take-up into HCl, which does not give recoveries of B, S, and I, however. The soil data have been already presented in detail within a special report (Sager, 2012)

In addition, the soils were characterized at the AGES-Institute for Sustainable Plant Production Vienna by standard soil analytical procedures, to ensure comparability with other data, like soil pH (ÖNORM L 1083), organic carbon (ÖNORM L 1080), total nitrogen (ÖNORM L 1095), K and P in CAL-extract (ÖNORM L 1087), Mg in $CaCl_2$-extract (ÖNORM L 1093), and boron in the Baron-extract (ÖNORM L 1090).

2.3 Leaves and blossom leaves

Leaves and blossom leaves were picked wearing gloves, rinsed with distilled water at a nylon sieve, freeze dried, crashed, and homogenized. Contact with skin and with metal surfaces should be avoided (see Sager and Mittendorfer, 1997).

Several blossom leaves were still white during sampling, but turned brown during lyophilization.

The leaves were picked at the end of May/ beginning of June, shortly after reaching their final size, and around the trees at variable heights at sunny and shadow positions, to obtain a representative sample, as recommended (Keppel et al., 1998). Because of different rates of photosynthesis and transpiration, at sunny positions higher levels of N, Ca, and Mg, as well as lower levels of K might be expected (Haynes and Groh, 1980; Keutgen and Keutgen, 2001). Luckily, there was no Cu-pesticide spraying before sampling, because this could change the composition of other elements as well (Sager and Spornberger 2017). At 2 locations (Klosterneuburg-Haschhof and St. Andrä/Lavanttal Carinthia), samples from the same trees were also picked in August of the same year (2012), to document concentration changes due to aging.

2.4 Fruits

Wearing gloves, fruits were rinsed with distilled water, cut into 4 or 6 parts with a ceramic knife, stalks and kernels removed, and finally smashed and freeze-dried, which lasted 2-3 nights. The weight loss was noted, to permit recalculation of fresh weight based element contents, which is usual in analysis of food (see Sager, 2014a). Water contents averaged about at 85%.

Within subsequent tables, concentrations refer to dry mass for reasons of more objective comparisons. Concentrations obtained for fresh weight are about 1/7 lower.

2.5 Digestions and determinations

Dried leaves, blossom leaves and fruits were pressure digested in double both with HNO_3 (0,25 g + 3,5 ml HNO_3 + 0,2ml HF) and with $KClO_3/HNO_3/H_2O$ (1g + 8 ml digestion solution). The digestion solution contained 20g $KClO_3$ (Merck p.a.) + 200 ml H_2O + 80ml HNO_3 suprapure, which makes a 7% $KClO_3$ in 4,5 M HNO_3 (Sager and Hammerschmidt 2015). Determinations by ICP-OES (inductively coupled plasma optical emission spectrometry) were done in 2-3 dilutions, and matrix-matched for respective digests with $KClO_3$. Determinations of Cd, Co, Mo, Pb, Rb, Cs and the Rare

Earths were done by ICP-MS (inductively coupled plasma mass spectrometry) in 1/10 dilution, corrected by addition of In as an internal standard. Whereas main- and trace metal data were available from both kinds of digests, except K-Rb-Cs from the $KClO_3$, for the non-metals B-S-Si-I just $KClO_3$ digests were suitable. B, Si, and S were obtained from ICP-OES, and I as the iodate from ICP-MS by standards addition. Memory effects of B and I, as well as Si-blanks from the HNO_3 (delivered in glass) have to be considered by running sufficient blank solutions and avoidance of contacts with glass.

On case of Ti only, digestion of leaves with HF yielded about 3 times higher concentrations (table 3). Due to the lack of respective reference material, however, it could not be decided which one is more correct.

2.6 Data processing

At first, results for each digest were summed up, and then the mean for each sample was calculated. Because at least 4 digests were available for most samples, flyers could be rejected, resp. procedures repeated. Statistical data treatments and box plot presentations were obtained by SPSS program version 19.

RESULTS AND DISCUSSIONS

3.1 Quality control

For reasons of quality control, the standard reference material NIST-1515 (apple leaves, picked from orchards at Rock Springs PA) was treated several times like a common sample, leading to satisfactory results (Table 2).

3.2 Concentration ranges

When the data obtained from leaves, blossom leaves, and fruits were compiled in one table (table 3), the fruits were always at the lowest level, particularly for Ca, Sr, Si, and surprisingly Co. Concentration ranges of leaves and blossom leaves were largely overlapping. The leaves contained higher concentrations of total N, alkaline earths and Na, but lower B, Cu, and Al. Higher median values for K, Rb, P, Zn and I should not be interpreted too much.

At optimum nutrient supply, the fruits should contain 0,23-0,40% N, 0,67-0,87% K, 600-740 mg kg^{-1} P and 260-370 mg kg^{-1} Mg in dry mass (Keppel et al., 1998), which happened in most cases. Some locations had low available K within their soil, which was also seen in the fruits.

As far as reference data have been available, data for the fruits were in the range given by Kabata-Pendias and Pendias (2001), but in this work, much more elements were determined. Similar apple fruit samples from Romania (Cluj district; Todea et al., 2014) contained similar concentration ranges. In apples from the region of Larissa, however, higher concentration ranges were found throughout (Skordas et al., 2013), except for Mo, Ba and Sr, which might be due to environmental contaminations.

3.3 Aging of apple leaves

In the course of a growing period, slow decreases of N- and P concentrations, as well as about concent Mg, B, Mn and Zn in apple leaves grown in Alto Adige Province (Italy) were noted, whereas Ca increased, and Cu varied. After 40 days of full leave size, K passed a slight maximum (Aichner and Stimpfl, 2002; Nagy and Holb, 2006). Therefore it is important to define a proper period for leaf sampling to ensure comparable results. Table 4 contains data ranges from leaves of the same variety, same year (2012), and same location. Lower medians than means indicate asymmetric frequency distributions, i.e. largely low plus a few high values.

Table 2

Quality control sample data (mg kg^{-1}) obtained from different runs by 10-fold digests of NIST-1515 Apple leaves

´mg kg-1	Found	Certified
Al	238 ± 45	284 ± 6
B	25,7 ± 7,3	27,6 ± 2,8
Ba	46,5 ± 9,7	48,8 ± 2,3
Be	0,019 ± 0,005	
Ca	15245 ± 420	15250 ± 100
Cd	0,0145 ± 0,0020	0,0132 ± 0,0015
Ce	3,25 ± 0,32	
Co	0,132 ± 0,009	
Cr	0,194 ± 0,088	
Cu	5,53 ± 1,31	5,69 ± 0,13
Er	0,646 ± 0,017	
Eu	0,261 ± 0,007	
Fe	77,2 ± 3,7	82,7 ± 2,6
Gd	3,24 ± 0,09	
Ho	0,290 ± 0,010	
J	0,541 ± 0,099	
K	12794 ± 834	16080 ± 210
La	20,1 ± 1,5	
Li	0,129 ± 0,037	
Lu	0,025 ±0,001	
Mg	2556 ± 114	2710 ± 120
Mn	50,6 ± 9,9	54,1 ± 1,1
Mo	0,086 ± 0,010	0,095 ± 0,011
Na	32,3 ± 6,8	24,4 ± 2,1
Nd	15,7 ± 0,3	
Ni	0,85 ± 0,20	0,94 ± 0,09
P	1427 ± 144	1593 ± 68
Pb	0,443 ± 0,020	0,470 ± 0,024
Pr	4,06 ± 0,09	
Rb	9,34 ± 0,16	10,2 ± 1,6
S	2216 ± 27	
Sc	0,020 ± 0,011	
Si	370 ± 57	
Sm	2,76 ± 0,09	
Sr	25,3 ± 1,5	25,1 ± 1,1
Tb	0,400 ± 0,011	
V	0,24 ± 0,08	0,25 ± 0,03
Y	11,1 ± 2,0	
Zn	11,5 ± 2,9	12,4 ± 0,4

Table 3

Concentrations in apple leaves, blossom leaves and fruits in dry mass, mg kg^{-1}

	Leaves		Blossom leaves		Fruits	
	Median	Range	Median	range	Median	range
N%	2,58	1,99 – 3,18	1,80	1,32 - 2,42	0,31	0,19 - 0,48
Al	34,8	16,9 - 121,6	46,3	22,2 - 176,3	2,31	0,57 - 7,36
B	24,1	16,4 – 36,4	69,0	38,2 - 144,7	15,7	8,55 - 38,5
Ba	37,4	19,3 – 71,1	5,50	2,30 – 15,2	0,83	0,33 - 2,02
Be	0,001	< 0,001 – 0,007	0,006	< 0,001 - 0,011	< 0,001	< 0,001 - 0,004
Ca	12246	8136 - 18280	2684	1463 - 4941	272	180 – 637
Cd	0,009	0,005 - 0,044	0,026	0,009 – 0,119	0,003	< 0,001 - 0,012
Ce	0,088	0,026 - 0,612	0,084	0,043 – 0,304	0,0091	0,0021 - 0,218
Co	0,104	0,065 - 0,150	0,133	0,067 – 0,268	0,0085	0,0013 - 0,0173
Cr	0,082	< 0,01 – 0,281	0,149	0,068 – 0,445	0,018	< 0,01 - 0,073
Cs	0,012	0,0003 – 0,097	0,015	0,0070 - 0,052	0,0070	0,0009 - 0,0736
Cu	8,16	5,02 – 14,14	20,8	9,57 – 39,1	2,44	1,50 - 4,43
Er	0,0025	0,0004 - 0,0165	0,0021	0,0004 - 0,0084	0,0003	< 0,0001 - 0,0034
Eu	0,0092	0,0047 - 0,0261	0,0025	0,0016 - 0,0091	0,0005	0,0001 - 0,0032
Fe	62,6	38,3 - 106,0	61,2	28,2 - 189,7	5,10	2,62 - 8,67
Gd	0,007	0,002 - 0,075	0,006	0,003 - 0,024	0,0008	0,0002 - 0,0123
Ho	0,0009	< 0,0001 – 0,0071	0,0008	0,0004 - 0,0034	0,0001	< 0,0001 - 0,0011
J	0,199	0,109 - 0,402	0,347	0,059 - 0,740	0,046	< 0,005 - 0,426
K	11280	7479 - 18242	15581	3234 - 25888	5069	3356 - 7664
La	0,062	0,018 - 0,516	0,046	0,021 – 0,176	0,0084	0,0012 - 0,058
Li	0,112	0,040 - 0,430	0,062	0,028 - 0,282	0,0066	0,0005 - 0,024
Lu	0,0003	< 0,0001 – 0,0012	0,0003	0,0001 - 0,0010	< 0,0001	< 0,0001 - 0,0005
Mg	2864	1994 - 4148	1931	1463 - 2740	295	218 – 422
Mn	33,2	17,0 – 72,8	26,2	14,7 - 144,6	1,95	1,12 - 3,18
Mo	0,150	0,059 - 0,631	0,125	0,056 – 0,495	0,069	0,027 - 0,228
Na	25,4	8,7 – 55,2	56,3	23,2 - 299	6,59	2,17 - 17,9
Nd	0,040	0,011 - 0,492	0,034	0,017 - 0,138	0,0049	0,0009 - 0,0883
Ni	0,96	0,24 – 3,89	0,76	0,24 - 2,22	0,08	< 0,02 - 0,33
P	2102	1460 - 3154	2653	1951 - 3601	606	416 – 861
Pb	0,164	0,056 - 0,321	0,212	0,085 - 0,598	0,018	< 0,01 - 0,091
Pr	0,011	0,003 - 0,090	0,009	0,005 - 0,035	0,0012	0,0002 - 0,0246
Rb	3,51	1,49 – 26,92	6,52	2,73 - 17,11	2,59	0,78 - 19,87
S	1650	1035 - 2494	1415	891 - 2266	235	151 - 344
Sc	< 0,02	< 0,02 – 0,05	< 0,02	< 0,02 - 0,06	< 0,02	< 0,02
Si	161	94 - 389	120	50 - 266	5,55	0,76 - 14,4
Sm	0,008	0,002 - 0,066	0,0064	0,0033 - 0,0274	0,0012	< 0,0002 - 0,0155
Sr	46,4	21,6 – 79,9	5,18	2,29 - 12,27	0,89	0,43 - 3,07
Tb	0,0010	0,0002 - 0,0099	0,0009	0,0004 - 0,0034	< 0,0001	< 0,0001 - 0,0024
Ti*	2,50	0,58 - 8,95	3,31	1,03 - 12,45	0,49	< 0,02 - 4,52
Ti**	0,81	0,048 – 2,33	1,06	0,26 - 4,71	0,062	< 0,01 - 0,34
V	0,057	0,013 - 0,132	0,080	0,022 - 0,329	0,003	<0,01 - 0,025
Y	0,027	0,009 - 0,241	0,025	0,013 - 0,085	0,003	0,001 - 0,014
Zn	18,7	11,9 – 29,8	33,0	13,5 - 76,7	1,82	1,24 - 3,36

Element symbols given in italics mark data obtained by ICP-MS, others by ICP-OES

Ti*: digest of 0,25g with 3,5 ml HNO_3+ 0,2ml HF

Ti**: digest of 1,0g with $KClO_3/HNO_3/H_2O$

Elements of low metabolic interactions are presumably passively transported to the leaves, like Al, Ba, Ca, Co, Cr, Fe, I, Li, Ni, Pb, Si, Sr and the rare earths, increase with the age of the leaf. To the contrary, levels metabollically important elements like K, Mg, Mn, and Zn, remain constant or decrease only slightly, like P, S, Cu, Mo, Na and Rb. The latter can be explained from relocation into stalks and roots, as a reaction of the plant because of decrease of periods of daylight in the temperate climatic zone, to be prepared for the winter time.

Table 4

Concentrations found in apple leaves from May and August 2012, at Klosterneuburg and St. Andrä. Reference data from Experimental Station at Laimburg (Aichner and Stimpfl, 2002) and Plant-Fruit-Centre Gorsem (Marulle and Dechers, 1988)

	May		**Reference**	**August**		**Reference**
´mg kg-1	Median	Mittel ± Stabw		Median	Mittel ± Stabw	
Al	27,2	30,2 ± 12,5		46,8	47,0 ± 14,0	
B	23,4	24,1 ± 4,9	30-50	26,6	27,0 ± 5,1	25-50
Ba	34,0	38,2 ± 17,1		53,9	57,0 ± 21,2	
Ca	11557	11757 ± 3040		18455	20276 ± 7187	
Cd	0,011	0,019 ± 0,021		0,010	0,014 ± 0,014	
Co	0,107	0,105 ± 0,027		0,123	0,126 ± 0,033	
Cr	0,061	0,079 ± 0,066		0,088	0,093 ± 0,063	
Cu	8,56	8,89 ± 2,84	8 – 15	7,77	8,90 ± 5,34	5 – 12
Fe	59,5	59,3 ± 16,0	60-150	70,9	71,0 ± 25,8	60-100
J	0,160	0,170 ± 0,065		0,256	0,268 ± 0,116	
K	11031	11146 ± 2329	15000-20000	11176	11908 ± 3447	12000-17000
Li	0,079	0,113 ± 0,106		0,153	0,213 ± 0,180	
Mg	2536	2624 ± 463	> 2400	2595	2780 ± 795	2000-3600
Mn	36,8	42,8 ± 18,7	50-100	37,6	41,3 ± 20,2	40-100
Mo	0,139	0,168 ± 0,106		0,120	0,162 ± 0,141	
Na	23,6	23,8 ± 10,5		19,6	25,8 ± 25,7	
Ni	1,05	1,55 ± 1,40		1,62	2,65 ± 2,30	
P	2116	2227 ± 491	> 2600	1921	2082 ± 630	1600-2600
Pb	0,094	0,104 ± 0,058		0,184	0,216 ± 0,127	
S	1791	1800 ± 371		1672	1694 ± 302	
Si	161	165 ± 56		373	380 ± 114	
Sr	52,2	51,3 ± 20,1		78,4	81,5 ± 35,9	
Zn	21,7	21,2 ± 6,8	25 – 50	20,2	20,4 ± 5,5	20-50
	Median	Range		Median	Range	
Be	< 0,002	< 0,002 - 0,0103		0,005	< 0,002 - 0,020	
Ce	0,070	0,022 - 0,759		0,121	0,045 - 1,134	
Cs	0,007	< 0,001 – 0,150		0,011	0,005 - 0,212	
Er	0,0015	0,0004 - 0,0187		0,0025	0,0010 - 0,0313	
Eu	0,0080	0,0042 - 0,0263		0,0141	0,0086 - 0,0370	
Gd	0,0054	0,0016 - 0,0815		0,0078	0,0028 - 0,1357	
Ho	0,0006	< 0,0001 – 0,0081		0,0008	0,0004 - 0,0135	
La	0,058	0,015 - 0,521		0,080	0,026 - 0,784	
Lu	0,0002	< 0,0001 – 0,0013		0,0003	0,0001 - 0,0019	
Nd	0,031	0,010 - 0,586		0,054	0,018 - 0,594	
Pr	0,009	0,003 - 0,092		0,015	0,005 - 0,154	
Rb	3,72	1,29 – 38,7		3,11	0,91 - 32,5	
Sc	< 0,02	< 0,02		< 0,02	< 0,02	
Sm	0,006	0,002 - 0,070		0,010	0,004 - 0,123	
Tb	0,0006	0,0002 - 0,0105		0,0010	0,0004 - 0,0182	
Ti*	1,58	0,51 - 2,95		2,71	0,40 - 6,54	
Ti**	0,60	0,04 - 1,13		1,23	0,40 - 5,56	
Tl	< 0,003	< 0,003 – 0,027		0,004	< 0,003 - 0,048	
V	0,056	0,013 - 0,107		0,065	0,032 - 0,355	
Y	0,022	0,009 - 0,281		0,027	0,008 - 0,378	

Element symbols given in italics mark data obtained by ICP-MS, others by ICP-OES

Ti*: digest of 0,25g with 3,5 ml HNO_3+ 0,2ml HF

Ti**: digest of 1,0g with $KClO_3/HNO_3/H_2O$

3.4 Shape of the tree

It is interesting to know, if the shape of the apple tree, like standard or spindlebush, does effect the composition of fruits and leaves. At the varieties Red and Golden Delicious grown in Italy, elevated concentrations of N, P, K, Ca, Mg in the leaves were observed, and explained by enrichments within a smaller top (Tagliavini et al., 1992). At a podsol in Poland, leaves from small shaped trees contained more N, Ca, Mg and Fe, but less K and B (Kruczynska et al., 1990).

Within the current dataset, just 8 varieties were grown as both tree shapes (Cellini, Gloster, Idared, Jonathan, Kronprinz, Luxemburger Rambour, Schmidberger Renette, Zigeunerapfel).

Considering different soils and fertilization regimes, fruits from spindlebush trees tended to contain higher levels of N, Al, Cu and Zn, and respective leaves higher levels of N, Cu, S, and Zn, which might be also explained by higher fertilization rates in intense fruit farming. To the contrary, the spindlebush leaves tended towards lower Al, Ce, La, and Y, whereas no differences with respect to other main and trace element contents were noted (Tables 5, 6).

3.5 Blossom leaves

With respect to concentrations found in blossom leaves, no reference data were available. Many concentration ranges were overlapping with green leaves, just Ca-Sr-Ba were significantly lower, and B was significantly higher than in the green leaves. With respect to most elements determined, blossom leaves contained significantly higher levels than fruits, above all Si-Ti-Fe-Al. Ranges of K-Rb-Cs, as well as B-I-Mo-Cd-V were only slightly overlapping (table 3).

If the varieties get grouped (table 7) according to increasing expectable acid contents of fruits, concentration trends remain marginal, just Co tends to increase, and Cr-Mg-P tend to decrease. Ni and Mo tended to decrease with later flowering periods. The later the expectable ripening period, the more N, and the less Ni and Pb were found in the blossom leaves.

3.6 Classification of varieties

Effects of various rootstocks upon the composition of leaves and fruits of the variety Topaz at location Jedlersdorf have been already published (Sager and Spornberger, 2015b). Other differences emerged from an investigation about element contents of cloudy varietal apple juices, which were obtained from the same location and the same rootstock, but from different varieties, particularly for P and S (Sager and Gössinger, 2015a).

None of the varieties investigated were grown at more than 3 locations, and the dataset contained much more varieties than locations. In order to detect some general effects of the varieties upon the composition of leaves, blossom leaves and fruits, they were classified according to expectable acid contents of the fruits, the flowering period, and the period of harvest. Because these parameters vary in absolute terms (France is e.g. earlier than Germany), some frequently varieties like Idared, Golden Delicious, or Jonathan, were used as reference. In table 7, these estimations were scaled as low-medium-high (1-2-3), resp. early- medium early – medium late- late (1-2-3-4), and the concentrations grouped respectively, to recognize further trends.

Table 7

Varieties (alphabetical) and their classification due to expectable acid contents of fruits, flowering and harvest period (Götz and Silbereisen 1989; Keppel et al., 1998; Jackson, 2003; Wu et al., 2007; Kunradi-Vieira et al., 2009)

	Acid	Flowering	Harvest
Alkmene			
Ananas Renette	2	2	3
Braeburn	2	3	3
Brünnerling	3	1	4
Cellini	3	1	2
Eiserapfel, roter	1	4	3
Elise Rathke	3	2	2
Enterprize	2	4	4
Frühapfel			1
Fuji Kiku	2	3	4
Gelber Bellefleur		3	3
Gloster	1	3	3
Goldparmene	2	2	2
Goldrush	2	3	4
Hana	3	1	1
Hausmütterchen	1	4	3
Hidala Hillwell	3	2	4
Idared	1	1	4
Jamba	2	2	1
Jonagold	1	1	3
Jonared		3	3
Jonathan	2	2	3
Klarapfel	3	1	1
Kronprinz	2	2	3
Landsberger Renette	2	2	3
Lavanttaler Bananenapfel	3	4	2
Luxemburger Rambour			3
Maigold		1	3
McIntosh	1	1	2
Pilot	3	1	3
Pinova	2	3	3
Prima	1		2
Purpurroter Cousinot	2		3
Remo	3	1	2
Roter Boskoop	3	1	3
Roter Winterrambour	1	4	3
Royal Gala	1	4	2
Rubinette Rosso	3	3	2
Schmidberger Renette	2	2	3
Stark Earliest	1	2	1
Topaz	2	3	3
Waltz		3	3
Welschbrunner	2		3
Zigeunerapfel	3		4

Organic acids are excellent complexants for trace elements, and could take part in their metabolism. On the other hand, they are formed inside the fruits. It is already known that organic farming might increase the contents of sugars and phenols, without change of acid contents (Hecke et al., 2006).

Later flowering means longer time of transport from stem and soil into the stalks.

3.7 Interelement effects

Within the entire dataset, very low correlations between element contents were found, and correlation coefficents were largely below 0,3. But after classification given in table 7, some more conclusions can be drawn.

3.7.1 Interelement relations in fruits

It may be not surprising that the rare earth elements were strongly intercorrelated, but other relations among element concentrations in fruits as well as between fruits and leaves were rather modest (Tab. 8). When the fruits get categorized, early flowering varieties tend towards higher levels of Ba, Ca, Cr, Mo, Na, Pb, S, Sr and Zn, contrary to lower Cd and Ti. No differences due to expectable acid contents nor harvesting period were noticeable.

Fruits of late harvest varieties contained some less N than the other 3 ones. The later the ripening period, the lower K and S, but the higher Cd, but insignificant.

Table 8

Correlation coefficients among fruit data > 0,35

	N	K	Li	Cs	Mg	Ca	Fe	Mn	P	Si
Al										0,637
Mg	0,351	0,459			X			0,528		
Mn	0,413				0,527		0,374	X		
S	0,417						0,380	0,398	0,408	0,450
P		0,547			0,394		0,391		X	
Zn					0,367			0,426		
Na			0,444							
Sr			0,403			0,794				
Ba						0,605				
Pb										-0,418
Cd				0,629						

3.7.2 Interelement relations in blossom leaves

With respect to concentrations met in blossom leaves, the rare elements were strongly intercorrelated, as well with Al, Fe, Li, Cr and V. This can also be statistically expressed as a result of principal component analysis, which yields high factor weights of the geogenics Al-Fe-Si-Li-Cr-rare earths in the first, B and Cu in the second, and Ca-Sr-Ba in the third component. In some cases, interelement correlations decreased towards a later flowering period (Tab 9), for others, no trends were noticed.

Later expectable ripening of fruits led to a trend towards increase of N, and of lower Pb and Ni in the blossom leaves. Among element proportions were found, just B/P tended to increase from early to late flowerings, and Ca/Sr was lower for late flowerings.

More expectable acid in the fruits led to a trend of increasing Fe, Co, Mo and Si, and to decreasing P, B, N, Cr, Mn in the blossom leaves.

Table 9

Correlation coefficients among blossom leaf data

	B-Cu	B-P	Cu-P	Mg-P	Mg-K	Mg-Ca
Total	0,582	0,642	0,476	0,476	0,791	0,595
Early flowering	0,777	0,879	0,693	0,771	0,859	0,719
Early-medium flowering	0,435	0,145	0,627	0,514	0,762	0,760
Medium-late flowering	0,313	0,506	0,373	0,224	0,777	0,469
Late flowering	-0,148	0,870	-0,346	0,045	0,187	0,383

3.7.3 Interelement relations in leaves

Apart from the rare earths, including Y, just a few significant interelement correlations in the leaves emerged, which do not depend on the classification of the variety (acid, flowering, harvest) (Tab. 10). In the leaves picked in August, the relations N-S, Ba-Si and Sr-Si got stronger, and the relations with Al got weaker. Principal component analysis yielded high factor weights for Al-Fe-Cr-Pb-V in the first component, excluding the rare earths contrary to blossom leaves. Ca was more related to Mg than to Sr and Ba. Contrary to blossom leaves, Cu and B were independent.

Tl was largely at or below detection limit, but in case of larger values, a fairly good correlation with Rb (r= 0,770) could be established, which is plausible due to equal charge and ionic radius.

If the leaves are assigned to the flowering period, early flowering varieties tend towards increased Fe and Al contents in their leaves. Grouping due to increasing expectable acid contents of the fruits, an increase of Mn and Si, and at a lower rate also of Ce, La, Nd, Ni and S in the respective leaves was observed, and to the contrary, a decrease of Al, B, Cr, Ti, and Iodine.

Table 10

Correlation coefficients (> 0,45) among leaf concentrations (May leaves only)

	N	Al	Ba	Ca	Cd	Cr	Cs	Cu	Fe	Nd	Ni
Cr		0,489				1					
Cs	0,466						1				
Eu			0,644								0,697
Fe		0,662				0,487			1		
Mg				0,456							
Mo		0,463									
Nd					0,522		0,783			1	
Pb		0,530									
Pr											0,514
Rb							0,835			0,680	
S								0,530			
Si		0,581							0,531		
Sm											0,536
Sr				0,485							
Tb											0,566
V		0,754							0,607		
Y											0,565
Zn								0,470			

3.7.4 Relations fruits-leaves

All investigated elements were enriched in the leaves versus the fruits, at least Rb-Cs-K, and at most Fe-Sr-Al-Ba-Ca-Si-Ti. But from the entire dataset, relations between concentrations in leaves and corresponding fruits can hardly be concluded (Table 11). In varieties of early ripening, element correlations between leaves and corresponding fruits were higher for Ba, Ca, Cu, Fe, K, Mo, and Pb, and for Mn it was reverse (Table 12).

If the fruit-leaf data pairs are grouped due to the rootstocks, only Li, Mn, Rb, and Sr correlate positively at the most frequent used M9, MM111, and seedlings. Further on, at M9 and seedlings, Al, Ba, K, and Cs in leaves and fruits correlated positively with one another, and at seedling also Mo and P. The proportion of fruit over leaf element concentrations tends towards higher values with higher expectable acid in the fruits for Al, Fe, and Mo, and towards lower values for Ni.

The proportion of elements contents in fruits over leaves tends to increase with expectable acid contents for Al, Fe, and Mo, and tends to decrease for Ni.

Varieties with early expectable flowering period tend to increase Fe in their leaves. The proportion of element contents in fruits over leaves tended to increase with later flowering period for Li, but to decrease for K and Cu. Varieties of early flowering tend to contain higher levels of Ba, Ca, Cr, Mo, Na, Pb, S, Sr, and Zn in their fruits, but lower Cd and Ti. Correlations of concentrations between leaves and corresponding fruits of early ripening varieties were much higher for Ba, Ca, Cu, Fe, K, Mo, and Pb, then for later ripening varieties, but for Mn it was reverse.

Table 11

Correlation coefficients of fruits with corresponding leaves > 0,4

↓Fruit	Leaf →							
	Ba	Cs	Cu	K	Mn	Mo	Na	I
Ba	0,550							
Cs		0,489						
Cu			0,458					
K				0,477				
Mn					0,438			
Mo						0,693		
Co			0,456				0,685	
B						0,400		0,421

The amount of expectable acid in the fruits did not influence the proportion of total element contents in fruits/leaves for all elements investigated.

Later ripening periods of fruits tend to decrease the proportion of element contents in fruits/leaves for K, N, and Cu, but not for the others. For the most early ripening varieties, Al in fruits/leaves was lower (Table 12), and S and Zn were higher.

Element proportion of N/P, Ca/Mg, B/Si, Zn/Cd, and Fe/Mn in leaves versus the respective element proportions in the fruits did not depend the expectable ripening period, acid contents nor flowering period. Just for K/Rb and K/Cs, the respective proportions in leaves and fruits correlated quite well.

Table 12

Overview about effects on element contents due to various categories of varieties

	Decrease with acid	Increase with acid	Decrease with later flowering period	Increase with later flowering period	Decrease with later ripening	Increase with later harvest
Fruits			K, P			
Leaves	Al, B, J, Ti	Ce, La, Mn, Nd, Ni, S	Fe			
Blossom leaves	Cr, Mg, P	Co	Ni, Mo		Ni, Pb	N
Proportions fruits/leaves	Ni	Al, Fe, Mo	K, Cu	Li	K,N,S,Cu,Zn	Al
Proportions fruits/blossom leaves			Mg		N,P, B, Mn	

Table 13

Correlation coefficients of concentrations found in fruits versus respective blossom leaves > 0,4

↓Blossom leaves	**Fruits →**								
	Al	**B**	**Co**	**Fe**	**J**	**Mo**	**Na**	**Rb**	Ti(HF)
N	0,472			0,716			0,563	-0,482	
Al		0,590				0,474			
Be		0,484		-0,348					
Ce		0,407							
Co			**0,499**						
Cr		0,583		-0,382		0,492			
Cs		0,354		-0,428					
Er		0,495							
Fe						0,425			
Gd						0,406			0,491
Ho									0,425
La					0,456	0,390			0,370
Lu						0,610			0,460
Mn			0,464						
Mo		0,549				**0,698**			0,496
Nd						0,501			0,492
Ni		0,404				0,343			
Pb						0,450			
Pr						0,496			0,495
Si		0,422							
Sm						0,388			0,520
Tb						0,431			0,494
Ti						0,522			0,394
Y					0,396	0,461			0,376

3.7.5 Relations fruits- blossom leaves

After picking the blossom leaves in springtime, corresponding fruits from the same trees were sampled after harvest, which made 80 data pairs. Just a few relations were found for B, Mo, Fe, and Ti. Just Co and Mo in fruits correlate with corresponding data in blossom leaves (tables 13 and 13A). Also, the element proportions N/P, Na/K, Ca/Mg, Ca/Sr, Fe/Mn, Ca/La, B/Si, and K/Rb did not significantly correlate with each other.

Slightly positive correlations between concentrations found in fruits and blossom leaves could be detected only for varieties of early flowering in case of Cd, Co, Li, and Mo, but not for others. In late flowering varieties, a positive correlation between fruits and blossom leaves for B, and a negative for Mg was found.

The proportions of fruit/blossom leave data slightly decrease with increasing ripening period for N, P, B and Mn, and increased for Fe, Li, Mo and Si with expectable acid contents of the fruits.

Table 13A

Detail of correlation coefficients of blossom-leaves versus fruits

	Mo-Mo	Co-Co
Low acid fruits	0,793	0,310
Medium acid fruits	0,370	0,475
High acid fruits	0,907	0,453
Early ripening		0,286
Early-medium ripening		0,624
Medium-late ripening		0,512
Late ripening		0,437

3.7.6 Relations leaves –blossom leaves

Table 14

Concentrations (mg kg^{-1} in dry mass) met in leaves and corresponding blossom leaves, all varieties on site (only elements showing differences)

	Haschhof		Kierling		Stammersdorf	
	Leaves	Blossom leaves	Leaves	Blossom leaves	Leaves	Blossom leaves
Li	0,085 ± 0,036	0,070 ± 0,040	0,169 ± 0,097	0,069 ± 0,028	0,213 ± 0,046	0,151 ± 0,116
Na	26,4 ± 5,9	47,9 ± 19,7	13,3 ± 5,6	46,7 ± 17,4	37,06 ± 6,61	143,4 ± 48,9
Rb	4,06 ± 1,74	7,81 ± 3,47	2,45 ± 0,86	5,10 ± 2,00	2,50 ± 0,37	6,63 ± 1,42
Ca	12732 ± 2800	2896 ± 1380	10169 ± 1829	2912 ± 815	16163 ± 2557	2744 ± 726
Sr	61,4 ± 13,5	7,2 ± 3,2	41,1 ± 14,9	6,7 ± 3,2	35,1 ± 5,5	4,6 ± 1,8
Ba	32,2 ± 10,9	5,9 ± 3,4	38,2 ± 16,0	6,9 ± 3,4	50,5 ± 18,3	7,3 ± 3,6
Eu	0,0069 ± 0,0020	0,0026 ± 0,0014	0,0186 ± 0,0074	0,0031 ± 0,0012	0,0088 ± 0,0023	0,0061±0,0036
Cu	10,36 ± 2,22	21,05 ± 6,56	6,12 ± 0,73	10,06 ± 1,87	5,81 ± 1,19	18,7 ± 3,4
Zn	24,5 ± 5,12	35,0 ± 8,9	15,0 ± 2,2	16,0 ± 4,2	15,3 ± 3,4	29,7 ± 5,8
Cd	0,0114 ± 0,0059	0,0314 ± 0,0210	0,0178 ± 0,0201	0,0569 ± 0,0345	0,010 ± 0,003	0,012 ± 0,004
Pb	0,066 ± 0,021	0,213 ± 0,046	0,168 ± 0,026	0,208 ± 0,030	0,336 ± 0,105	0,482 ± 0,223
B	24,8 ± 4,5	73,8 ± 20,9	23,7 ± 4,0	56,1 ± 17,3	18,4 ± 1,6	57,2 ± 15,4
Si	167 ± 40	132 ± 38	156 ± 39	80 ± 18	349 ± 92	251 ± 137
Ti	0,54 ± 0,22	1,27 ± 0,49	0,93 ± 0,22	0,89 ± 0,52	2,36 ± 0,47	3,90 ± 1,78

Composition of leaves and corresponding blossom leaves turned out to be almost independent from one another, and also the element proportions N/P, Na/K, Ca/Mg, Ca/Sr, Fe/Mn, Ca/La, B/Si and K/Rb, irrespective from the flowering period. At the locations at Klosterneuburg (both at Haschhof and Kierling) and Stammersdorf, where many different varieties were grown, leaves contained more Li, Ca, Sr, Ba, Eu and Si than the respective blossom leaves. It was reverse, however, in case of B, as well as for Na, Rb, Cu, Zn, Cd, Pb and Ti (Table 14).

The flowering period did not influence the proportion leaf/blossom leaf of a given element, just N tended to decrease for late flowerings.

3.8 Effect of the soil

Soil analytical data in detail have been already reported elsewhere. (Sager, 2012; Sager, 2014b; Sager, 2016). Table 15 is therefore restricted to traditional standard soil parameters, which indicate a wide range of nutrient supply among the sampled locations. In some cases, deeper layers have been cored also, which are slightly different to the recommended 0-25 cm.

Table 15

Traditional soil parameters

		Profile- cm	Plant cover	pH $CaCl_2$	% $CaCO_3$	%N	%Humics	´mg kg-1			
								P-CAL	K-CAL	Mg-$CaCl_2$	B-Baron
Kierling	Young uphill	0-25	Grass	6,0	< 0,5	0,114		41	167	97	0,4
Kierling	Young downhill	0-25	Grass	5,8	< 0,5	0,123		73	246	150	0,3
Kierling	Old uphill	0-25	Grass	4,9	< 0,5	0,139		32	163	90	0,3
Kierling	Old downhill	0-25	Grass	4,5	< 0,5	0,104		29	144	84	0,3
Haschhof	Site 030	0-25	Bare soil	7,2			4,9	117	320		
Haschhof	Site 030	25-50	Bare soil	7,3			4,2	82	300		
Haschhof	Site 091	0-25	Bare soil	7,1			3,5	60	236		
Haschhof	Site 091	25-50	Bare soil	7,1			2,8	39	219		
Innermanzing	Renette	0-25	Green feed	6,8	< 0,5	0,226		< 20	115	223	0,6
Innermanzing	Klarapfel	0-25	Green feed	6,2	< 0,5	0,282		< 20	119	151	0,6
Innermanzing	Zigeunerapfel	0-25	Green feed	5,4	< 0,5	0,336		< 20	82	175	0,4
Innermanzing	Idared	0-25	Grass	6,1	< 0,5	0,304		< 20	573	215	0,8
Laaben	Lower seedling	0-25	Green feed	6,2	< 0,5	0,206		< 20	319	126	0,5
Laaben	Upper seedling	0-25	Green feed	7,2	0,8	0,309		< 20	114	184	1,5
Jedlersdorf	BOKU- experimental site	0-25	Grass	7,6	13,5		3,8	72	90	109	2,7
Jedlersdorf		25-50	Grass	7,8			2,8	23	27	84	2,0
M. Lanzendf		0-25	Grass	7,2	20,2	0,386	7,5	254	606	281	3,6
M. Lanzendf		25-40	Grass	7,3			7,4	254	655	272	3,6
Hirschstetten	AGES-site	0-25	Grass	7,4	25,0	0,267	7,4	24	183	294	1,7

Unterwalters-dorf	In the wetland	0-25	Grass	7,4	16,7	0,339	5,3	110	267	215	2,8
Unterwalters-dorf	In the wetland	25-50	Grass	7,4	15,7	0,314	5,1	102	207	214	2,8
Mattersburg	Red vineyard	0-25	Grass	6,5	< 0,5	0,211	3,6	92	395	288	0,8
Mattersburg	Red vineyard	25-50	Grass	6,2	< 0,5	0,173	3,0	88	322	297	0,8
Gaisbach	Gaisbach 2 u.3	0-50	Grass	7,0	1,6	0,316	5,5	102	338	284	1,7
Forchtenstein	the garden	0-25	Grass	7,0	1,8	0,238	3,5	36	301	258	1,4
Forchtenstein	the garten	25-50	Grass	7,1	1,6	0,187	2,8	25	215	245	1,2
Hofstetten	Meadow downhill	0-25	Green feed	6,5	< 0,5		4,9	< 20	244	265	1,0
Hofstetten	Meadow uphill	0-25	Green feed	5,7	< 0,5		3,8	< 20	82	195	0,5
Grünau		0-25	Grünfutter	6,3	< 0,5		5,3	24	241	256	0,6
Haidegg	Row 1138	0-30	Grass	6,6	< 0,5	0,185		100	289	218	0,5
Haidegg	Row 1138	30-40	Grass	6,3	< 0,5	0,197		87	254	139	0,4
Haidegg	Row 1138	50-60	Grass	5,6	< 0,5	0,256		105	265	107	0,4
St. Andrä	Standard tree		Grass	6,1	< 0,5	0,237	1,6	85	46	176	0,7
St. Andrä	Spindlebushes		Grass	6,8	< 0,5	0,164	1,4	47	53	194	0,6
Stammersdorf	Apple	0-30	Grass	7,6			3,2	61	330	69	1,2
Stammersdorf	Apple	30-60	Grass	7,7			2,0	40	184	73	0,8

Classifications: very low; low; medium; high; very high

Factor analysis of soil data groups the exchangeables (0,16M acetic acid) into B-Ba-Mg-pH, K-P, and Fe-Mn-Li. The components of data from the subsequent extracts in acid oxalate contain main the data from Al-Fe-Mn-Ba-Li-Zn, B-S-Si, and P-Cu.

3.8.1 Soil - fruit interactions

As fruit farming cycles are stretching over several years, it might be that soil deficiencies emerge at long term, and success might not develop immediately. Mobilization of nutrients from wood and bark from April to June, when there is maximum need, takes also place from reserves obtained in preceding autumn, and cannot fully substituted by pulse fertilization in springtime.

Increasing P (CAL) in the soil led to increase of N and K in the fruits, whereas Ba, Rb and I decreased, but it was of no influence upon P and all others.

3.8.2 Soil – leaf interactions

If all kinds of varieties, rootstocks, and locations are put together, just a few correlations between element concnetrations in leaves and standard soil parameters could be recognized (table 16). Nutrient supply, indicated by the K and P extracts of the topsoil into CAL, had only marginal effects upon the elemental composition of the leaves. More avaiable nutrients decrease the rare earths in the leaves, and might increase the level of nutrient elements. Increasing P-CAL increased S and Mg in the leaves, but P at medium class of nutrient availability (at sufficient supply) was at maximum, and decreased at higher P supply. The proportion leaf/fruit increased with increasing P-CAL only in case of Rb, and decreased in case of Si. Increase of K-CAL in the topsoil resulted in slight increases of K, Ca, and Sr in the leaves (Table 16).

Among mobile soil fractions (Sager 2016), Ca dissolved by dilute acetic acid and Si dissolved by oxalate correlated well with Ca resp. Si in the leaves.

Table 16

Correlation coefficients > 0,4 between concentrations in the leaves and standard soil parameters

	Positively	Negatively
pH	-	Ce, La, Ni, Pr, Sm, Y
Humics	B, K, Mn	Rb, Cs, Nd
Total N	B, Cu, Li, Na, Zn	Ce, La, Nd, Pr, Sm, Y
K-CAL	K, Na	Nd, Rb
Mg in CaCl$_2$	Co, Zn	Si
B (Baron-extract)	-	Ce, Li, Nd, Pr, Sm, Y

Correlation coefficients > 0,45 between concentrations in leaves and soil

leaf -->	Al	Be	Ca	Ce	Cr	Cu	La	Li	Mg	Mn	Na	Ni	Pb	Sr	Zn
Soil extract with 0,16M acetic acid															
Al				,561											
B				-,492			-,490								
Ba						,496									
Cd														,593	
Fe													-,561		
La										,664			-,479		
Li				-,565			-,517						-,527		,526
Mn													-,585	,456	,476
Na								,550							
Ni					-,627										
P											,491				
Pb						,497									
S											,497				
Si		-,564	,538	-,572			-,488		,526	-,510		-,674			
Ti	,553		,541		,491						,631				
Zn								,529							

Soil extract with 0,2M oxalate pH 3															
leaf -->	Al	Be	Ce	La	Li	Mg	Mn	Mo	Na	Ni	P	Pb	Si	Ti	Zn
Al														-,500	
Be			-,560												,504
Cr														-,491	
Cu	,779	-,514						,658					,503	,523	
Fe						-,508						-,528		-,502	
K			-,509												
Mg					,595										
Mo											,499				
Na							,513								
Ni		-,521	-,578												
P		-,479	-,489	-,518											
S					,549										
Si	,490		-,529	-,603				,523	,543	-,528			,479	,583	

KClO$_3$/HNO$_3$/H$_2$O digest																
	Al	Be	Ca	Ce	Cr	Cu	K	La	Li	Mg	Mn	Mo	Na	Pb	Si	Ti
Al				-,560				-,498								
B				-,485	,498											
Ba														-,726		
Cd	,679				,552							,536		,507		,545
Fe			-,480											-,523		-,520
La							-,480									
Li	,710	-,532								,481		,623				

Mn	-,510												-,545		-,502	
Na									,505							
Ni											,493					
P				-,476												
Pb					,481								,482			
S										,476	-,527					
Si	,730				,525							,553				,515
Ti						,505			,538							
Zn				-,509									,485			

Total digest $HClO_3/HNO_3/HF$

	Al	Be	Ce	Cr	Cu	Fe	Li	Mg	Mo	Na	Pb	Ti	V		
Al	-,473					-,488							-,527		
Ca	,564			,558			,483								
Cd			-,504							,493					
Cu	,674	-,515						,502	,593						
J					,535										
K	-,475					-,564									
Li											-,566				
Mg							,484								
Ni													-,494		
P										,486					
Pb					,490										
Rb	-,499					-,500							-,504		
Sr	,618			,528					,495						
V												-,497	-,457		
Zn			-,545												

3.8.3 Soil – blossom leaf interactions

For most of the elements, no relations between element contents in blossom leaves and respective topsoils were found, except Cr in the blossom leaves, which correlated positively with P-CAL (r=0,853), K-CAL (r=0,693), Mg-$CaCl_2$ (r=0,600) and B-Baron (r=0,699) in the soil. No relations between concentrations of equal elements were detected.

Parted due to flowering periods, early flowering blossom leaves showed more correlations than the entire dataset (table 17).

P in the blossom leaves correlated positively with total N (r=0,666), Mg-$CaCl_2$ (r=0,606) and B (in Baron-extract; r=0,699) and soil pH (r=0,713). The latter is somewhat surprising, because phosphate mobility gets lowered by increase of pH.

3.9 Anomalies of the Rare Earths

The Rare Earth elements occur strongly intercorrelated, thus the occurrence of a missing one can be estimated from the occurrence of neighbouring elements. Deviations of real data from theses estimations are called anomalies. Anomalies of Ce are caused by oxidation to more immobile Ce(IV), and anomalies of Eu are caused by reduction to more mobile Eu(II), the mobility of which resembled Ca or Sr.

This study contains locations of negative as well as positive Ce and Eu-anomalies, if referred to Standard European Shale (Bau et al., 2018). This contains 44,3 mg kg^{-1} La, 88,5 mg kg^{-1} Ce, and 10,6 mg kg^{-1} Pr, and further 7,3 mg kg^{-1} Sm, 1,48 mg kg^{-1} Eu, and 6,34 mg kg^{-1} Gd. At the sampled locations, the median of Ce anomalies was 1,038 (range 0,758-1,448), and the median of Eu anomalies 1,021 (range 0,954-1,448). Both in leaves and fruits, trends of negative Ce-anomalies and positive Eu-anomalies appeared, but no significant correlations could be established.

Table 17

Correlation coefficients of concentration in blossom leaves with soil data > 0,5 (at 0,01 significance level)

Blossom leaf -->	Fe	K	P	Ba	Cr	Cu	Mn	Zn
	All			Early flowering only				
Soil extract with 0,16M acetic acid								
Co			-0,675		-0,584	0,572		
Cr					-0,570			
K			0,607		0,712			
Li			0,663					
Mn							-0,771	
P					0,865			
Si	-0,609	-0,929						
Soil extract with 0,2M oxalate pH 3								
Be			0,566		0,811			
Cd			-0,637					
K					0,708			
La					-0,592			
Li				0,812				
Mn				0,603				
Ni					0,701			
Si	-0,683	-0,778		0,764				
Zn				0,681				
$KClO_3/HNO_3/H_2O$ digest								
Ba					0,802			
S	-0,736	-0,924	0,607		0,762			
Sc						0,691		
Sr					0,838			
P			0,606		0,876			
Y	-0,644					0,513		
Zn					0,794			0,510
Total digest ($HClO_4/HNO_3/HF$)								
Ba			-0,581		-0,725			
Cd			0,636		0,605			
Ce					-0,684			-0,567
Eu					-0,593			
K					-0,798			-0,792
Li				0,791				
La					-0,698			
Mo					0,856			
Na					-0,658			-0,664
Pr					-0,688			
Rb					-0,762			-0,725

Positive Ce-anomalies in soils were found at Haidegg, Klosterneuburg, Maria Lanzendorf, Hirschstetten, St. Andrä, Mattersburg, Innermanzing and Hofstetten, whereas negative Ce-anomalies in the soils occurred at Pielachtal Grünau, Weigelsdorf, Stammersdorf, Jedlersdorf, and Laaben. The locations Haidegg, Hirschstetten, Klosterneuburg, Maria Lanzendorf, Mattersburg, Innermanzing, and St. Andrä had positive Eu-anomalies in soils, whereas negative Eu-anomalies in the soils were found at Stammersdorf, Jedlersdorf, Laaben and Grünau. No anomaly appeared at Unterwaltersdorf.

Rare earth anomalies, however, were not transferred to fruits, blossom leaves and leaves, however, which means, that this parameter cannot be used to identify unknown locations. Remarkably, Ce in the plant gets depleted with respect to the other rare earths, particularly in the blossom leaves, whereas Eu gets enriched, particularly in the leaves. Low precision of the data for Sm, however, which are close to the detection limit, leads to high uncertainties of the Eu anomalies in the green plants (Table 18).

Table 18

Calculated Ce and Eu-anomalies, all data

	Ce-anomalies		Eu-anomalies	
	Median/range	Mean-Stddev	Median/range	Mean-Stddev
Soils	1,039/0,758 – 1,448	1,047 ± 0,181	1,021/0,954-1,448	1,025 ± 0,050
Leaves	0,820/0,285 – 1,093	0,777 ± 0,282	5,45/1,49 – 19,31	7,08 ± 6,26
Blossom leaves	0,49 /0,39 – 0,57	0,49 ± 0,059	1,29/0,85 – 2,63	1,49 ± 0,79
Fruits	0,770/0,286 - 1,691	0,833 ± 0,538	1,97/0,59 – 8,38	2,88 ± 3,64

CONCLUSIONS

Within this work, leaves, blossom leaves and fruits from apple trees together with respective topsoils were sampled at non-contaminated sites in the East of Austria, in order to find interelement relations within the same plant, as well with total contents and mobile fractions of adjacent surface soils. In addition to usually determined main and essential elements and toxic metals, also data from Li, Rb, Cs, Si, I and the Rare Earths have been compiled, which occur at low levels in biological matrices. Their importance for the plant metabolism is still unknown, or not relevant, but, as no other respective data for reference were found, the current dataset should encourage for further research.

Fruits were sampled after harvest, blossom leaves were available just within a short period, and green leaves were taken young at the end of May, and some of them also in the mid of August. Aging of green leaves lowered total N, and increased Al, Si, Ca, Sr, Ba, Li and the Rare Earths vice-versa. Thus it is essential to sample the leaves within a standardized period.

The shape of plant growth, high or low, did not have significant effects upon the concentrations obtained in leaves, blossom leaves, nor fruits, and some trends can also be explained by fertilization. Increased nutrient supply, indicated by organic C, total N, as well as P or K-soil extracts into CAL-solution, tended to increase the physiologically more important elements in the leaves, and decreased the Rare Earths.

With respect to usual proportions encountered in rocks and soils (Wedepohl, 1995), K was found to be enriched versus Rb and Cs in plant tissues, particularly in the leaves, whereas the proportion Ca/Sr remained within the same range. Iodine contents did not yield any relations to other parameters determined, but F, Cl, and Br were not included within this study. Silicate could be an important parameter to indicate mechanical stability.

Table 5

Concentrations found in fruits from standard and spindlebush-shaped trees, means from different sites (Ti from $KClO_3$)

Variety	**Cellini**		**Gloster**		**Idared**		**Jonathan**		**Kronprinz**		**Luxemburger Rambour**		**Schmidberger Renette**		**Zigeunerapfel**	
Location	Kierling	Haschhof	Stammersdorf	Weigelsdorf	Stammersdorf	Unterwaltersdorf Weigels-dorf Ma.Lanzendorf	Hirschstetten Stammersdorf	Ma.Lanzendorf	Kierling	Ma.Lanzendorf St.Andrä Haschhof	Kierling	Haschhof	Kierling Hofstetten	Haschhof St. Andrä	Kierling Innermanzing	Haschhof
Year	2011	2011	2014	2012	2014	2011/12	2012/14	2012	2011	2011/12	2011	2011	2011	2011/2012	2011	2011
Shape	Standard	Spindle-bush	Standard	Spindle-bush	Standard	Spindle-bush	Standard	Spindle-bush	Standard	Spindle-bush	Standard	Spindle-bush	Standard	Spindle-bush	Standard	Spindle-bush
%N	0,347	0,542		0,325		0,321	0,325	0,405	0,263	0,395	0,289	0,485	0,267	0,337	0,213	0,289
Al	1,73	2,90	3,07	3,76	4,31	2,08	1,13	2,31	5,99	3,41	2,57	1,89	1,78	4,05	1,57	6,74
B	17,2	14,2	39,1	8,55	23,8	15,5	26,6	11,9	13,3	20,9	8,79	8,38	16,6	16,2	25,4	14,4
Ba	1,33	0,57	0,68	1,96	1,01	0,78	1,05	0,78	1,07	1,03	0,62	0,28	0,69	1,11	1,50	1,53
Ca	346	333	358	736	340	269	231	290	672	292	205	180	378	238	334	628
Cd	0,0061	0,0029	0,0013	0,0021	0,0020	0,0000	0,0117	0,0010	0,0088	0,0087	0,0048	0,0037	0,0059	0,0175	0,0041	0,0048
Ce	0,0584	0,0106	0,0085	0,0304	0,0194	0,0046		0,0031	0,0052	1,3662	0,3045	0,0125	0,3839	0,1125	1,5736	0,0152
Co	0,0064	0,0149	0,0039	0,0128	0,0041	0,0080	0,1937	0,0024	0,0024	0,0121	0,0074	0,0114	0,0055	0,0129	0,0075	0,0095
Cr	0,041	0,041	0,032	<0,01	0,027	<0,01	<0,01	<0,01	<0,01	< 0,01	0,053	0,086	0,013	0,048	0,030	0,085
Cs	0,0043	0,0123	0,0097	0,0043	0,0097	0,0080		0,0020	0,0017	0,0485	0,0073	0,0069	0,0050	0,0966	0,0199	0,0073
Cu	2,30	4,43	1,50	3,44	2,01	2,23	3,03	2,18	2,14	2,59	1,12	3,96	2,04	2,80	1,32	2,93
Er	0,0014	0,0004	0,0000	0,0002	0,0002	0,0002		0,0000	0,0002	0,0129	0,0036	0,0003	0,0039	0,0006	0,0143	0,0005
Eu	0,0013	0,0009	0,0002	0,0005	0,0004	0,0004		0,0001	0,0004	0,0076	0,0043	0,0008	0,0022	0,0019	0,0095	0,0010
Fe	8,00	6,45	4,37	3,84	3,63	5,93	2,32	4,09	7,25	5,41	7,11	7,25	4,48	7,40	4,06	6,60
Gd	0,0040	0,0008	0,0003	0,0016	0,0008	0,0006		0,0002	0,0005	0,0955	0,0208	0,0010	0,0254	0,0062	0,0419	0,0014
Ho	0,0005	0,0001	0,0000	0,0005	0,0001	0,0000		0,0000	0,0000	0,0051	0,0013	0,0001	0,0015	0,0002	0,0060	0,0002
I	0,106	0,283	0,063	0,021	0,031	0,090	0,040	-0,003	0,053	0,071	0,579	0,112	0,102	0,048	0,125	0,345
K	7036	5203	5637	7664	3972	5154	4573	6588	3220	4232	5981	5942	5055	3809	3875	4712
La	0,034	0,009	0,001	0,018	0,007	0,005		0,001	0,005	0,677	0,155	0,009	0,032	0,025	0,257	0,012
Li	0,0075	0,0135	0,0064	0,0066	0,0080	0,0077	0,0052	0,0182	0,0408	0,0069	0,0072	0,0023	0,0068	0,0038	0,0142	0,0091
Lu	0,0003	0,0001	0,0001	0,0001	0,0001	0,0000		0,0000	<0,0001	0,0009	0,0005	0,0001	0,0004	0,0000	0,0010	0,0001
Mg	292	366	285	474	234	319	313	374	279	317	302	342	299	345	254	274
Mn	2,14	3,44	1,71	3,12	1,54	1,59	1,75	2,64	2,72	2,46	2,32	2,56	2,00	1,93	2,20	2,47
Mo	0,055	0,051	0,197	0,041	0,161	0,085	0,137	0,082	0,022	0,087	0,050	0,039	0,055	0,067	0,075	0,063
Na	7,73	2,49	8,49	7,14	6,61	8,34	4,87	7,26	1,55	5,19	7,62	2,17	12,48	5,53	6,21	5,83
Nd	0,026	0,007	0,001	0,002	0,006	0,003		0,001	0,002	0,002	0,131	0,006	0,165	0,046	0,260	0,009
Ni	0,082	0,154	0,136	0,234	0,136	0,120	0,099	1,095	0,120	0,041	0,137	0,088	0,257	0,073	0,091	0,082
P	759	699	673	813	583	527	776	602	506	569	822	853	529	667	413	529
Pb	0,058	0,022	0,017	0,024	0,025	0,018		0,075	0,026	0,032	0,027	0,019	0,015	0,121	0,057	0,027
Pr	0,0066	0,0015	0,0001	0,0036	0,0015	0,0007		0,0004	0,0006	0,1533	0,0340	0,0016	0,0062	0,0128	0,0696	0,0020
Rb	1,47	6,25	1,40	2,55	1,61	2,65		1,40	2,02	7,99	1,00	2,77	2,17	14,54	7,45	2,34
S	132	323	279	230	232	203	259	234	333	285	161		197	260	219	275

Si	2,45	7,81	11,94	4,97	11,66	3,48	<0,2	2,30	10,42	6,77	5,10		4,05	7,31	5,91	11,70
Sm	0,0064	0,0026	0,0002	0,0025	0,0011	0,0005		0,0003	0,0002	0,1054	0,0258	0,0021	0,0050	0,0080	0,0472	0,0033
Sr	1,15	0,99	0,87	1,32	0,83	0,70	1,02	1,13	5,73	1,03	0,62	0,36	2,23	0,86	1,47	2,99
Tb	0,0006	0,0002	0,0000	0,0001	0,0001	0,0000		0,0000	0,0000	0,0108	0,0024	0,0002	0,0029	0,0006	0,0121	0,0002
Ti	0,077	0,113	0,051	0,078	0,342	0,105	0,044	0,038	0,091	0,082	0,088	0,069	0,045	0,122	0,035	0,170
V	<0,002	0,004	<0,002	0,016	<0,002	<0,002	0,009	0,002	0,003	0,015	0,005	<0,002	<0,002	0,010	0,029	0,019
Y	0,0071	0,0015	0,0015	0,0039	0,0028	0,0020		0,0013	0,0028	0,0381	0,0089	0,0011	0,0174	0,0082	0,0298	0,0027
Zn	2,43	2,54	2,68	2,89	1,97	1,48	1,70	1,98	1,84	2,15	1,18	1,97	1,85	2,59	1,50	3,15

Table 6

Concentrations found in leaves from standard and spindlebush-shaped trees, means from different sites (Ti from $KClO_3$)

Variety	**Cellini**		**Gloster**	**Idared**		**Jonathan**		**Kronprinz**		**Luxemburger Rambour**		**Schmidberger Renette**		**Zigeunerapfel**	
Location	Kierling	Haschhof	Weigels-dorf	Stammersdorf Innermanzing	Unterwaltersdorf Weigels-dorf Ma.Lan-zendorf	Hirschstetten Stammersdorf	Ma.Lan-zendorf	Kierling	Ma.Lan-zendorf St.Andrä Haschhof	Kierling	Haschhof	Kierling Hofstetten	Haschhof St. Andrä	Kierling Innermanzing	Haschhof
Year	2011	2011	2012	2012/14	2011/12	2012/14	2012	2011	2011/12	2011	2011	2011	2011/2012	2011	2011
	Standard	Spindle-bush	Spindle-bush	Standard	Spindle-bush	Standard	Spindle-bush	Standard	Spindle-bush	Standard	Spindle-bush	Standard	Spindle-bush	Standard	Spindle-bush
%N	2,25	2,56	2,72	2,16	2,72		3,11	2,43	2,90	2,07	2,32	2,06	2,60	2,12	2,48
Al	36,9	40,8	41,6	96,5	44,3	186,8	42,7	50,9	34,3	39,4	23,0	30,8	43,9	42,6	24,3
B	22,4	19,8	26,4	18,1	24,8	18,9	28,9	22,2	19,6	21,9	21,5	32,1	28,0	29,8	21,5
Ba	44,3	27,6	58,3	44,6	51,8	75,5	42,8	66,8	45,8	31,0	22,5	23,9	26,3	52,0	37,1
Ca	11680	15497	17376	15888	13631	16293	10956	11423	14379	8026	13600	12069	12944	11127	15187
Cd	0,0186	0,0077	0,0040	0,0101	0,0066	0,0098	0,0097	0,0873	0,0280	0,0155	0,0100	0,0065	0,0129	0,0147	0,0094
Ce	0,302	0,091	0,062	0,160	0,099	0,268	0,050	0,574	0,069	0,485	0,029	0,268	0,048	0,543	0,043
Co	0,087	0,113	0,128	0,070	0,112	0,090	0,089	0,138	0,087	0,081	0,124	0,116	0,119	0,102	0,120
Cr	0,118	0,157	0,083	0,196	0,058	0,310	0,236	0,095	0,166	0,052	0,127	0,053	0,101	0,082	0,051
Cs	0,0002	0,0147	0,0126	0,0119	0,0158	0,0173	0,0022	0,0080	0,0540	0,0085	0,0096	0,0015	0,0072	0,0191	0,0078
Cu	6,74	13,19	8,20	6,07	7,35	6,83	10,49	6,43	9,55	4,90	10,23	6,22	9,79	6,29	12,28
Er	0,0118	0,0011	0,0018	0,0044	0,0026	0,0078	-0,0164	0,0167	-0,0027	0,0115	0,0005	0,0056	0,0013	0,0115	0,0012
Eu	0,0187	0,0052	0,0122	0,0088	0,0104	0,0124	0,0102	0,0229	0,0129	0,0158	0,0047	0,0101	0,0060	0,0199	0,0087
Fe	80,8	65,0	53,3	81,3	77,6	127,5	76,9	71,2	51,7	59,1	65,2	60,6	61,0	72,2	51,6
Gd	0,0566	0,0037	0,0042	0,0094	0,0066	0,0167	0,0050	0,0610	0,0148	0,0491	0,0018	0,0253	0,0038	0,0489	0,0034
Ho	0,0047	0,0000	0,0006	0,0014	0,0009	0,0027	-0,0039	0,0069	-0,0008	0,0048	0,0002	0,0023	0,0002	0,0047	0,0003
I	0,203	0,164	0,233	0,278	0,281	0,353	0,117	0,196	0,138	0,195	0,085	0,229	0,147	0,267	0,171
K	10751	7834	14206	12779	10775	12055	15700	16849	10131	15009	11582	13124	10173	12080	10285
La	0,357	0,045	0,033	0,086	0,052	0,140	0,076	0,441	0,237	0,297	0,014	0,192	0,033	0,349	0,028
Li	0,108	0,164	0,107	0,209	0,331	0,220	0,056	0,509	0,075	0,248	0,120	0,061	0,094	0,266	0,085
Lu	0,0008	0,0001	0,0002	0,0006	0,0004	0,0010	-0,0054	0,0011	-0,0016	0,0009	0,0001	0,0005	0,0001	0,0009	0,0001

Mg	2832	3465	3987	3773	3289	3244	2636	2447	2542	2161	2762	2731	3202	2667	2908
Mn	35,9	82,2	18,9	28,3	31,4	31,9	62,0	80,4	54,4	47,0	52,0	26,48	49,4	39,7	56,3
Mo	0,094	0,129	0,153	0,434	0,237	0,744	0,098	0,045	0,131	0,112	0,108	0,145	0,139	0,104	0,126
Na	14,8	23,8	16,3	41,3	21,2	57,2	153,7	16,2	46,0	15,6	18,7	10,6	28,6	18,7	28,1
Nd	0,252	0,024	0,026	0,060	0,042	0,104	0,034	0,252	0,295	0,206	0,011	0,123	0,022	0,224	0,017
Ni	3,29	2,90	0,37	0,41	0,74	0,45	1,11	4,60	0,74	2,60	0,78	0,95	0,59	2,07	1,13
P	1946	2060	2707	2219	1728	3442	2631	1503	1879	2056	1988	1756	2205	1685	2542
Pb	0,139	0,063	0,138	0,223	0,186	0,470	0,141	0,176	0,128	0,177	0,063	0,176	0,080	0,235	0,091
Pr	0,070	0,007	0,007	0,017	0,011	0,029	0,010	0,070	0,025	0,056	0,003	0,034	0,006	0,062	0,005
Rb	1,84	7,77	3,96	3,01	3,63	2,50	1,79	2,87	10,54	1,47	4,09	2,75	3,75	7,75	4,41
S	1716	2317	1525	1312	1677	1404	2729	1390	1618	1377	1617	1435	2015	1265	2025
Si	150	217	127	268	158	484	202	197	142	144	110	96	199	172	174
Sm	0,045	0,003	0,005	0,011	0,008	0,017	0,006	0,049	0,014	0,042	0,002	0,025	0,004	0,044	0,003
Sr	43,9	60,0	57,0	39,1	40,2	40,6	21,6	48,9	40,1	26,8	53,3	71,8	57,1	53,1	76,1
Tb	0,0072	0,0004	0,0006	0,0015	0,0010	0,0025	-0,0001	0,0085	0,0015	0,0065	0,0002	0,0033	0,0004	0,0064	0,0004
Ti	0,98	0,43	1,19	1,57	1,13	3,10	0,13	1,06	0,20	1,18	0,63	0,88	0,67	1,14	0,60
V	0,062	0,057	0,011	0,100	0,090	0,201	0,116	0,090	0,047	0,056	0,068	0,078	0,089	0,084	0,034
Y	0,202	0,015	0,017	0,038	0,024	0,068	0,036	0,277	0,054	0,164	0,009	0,078	0,015	0,160	0,015
Zn	16,9	29,8	16,7	15,3	16,0	22,7	33,0	12,2	21,4	13,0	25,1	13,8	30,9	16,1	27,0

The concentrations of rare earths were strongly intercorrelated in all matrices investigated, but at the detection limits in bio-matrices, and therefore determinations of La and possibly Eu would be sufficient for further studies. With respect to other rare earths, Eu was found to be enriched in the plant tissues, which may need further detailed investigations. It might be transferred as a divalent cation like Ba or Sr. The transfer of the Rare Earths into the apple plants was low, there was no carry-over of Ce- and Eu- anomalies found in the adjacent soils. Compared with other Rare Earths, transfer of Eu into the apple plant was preferred, and Ce was rather prevented.

If the entire dataset is used, the number of significant correlations betwen fruits, leaves, blossom leaves and soil parameters remained low. In particular, the composition of the blossom leaves turned out to be largely independent from respective green leaves and fruits. Only relations to B and Mo in the fruits, as well as to P, K, and Fe in the leaves were noted, preferably for early flowering varieties.

As it could be shown in a preceding paper, the rootstock, which is not known in any case, mainly influences the uptake of Co and Mo, and in some cases also K, B, Si, and Mn. Because many of the samples were grown on the rootstocks M9 and MM111, the samples were grouped according to varieties, and classified due to expectable acid contents of the fruits, as well as the flowering and the harvesting period, to detect possible further trends.

The composition of blossom leaves was largely independent from the corresponding leaves, except for Co and Mo. In the fruits, only B and Mo correlated with some more elements in the blossom leaves, and vice-versa the nitrogen in the blossom leaves with Al, Fe, Na, and Rb in the fruits.

Further on, only few interrelations between the composition of surface soils with leaves and fruits were obtained, which prevents conclusions to find the sampling site from the chemical analyses.

Numerous varieties have been classified according to expectable acid contents, the period of harvest, and the period of flowering, to indicate possible differences among interelement effects. Presumable acid contents and harvesting period may lead to different leaf/fruit proportions in particular.

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