# Apple Peel as a Contributor to Whole Fruit Quantity of Potentially Healthful Bioactive Compounds. Cultivar and Year Implication 

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#### Abstract

On the basis of the fresh weight of apple fruit and its peel and the concentration of bioactive compounds, the total quantity of L-cysteine, glutathione, ascorbate, flavonols, and anthocyanins as well as phenolics was evaluated in a wide range of cultivars and two growing seasons. Apple peel as a contributor to the entire apple quantity of the examined components considerably differed in relation to the investigated compounds and was also highly cultivar dependent. A great amount of flavonols was found in apple peel ( $\sim 40 \%$ ), followed by ascorbate ( $\sim 30 \%$ ) and total phenolics ( $\sim 20 \%$ ), while the lowest contribution was assessed for thiols ( $\sim 11 \%$ and $14 \%$ for L-cysteine and total quantity of glutathione, respectively), based on average values for both years. Seasonal variations in the quantity of antioxidants was more pronounced in apple peel, whereas the contribution of apple peel to the whole fruit was predominantly affected by the genotype. A very high positive correlation existed between apple peel and the whole fruit quantity of antioxidants.


## KEYWORDS: Malus domestica Borkh; cultivar; antioxidant amount; vitamin C; phenolics; glutathione

## INTRODUCTION

Bioactive, mainly nonnutrient plant compounds, also called phytochemicals, which are present in fruit and vegetables may provide desirable health benefits, beyond basic nutrition, such as reducing the risk of cancer, cardiovascular diseases, stroke, Alzheimer disease, or some of the functional declines associated with aging. Prevention is a more effective strategy than treatment of chronic diseases ( 1,2 ). To reach such a protective effect, it is recommended to consume five or even more servings of fruit and vegetables per day. A proper determination of the quality and quantity of plant-origin food in a diet requires knowledge of the range of bioactive compound content, as well as the recognition of factors influencing them. These elements, as the antioxidative stress metabolites in plant tissues, are strongly affected by many outside factors, mainly growing conditions in a vegetative season (3-7). Availability throughout the year and maintenance of a high-quality antioxidant status during storage or processing is another significant issue ( 8,9 ). There are a few reports about the daily intake of flavonoids, anthocyanins, or total phenolics (10-13), although it is still an open question about the minimum daily requirement of antioxidants, which may be a protective factor in the prevention of diseases. Although the contribution of a particular phytochemical to the total antioxidant capacity differs considerably, it is proposed

[^0]that their potent antioxidant and anticancer traits are attributed to the complex mixture of phytocompounds present in fruit and vegetables ( 1,14 ).

Apple fruit is an unquestionable leading horticultural product and an important fruit in people's diet, used in the European, American, and many other national cuisines throughout the year. According to the current knowledge and our own evaluation there are few main factors that affect the concentration of potentially healthful apple bioactives, which could be classified in a following way: first, the content of phytocompounds is highly tissue-type dependent (15-17); second, great differences are observed between cultivars, which belong to Malus genus (7, 15, 18-20). However, it should also be stressed that the impact of growing season, the third factor, could exceed the genotype effect in many cultivars (7,17). Finally, the time and storage condition dependent changes in the antioxidant status seem to be highly cultivar dependent, and the growing season impact observed after harvest is reduced to a less important level during storage (21, 22).

The evaluation of the content of apple bioactives in different parts of fruit: peel, flesh, flesh + peel was discussed in many papers ( $15,17,20,22-24$ ). It is commonly known that the apple peel content of those compounds is from a few to several times higher as compared to the flesh or entire fruit, depending on the constituent, genotype, year, or, to a lesser degree, other conditions of the experiment. More interesting is the real proportion of epidermal zone of apple fruit (based on its weight) to the whole apple quantity, especially as this part of fruit is frequently discarded as a waste product during apple manufac-
turing or before eating. No information was found on that subject in the literature except some fragmentary data (25). Thus it seemed sensible to perform such an estimation. This paper, therefore, presents the results concerning antioxidant amount in relation to both, the whole fruit weight and its peel, in a wide range of cultivars monitored over two seasons to assess their importance and/or contribution as potential donors of bioactive compounds. We hoped that these results could be a good supplement to the present knowledge in this area.

## MATERIALS AND METHODS

Plant Material. The analyzed apple cultivars were obtained from the Experimental Orchard of the Department of Pomology, Warsaw University of Life Sciences (SGGW) in Warsaw-Wilanow ( $52{ }^{\circ} \mathrm{N}$ and $21^{\circ} \mathrm{E}$ ). All trees were planted in the spring of 1998 on rootstock M9. Trees were grown on the same type of soil and subjected to standard horticultural practices (fertilization, plant protection, orchard was not irrigated). Apples of the examined cultivars were harvested successively as they ripened from Sept 23 to Oct 28, 2004, and from Oct 3 to Nov 3,2005 , in the morning. Fruits were picked from the outer layer, from the designated trees, the same in both years, avoiding the tops and bottoms of the trees, and fruits typical and of similar size/diameter for a given apple cultivar were selected. Mature fruit were picked (according to starch test values, which was between 6 to 8 ). After harvest fruits were transferred into the laboratory, tissue samples for chemical analyses were collected and immediately frozen in liquid nitrogen and stored at $-80^{\circ} \mathrm{C}$ until analyses.

The detailed harvest dates, mean monthly temperature, and rainfall in 2004 and 2005 were already described (17).

Sample Preparation. Apples were cleaned with tissue paper. Then, each apple was divided into four sections, along a longitudinal axis, to remove core and seeds, and next, "sectors" from opposite sides were cut into small pieces. The other two parts of fruit were peeled with a peeler, with a thin layer of apple flesh (ca. $30-35 \%$ in relation to the weight of apple peel) remaining adhered to the peel. Thus the peel sample should be considered as the epidermic zone of apple fruit. Five replicates for the antioxidant content for each cultivar and type of tissue were conducted. Each of them included tissue samples from two fruits. The weight of a whole fruit of the investigated cultivars in consecutive seasons was measured in four replicates; each of them included ten fruits. The proportion of apple peel was calculated after weighing the whole fruit and its peel.
Determination of Bioactive Constituents. Frozen apple powder obtained by homogenization of the examined tissue type in liquid nitrogen was used for all determinations.
Thiols (total glutathione, GSH + GSSG, reduced and oxidized glutathione referred to as GSH in the text and its precursor L-cysteine) and ascorbate (the sum of ascorbate, AA, and dehydroascorbate, DHA, referred to as ASC). For both constituents the extraction was made in 0.1 M HCl containing PVPP, and they were centrifuged at 21900 g (for thiols) or 48000 g (for ASC) for 20 min at $4^{\circ} \mathrm{C}$. GSH and L-cysteine contents were determined in the same supernatant after the reduction with DTT (DL-dithiothreitol) and derivatization with monobromobimane. ASC content was measured after the complete oxidation of AA to DHA with ascorbate oxidase. DHA was then derivatized with o-phenylenediamine (OPDA).

Thiol derivatives were separated on a Symmetry $\mathrm{C}_{18}$ column (250 $\mathrm{mm} \times 4.6 \mathrm{~mm}, 5 \mu \mathrm{~m}$; Waters) by applying a solution of $10 \%$ methanol containing $0.25 \%(\mathrm{v} / \mathrm{v})$ glacial acetic acid (solvent A, pH 4.3 ) and $90 \%$ methanol with the same acetic acid concentration (solvent B, pH 3.9 ); the flow rate was $1 \mathrm{~mL} \mathrm{~min}^{-1}$. The eluent for ASC constituted 20\% methanol containing $800 \mathrm{mM} \mathrm{K}_{2} \mathrm{HPO}_{4}(\mathrm{pH} 7.8)$ with the same flow rate and column used.
For both ASC and thiols (GSH, l-cysteine) their derivatives were detected fluorometrically at 450 nm by excitation at 350 nm , and at 480 nm by excitation at 380 nm , respectively.

Phenolics were measured spectrophotometrically. Extraction was made in a mixture of methanol, formic acid, and distilled water (50: 1.5:48.5, pH 2.6 ). After centrifugation ( $24000 \mathrm{~g}, 4^{\circ} \mathrm{C}, 10 \mathrm{~min}$ ), the
supernatant was filtered through a $0.45 \mu \mathrm{~m}$ membrane and diluted with $10 \%$ ethanol ( $1: 4 \mathrm{v} / \mathrm{v}$ ). For the estimation of some subgroups of phenolics, the absorbance of the extracted solution was read at 280, 360 , and 520 nm to measure the total content of phenolics, flavonols, and anthocyanins, respectively. Gallic acid, quercetin, and cyanidin 3,5diglucoside chloride were used as standards for the total phenolics, flavonols, and anthocyanins, respectively. Chemicals, apparatus, and more detailed description of all chemical analyses were presented in the previous paper (17).

In the paper the antioxidant concentration is related to $\mathrm{a} w / \mathrm{w}$ ratio, that is in micrograms (for L-cysteine) or for other compounds in milligrams per gram fresh weight of the tested sample. The amount or quantity of antioxidant is referred to as micrograms or milligrams of a given compound per the entire apple fruit or its whole peel weight ("yield" of a constituent). The quantity (=amount) is counted on the basis of mean apple weight and its peel in relation to a particular cultivar and antioxidant concentration in these two tissue types.

Statistical Analysis and Data Presentation. To test the effect of cultivar and growing season, the obtained results of the quantity of phytocompounds in the tested types of tissue were elaborated by a twoway factorial ANOVA of Statgraphics Plus 4.1, separately for whole fruit (WF) and apple peel (AP). The significance of differences between means of the main effects (cultivar, year, and its interactions) was evaluated using the Newman-Keuls test at $5 \%$ probability level. Seasonal differences for both the whole fruit and apple peel were also expressed as a more informative 04/05 index. Additionally, a correlation between the antioxidant amount of apple peel and whole fruit and between fruit weight and the concentration or amount of antioxidants was calculated. Correlation coefficients of linear regression analyses were computed using the regression procedure in Microsoft Excel for Windows.

Antioxidant amounts in WF and AP were presented as means $\pm$ SD separately for each tested year, since growing seasons had a significant impact on the constituents tested.

## RESULTS

Statistical Analysis: Total ANOVA Results. Conditions of growing season had several times higher impact on the amounts of apple peel ascorbate and total phenolics as compared to WF ones (Table 1). A comparable year effect on thiols, irrespective of tissue type, was revealed. However, it should be stressed that the amount of thiols, especially L-cysteine, was more influenced by growing season as compared to cultivar, irrespective of the tested part of fruit. A contribution of apple peel to the WF quantity of tested components was highly cultivar dependent, whereas year effect concerned only total phenolics and ascorbate (Table 2).

Fruit Weight. Apple weight (g fruit ${ }^{-1}$ ) varied between 165 (cv. Pinova) and 276 (cv. Rubin) and from 139 (cv. Jonamac) to 252 (cv. Red Rome) in the consecutive years (Table 3). The extent of differences between the tested years in the size of apple fruit ranged from $0 \%$ (cvs. Elan, Granny Smith) up to $30 \%$ (cv. Prima). The peel comprised from $5.31 \pm 0.32 \%$ (cv. Fuji) to $8.16 \pm 1.06 \%$ (cv. Golden Delicious) share of the whole apple fruit. A weak negative correlation was found between fruit weight and peel content (data not shown).

Quantity of Bioactive Compounds in Whole Fruit (WF) and Entire Apple Peel (AP) in Relation to Genotype and Growing Season. Ascorbate $(A A+D H A)$. The mean quantity of ASC varied from 11.5 (cv. Gloster) to 49.4 (cv. Pilot) mg and from 8.75 (cv. Jonamac) to 50.2 (cv. Fiesta) mg per fruit in 2004 and 2005, respectively (Table 4). The entire peel ASC ranged from 3.13 (cv. McIntosh) to 12.4 (cv. Golden Delicious) mg and from 2.35 (cv. McIntosh) to 8.51 (cv. Granny Smith) mg per AP in the consecutive growing seasons. Only a small number of cultivars (e.g., Fuji, Granny Smith, and Priscilla) maintained (differences between growing seasons did not exceed

Table 1. Summary of Analysis of Variance (ANOVA) for Components Tested and Values of $F$ for Particular Sources of Variation in Relation to Whole Fruit (WF) and Apple Peel (AP) Antioxidant Amount and Their Significance

| component | WF antioxidant amount at source of variation |  |  | AP antioxidant amount at source of variation |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | cultivar (A) | year (B) | AB | cultivar (A) | year (B) | $A B$ |
| df | 18 | 1 | 18 | 18 | 1 | 18 |
| AA + DHA | $59.4{ }^{\text {a }}$ | $9.38{ }^{\text {b }}$ | $13.1{ }^{\text {a }}$ | $63.2{ }^{\text {a }}$ | $140^{\text {a }}$ | $8.74{ }^{\text {a }}$ |
| L-cysteine | $12.7^{\text {a }}$ | $116^{\text {a }}$ | $12.0^{\text {a }}$ | $9.71{ }^{\text {a }}$ | $112^{\text {a }}$ | $4.15{ }^{\text {a }}$ |
| GSH + GSSG | $23.3{ }^{\text {a }}$ | $35.4{ }^{\text {a }}$ | $9.23{ }^{\text {a }}$ | $18.9{ }^{\text {a }}$ | $40.2^{\text {a }}$ | $7.33{ }^{\text {a }}$ |
| phenolics | $16.6^{\text {a }}$ | $10.9{ }^{\text {b }}$ | $17.5^{\text {a }}$ | $48.2^{\text {a }}$ | $244{ }^{\text {a }}$ | $19.5{ }^{\text {a }}$ |
| flavonol | $20.6{ }^{\text {a }}$ | $33.4{ }^{\text {a }}$ | $24.1{ }^{\text {a }}$ | $57.4{ }^{\text {a }}$ | $28.8{ }^{\text {a }}$ | $17.7^{\text {a }}$ |
| anthocyanins | na | na | na | $81.4{ }^{\text {a }}$ | $2.23{ }^{\text {c }}$ | $17.9^{a}$ |
| fruit weight | $33.6{ }^{\text {a }}$ | $24.8{ }^{\text {a }}$ | $11.0^{a}$ | na | na | na |

${ }^{a}$ Significant at $\alpha=0.001 .{ }^{b}$ Significant at $\alpha=0.01$. ${ }^{c}$ Insignificant. na, not analyzed.

Table 2. Summary of Analysis of Variance (ANOVA) for Apple Peel Contribution to the Total Quantity of Components Tested and Values of $F$ for Particular Sources of Variation and Their Significance

|  | source of variation |  |  |
| :--- | :---: | :---: | :---: |
| component | cultivar (A) | year $(\mathrm{B})$ | AB |
| df | 18 | 1 | 18 |
| AA + DHA | $10.1^{a}$ | $11.2^{b}$ | $4.65^{a}$ |
| L-cysteine | $2.23^{b}$ | $2.89^{c}$ | $3.45^{a}$ |
| GSH + GSSG | $2.55^{b}$ | $0.11^{c}$ | $0.93^{c}$ |
| phenolics | $14.9^{a}$ | $57.2^{a}$ | $12.5^{a}$ |
| flavonol | $21.6^{a}$ | $0.22^{c}$ | $17.5^{a}$ |

${ }^{a}$ Significant at $\alpha=0.001$. ${ }^{b}$ Significant at $\alpha=0.01$. ${ }^{c}$ Not significant.
Table 3. Fruit Weight Depending on Cultivar and Growing Season $\left(\mathrm{g} \text { Fruit }{ }^{-1}\right)^{a}$

|  | year |  |  |
| :--- | :--- | :--- | :---: |
| cultivar | 2004 |  | 2005 |
| Elan | $225 \pm 14.1$ | $224 \pm 17.6$ | $04 / 05^{b}$ |
| Elstar | $194 \pm 2.8$ | $180 \pm 12.5$ | 1.00 |
| Fiesta | $181 \pm 7.0$ | $201 \pm 7.5$ | 0.90 |
| Fuji | $209 \pm 10.2$ | $189 \pm 3.0$ | 1.11 |
| Gala | $187 \pm 8.7$ | $163 \pm 7.6$ | 1.15 |
| Gloster | $194 \pm 13.7$ | $237 \pm 8.7$ | 0.82 |
| Golden Delicious | $198 \pm 13.1$ | $182 \pm 9.3$ | 1.09 |
| Granny Smith | $214 \pm 5.8$ | $215 \pm 4.9$ | 0.99 |
| Idared | $210 \pm 17.0$ | $195 \pm 13.3$ | 1.08 |
| Jonamac | $174 \pm 7.3$ | $139 \pm 12.3$ | 1.25 |
| McIntosh | $189 \pm 1.7$ | $197 \pm 15.7$ | 0.96 |
| Monroe | $191 \pm 9.7$ | $186 \pm 10.1$ | 1.03 |
| Pilot | $204 \pm 16.2$ | $158 \pm 8.0$ | 1.29 |
| Pinova | $165 \pm 10.7$ | $204 \pm 7.1$ | 0.81 |
| Prima | $210 \pm 4.1$ | $161 \pm 14.8$ | 1.30 |
| Priscilla | $177 \pm 21.5$ | $164 \pm 5.0$ | 1.08 |
| Red Rome | $226 \pm 15.1$ | $252 \pm 9.0$ | 0.90 |
| Rubin | $276 \pm 16.8$ | $235 \pm 8.1$ | 1.17 |
| Starking Delicious | $202 \pm 7.2$ | $159 \pm 25.0$ | 1.27 |
| average | $201 \mathrm{~b}^{c}$ | 192 a | 1.07 |
|  |  |  |  |

[^1]20\%) their ascorbic acid quantity over years both in WF and AP. On average, a significantly higher amount of ASC was noted in 2004, irrespective of the tissue tested. The proportion of AP in the WF quantity also varied significantly, depending on the year, from $17.8 \%$ to $52.4 \%$ (cvs. Pilot-Rubin) and from $14.3 \%$ to $37.4 \%$ (cvs. Fiesta-Granny Smith). Differences in seasonal variation of apple peel ASC share strictly depended on the genotype and expanded from unchangeable level (cvs. Gala and Granny Smith) up to $110 \%$ in the case of Fiesta cv. The AP
contribution in WF ASC amount in 2004 was significantly higher as compared to that in 2005.

A very high correlation existed between AP and WF quantity of ascorbate, regardless of the growing season (Table 4).

Glutathione $(G S H+G S S G)$. The amount of this tripeptide ranged from 0.89 (cv. McIntosh) to 3.00 (cv. Starking Delicious) mg and from 1.04 (cv. Golden Delicious) to 4.46 (cv. Red Rome) mg per WF in 2004 and 2005, respectively (Table 5), whereas the AP amount of GSH was ca. 8 times lower, on average, showing values from 0.12 (cv. McIntosh) to 0.35 (cvs. Granny Smith and Starking Delicious) mg and from 0.16 (cvs. Elstar and Gala) to 0.55 (cv. Gloster) mg in the consecutive tested years. The mean GSH value in 2005 was significantly higher as compared to that in 2004, regardless of the examined part of fruit. Moreover, a similar increase, i.e., $24 \%$ and $29 \%$, was noted for WF and AP, respectively. Only a few genotypes, Gloster, Golden Delicious, McIntosh, Pinova, Prima, and Red Rome cvs. expressed differences between years exceeding $30 \%$. The proportion of AP in the whole fruit GSH quantity varied from $10.1 \%$ to $20.7 \%$ (cvs. Gala-Rubin) and from $9.0 \%$ to $17.7 \%$ (cvs. Gala-Pilot) in 2004 and 2005, respectively. It should be noted, however, that the AP contribution to the whole apple GSH quantity was as a rule stable over the years within a cultivar (with only two exceptions: Monroe and Pilot) and amounted approximately to $14 \%$, on average.

As in the case of ascorbate a high correlation between AP and WF amount of glutathione was proved (Table 5).

L-Cysteine. The whole fruit quantity of L-cysteine amounted to from 56.0 (cv. McIntosh) to 166 (cv. Pilot) $\mu \mathrm{g} \mathrm{WF}{ }^{-1}$ in 2004 and from 70 (cv. Jonamac) to 566 (cv. Gloster) $\mu \mathrm{g} \mathrm{WF}{ }^{-1}$ in 2005 (Table 6). So, the diversity between cultivars was considerably bigger in 2005 as compared to 2004, i.e., 8.1- and 3.0-fold. AP L-cysteine amount was several times lower and varied from 6.3 (cv. McIntosh) to $16.2 \mu \mathrm{~g}$ (cv. Golden Delicious) in 2004 and from 8.1 (cv. McIntosh) to $28.4 \mu \mathrm{~g} \mathrm{AP}{ }^{-1}$ (cv. Gloster) in 2005.

A significantly higher amount of this amino acid was displayed by apples harvested in 2005, greater or smaller increase was observed in almost all cultivars, and a similar impact of growing season concerned both WF and AP.

The mean proportion of AP L-cysteine in WF was between $10 \%$ and $11 \%$, depending on growing season with the range of cultivar variability between $7.5 \%$ and $14.7 \%$ and between $5.4 \%$ and $15 \%$ in 2004 and 2005, respectively (Table 6). Greater fluctuations of L-cysteine were observed between years in particular examined cultivars as compared to GSH. Contrary to ascorbate the increased quantity of both thiols in 2005 was accompanied by a slight decrease of its share in WF (Tables 5 and 6).

Table 4. Total Amounts of Ascorbate (AA + DHA) in Whole Fruit and Apple Peel (mg) as Well as Apple Peel as a Contributor to Whole Fruit Amount of Ascorbate (\%) Depending on Cultivar and Growing Seasona

| cultivar | amount of ascorbate ${ }^{\text {b }}$ |  |  |  |  |  | contribution of apple peel to whole fruit amount of ascorbate |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | whole fruit (WF) |  |  | apple peel (AP) |  |  |  |  |  |
|  | 2004 | 2005 | 04/05 ${ }^{\text {c }}$ | 2004 | 2005 | 04/05 | 2004 | 2005 | 04/05 |
| Elan | $27.1 \pm 3.63$ | $14.3 \pm 3.70$ | 1.90 | $6.94 \pm 1.53$ | $3.99 \pm 1.15$ | 1.74 | $25.5 \pm 3.6$ | $28.0 \pm 3.9$ | 0.91 |
| Elstar | $28.6 \pm 5.56$ | $20.2 \pm 2.99$ | 1.42 | $6.18 \pm 0.42$ | $2.95 \pm 0.49$ | 2.09 | $22.3 \pm 4.8$ | $14.8 \pm 2.6$ | 1.51 |
| Fiesta | $34.4 \pm 1.47$ | $50.2 \pm 9.19$ | 0.69 | $10.4 \pm 2.52$ | $7.02 \pm 0.82$ | 1.48 | $30.1 \pm 7.4$ | $14.3 \pm 2.8$ | 2.10 |
| Fuji | $20.5 \pm 1.28$ | $21.5 \pm 3.03$ | 0.95 | $3.99 \pm 0.51$ | $4.65 \pm 0.62$ | 0.86 | $19.5 \pm 1.5$ | $22.1 \pm 4.8$ | 0.88 |
| Gala | $18.8 \pm 0.56$ | $13.5 \pm 3.50$ | 1.39 | $4.34 \pm 0.61$ | $2.88 \pm 0.43$ | 1.51 | $23.2 \pm 3.7$ | $22.4 \pm 5.8$ | 1.04 |
| Gloster | $11.5 \pm 1.38$ | $20.5 \pm 4.65$ | 0.56 | $4.28 \pm 0.34$ | $5.30 \pm 0.85$ | 0.81 | $37.8 \pm 5.5$ | $27.5 \pm 10$ | 1.37 |
| Golden Delicious | $40.6 \pm 4.77$ | $37.8 \pm 4.01$ | 1.07 | $12.4 \pm 0.37$ | $8.35 \pm 1.23$ | 1.49 | $31.0 \pm 4.8$ | $22.3 \pm 4.5$ | 1.39 |
| Granny Smith | $25.2 \pm 3.14$ | $22.8 \pm 1.60$ | 1.11 | $9.56 \pm 0.62$ | $8.51 \pm 1.18$ | 1.12 | $38.6 \pm 6.7$ | $37.4 \pm 3.7$ | 1.03 |
| Idared | $27.7 \pm 3.42$ | $21.0 \pm 3.31$ | 1.32 | $10.1 \pm 1.02$ | $5.42 \pm 1.23$ | 1.86 | $37.3 \pm 7.7$ | $26.3 \pm 6.9$ | 1.42 |
| Jonamac | $13.4 \pm 1.32$ | $8.75 \pm 0.89$ | 1.53 | $3.58 \pm 0.31$ | $2.71 \pm 0.42$ | 1.32 | $26.8 \pm 1.4$ | $31.1 \pm 4.8$ | 0.86 |
| Mclntosh | $13.9 \pm 1.02$ | $8.81 \pm 3.60$ | 1.58 | $3.13 \pm 0.17$ | $2.35 \pm 0.38$ | 1.33 | $22.6 \pm 2.7$ | $31.7 \pm 16.3$ | 0.71 |
| Monroe | $20.0 \pm 2.30$ | $21.2 \pm 3.79$ | 0.94 | $6.73 \pm 0.81$ | $4.36 \pm 0.65$ | 1.54 | $34.4 \pm 8.8$ | $20.8 \pm 2.7$ | 1.65 |
| Pilot | $49.4 \pm 2.39$ | $33.2 \pm 6.36$ | 1.49 | $8.79 \pm 0.36$ | $6.28 \pm 1.49$ | 1.40 | $17.8 \pm 0.4$ | $18.9 \pm 3.4$ | 0.94 |
| Pinova | $21.5 \pm 2.33$ | $33.3 \pm 3.79$ | 0.65 | $5.62 \pm 0.79$ | $5.96 \pm 1.01$ | 0.94 | $26.6 \pm 6.0$ | $18.0 \pm 3.1$ | 1.48 |
| Prima | $22.1 \pm 4.07$ | $12.1 \pm 1.18$ | 1.83 | $4.33 \pm 0.55$ | $4.39 \pm 0.80$ | 0.99 | $20.5 \pm 6.4$ | $37.1 \pm 11$ | 0.55 |
| Priscilla | $19.7 \pm 5.04$ | $18.6 \pm 5.02$ | 1.06 | $4.30 \pm 1.02$ | $4.28 \pm 0.33$ | 1.00 | $23.5 \pm 10.9$ | $24.9 \pm 9.2$ | 0.94 |
| Red Rome | $20.7 \pm 1.89$ | $30.7 \pm 4.69$ | 0.67 | $7.07 \pm 0.26$ | $7.37 \pm 0.81$ | 0.96 | $34.3 \pm 3.1$ | $24.4 \pm 3.9$ | 1.41 |
| Rubin | $21.8 \pm 2.68$ | $25.0 \pm 6.85$ | 0.87 | $11.4 \pm 1.69$ | $8.36 \pm 0.97$ | 1.36 | $52.4 \pm 6.0$ | $36.2 \pm 12$ | 1.45 |
| Starking Delicious | $19.0 \pm 3.22$ | $10.9 \pm 1.18$ | 1.74 | $5.91 \pm 0.66$ | $4.00 \pm 0.44$ | 1.48 | $31.8 \pm 6.6$ | $37.0 \pm 6.5$ | 0.86 |
| average | $24.0 \mathrm{~b}^{\text {d }}$ | 22.3 a | 1.08 | 6.79 b | 5.22 a | 1.30 | 29.3 b | 26.1 a | 1.12 |
| WF-AP ${ }^{e}$ ascorbate | $0.690^{f}$ | $0.728^{f}$ |  |  |  |  |  |  |  |

${ }^{a}$ Data are presented as means $\pm \mathrm{SD}, n=5 .{ }^{b}$ Amount of ascorbate was calculated on the basis of the concentration (mg g ${ }^{-1} \mathrm{FW}$ ) and the mean weight of whole fruit and its entire peel. ${ }^{c} 04 / 05=$ the value obtained by dividing the amount noted in 2004 by 2005. ${ }^{d}$ Mean separation for years by Newman-Keuls test ( $p<0.05$ ). ${ }^{e}$ Correlation between whole fruit and the apple peel quantity of ascorbate in the consecutive years. ${ }^{f}$ Significant at $\alpha=0.001$. Bold type indicates the highest and the lowest values.

Table 5. Total Amounts of Glutathione (GSH + GSSG) in Whole Fruit and Apple Peel (mg) as Well as Apple Peel as a Contributor to Whole Fruit Amount of Glutathione (\%) Depending on Cultivar and Growing Season ${ }^{a}$

| cultivar | amount of glutathione ${ }^{b}$ |  |  |  |  |  | contribution of apple peel to whole fruit amount of glutathione |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | whole fruit (WF) |  |  | apple peel (AP) |  |  |  |  |  |
|  | 2004 | 2005 | 04/05 ${ }^{\text {c }}$ | 2004 | 2005 | 04/05 | 2004 | 2005 | 04/05 |
| Elan | $2.34 \pm 0.42$ | $2.30 \pm 0.33$ | 1.02 | $0.25 \pm 0.04$ | $0.27 \pm 0.07$ | 0.93 | $11.3 \pm 4.1$ | $11.7 \pm 2.6$ | 0.97 |
| Elstar | $1.19 \pm 0.28$ | $1.06 \pm 0.11$ | 1.12 | $0.14 \pm 0.01$ | $0.16 \pm 0.01$ | 0.87 | $11.9 \pm 3.0$ | $15.6 \pm 2.3$ | 0.76 |
| Fiesta | $2.09 \pm 0.53$ | $2.84 \pm 0.23$ | 0.73 | $0.21 \pm 0.05$ | $0.27 \pm 0.05$ | 0.78 | $10.4 \pm 1.8$ | $9.6 \pm 2.1$ | 1.08 |
| Fuji | $1.94 \pm 0.32$ | $2.15 \pm 0.38$ | 0.90 | $0.20 \pm 0.02$ | $0.25 \pm 0.03$ | 0.80 | $10.5 \pm 2.2$ | $11.9 \pm 3.7$ | 0.88 |
| Gala | $1.47 \pm 0.21$ | $1.76 \pm 0.11$ | 0.83 | $0.15 \pm 0.00$ | $0.16 \pm 0.03$ | 0.94 | $10.1 \pm 1.4$ | $9.0 \pm 1.6$ | 1.12 |
| Gloster | $1.76 \pm 0.37$ | $3.94 \pm 0.87$ | 0.45 | $0.24 \pm 0.02$ | $0.55 \pm 0.09$ | 0.44 | $14.2 \pm 4.7$ | $14.5 \pm 4.6$ | 0.98 |
| Golden Delicious | $1.53 \pm 0.05$ | $1.04 \pm 0.01$ | 1.47 | $0.27 \pm 0.06$ | $0.18 \pm 0.01$ | 1.50 | $17.9 \pm 4.1$ | $17.6 \pm 1.5$ | 1.02 |
| Granny Smith | $2.80 \pm 0.49$ | $3.16 \pm 0.37$ | 0.89 | $0.35 \pm 0.07$ | $0.42 \pm 0.02$ | 0.83 | $12.4 \pm 2.4$ | $13.3 \pm 1.0$ | 0.93 |
| Idared | $1.33 \pm 0.41$ | $1.86 \pm 0.40$ | 0.72 | $0.21 \pm 0.01$ | $0.25 \pm 0.04$ | 0.84 | $16.3 \pm 4.6$ | $14.2 \pm 4.6$ | 1.15 |
| Jonamac | $1.34 \pm 0.30$ | $1.06 \pm 0.10$ | 1.26 | $0.21 \pm 0.03$ | $0.18 \pm 0.03$ | 1.17 | $15.8 \pm 3.1$ | $17.5 \pm 4.3$ | 0.90 |
| Mclntosh | $0.89 \pm 0.11$ | $1.33 \pm 0.19$ | 0.67 | $0.12 \pm 0.01$ | $0.17 \pm 0.03$ | 0.71 | $13.9 \pm 3.1$ | $12.9 \pm 4.0$ | 1.08 |
| Monroe | $1.00 \pm 0.29$ | $1.84 \pm 0.04$ | 0.54 | $0.18 \pm 0.01$ | $0.23 \pm 0.01$ | 0.78 | $18.6 \pm 6.1$ | $12.3 \pm 0.8$ | 1.51 |
| Pilot | $2.65 \pm 0.47$ | $1.55 \pm 0.15$ | 1.71 | $0.31 \pm 0.06$ | $0.27 \pm 0.01$ | 1.15 | $11.8 \pm 2.5$ | $17.7 \pm 1.1$ | 0.67 |
| Pinova | $0.90 \pm 0.13$ | $1.49 \pm 0.17$ | 0.60 | $0.13 \pm 0.01$ | $0.19 \pm 0.03$ | 0.68 | $14.7 \pm 2.1$ | $13.1 \pm 2.5$ | 1.12 |
| Prima | $1.00 \pm 0.12$ | $1.34 \pm 0.09$ | 0.75 | $0.14 \pm 0.04$ | $0.20 \pm 0.01$ | 0.70 | $14.1 \pm 5.3$ | $15.1 \pm 1.4$ | 0.93 |
| Priscilla | $1.27 \pm 0.19$ | $2.03 \pm 0.34$ | 0.63 | $0.19 \pm 0.04$ | $0.23 \pm 0.02$ | 0.83 | $15.4 \pm 4.7$ | $11.6 \pm 1.1$ | 1.33 |
| Red Rome | $1.82 \pm 0.75$ | $4.46 \pm 0.25$ | 0.41 | $0.21 \pm 0.03$ | $0.51 \pm 0.08$ | 0.41 | $12.6 \pm 4.6$ | $11.5 \pm 2.1$ | 1.10 |
| Rubin | $1.08 \pm 0.11$ | $1.36 \pm 0.05$ | 0.79 | $0.22 \pm 0.03$ | $0.22 \pm 0.01$ | 1.00 | $20.7 \pm 5.1$ | $16.3 \pm 1.3$ | 1.27 |
| Starking Delicious | $3.00 \pm 0.66$ | $2.35 \pm 0.62$ | 1.28 | $0.35 \pm 0.09$ | $0.34 \pm 0.12$ | 1.03 | $12.4 \pm 6.2$ | $15.5 \pm 8.2$ | 0.80 |
| average | $1.65 \mathrm{a}^{\text {d }}$ | 2.05 b | 0.80 | 0.21 a | 0.27 b | 0.78 | 13.9 a | 13.7 a | 1.01 |
| WF-AP ${ }^{\text {e }}$ glutathione | $0.872^{f}$ | $0.930^{f}$ |  |  |  |  |  |  |  |

[^2]A high correlation was proved between AP and WF amount of L-cysteine (Table 6).
Phenolics. Apple phenolic quantity varied from 35.7 (cv. Elan) to 149 (cv. Idared) $\mathrm{mg} \mathrm{WF}^{-1}$ and from 44.5 (cv. Fiesta) to 150 (cv. Granny Smith) $\mathrm{mg} \mathrm{WF}^{-1}$ in 2004 and 2005, respectively (Table 7). A total AP amount of phenolics ranged from 6.33 (cv. Elan) to 24.5 (cv. Granny Smith) $\mathrm{mg} \mathrm{AP}^{-1}$ in

2004 and from 6.94 (cv. Fiesta) to 49.2 (cv. Starking Delicious) $\mathrm{mg} \mathrm{AP}{ }^{-1}$ in 2005.

Although, on average, a significantly higher amount of phenolics for both tested parts of fruits was noted in 2005, the pattern of its fluctuation in particular growing seasons was highly cultivar as well as tissue-type dependent. The more consistent increase was observed for apple peel, since almost all cultivars were character-

Table 6. Total Amounts of l-Cysteine in Whole Fruit and Apple Peel ( $\mu \mathrm{g}$ ) as Well as Apple Peel as a Contributor to Whole Fruit Amount of l-Cysteine (\%) Depending on Cultivar and Growing Seasona

| cultivar | amount of L-cysteine ${ }^{\text {b }}$ |  |  |  |  |  | contribution of apple peel to whole fruit amount of L-cysteine |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | whole fruit (WF) |  |  | apple peel (AP) |  |  |  |  |  |
|  | 2004 | 2005 | 04/05 ${ }^{\text {c }}$ | 2004 | 2005 | 04/05 | 2004 | 2005 | 04/05 |
| Elan | $125 \pm 25$ | $181 \pm 26$ | 0.69 | $11.2 \pm 0.5$ | $18.7 \pm 1.4$ | 0.60 | $9.3 \pm 2.4$ | $10.6 \pm 2.4$ | 0.88 |
| Elstar | $107 \pm 31$ | $281 \pm 49$ | 0.38 | $9.2 \pm 0.8$ | $21.6 \pm 3.4$ | 0.43 | $9.2 \pm 2.9$ | $7.9 \pm 2.2$ | 1.16 |
| Fiesta | $121 \pm 35$ | $168 \pm 11$ | 0.72 | $11.7 \pm 1.5$ | $13.4 \pm 2.2$ | 0.87 | $10.1 \pm 2.2$ | $7.9 \pm 0.8$ | 1.28 |
| Fuji | $94 \pm 15$ | $136 \pm 33$ | 0.69 | $6.9 \pm 0.7$ | $14.5 \pm 0.9$ | 0.48 | $7.5 \pm 1.6$ | $11.1 \pm 3.1$ | 0.68 |
| Gala | $102 \pm 19$ | $105 \pm 26$ | 0.97 | $9.7 \pm 0.3$ | $10.2 \pm 2.8$ | 0.95 | $9.7 \pm 1.6$ | $9.7 \pm 0.7$ | 1.00 |
| Gloster | $89 \pm 9.3$ | $566 \pm 203$ | 0.16 | $12.6 \pm 4.4$ | $28.4 \pm 3.7$ | 0.44 | $14.7 \pm 6.9$ | $5.5 \pm 2.2$ | 2.67 |
| Golden Delicious | $111 \pm 14$ | $100 \pm 22$ | 1.11 | $16.2 \pm 6.1$ | $14.3 \pm 1.3$ | 1.13 | $14.4 \pm 4.0$ | $15.0 \pm 2.2$ | 0.96 |
| Granny Smith | $156 \pm 30$ | $183 \pm 37$ | 0.85 | $14.8 \pm 4.5$ | $25.4 \pm 0.3$ | 0.58 | $9.3 \pm 1.3$ | $14.3 \pm 3.0$ | 0.65 |
| Idared | $61 \pm 7.8$ | $195 \pm 32$ | 0.31 | $7.8 \pm 0.4$ | $15.2 \pm 4.2$ | 0.51 | $13.0 \pm 0.9$ | $7.9 \pm 2.3$ | 1.64 |
| Jonamac | $73 \pm 12$ | $70 \pm 15$ | 1.04 | $9.0 \pm 1.3$ | $9.0 \pm 2.1$ | 1.00 | $12.4 \pm 1.5$ | $13.4 \pm 4.9$ | 0.92 |
| Mclntosh | $56 \pm 6.0$ | $79 \pm 7.6$ | 0.71 | $6.3 \pm 0.3$ | $8.1 \pm 1.4$ | 0.78 | $11.3 \pm 1.8$ | $10.3 \pm 2.7$ | 1.10 |
| Monroe | $74 \pm 9.5$ | $168 \pm 18$ | 0.44 | $9.5 \pm 0.6$ | $8.9 \pm 3.1$ | 1.07 | $13.0 \pm 2.6$ | $5.4 \pm 2.2$ | 2.41 |
| Pilot | $166 \pm 15$ | $171 \pm 14$ | 0.97 | $14.9 \pm 2.7$ | $18.8 \pm 2.1$ | 0.79 | $9.0 \pm 1.0$ | $11.0 \pm 1.3$ | 0.82 |
| Pinova | $73 \pm 9.2$ | $154 \pm 23$ | 0.47 | $8.1 \pm 0.6$ | $16.9 \pm 1.8$ | 0.48 | $11.3 \pm 2.0$ | $11.0 \pm 0.5$ | 1.03 |
| Prima | $75 \pm 7.5$ | $126 \pm 4.5$ | 0.59 | $7.9 \pm 2.1$ | $16.6 \pm 1.3$ | 0.48 | $10.7 \pm 3.3$ | $13.2 \pm 1.3$ | 0.81 |
| Priscilla | $89 \pm 3.4$ | $173 \pm 33$ | 0.51 | $10.8 \pm 1.1$ | $19.1 \pm 0.7$ | 0.56 | $12.2 \pm 1.7$ | $11.3 \pm 1.9$ | 1.08 |
| Red Rome | $100 \pm 25$ | $335 \pm 48$ | 0.30 | $13.7 \pm 0.4$ | $18.0 \pm 10.1$ | 0.76 | $14.1 \pm 3.1$ | $5.7 \pm 3.5$ | 2.47 |
| Rubin | $91 \pm 13$ | $127 \pm 13$ | 0.72 | $11.2 \pm 1.4$ | $16.9 \pm 0.8$ | 0.66 | $12.5 \pm 3.0$ | $13.5 \pm 2.0$ | 0.93 |
| Starking Delicious | $131 \pm 31$ | $137 \pm 43$ | 0.96 | $9.8 \pm 3.5$ | $13.4 \pm 1.6$ | 0.73 | $7.8 \pm 3.7$ | $10.7 \pm 3.1$ | 0.73 |
| average | $99.6 \mathrm{a}^{\text {d }}$ | 182 b | 0.55 | 10.6 a | 16.2 b | 0.65 | 11.1 a | 10.3 a | 1.08 |
| WF-AP ${ }^{\text {L }}$-Cys | $0.709^{f}$ | $0.729^{f}$ |  |  |  |  |  |  |  |

${ }^{a}$ Data are presented as means $\pm \mathrm{SD}, n=5 .{ }^{b}$ Amount of L-cysteine was calculated on the basis on the concentration ( $\mu \mathrm{g} \mathrm{g}^{-1} \mathrm{FW}$ ) and the mean weight of whole fruit and its entire peel. ${ }^{c} 04 / 05=$ the value obtained by dividing the amount noted in 2004 by 2005. ${ }^{d}$ Mean separation for years by Newman-Keuls test ( $p<0.05$ ). ${ }^{e}$ Correlation between whole fruit and the apple peel quantity of L-cysteine in the consecutive years. ${ }^{f}$ Significant at $\alpha=0.001$. Bold type indicates the highest and the lowest values.

Table 7. Total Amounts of Phenolics in Whole Fruit and Apple Peel (Expressed in mg of Gallic Acid Equivalent) as Well as Apple Peel as a Contributor to Whole Fruit Amount (\%) Depending on Cultivar and Growing Seasona ${ }^{\text {a }}$

| cultivar | amount of phenolics ${ }^{\text {b }}$ |  |  |  |  |  | contribution of apple peel to whole fruit amount of phenolics |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | whole fruit (WF) |  |  | apple peel (AP) |  |  |  |  |  |
|  | 2004 | 2005 | 04/05 ${ }^{\text {c }}$ | 2004 | 2005 | 04/05 | 2004 | 2005 | 04/05 |
| Elan | $35.7 \pm 2.61$ | $91.0 \pm 18.7$ | 0.39 | $6.33 \pm 1.18$ | $17.9 \pm 2.68$ | 0.35 | $17.9 \pm 4.0$ | $20.1 \pm 4.0$ | 0.89 |
| Elstar | $73.8 \pm 11.6$ | $103 \pm 29.1$ | 0.72 | $14.4 \pm 0.52$ | $19.2 \pm 1.65$ | 0.75 | $20.0 \pm 3.6$ | $19.9 \pm 6.2$ | 1.00 |
| Fiesta | $69.0 \pm 5.25$ | $44.5 \pm 14.8$ | 1.55 | $8.77 \pm 2.17$ | $6.94 \pm 0.99$ | 1.26 | $13.0 \pm 4.4$ | $17.2 \pm 6.9$ | 0.75 |
| Fuji | $60.1 \pm 10.2$ | $90.6 \pm 14.9$ | 0.66 | $11.4 \pm 0.31$ | $9.88 \pm 2.64$ | 1.15 | $19.4 \pm 3.1$ | $11.1 \pm 3.4$ | 1.75 |
| Gala | $76.3 \pm 5.58$ | $76.5 \pm 11.8$ | 1.00 | $10.8 \pm 0.68$ | $14.6 \pm 1.83$ | 0.74 | $14.2 \pm 1.6$ | $19.6 \pm 4.0$ | 0.72 |
| Gloster | $58.0 \pm 6.37$ | $96.3 \pm 17.2$ | 0.60 | $15.0 \pm 1.41$ | $30.4 \pm 2.78$ | 0.49 | $26.3 \pm 5.1$ | $32.6 \pm 7.7$ | 0.81 |
| Golden Delicious | $88.1 \pm 6.63$ | $53.6 \pm 15.8$ | 1.64 | $15.5 \pm 1.19$ | $10.6 \pm 1.73$ | 1.46 | $17.6 \pm 1.1$ | $21.6 \pm 8.3$ | 0.81 |
| Granny Smith | $45.1 \pm 5.40$ | $150 \pm 25.4$ | 0.30 | $24.5 \pm 2.49$ | $33.8 \pm 6.83$ | 0.72 | $55.2 \pm 12$ | $23.2 \pm 6.7$ | 2.38 |
| Idared | $149 \pm 6.60$ | $80.5 \pm 12.2$ | 1.85 | $21.0 \pm 3.78$ | $26.8 \pm 8.06$ | 0.78 | $14.1 \pm 2.4$ | $33.9 \pm 11$ | 0.42 |
| Jonamac | $77.3 \pm 9.22$ | $60.3 \pm 11.1$ | 1.28 | $8.99 \pm 1.03$ | $8.96 \pm 2.36$ | 1.00 | $11.7 \pm 1.0$ | $15.2 \pm 4.4$ | 0.77 |
| Mclntosh | $120 \pm 10.0$ | $68.2 \pm 14.1$ | 1.76 | $11.4 \pm 1.54$ | $23.4 \pm 2.14$ | 0.49 | $9.7 \pm 2.2$ | $35.8 \pm 9.2$ | 0.27 |
| Monroe | $73.7 \pm 12.6$ | $84.6 \pm 8.83$ | 0.87 | $13.1 \pm 3.36$ | $32.0 \pm 1.23$ | 0.41 | $18.0 \pm 4.6$ | $38.1 \pm 3.7$ | 0.47 |
| Pilot | $69.7 \pm 17.2$ | $93.3 \pm 25.6$ | 0.75 | $9.09 \pm 1.68$ | $11.8 \pm 1.19$ | 0.77 | $13.5 \pm 3.3$ | $13.6 \pm 4.5$ | 0.99 |
| Pinova | $84.5 \pm 7.86$ | $122 \pm 41.3$ | 0.69 | $7.60 \pm 0.07$ | $17.3 \pm 4.95$ | 0.44 | $9.1 \pm 0.9$ | $15.7 \pm 6.7$ | 0.58 |
| Prima | $76.5 \pm 10.5$ | $47.0 \pm 15.2$ | 1.63 | $15.4 \pm 1.56$ | $15.8 \pm 1.34$ | 0.97 | $20.6 \pm 4.7$ | $36.0 \pm 9.6$ | 0.57 |
| Priscilla | $70.1 \pm 15.0$ | $85.5 \pm 5.57$ | 0.82 | $8.43 \pm 0.71$ | $15.3 \pm 3.06$ | 0.55 | $12.4 \pm 2.2$ | $18.1 \pm 4.4$ | 0.68 |
| Red Rome | $114 \pm 17.7$ | $109 \pm 17.5$ | 1.04 | $17.8 \pm 2.66$ | $26.5 \pm 7.65$ | 0.67 | $15.7 \pm 0.8$ | $25.8 \pm 11$ | 0.61 |
| Rubin | $60.7 \pm 3.31$ | $51.5 \pm 1.90$ | 1.18 | $8.02 \pm 0.90$ | $10.7 \pm 2.86$ | 0.75 | $13.2 \pm 1.1$ | $20.8 \pm 5.6$ | 0.63 |
| Starking Delicious | $108 \pm 12.9$ | $143 \pm 25.8$ | 0.75 | $14.8 \pm 1.66$ | $49.2 \pm 8.58$ | 0.30 | $13.8 \pm 1.5$ | $34.8 \pm 5.1$ | 0.40 |
| average | $79.4 \mathrm{a}^{\text {d }}$ | 86.9 b | 0.91 | 12.8 a | 20.1 b | 0.64 | 17.6 a | 23.8 b | 0.74 |
| WF-AP ${ }^{\text {e }}$ phenolics | $0.346{ }^{f}$ | $0.564^{g}$ |  |  |  |  |  |  |  |

${ }^{a}$ Data are presented as means $\pm$ SD, $n=5 .{ }^{b}$ Amount of phenolics was calculated on the basis of the concentration (mg g ${ }^{-}$( FW) and the mean weight of whole fruit and its entire peel. ${ }^{c} 04 / 05=$ the value obtained by dividing the amount noted in 2004 by 2005. ${ }^{d}$ Mean separation for years by Newman-Keuls test ( $p<0.05$ ). ${ }^{e}$ Correlation between whole fruit and the apple peel quantity of phenolics in the consecutive years. ${ }^{f}$ Not significant. ${ }^{g}$ Significant at $\alpha=0.01$. Bold type indicates the highest and the lowest values.
ized by the higher AP global phenolics in 2005 as compared to WF. The marked increase of AP total phenolic amount in 2005 was accompanied by an increase of AP share in WF from $17.6 \%$ (2004) to $23.8 \%$ (2005). Nevertheless, this index was highly cultivar dependent and varied from $9.1 \%$ (cv. Pinova) to $55.2 \%$ (cv. Granny Smith) in 2004 and from $11.1 \%$ (cv. Fuji) to $38.1 \%$ (cv. Monroe) in 2005. Differences between years reflected the extent of calculated
relationship ( $04 / 05$ ratio), which amounted to from 0.27 (cv. McIntosh) to 2.38 (cv. Granny Smith).

A great diversity occurred in flavonols, especially in AP flavonol quantity, and its contribution to WF amount (Table 8). The WF amount varied between 4.63 and $69.8 \mathrm{mg} \mathrm{WF}^{-1}$ (cvs. Prima-Idared) and from 11.0 to $36.9 \mathrm{mg} \mathrm{WF}^{-1}$ (cvs. Fiesta-Pinova) in 2004 and 2005, respectively. The fluctuation

Table 8. Total Amounts of Flavonols in Whole Fruit and Apple Peel (Expressed in mg of Quercetin) as Well as Apple Peel as a Contributor to Whole Fruit Amount of Flavonols (\%) Depending on Cultivar and Growing Season ${ }^{a}$

| cultivar | amount of flavonols ${ }^{\text {b }}$ |  |  |  |  |  | contribution of apple peel to whole fruit amount of flavonols |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | whole fruit (WF) |  |  | apple peel (AP) |  |  |  |  |  |
|  | 2004 | 2005 | 04/05 ${ }^{\text {c }}$ | 2004 | 2005 | 04/05 | 2004 | 2005 | 04/05 |
| Elan | $33.5 \pm 2.97$ | $19.4 \pm 7.05$ | 1.73 | $1.70 \pm 0.49$ | $6.00 \pm 2.17$ | 0.28 | $5.0 \pm 1.1$ | $32.9 \pm 12$ | 0.15 |
| Elstar | $18.2 \pm 3.03$ | $12.0 \pm 1.76$ | 1.52 | $6.75 \pm 0.84$ | $4.75 \pm 0.66$ | 1.42 | $37.2 \pm 2.0$ | $40.4 \pm 9.1$ | 0.92 |
| Fiesta | $37.7 \pm 6.88$ | $11.0 \pm 3.28$ | 3.43 | $4.23 \pm 1.29$ | $2.40 \pm 0.79$ | 1.76 | $12.1 \pm 6.4$ | $22.7 \pm 7.3$ | 0.53 |
| Fuji | $23.6 \pm 6.27$ | $16.1 \pm 2.10$ | 1.47 | $4.42 \pm 0.60$ | $6.23 \pm 1.26$ | 0.71 | $20.1 \pm 6.8$ | $38.5 \pm 3.7$ | 0.52 |
| Gala | $23.8 \pm 5.60$ | $14.0 \pm 3.14$ | 1.70 | $4.15 \pm 0.38$ | $4.69 \pm 1.19$ | 0.88 | $18.1 \pm 3.6$ | $35.8 \pm 15$ | 0.50 |
| Gloster | $16.4 \pm 1.67$ | $26.4 \pm 6.13$ | 0.62 | $9.52 \pm 0.86$ | $9.98 \pm 2.10$ | 0.95 | $58.7 \pm 9.6$ | $41.5 \pm 21$ | 1.41 |
| Golden Delicious | $16.2 \pm 2.81$ | $11.5 \pm 2.51$ | 1.41 | $5.63 \pm 1.03$ | $3.74 \pm 0.13$ | 1.50 | $34.8 \pm 1.7$ | $33.8 \pm 8.0$ | 1.03 |
| Granny Smith | $13.0 \pm 2.18$ | $33.1 \pm 4.14$ | 0.39 | $20.2 \pm 3.75$ | $16.7 \pm 3.49$ | 1.21 | $158 \pm 33$ | $50.4 \pm 8.7$ | 3.13 |
| Idared | $69.8 \pm 15.6$ | $11.7 \pm 2.47$ | 5.97 | $9.95 \pm 2.15$ | $7.42 \pm 1.30$ | 1.34 | $15.4 \pm 6.7$ | $66.8 \pm 26$ | 0.23 |
| Jonamac | $23.5 \pm 4.69$ | $12.8 \pm 3.99$ | 1.84 | $4.03 \pm 1.01$ | $1.25 \pm 0.32$ | 3.22 | $17.5 \pm 4.1$ | $10.4 \pm 3.0$ | 1.68 |
| Mclntosh | $44.1 \pm 4.80$ | $22.2 \pm 7.01$ | 1.99 | $6.72 \pm 1.02$ | $12.6 \pm 3.29$ | 0.53 | $15.6 \pm 4.4$ | $62.5 \pm 26$ | 0.25 |
| Monroe | $23.9 \pm 0.47$ | $30.6 \pm 6.19$ | 0.78 | $7.53 \pm 1.91$ | $17.5 \pm 3.31$ | 0.43 | $31.4 \pm 7.5$ | $57.8 \pm 7.3$ | 0.54 |
| Pilot | $6.25 \pm 1.15$ | $17.0 \pm 3.59$ | 0.37 | $3.69 \pm 0.87$ | $4.17 \pm 0.70$ | 0.88 | $59.1 \pm 9.2$ | $26.0 \pm 8.3$ | 2.27 |
| Pinova | $33.3 \pm 4.48$ | $36.9 \pm 19.8$ | 0.90 | $3.80 \pm 0.64$ | $4.58 \pm 1.52$ | 0.83 | $11.6 \pm 2.9$ | $17.3 \pm 13$ | 0.67 |
| Prima | $4.63 \pm 1.29$ | $16.6 \pm 3.06$ | 0.28 | $4.35 \pm 0.89$ | $5.72 \pm 1.00$ | 0.76 | $104 \pm 48$ | $36.2 \pm 13$ | 2.87 |
| Priscilla | $17.8 \pm 4.32$ | $15.0 \pm 1.16$ | 1.19 | $3.44 \pm 0.32$ | $6.16 \pm 2.51$ | 0.56 | $20.2 \pm 5.4$ | $40.7 \pm 15$ | 0.50 |
| Red Rome | $35.7 \pm 4.13$ | $25.6 \pm 6.06$ | 1.39 | $7.28 \pm 0.86$ | $8.52 \pm 1.88$ | 0.85 | $20.5 \pm 1.8$ | $35.1 \pm 13$ | 0.58 |
| Rubin | $14.4 \pm 5.14$ | $15.1 \pm 4.59$ | 0.95 | $4.33 \pm 0.71$ | $3.09 \pm 1.36$ | 1.40 | $35.1 \pm 18.2$ | $24.2 \pm 18$ | 1.45 |
| Starking Delicious | $17.4 \pm 1.86$ | $33.8 \pm 5.59$ | 0.51 | $4.41 \pm 0.51$ | $15.1 \pm 2.57$ | 0.29 | $25.6 \pm 3.5$ | $45.2 \pm 8.3$ | 0.57 |
| average | $24.9 \mathrm{~b}^{\text {d }}$ | 20.0 a | 1.25 | 6.11 a | 7.40 b | 0.83 | 36.8 a | 37.8 a | 1.04 |
| WF-AP ${ }^{\text {e flavonols }}$ | $0.051{ }^{f}$ | $0.716^{g}$ |  |  |  |  |  |  |  |

${ }^{a}$ Data are presented as means $\pm \mathrm{SD}, n=5 .{ }^{b}$ Amount of phenolics was calculated on the basis of the concentration (mg g ${ }^{-1} \mathrm{FW}$ ) and the mean weight of whole fruit and its entire peel. ${ }^{c} 04 / 05=$ the value obtained by dividing the amount noted in 2004 by 2005. ${ }^{d}$ Mean separation for years by Newman-Keuls test ( $p<0.05$ ). ${ }^{e}$ Correlation between whole fruit and the apple peel quantity of flavonols in the consecutive years. ${ }^{f}$ Not significant. ${ }^{g}$ Significant at $\alpha=0.001$. Bold type indicates the highest and the lowest values.

Table 9. Total Amounts of Anthocyanins in Apple Peel (Expressed in mg of Cyanidin 3,5-Diglucoside) Depending on Cultivar and Growing Season ${ }^{a}$

| cultivar | apple color description for year |  | anthocyanin amount ${ }^{\text {b }}$ for year |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
|  | 2004 | 2005 | 2004 | 2005 | 04/05 ${ }^{f}$ |
| Elan | $2^{c} / 4^{d}$ | 2/3 | $1.19 \pm 0.05$ | $1.73 \pm 0.67$ | 0.69 |
| Elstar | 2/4 | 2/4 | $2.27 \pm 0.16$ | $2.55 \pm 0.60$ | 0.89 |
| Fiesta | 2/4 | 2/4 | $1.59 \pm 0.37$ | $0.72 \pm 0.31$ | 2.21 |
| Fuji | 3/4 | 3/4 | $1.65 \pm 0.05$ | $0.33 \pm 0.11$ | 5.00 |
| Gala | 2/4 | 2/3 | $1.58 \pm 0.44$ | $0.86 \pm 0.70$ | 1.84 |
| Gloster | 5/5 | 5/5 | $5.53 \pm 0.56$ | $5.40 \pm 0.70$ | 1.02 |
| Golden Delicious | 1/2 | 1/2 | nd | nd | nd |
| Granny Smith | 3/2 | 3/2 | $0.91 \pm 0.26$ | $0.48 \pm 0.09$ | 1.90 |
| Idared | 4/5 | 4/5 | $7.82 \pm 1.14$ | $4.86 \pm 0.66$ | 1.61 |
| Jonamac | 5/5 | 5/5 | $2.52 \pm 0.36$ | $3.06 \pm 0.85$ | 0.82 |
| McIntosh | 3/4 | 3/4 | $1.45 \pm 0.07$ | $1.69 \pm 0.63$ | 0.86 |
| Monroe | 5/5 | 4/5 | $3.71 \pm 0.82$ | $4.44 \pm 0.70$ | 0.83 |
| Pilot | 2/4 | 4/4 | $0.46 \pm 0.12$ | $0.91 \pm 0.13$ | 0.50 |
| Pinova | 2/3 | 2/4 | $0.38 \pm 0.18$ | $0.96 \pm 0.21$ | 0.40 |
| Prima | 5/5 | 5/4 | $3.72 \pm 0.78$ | $3.00 \pm 0.18$ | 1.24 |
| Priscilla | 5/5 | 5/5 | $1.20 \pm 0.20$ | $1.98 \pm 0.53$ | 0.76 |
| Red Rome | 4/5 | 4/4 | $2.27 \pm 0.04$ | $2.98 \pm 1.02$ | 0.76 |
| Rubin | 2/5 | 2/5 | $1.87 \pm 0.42$ | $1.11 \pm 0.52$ | 1.64 |
| Starking Delicious | 5/5 | 5/5 | $2.24 \pm 0.24$ | $7.77 \pm 2.06$ | 0.29 |
| average |  |  | $2.35 \mathrm{a}^{e}$ | 2.49 a | 0.94 |

${ }^{a}$ Data are presented as means $\pm \mathrm{SD}, n=5 .{ }^{b}$ Amount of anthocyanins was calculated on the basis of the concentration ( $\mathrm{mg} \mathrm{g}^{-1} \mathrm{FW}$ ) and the mean weight of entire peel. ${ }^{c}$ Over color of the skin: $1=$ orange, $2=$ orange-red, $3=$ pink-red, $4=$ red, and $5=$ dark red. ${ }^{d} \%$ of over color: $1=$ no, $2=<\frac{1}{4}, 3=1 / 4-1 / 2,4=1 / 2-3 / 4$, and $5=>{ }^{3} / 4$. ${ }^{e}$ Mean separation for years by Newman-Keuls test ( $p<0.05$ ). Bold type indicates the highest and the lowest values. nd $=$ not detected. ${ }^{f} 04 / 05=$ the value obtained by dividing the amount noted in 2004 by 2005.
between AP quantity was 1.7-20.2 (cvs. Elan-Granny Smith) mg per entire AP and from 1.25 to 17.5 (cvs. Jonamac-Monroe) mg per entire AP in the consecutive years. Apple peel share ranged between 5\% (cv. Elan) and 158\% (cv. Granny Smith) in 2004. Lower range, i.e., from $10.4 \%$ (cv. Jonamac) to $66.8 \%$ (cv. Idared), appeared in 2005.

A positive correlation between AP and WF phenolics as well as flavonol quantity was statistically proven only in the second of the two examined growing seasons (Tables 7 and 8).

The average content of anthocyanins amounted to from 0.67 (cv. Pinova) to 6.34 (cv. Idared) mg per entire apple peel (Table 9). Idared, followed by Gloster, Starking Delicious, Monroe, Prima, and Jonamac cultivars, was characterized by the highest anthocyanin quantity. Apple peel of all these cultivars was predominantly dark red, but each constituted a separate homologue item with respect to anthocyanin amount, based on the average values (mean separation by Newman-Keuls test; data not shown). Year effect was statistically not significant, as about half of the tested cultivars expressed a
higher amount in the first tested season and the rest in the second growing season.

## DISCUSSION

Accurate quantification of bioactive compounds in fruit, vegetable, and cereals as well as other plant-origin food seems to be crucial in promoting strategy of a diet rich in such constituents. The problem might be that the calculation is frequently conducted on the data derived from different databases. A daily consumption of phenolics and total antioxidant capacity derived from 14 fruits and 20 vegetables was recently estimated in the American diet by Chun et al. (26). American daily intake of phenolics, flavonoids, and antioxidants (vitamin C equivalent) from fruit was estimated to be 320 mg of GAE (gallic acid), 86 mg of catechin, and 441 mg of vitamin C equivalents. Apples comprised relatively high levels of total phenolics and antioxidant capacity, comparable to oranges (specified as the first), and their phenolic and antioxidant contribution was the second highest. It was not specified which cultivar or cultivars were examined. Total phenolic amount per one apple fruit, in the present study, varied from 56 (cv. Rubin) to 125 (cv. Starking Delicious) mg of GAE. Flavonol quantity, an important subgroup of phenolics, ranged from 10.6 to 40.8 mg fruit ${ }^{-1}$ and consisted of $\sim 30 \%$ global phenolics, on average. This finding confirms the above-described data about apple as an important contributor of these compounds to human diet. Those results should be checked by HPLC analysis to obtain detailed profiles of phenolics, as each cultivar exhibited its own defined chemical composition and, furthermore, each individual compound differed considerably in its activity, stability, and bioavailabilty, which is crucial in health protection. Greater amounts of phenolics (97.7-263.1 mg per apple) and, similar to present study scope, quantity of flavonols (17.7-33.0 mg fruit ${ }^{-1}$ ) were obtained by McGhie et al. (25) after testing 10 cvs. using HPLC analysis. The daily intake of anthocyanins was estimated to be 12.5 mg per day per person in the United States (13). Out of the different aglycons, cyanidin comprised up to $45 \%$ of their total uptake. It is the main anthocyanidin identified in the apple peel (15). According to McGhie et al. (25) the quantity of anthocyanins amounted to from 0.9 to 6.5 mg fruit ${ }^{-1}$ and in $100 \%$ were present in apple skin, whereas in our research the range was at the level $0.7-6.3 \mathrm{mg}$ per entire apple peel.

Attention should be paid to what extent a cultivar might differ as a source of bioactives and to what degree the impact of growing season might be expected. In our study the differences between the poorest and the richest cultivars in WF quantity of phytocompounds reached the following values, depending on growing season: $330-470 \%, 240-330 \%, 200-710 \%$, and $240-320 \%$ for ascorbate, glutathione, L-cysteine, and global phenolics, respectively. The corresponding amounts for AP quantity were $260-300 \%, 190-240 \%, 160-250 \%$, and $290-610 \%$. The diversity in anthocyanin quantity among the examined genotypes reached such a high level as 14.5- and 23.5-fold variation in 2004 and 2005, respectively. These results confirmed that the accumulation of bioactive compounds is defined by internal factor (genotype) but that the influence could be strongly modified by the conditions of growing season. Such a high biodiversity was well documented in the recent years $(7,15,17,18,27)$.

Apple peel as a contributor to WF quantity of the tested elements fluctuated considerably from compound to compound and was also highly cultivar dependent. On the basis of average values for both years, a great amount of flavonols was found in AP ( $\sim 40 \%$ ), followed by ascorbate ( $\sim 30 \%$ ) and total phenolics ( $\sim 20 \%$ ), and the lowest contribution was calculated for thiols
( $\sim 11 \%$ and $14 \%$, for l-cysteine and total quantity of glutathione, respectively). Moreover, almost half of the tested cultivars expressed a higher value of the above index than the calculated mean for ascorbate and thiols, and in the case of phenolics this statement was true only in 2005. This finding provided rather convincing proof that peel might be a significant contributor to the total apple bioactive components; however, it could be difficult to predict the value of this index. Apple peel as a contributor to total phenolics assessed by McGhie et al. (25) was even bigger and varied between $38 \%$ and $55 \%$ (ten cvs. commercially grown in New Zealand were tested). Also, flavonols, in apple mainly different glycosides of quercetin, were predominantly identified in the external layer of apple peel (15, 24, 25). We were unable to find the respective values as well as calculation of ascorbate or thiols per entire apple fruit. The impact of environmental condition on antioxidant quantity was more pronounced in apple peel (an exception was L-cysteine), especially in the case of ascorbate and phenolics. The differences between growing seasons in ascorbate and phenolic quantity in apple peel amounted to ca. $30 \%$ and $57 \%$, respectively. The corresponding values for the entire fruit amount were only $8 \%$ and $9 \%$. This strengthens the theory that peel constitutes an important barrier against biotic and abiotic outside stress that fruits are frequently subjected to. The influence of cultivar on the contribution of AP to WF antioxidant amount was considerably lower as compared to the antioxidant quantity in both tested fruit parts, but still significant, while year effect was lost in many cases or markedly lowered.

Correlation coefficients between AP and WF quantity of antioxidant were generally higher as compared to those previously calculated for the concentrations of these bioactive compounds (17). A weak, not statistically proven, negative relationship, which existed between fruit weight and the concentration of the examined constituents, was lost after their calculation per whole fruit (data not shown).

Summarizing, apples contain a high quantity of bioactive compounds as compared to the described data related to their daily intake, although it might be difficult to precisely predict their amounts as they are subject, in a significant way, to seasonal and cultivar variability. However, it is possible to select the richest sources of particular compounds. Apple peel seems to be an impressive contributor (especially in relation to phenolics and vitamin C) to the entire fruit quantity.

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[^1]:    ${ }^{\text {a }}$ Data are presented as means $\pm$ SD, $n=4$ (one replicate included 10 fruits). ${ }^{b} 04 / 05=$ the value obtained by dividing the weight obtained in 2004 by 2005. ${ }^{c}$ Mean separation for years by Newman-Keuls test ( $p<0.05$ ). Bold type indicates the highest and the lowest values.

[^2]:    ${ }^{a}$ Data are presented as means $\pm \mathrm{SD}, n=5 .{ }^{b}$ Amount of glutathione was calculated on the basis of the concentration ( $\mathrm{mg} \mathrm{g}^{-1} \mathrm{FW}$ ) and the mean weight of whole fruit and its entire peel. ${ }^{c} 04 / 05=$ the value obtained by dividing the amount noted in 2004 by 2005. ${ }^{d}$ Mean separation for years by Newman-Keuls test ( $p<0.05$ ). ${ }^{e}$ Correlation between whole fruit and the apple peel quantity of glutathione in the consecutive years. ${ }^{f}$ Significant at $\alpha=0.001$. Bold type indicates the highest and the lowest values.

