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Effect of milling, pasta making and cooking on minerals in durum wheat

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ABSTRACT

The effect of technological processing on the contents of eight minerals – i.e., calcium, copper, iron, magnesium, phosphorous, potassium, selenium, and zinc – was investigated in pasta making. Milling of durum wheat as well as pasta making were carried out in a pilot plant by using three different grain samples. Pasta samples purchased on the market were also surveyed to gain information on the mineral content of commercial products. The effect of cooking was also investigated in order to determine the retention of the selected elements in the final ‘ready-to-eat’ product. Analyte concentrations in whole grains, semolina, pasta and cooked pasta were determined by inductively coupled plasma-mass spectrometry.

Conventional roller milling significantly reduced the content of each mineral in durum wheat grains. However concentration losses as a consequence of milling widely differed among elements, from 16% for Se to 66% for Mg and Zn on a dry weight basis. Retention of elements after milling followed the order $Se > Ca > Cu > P \approx K > Fe > Mg \approx Zn$. Pasta making had little effect on element concentrations in semolina. Cooking caused an increase in the calcium content of pasta whereas the concentrations of the other elements were either unchanged or slightly reduced (0–18% on a dry weight basis) except potassium, which showed a decrease of 74%.

Commercial pasta samples showed concentrations of minerals similar to those of the experimental samples, except selenium which was higher due to the use of imported wheat with higher levels of selenium in industrial semolina production. Overall, pasta appears to be a valuable source of several minerals, especially selenium, copper, magnesium, and zinc.

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1. Introduction

Cereals and derived products are among the major dietary sources of essential elements for humans. The contribution of cereal products to the estimated dietary intake of several minerals and nutritionally beneficial trace elements is about 20–30% of the total intake in Western countries (Carcea et al., 2007). In the case of iron and manganese the contribution is as high as 40–50% (Carcea et al., 2007). These figures are even higher in other regions of the world (Choi and Kim, 2007; Hattori et al., 2004) and especially in developing countries (Hussein and Brüggemann, 1997).

Wheat is the main cereal crop used for human consumption in many areas worldwide. Common wheat (*Triticum aestivum* L.) is widely used for breadmaking, whereas durum wheat, i.e., *Triticum turgidum* L. subsp. *durum* (Desf.) Husn., is mainly employed in the production of other food items, pasta being the most popular. In Italy, the main pasta producer, pasta is a staple food. However pasta

consumption has become widespread in several countries (UNIFI, 2007). Notwithstanding its popularity, the mineral profile of pasta as influenced by processing (i.e., milling and pasta making) and cooking has been the subject of systematic investigations mainly in the 1980s (Albrecht et al., 1987; Brondi et al., 1984; Ranhotra et al., 1984, 1985; Toepfer et al., 1972; Yaseen, 1993). The introduction of new cultivars as well as alterations in agronomic practices and changes in the processing conditions do require updated studies. These studies should employ state-of-the-art techniques and include analytical quality control schemes allowing, for instance, precise and accurate determinations of essential microelements such as selenium.

Milling is the critical process affecting the concentrations of inorganic elements in wheat-derived food products. As the outer parts of the kernel, especially the aleurone layer and the germ, are richer in minerals when compared to the starchy endosperm, conventional milling reduces their content in flour (semolina, in the case of durum wheat) and concentrates them in the milling residues (Brondi et al., 1984). However, it has been reported that differences in the mineral content likely exist even between the inner endosperm and the outer endosperm (Pomeranz, 1988). The grain shape and texture (which both depend also on cultivar) and

Abbreviations: RDA, daily recommended dietary allowance.

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the technical conditions of milling, primarily the extraction rate, are important in determining the extent of mineral loss. However, when all these variables are fixed, the distribution of the mineral in the various milling fractions ultimately depends on how the element is unevenly distributed within the kernel. Therefore, it will vary on an element-specific basis.

There is little information on the effect of milling on durum wheat minerals (Brondi et al., 1984; Toepfer et al., 1972). This information is needed to assess the nutritional significance of mineral loss as a consequence of conventional roller milling and to provide basic knowledge in order to establish, for instance, whether there is a need for fortification, which minerals should be supplemented (in bioaccessible form), and at what levels. Limited and sometimes contradictory data are available on the effect of further processing of semolina into pasta as well as pasta cooking (Albrecht et al., 1987; Ranhotra et al., 1984, 1985; Yaseen, 1993).

The present study was undertaken to determine the effect of conventional roller milling, pasta making and cooking on eight nutritionally important minerals (namely calcium, copper, iron, magnesium, phosphorous, potassium, selenium, and zinc) in durum wheat. Milling and pasta making pilot plants were employed for the manufacture of semolina and long ('spaghetti' type) pasta in order to be able to control the whole processing chain. Commercial pasta samples from major Italian brands were purchased on the market and included in this study for comparison. The effect of cooking was investigated in order to gain information on the retention of the selected elements in the final 'ready-to-eat' product.

2. Experimental

2.1. Milling and pasta making

Three samples of durum wheat grain of about 10 kg each were included in the study. The samples belonged to three different cultivars, namely, Appio, Duilio, and Simeto (hereafter indicated as samples 1, 2, and 3) grown in Southern Italy and widely used in Italy for industrial pasta production.

Semolina was obtained from each sample by cleaning and tempering the grains for 36–40 h to 16.5% moisture and then milling them in a pilot mill (Model MLU 202, Bühler, Uzwil, Switzerland) equipped with three breaks, three reduction rolls, six steel screens and coupled with a purifier to give standard grade semolina, following Approved Methods 26-10 A and 26-41 (AACC, 2000). Semolina yield (ash <0.90% d.m.) was about 66% for the three samples, and granulation was within Italian legal limits (25% maximum passed through a 180 μm sieve).

Semolina was used to manufacture long pasta (spaghetti) by means of a pilot pasta making apparatus (Pavan, Padova, Italy) composed of a press and a dryer. The press (capacity 5–20 kg) was equipped with a vacuum mixing and extruding system, and a water-cooling jacket on the barrel and the extrusion head to reduce heat and to maintain a constant extrusion temperature of no more than 50 °C.

Semolina was mixed with tap water for about 15 min to obtain a dough suitable for extrusion. The moisture content of the dough was about 30%. After extrusion, spaghetti were dried according to a 27 h drying cycle during which relative humidity was kept under control and maximum drying temperature was 58 °C for a period of 4 h. The diameter of dry spaghetti was 1.65–1.70 mm. At the end of the drying cycle pasta was conditioned at room temperature (20 °C) for 24 h and packed in polyethylene bags.

2.2. Cooking

Experimental pasta samples were cooked in Pyrex flasks previously decontaminated with a 12 h treatment with nitric acid (ultrapure, 10% v/v solution). A single batch of soft tap water

(0.68 meq L⁻¹ hardness) with low levels of the elements being investigated, was used for all cooking. Common kitchen salt taken from a single commercial packet was added at a concentration of 9 g L⁻¹. The analyte levels were determined in water samples before cooking and were constant throughout the study. The optimum cooking time was taken as that required for the white core in the strands to disappear when they were squeezed between two test glasses (AACC, 2000).

Cooked samples were drained in a plastic drainer to avoid contamination and aliquots of pasta strands were placed in suitable containers for moisture determination.

2.3. Sample preparation for analytical determinations

Sample handling was carried out under clean room conditions.

Tap water used in dough preparation and for cooking was acidified soon after sampling with ultrapure HNO₃ (1% v/v) and stored at 4 °C pending analysis.

Grain and pasta samples were ground in order to obtain a fine flour. As a previous study demonstrated that the use of common laboratory mills may lead to sample contamination at this step (Cubadda et al., 2001), an automatic pestle mill with internal parts made in agate – model RM100 by Retsch GmbH & Co. (Haan, Germany) – was used. A preliminary study on wheat grain samples milled by means of this device indicated the absence of any detectable contamination for the elements investigated in the present study.

Aliquots of about 100 g of grain and dry pasta samples were ground. For each sample, grinding was carried out twice and the flour obtained in the first run was discarded. After each batch, the mortar was thoroughly cleaned with laboratory wipers and then rinsed with ultrapure water. This procedure was adopted in order to avoid carry-over contamination from preceding samples. In addition to experimental samples, 12 commercial pasta samples from eight different makers were identically ground and subsequently submitted to the same analytical procedure.

Cooked and drained aliquots of pasta were similarly homogenized before being submitted to elemental analysis. Transfer of samples from one container to another was always performed with suitable plastic tools in order to avoid contamination.

Sample digestion was performed by means of a closed vessel system, a Milestone MLS-1200 Mega MW oven (FKV, Bergamo, Italy), as described elsewhere (Cubadda et al., 2002). The MW system utilized was able to handle pressures as high as 110 bar. Sample weight was 0.3–0.4 g on a dry weight basis, depending on the material. The reagents used in sample digestion were ultrapure concentrated HNO₃ (Carlo Erba Reagenti, Milan, Italy) and H₂O₂ (Merck, Darmstadt, Germany), 3 and 1 ml respectively. Each sample was digested in duplicate and made up to 30 ml in polypropylene disposable tubes with high purity deionized water (18.2 M Ω cm resistivity at 25 °C) obtained by a Milli-Q apparatus (Millipore, Molsheim, France).

Dry weight determinations were performed for each sample on separate 10-g aliquots by oven drying at 103 °C until constant weight.

Two reference materials were included randomly in analytical batches from digestion onward. These were the RM 8436 (durum wheat flour), from the National Institute of Standards and Technology (Gaithersburg, MD), and the BCR CRM 189 (wholemeal flour), from the Institute for Reference Materials and Measurements (Geel, Belgium).

2.4. Instrumentation and analytical measurements

A quadrupole Sciex Elan 6000 ICP mass spectrometer (Perkin-Elmer, Norwalk, CT, USA), equipped with an ASX-500 autosampler

(model 510) and an ADX-500 autodilutor (both from CETAC Technologies, Omaha, NE, USA), was used for quantification of the analytes. Details of the instrumentation and the operating conditions are reported elsewhere (Cubadda et al., 2002). The analytical masses were ^{43}Ca , ^{63}Cu , ^{57}Fe , ^{39}K , ^{24}Mg , ^{31}P , $^{77+82}\text{Se}$, and ^{64}Zn .

Multielemental calibration standards were prepared from 1000 mg L⁻¹ stock solutions of individual elements (BDH, Poole, England) by dilution with 3% v/v ultrapure concentrated HNO₃. In all measurements, rhodium (20 µg L⁻¹) was selected as internal standard for correction of matrix effects and instrumental drift. Correction of $^{44}\text{Ca}^{16}\text{OH}$ interference on ^{57}Fe was accomplished by application of a mathematical equation calculated daily as reported previously (Cubadda et al., 2002).

Randomly selected samples were analysed on different days to verify the precision of results. Samples of the two reference materials were analysed in each analytical run to check accuracy of measurements. Digestion blanks were run together with samples belonging to the same analytical batch and their signal was subtracted from that of the sample when calculating analyte concentrations.

2.5. Statistical analysis

The existence of significant differences in the element concentrations (on a dry weight basis) among the studied matrixes on account of the various treatments (i.e., milling, pasta making, cooking) was determined by analysis of variance. The test resulted significant for all metals ($p = 0.05$) and thus a multiple comparison test (Scheffé test) was performed to identify which treatments caused significant variations ($p = 0.05$).

3. Results and discussion

The results obtained for the reference materials analysed for quality control purposes are summarized in Table 1. Good agreement was observed with the certified or best estimated values of each element, indicating effective recovery of analytes after digestion and subsequent accurate detection. Precision expressed as the coefficient of variation (CV) was, on average, 6% for calcium, 3% for copper, 2% for iron, 1% for potassium, 1% for magnesium, 2% for phosphorous, 2% for selenium, and 4% for zinc.

Tables 2–4 show the element concentrations measured in the three grain samples selected for this study and in their derived products, including cooked pasta. Each result is the average of four experimental replicates, on which duplicate subsampling was carried out for analyses. Data are reported both on a dry and on a fresh weight basis. Average moisture content of samples was 9.8%,

12.6%, 10.1% and 61.1% for grain, semolina, pasta and cooked pasta, respectively.

In order to allow easy recognition of the effects of processing and cooking, the overall percent variation in element concentrations caused by the different treatments in relation to their original levels in grain (=100%) is shown in Tables 2–4, together with the percent variation of the element concentrations in each type of sample as a consequence of a specific treatment.

3.1. Effect of milling

As expected, milling significantly reduced the concentrations of all elements ($p < 0.01$), with average losses ranging from 16% for selenium to 66% for magnesium and zinc on a dry weight basis (Tables 2–4).

A modest reduction of selenium concentration upon milling (8%–20%) has also been found in studies on common wheat (Lyons et al., 2005; Toepfer et al., 1972). Similar to sulphur, selenium, which occurs predominantly as selenomethionine in wheat grains, is mostly protein-bound and more evenly distributed throughout the kernel when compared to other minerals (Lyons et al., 2005). Therefore, due to a higher proportion being stored in the endosperm, lower proportions of Se are removed in the milling process.

Calcium showed an average loss of 41% in concentration terms, which is in agreement with the results obtained in earlier work on durum wheat (Toepfer et al., 1972). Studies on the distribution of minerals within the kernel of common wheat reported that the endosperm contains about 50% of calcium whereas about 25% is found in the aleurone layer (Pomeranz, 1988). For other elements, such as magnesium and zinc, only a minor proportion is found in the endosperm, whereas $\geq 70\%$ and $\sim 50\%$, respectively, is in the aleurone (Bock, 2000; Pieczonka and Rosopulo, 1985; Pomeranz, 1988). Accordingly, calcium was found to follow an entirely different pattern from that of magnesium, zinc and iron in industrially milled wheat flours (Lorenz et al., 1980). The level of calcium depended mainly on the calcium content of the wheat, whereas magnesium, zinc and iron depended more on milling variables (Lorenz et al., 1980).

Next to calcium, copper showed a concentration decrease of 47% in this study. This is similar to the results obtained in earlier work on durum wheat (Brondi et al., 1984; Toepfer et al., 1972) and matches studies showing that about 45% of copper is in the endosperm of common wheat kernels (O'Dell et al., 1972; Pieczonka and Rosopulo, 1985).

The concentration of phosphorous and potassium in semolina was 56% lower than that in parent grains. Phosphorous mainly occurs in wheat kernels as phytic acid and its salts. Potassium is associated with phosphorous as it forms, together with magnesium, a major part of the phytates found in the kernels (Bock, 2000). A sizeable reduction of phytic acid in semolina is achieved upon milling of durum wheat grains so that a major proportion of phosphorous is present as nucleoprotein, lipid, and inorganic phosphorous (Pomeranz, 1988). Since phytic acid is a metal-chelating agent which can lower the absorption of several essential metals (including iron, zinc, calcium and magnesium) its removal into milling by-products is nutritionally beneficial (Bock, 2000; O'Dell et al., 1972). Recently, low phytic acid mutants of wheat have been isolated with the view of improving the nutritional quality of wheat by reducing the major storage form of phosphorous and increasing the level of inorganic phosphorous, which is more readily absorbed by humans and other monogastric animals (Gutierrez et al., 2006).

A group of three elements showed a major decrease in concentration following milling, i.e., iron (63%), magnesium and zinc (66%). These metals are particularly abundant in the aleurone (O'Dell et al., 1972; Pieczonka and Rosopulo, 1985). Zinc is present

Table 1
Results obtained for the reference materials analysed ($N = 6$)

Element	CRM 189 (wholemeal flour)				RM 8436 (durum wheat flour)			
	Found		Certified		Found		Best estimated	
	Mean	(c.i.) ^a	Mean	(c.i.) ^a	Mean	(c.i.) ^a	Mean	(c.i.) ^a
Ca ^b	540	(22)	[520] ^c		276	(14)	278	(26)
Cu ^b	6.36	(0.13)	6.4	(0.2)	4.28	(0.10)	4.30	(0.69)
Fe ^b	69.2	(0.6)	68.3	(1.9)	41.1	(1.2)	41.5	(4.0)
K ^d	6.23	(0.09)	[6.3] ^c		3.20	(0.02)	3.18	(0.14)
Mg ^d	1.92	(0.01)	[1.9] ^c		1.12	(0.02)	1.07	(0.08)
P ^d	5.49	(0.03)	[5.3] ^c		2.91	(0.06)	2.90	(0.22)
Se ^b	0.137	(0.002)	0.132	(0.010)	1.25	(0.02)	1.23	(0.09)
Zn ^b	56.6	(1.1)	56.5	(1.7)	22.3	(1.1)	22.2	(1.7)

^a Uncertainty as half-width of the 95% confidence interval of the mean.

^b Concentrations in µg g⁻¹.

^c Indicative value.

^d Concentrations in mg g⁻¹.

Table 2

Variations of potassium, phosphorous, and magnesium concentration in durum wheat as a consequence of processing and cooking

Sample	On a fresh weight basis				On a dry weight basis			
	Grain	Semolina	Pasta	Cooked pasta	Grain	Semolina	Pasta	Cooked pasta
Potassium								
1 ^a	4.37 ± 0.04	1.99 ± 0.02	2.06 ± 0.02	0.22 ± 0.01	4.85 ± 0.04	2.28 ± 0.02	2.30 ± 0.02	0.58 ± 0.01
2 ^a	4.32 ± 0.04	1.80 ± 0.01	1.87 ± 0.01	0.20 ± 0.01	4.79 ± 0.04	2.06 ± 0.02	2.08 ± 0.02	0.52 ± 0.01
3 ^a	5.08 ± 0.04	2.07 ± 0.02	2.14 ± 0.02	0.25 ± 0.01	5.62 ± 0.05	2.37 ± 0.02	2.37 ± 0.02	0.64 ± 0.01
% vs prec ^b	100	43 (41–46)	104 (103–104)	11 (11–12)	100	44 (42–47)	101 (100–101)	26 (25–27)
% vs grain ^c	100	43 (41–46)	44 (42–47)	5 (5–5)	100	44 (42–47)	44 (42–47)	11 (11–12)
Phosphorous								
1 ^a	4.04 ± 0.07	1.70 ± 0.03	1.76 ± 0.03	0.65 ± 0.01	4.48 ± 0.07	1.95 ± 0.03	1.96 ± 0.03	1.68 ± 0.03
2 ^a	3.69 ± 0.06	1.68 ± 0.03	1.73 ± 0.03	0.61 ± 0.01	4.10 ± 0.07	1.92 ± 0.03	1.92 ± 0.03	1.57 ± 0.03
3 ^a	4.07 ± 0.07	1.69 ± 0.03	1.74 ± 0.03	0.59 ± 0.01	4.50 ± 0.07	1.93 ± 0.03	1.94 ± 0.03	1.52 ± 0.02
% vs prec ^b	100	43 (42–45)	103 (103–103)	36 (34–37)	100	44 (43–47)	100 (100–100)	82 (79–86)
% vs grain ^c	100	43 (42–45)	44 (43–47)	16 (15–17)	100	44 (43–47)	45 (43–47)	37 (34–38)
Magnesium								
1 ^a	1.20 ± 0.01	0.39 ± 0.01	0.40 ± 0.01	0.18 ± 0.01	1.33 ± 0.01	0.44 ± 0.01	0.45 ± 0.01	0.45 ± 0.01
2 ^a	1.04 ± 0.01	0.36 ± 0.01	0.38 ± 0.01	0.16 ± 0.01	1.15 ± 0.01	0.42 ± 0.01	0.43 ± 0.01	0.42 ± 0.01
3 ^a	1.20 ± 0.01	0.40 ± 0.01	0.41 ± 0.01	0.18 ± 0.01	1.33 ± 0.01	0.45 ± 0.01	0.46 ± 0.01	0.46 ± 0.01
% vs prec ^b	100	33 (32–35)	104 (104–105)	43 (43–44)	100	34 (33–36)	101 (101–102)	100 (99–101)
% vs grain ^c	100	33 (32–35)	35 (34–37)	15 (15–16)	100	34 (33–36)	35 (34–37)	35 (34–37)

^a Concentration in mg g⁻¹ ± 95% confidence interval of the mean.^b Percent variation versus preceding item: average of the three samples (range).^c Percent variation versus grain: average of the three samples (range).

at a relatively high concentration in the germ as well, this part accounting for over 10% of the zinc burden in the caryopsis compared to, e.g., 5% of copper (Pieczonka and Rosopulo, 1985). As a consequence, a major proportion of iron, magnesium and zinc in the grain is removed in the conventional roller milling process.

Overall, the retention of elements after milling followed the order Se > Ca > Cu > P ≈ K > Fe > Mg ≈ Zn. The sequence Ca > Cu > (P, K, Fe, Mg, Zn) was obtained in previous investigations on durum wheat by Toepfer et al. (1972) (in this case with an inversion between phosphorous and copper) and Brondi et al.

(1984). The same order results from studies on common wheat (Lorenz et al., 1980; Pomeranz and Dikeman, 1983; Toepfer et al., 1972), even though some investigations found a higher proportion of either potassium (Brondi et al., 1984; Lyons et al., 2005; Zhang et al., 1997) or iron (Brondi et al., 1984; Brüggemann and Kumpulainen, 1995; Rao and Deosthale, 1981; Zhang et al., 1997) in flour. In most studies the percentage retentions of copper and phosphorous in flour were found to be similar (Pomeranz and Dikeman, 1983; Rao and Deosthale, 1981; Toepfer et al., 1972; Zhang et al., 1997), although generally slightly higher for copper. Deviations from the

Table 3

Variations of calcium, iron, zinc, and copper concentration in durum wheat as a consequence of processing and cooking

Sample	On a fresh weight basis				On a dry weight basis			
	Grain	Semolina	Pasta	Cooked pasta	Grain	Semolina	Pasta	Cooked pasta
Calcium								
1 ^a	373 ± 18	210 ± 10	228 ± 11	169 ± 8	413 ± 20	241 ± 12	254 ± 12	436 ± 21
2 ^a	412 ± 20	224 ± 11	248 ± 12	193 ± 9	456 ± 22	256 ± 12	276 ± 13	496 ± 24
3 ^a	346 ± 17	206 ± 10	229 ± 11	180 ± 9	383 ± 18	235 ± 11	254 ± 12	462 ± 22
% vs prec ^b	100	57 (54–60)	110 (108–111)	77 (74–79)	100	59 (56–61)	107 (105–108)	178 (172–182)
% vs grain ^c	100	57 (54–60)	63 (60–66)	48 (45–52)	100	59 (56–61)	63 (61–66)	112 (105–121)
Iron								
1 ^a	42.0 ± 0.7	14.7 ± 0.2	15.7 ± 0.3	6.3 ± 0.1	46.6 ± 0.7	16.9 ± 0.3	17.5 ± 0.3	16.3 ± 0.3
2 ^a	33.7 ± 0.5	12.3 ± 0.2	13.4 ± 0.2	5.1 ± 0.1	37.4 ± 0.6	14.1 ± 0.2	14.9 ± 0.2	13.0 ± 0.2
3 ^a	37.0 ± 0.6	13.2 ± 0.2	14.5 ± 0.2	5.4 ± 0.1	41.0 ± 0.7	15.1 ± 0.2	16.1 ± 0.3	13.9 ± 0.2
% vs prec ^b	100	36 (35–36)	109 (107–110)	38 (37–40)	100	37 (36–38)	106 (104–107)	89 (86–93)
% vs grain ^c	100	36 (35–36)	39 (37–40)	15 (15–15)	100	37 (36–38)	39 (38–40)	35 (34–35)
Zinc								
1 ^a	39.5 ± 1.3	13.3 ± 0.4	13.7 ± 0.4	5.2 ± 0.2	43.8 ± 1.4	15.3 ± 0.5	15.3 ± 0.5	13.3 ± 0.4
2 ^a	33.6 ± 1.1	10.3 ± 0.3	10.7 ± 0.3	4.5 ± 0.1	37.3 ± 1.2	11.8 ± 0.4	11.9 ± 0.4	11.6 ± 0.4
3 ^a	29.8 ± 1.0	10.3 ± 0.3	10.8 ± 0.3	4.4 ± 0.1	33.0 ± 1.1	11.8 ± 0.4	12.0 ± 0.4	11.3 ± 0.4
% vs prec ^b	100	33 (31–35)	104 (103–104)	40 (38–42)	100	34 (32–36)	101 (100–101)	93 (87–97)
% vs grain ^c	100	33 (31–35)	34 (32–36)	14 (13–15)	100	34 (32–36)	34 (32–36)	32 (30–34)
Copper								
1 ^a	5.54 ± 0.13	2.92 ± 0.07	3.06 ± 0.07	1.13 ± 0.03	6.15 ± 0.15	3.35 ± 0.08	3.41 ± 0.08	2.92 ± 0.07
2 ^a	5.30 ± 0.13	2.62 ± 0.06	2.71 ± 0.07	0.98 ± 0.02	5.88 ± 0.14	3.00 ± 0.07	3.02 ± 0.07	2.52 ± 0.06
3 ^a	5.47 ± 0.13	2.87 ± 0.07	3.09 ± 0.07	1.08 ± 0.03	6.06 ± 0.15	3.28 ± 0.08	3.43 ± 0.08	2.76 ± 0.07
% vs prec ^b	100	52 (49–53)	105 (104–107)	36 (35–37)	100	53 (51–55)	102 (101–104)	83 (80–86)
% vs grain ^c	100	52 (49–53)	54 (51–56)	20 (18–20)	100	53 (51–55)	54 (51–57)	45 (43–47)

^a Concentration in µg g⁻¹ ± 95% confidence interval of the mean.^b Percent variation versus preceding item: average of the three samples (range).^c Percent variation versus grain: average of the three samples (range).

Table 4
Variations of selenium concentration in durum wheat as a consequence of processing and cooking

Sample	On a fresh weight basis				On a dry weight basis			
	Grain	Semolina	Pasta	Cooked pasta	Grain	Semolina	Pasta	Cooked pasta
1 ^a	85.8 ± 1.4	72.8 ± 1.2	74.5 ± 1.2	31.2 ± 0.5	95.2 ± 1.5	83.5 ± 1.3	83.1 ± 1.3	80.3 ± 1.3
2 ^a	99.1 ± 1.6	81.2 ± 1.3	83.5 ± 1.3	35.8 ± 0.6	109.8 ± 1.8	93.0 ± 1.5	93.0 ± 1.5	92.0 ± 1.5
3 ^a	110.6 ± 1.8	85.2 ± 1.4	87.5 ± 1.4	36.2 ± 0.6	122.5 ± 2.0	97.3 ± 1.6	97.2 ± 1.6	92.8 ± 1.5
% vs prec ^b	100	81 (77–85)	103 (102–103)	42 (41–43)	100	84 (79–88)	100 (99–100)	97 (95–99)
% vs grain ^c	100	81 (77–85)	83 (79–87)	35 (33–36)	100	84 (79–88)	84 (79–87)	81 (76–84)

^a Concentration in ng g⁻¹ ± 95% confidence interval of the mean.

^b Percent variation versus preceding item: average of the three samples (range).

^c Percent variation versus grain: average of the three samples (range).

common pattern occasionally observed for potassium, iron, and phosphorous may be due to varying milling conditions among studies, primarily extraction rate (Rao and Deosthale, 1981), and to an uneven release of some elements from milling equipment, especially iron (Cubadda et al., 2005). Furthermore, the proportion of each element in the morphological sections of the wheat kernel is dependent on the genotype and varies among cultivars (Lyons et al., 2005), and this can further explain the slightly different patterns from one study to another.

3.2. Effect of pasta making

Overall, pasta making had little effect on element concentrations in parent semolina. Slight, non-statistically significant enrichments of calcium (107%), iron (106%) and copper (102%) were observed. The concentrations of these elements in the water used for dough preparation were 52 ± 1, 0.10 ± 0.01, and 0.041 ± 0.02 mg L⁻¹, respectively, and explained the major part of the calcium increase, a low proportion of that of copper, and 1% of that of iron. Therefore, the release from pieces of equipment used in the pasta making process appeared to be the cause of the concentration increase of iron and, to a lesser extent, of copper.

The elemental concentrations found in the commercial pasta samples are summarized in Table 5. These concentrations closely match those of the experimental samples. The only differences were a slightly higher magnesium concentration ($p = 0.014$) and an almost double concentration of selenium ($p < 0.001$). Lower concentrations of selenium in the experimental samples compared to commercial samples are the consequence of the relatively low levels of plant-available selenium in the areas of Southern Italy from which experimental grain samples originated (Spadoni et al., 2007). The widespread use of wheat imported from selenium-rich areas in industrial semolina production results in a higher level of selenium in commercial pasta.

It was investigated as to whether differences in elemental levels between long pasta (spaghetti and related types) and short pasta (macaroni and related types) existed in commercial samples. Differences, indeed, turned out to be negligible, even though a slightly significantly higher content of copper and zinc in long pasta was detected ($0.01 < p < 0.05$).

Table 5
Element concentrations in commercial pasta samples ($N = 12$)^a

	Ca (μg g ⁻¹)	Cu (μg g ⁻¹)	Fe (μg g ⁻¹)	K (mg g ⁻¹)	Mg (μg g ⁻¹)	P (mg g ⁻¹)	Se (ng g ⁻¹)	Zn (μg g ⁻¹)
Median	266	3.30	12.9	2.07	430	1.66	141	12.7
Mean	260	3.21	13.0	2.07	430	1.67	154	12.9
Min	200	2.76	11.3	1.87	398	1.51	84	10.3
Max	314	3.56	14.7	2.29	457	1.82	227	15.4
CV(%)	11	9	9	6	5	6	34	14

^a Fresh weight basis (average water content for conversion to dry wt basis is 11.0%).

Perhaps of more importance is the variability of concentrations in commercial pasta, which differed widely among minerals. Potassium, magnesium and phosphorous exhibited the lowest CV (5–6%), followed by copper and iron (9%), calcium (11%), zinc (14%) and selenium (34%). The large spread of selenium levels is not surprising since this element is not essential for plants and its concentration in grains and derived cereal products correlates with plant-available selenium in the soil (Spadoni et al., 2007).

The mineral concentrations in pasta in this study are generally similar to those found in recent surveys elsewhere (USDA, 2007), even though more confidence can be attributed to the data presented here due to a more representative sampling. However, in earlier studies, substantially lower levels of calcium (Albrecht et al., 1987; Ranhotra et al., 1984, 1985; Yaseen, 1993), copper (Albrecht et al., 1987), potassium (Yaseen, 1993), magnesium (Yaseen, 1993), and phosphorous (Ranhotra et al., 1984; Yaseen, 1993) were reported. It is unclear whether the lower concentrations measured in these earlier studies are the result of analytical shortcomings or reflect actual differences due to, e.g., the introduction of new cultivars, modifications in agronomic practices, or changes in processing.

3.3. Effect of cooking

The effect of cooking can be best assessed considering data expressed on a dry weight basis in Tables 2–4. Cooking markedly increased calcium concentration of pasta ($p < 0.001$), which can be ascribed to the calcium content of the cooking water (26 ± 1 mg L⁻¹). Except for potassium, the concentrations of the other elements remained unchanged (magnesium) or showed a slight reduction in the range 79–97%, which turned out to be significant only for copper ($p < 0.001$). Potassium showed a sizeable decrease ($p < 0.001$), its concentration after cooking being reduced to about 1/4 of that in dry pasta.

The results obtained in this study can not be easily compared to those of previous investigations. When expressed on a dry weight basis, the retention values calculated in this study correspond to the 'apparent retention' of nutrients in cooked foods as defined by Murphy et al. (1975). Apparent retentions after pasta cooking were determined in an earlier study, where slightly lower values were found for all minerals (70–82%), including calcium, whereas potassium again displayed the highest loss (Yaseen, 1993). However, in this latter study, pasta was cooked in distilled deionized water without addition of salt, which does not allow easy comparison with the results of the present study. A similar approach was used by Ranhotra et al. (1984), but in this case no distilled water was used and calcium turned out to have the highest retention. Other studies (Albrecht et al., 1987; Ranhotra et al., 1985) took into account the loss of solids during cooking and calculated the so-called 'true retention' (Murphy et al., 1975). Albrecht et al. (1987) compared the effect of salt addition when pasta is cooked either in distilled or tap water. Calcium true retention increased from 89% to about 100% when salt was added to distilled water.

Calcium retention in unsalted tap water was about 129% (average of macaroni and spaghetti) and increased to 158% upon salt addition, with negligible differences following subsequent rinsing. In agreement with the other studies, potassium was found to have the lowest retention and salt addition decreased it, which probably explains the low retention value for this element obtained in the present study.

Studies on different cooking approaches may give insight into the effect of each specific medium on mineral retention and suggest explanations for different retention patterns. However, in this study pasta was cooked in the customary way, i.e., in salted tap water, in order to identify the actual mineral content of the final product when prepared according to common household practice.

Using the retention factors obtained in this study, the amount of each mineral provided by a standard serving of pasta (80 g of the uncooked product) containing each mineral at the average concentration found in the commercial samples (Table 5) was calculated. This amount was compared with the Italian daily recommended dietary allowance (RDA) for the adult population (SINU, 1996). It resulted that the proportion of the RDA provided by a daily serving of pasta is on average 22% for selenium, 18% for copper, 10%–14% for zinc (for males and females, respectively), 11% for phosphorus, 9%–5% for iron (for males and females, respectively), 4% for calcium, and 1% for potassium. For magnesium, only a range of intakes is established instead of a RDA; if a value one-third above the lower level of this range is chosen as a reference, the proportion of such an amount provided by a daily serving of pasta turns out to be 17%. Overall, pasta appears to be a valuable source of several minerals of importance in human nutrition and well-being.

4. Conclusions

This study led to a better understanding of the effect of durum wheat processing on the levels of eight minerals, namely, calcium, copper, iron, magnesium, phosphorous, potassium, selenium, and zinc. For selenium, no data on the changes induced by durum wheat processing were available so far, notwithstanding the ever increasing awareness of the importance of this element to human health. Furthermore, the effect of cooking was investigated in order to determine the retention factors to be used for the estimation of the content of each element in the final product (as consumed) when the element concentration in the uncooked product is known.

Milling was the most important processing step in the production of conventional pasta in regard to the change in content of minerals originally present in the durum wheat grains. At least six groups of elements could be distinguished on the basis of their concentration decrease upon milling. Selenium had the highest retention with concentrations in semolina equal to 77%–85% of that in grain (dry weight basis), followed by calcium (54%–60%), copper (49%–53%), potassium and phosphorous (42%–47%), iron (36%–38%), magnesium and zinc (32%–36%).

Pasta making had little effect on element concentrations in semolina whereas cooking caused negligible to small losses of elements, except for calcium and potassium which greatly increased and decreased their concentration, respectively. Using the retention factors determined by the cooking experiments and the average concentrations ascertained in the commercial pasta samples it was assessed that pasta can provide nutritionally important amounts of several minerals, especially selenium, copper, magnesium, and zinc.

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