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Adsorption of Cadmium and Lead by Various Cereals from Korea

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Heavy metals such as lead (Pb), cadmium (Cd), mercury (Hg), and arsenic (As) are widely found in natural environments. These contaminants are not biodegraded and accumulate in the food chain (Rashed 2001). People are exposed to heavy metals primarily through consumption of contaminated foods such as fish and cereals (Llobet et al. 2003). The occurrence of heavy metal contaminants in crops is especially concerning in countries that consume cereals as the primary source of nutrition, since chronic exposure to these toxic elements, at even low levels, may cause adverse effects. For this reason, the residues of heavy metals found in some cereal products in various countries have been vigorously investigated (Zhang et al. 1998; Shimbo et al. 2001).

Dietary fibers are indigestible complex carbohydrates, and may play role in preventing the occurrence of chronic diseases including colon cancer, obesity, and cardiovascular disease (Torsdottir et al. 1991). These compounds are commonly found in fruits and vegetables as well as cereals (Clay et al. 1996). The intake of dietary fibers from cereals could be higher than those from fruit and vegetables in the countries that cereals are the primary source of nutrition. Since dietary fibers are not fully digested in human body, they have been proposed as a mean for decreasing the residue of heavy metals in the body due to their strong binding capacity for these toxic chemicals (Claye et al. 1996; Eromoseie and Otitolaye 1994). In this study, we measured the contents of heavy metals found in 18 different kinds of cereals consumed in Korea, evaluated the binding capacity of various cereals to Pb and Cd *in vitro,* and assessed the effect of various amounts of barley on binding capacity with Pb or Cd.

MATERIALS AND METHODS

Fifty-five cereals of 18 kinds were purchased from the local grocery stores at Seoul and KyungKi-do, Korea. These cereals were considered to be harvested locally, although production sites could not be entirely identified. Each type of cereal obtained from different grocery stores was mixed together for sample preparation. Chitosan (Sigma Chemical Co., St. Louis, MO, USA), cellulose (Riedel de Haen, AG, Germany), and activated charcoal (Wako Pure Chemical Industry Ltd., Japan) were commercially obtained for comparison with cereals in the binding capacity of heavy metals. Samples were digested with nitric acid

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(Dong Woo Fine Chem. Co., Korea) and sulfuric acid (Dong Woo Fine Chem. Co., Korea) to extract Pb and As. Standard solution (Wako Pure Chemical Industry Ltd., Japan) was diluted with 0.0015% L-cystein for Hg; 0.2% nitric acid for Pb and As; and 0.2% or 0.3% nitric acid for Cd. Sodium chloride (67.5 g) was added into 1.04 L of sodium bicarbonated buffer (950 ml 0.5 M $NaHCO_3$ + 90 ml 0.75 M CH_3COOH). Homogenized sample was mixed into solution (50 ml nitric acid + 50 ml sulfuric acid) for decomposition of Pb, Cd, and As. Heavy metals were analyzed the following operating conditions: (1) Cd, ICP (Inductively coupled plasma spectrometer, Model MX2, GBC Co., Australia): wavelength, 214.4 nm; sample gas flow rate, 0.5 L/min; plasma gas flow rate,11.0 L/min; auxiliary gas flow rate, 0.9 L/min; and (2) Pb and As, Graphite-AAS (Graphite-Atomic Absorption Spectrophotometry, Model 5100 ZL, Model FIAS 400, Perkin Elmer Co., USA): wave length, 283.3 nm for Pb and 193.4 nm for As; low slit, 0.7 nm; pyrolysis temperature, 850°C for Pb and 1200°C for As; and atomization, 1600 for Pb and 2000 for Cd. Hg levels were measured using a mercury analyzer (SP-3D, Nippon Instrument Co., Japan) after being mixed with a mixture (1:1, w/w) of anhydrous sodium carbonate (Nakari Chem. Ltd., Japan) and calcium hydroxide (Nakari Chem. Ltd., Japan), which were then heated at 800°C for 2 hr, following cooling down. Uncooked cereals were used to prevent heavy metal contamination from the cooking utensils. Since binding capacity is dependent on pH, temperature, and reaction time, this study was conducted under the simulated gastric condition (Rose and Quarterman 1987). Each sample was transferred to a 50 ml centrifuge tube and then placed in a shaking water bath (KMC-1205S W1, Vision Scientific Co., Korea) at 37°C for 30 min followed by the addition of 0.1 N HCl solution and 100 μg each of Pb and Cd. The pH was adjusted to 6.8 using a buffered saline solution. After incubation at 37°C for 2 hr, samples were centrifuged at 9000 x g for 40 min (Allegra 21R centrifuge, Beckman Coulter, Inc., USA) for isolation of the soluble and insoluble fractions. The concentration of Pb and Cd were measured using Flame-AAS under the following conditions: lamp current, 10 mA for Pb and 4 mA for Cd; wavelength, 283.3 nm for Pb and 228.8 nm for Cd; and slit width, 0.7 nm.

RESULTS AND DISCUSSION

The average concentrations of toxic metal residues in cereals were 1.3, 48., 10.7, and 0.7 μg/kg for Hg, Pb, Cd, and As, respectively (Table 1). Our measurements for Hg concentration were higher than those (approximately 0.03 μg/kg) from previous studies (Chung et al. 2000; Llobet et al. 2003). The Hg concentration from black rice was 10 times higher than that of other cereals such as prosomillet, barley, and maize (0.3-0.4 μg/kg). The concentrations of Pb measured in this study were significantly higher than those (0.025-3 μg/kg) in previous studies (Shimbo et al. 2001; Llobet et al. 2003). In particular, black rice, job's tears, gutinous millet, and perilla contained higher levels (61.8-91.2 μg/kg) of Pb than other cereals. Our data also showed that the mean concentrations of As and Cd found in cereals from Korea were less than those found in cereals from Spain (50

Table 1. The residues (μg/kg) of heavy metals in various cereals from Korea.

	Hg	Pb	Cd	As
Rice	2.2*(1.4-2.8)	23.8 (13.99-30.5)	4.9 (2.5-9.2)	2.5 (ND-4.4)
Black rice	4.1 (2.1-5.7)	91.2 (59.2-151.3)	10.6 (8.0-12.6)	ND
Glutinous rice	2.8 (2.0-3.5)	39.4 (24.1-66.5)	7.6 (4.8-12.7)	10.0 (ND-19.5)
Brown rice	2.5(1.2-3.1)	41.2 (15.8-67.7)	10.4 (2.7-20.1)	ND
Brown glutinous rice	2.8 (1.8-4.4)	37.3 (11.1-54.0)	10.3 (8.0-13.9)	0.5 (ND-1.4)
Prosomillet	0.4 (0.3-0.4)	53.5 (23.5-89.8)	6.3 (6.2-6.6)	ND
Barely	0.4 (0.3-0.5)	49.7 (21.8-82.5)	10.3 (5.0-18.8)	0.3 (ND-1.9)
Sorghum	0.5 (0.4-0.7)	45.2 (39.0-49.2)	14.7 (7.9-26.7)	ND
Maize	0.3 (0.2-0.4)	52.1 (39.0-72.0)	9.0 (5.0-7.4)	ND
Job's tears	0.6 (0.5-0.7)	61.8 (29.8-122.4)	6.5 (0.7-13.2)	ND
Foxtail millet	0.7 (0.3-1.3)	51.4 (34.8-66.7)	9.1 (7.7-11.2)	ND
Gutinous millet	0.9 (0.9-1.0)	85.4 (58.2-119.8)	8.1 (6.7-9.7)	ND
Buckwheat	0.4 (0.3-0.5)	40.7 (38.2-43.2)	5.6 (4.6-6.5)	ND
Wheat	0.9 (0.9-1.0)	27.0 (20.9-33.0)	4.1 (2.4-5.9)	ND
Wheat flour	0.3 (0.1-0.4)	25.4 (6.0-51.5)	3.4 (2.0-5.7)	ND
Sesame	0.8 (0.7-1.2)	45.3 (13.0-75.3)	28.8 (15.2-37.4)	ND
Perilla	1.2 (0.8-1.5)	80.7 (23.0-194.7)	16.9 (7.3-27.8)	ND
Black sesame	1.3 (1.0-1.7)	41.0 (13.0-96.1)	30.3 (1.2-46.4)	ND

* The values are means (min~max). † ND: Not detected (Hg, Cd, As< 0.1 μg/kg, Pb<1 μg/kg)

Table 2. Adsorption of Pb and Cd in the soluble and insoluble fraction of various cereals, chitosan, cellulose, and activated charcoal.

	Content (μg/kg)				Proportion (%)			
	Pb		Cd		Pb		Cd	
	S*	INS†	S	INS	S	INS	S	INS
Rice	51.38	55.48	9.47	75.58	48.09	51.91	11.13	88.87
Brown rice	23.87	105.30	3.00	82.13	18.48	81.52	3.52	96.48
Glutinous rice	30.13	98.87	8.93	75.62	23.36	76.64	10.57	89.43
Brown glutinous rice	22.95	104.83	0.40	85.03	17.96	82.04	0.47	99.53
Black rice	22.07	111.28	2.48	82.40	16.55	83.45	2.93	97.07
Barley	24.50	50.88	12.65	73.98	32.50	67.50	14.60	85.40
Sorghum	29.62	80.93	3.10	83.68	26.79	73.21	3.57	96.43
Foxtail millet	29.57	89.80	7.92	79.95	24.77	75.23	9.01	90.99
Gutinous millet	26.32	87.20	6.57	79.57	23.18	76.82	7.62	92.38
Prosomillet	22.03	116.80	0.27	86.63	15.87	84.13	0.31	99.69
Job's tears	20.32	103.63	4.87	84.32	16.39	83.61	5.46	94.54
Buckwheat	22.47	101.60	8.75	75.80	18.11	81.89	10.35	89.65
Wheat	19.98	95.95	1.90	82.37	17.24	82.76	2.25	97.75
Maize	23.87	103.78	6.33	78.63	18.70	81.30	7.45	92.55
Sesame	35.08	86.52	17.20	59.38	28.85	71.15	22.46	77.54
Perilla	23.90	107.63	8.28	73.02	18.17	81.83	10.19	89.81
Black sesame	26.38	81.20	12.78	58.23	24.52	75.48	18.00	82.00
Chitosan	19.25	112.93	0.00	72.97	14.56	85.44	0.00	100.0
Cellulose	45.23	86.20	60.88	24.25	34.42	65.58	71.52	28.48
Activated charcoal	19.30	80.70	0.00	100.0	19.30	80.70	0.00	100.0

* S: Soluble fraction, † INS: Insoluble fraction

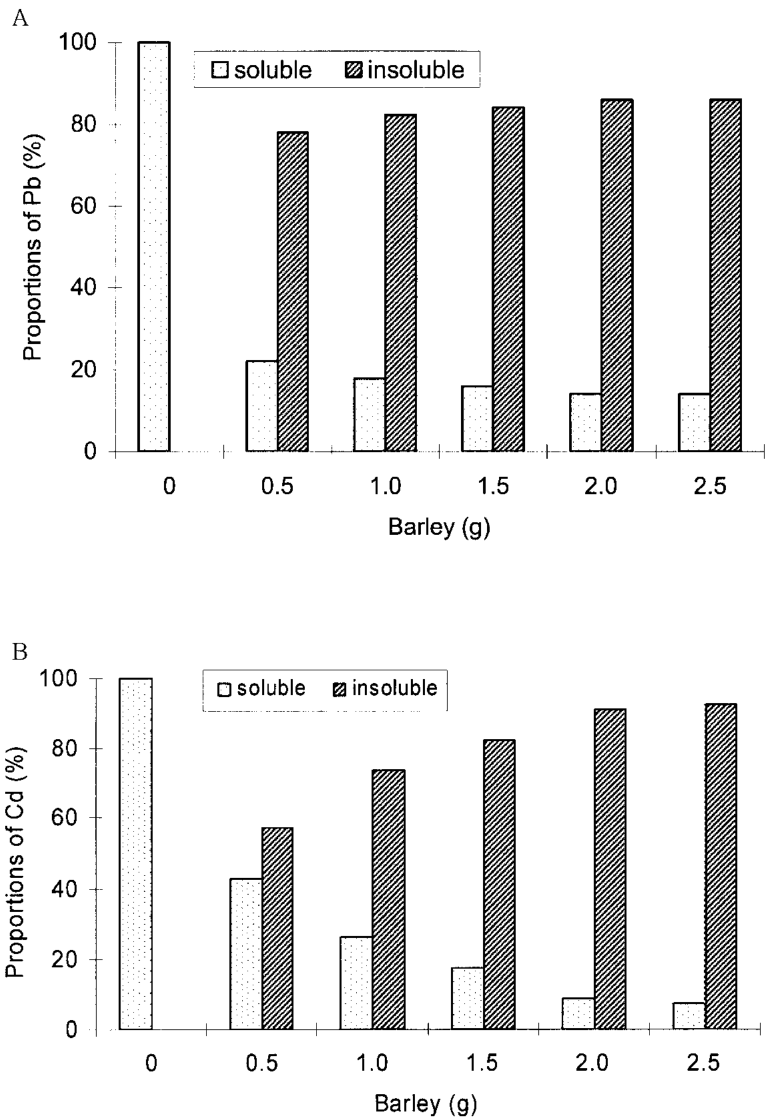

Figure 1. Adsorption of lead (Pb, A) and cadmium (Cd, B) to different amounts (0, 0.5, 1.0, 1.5, 2.0, and 2.5 g) of barley.

μg/kg for As, 350 μg/kg for Cd) and Japan (50 μg/kg for Cd) (Zhang et al. 1998; Shimbo et al. 2001; Watanae et al. 1989). Considering the fact that cereals are the primary source of carbohydrates in some countries, exposure to heavy metal, even at low level, through intake of cereals may be a significant health risk factor in these countries.

The binding capacity to Pb and Cd were compared between the soluble fraction and the insoluble fraction of cereals (Tables 2). Overall, the insoluble fraction of cereals had higher absorption with Pb and Cd than the soluble fraction. The insoluble fraction of prosomillet showed the strongest binding capacity to Pb (84.1%) and Cd (99.7%), while the insoluble fraction of black rice, job's tears, buckwheat, and wheat slightly adsorbed Cd and Pb. The insoluble fraction of rice and sesame exhibited 51% and 77.5% of adsorption levels with Pb and Cd, respectively. This data suggest that a dietary fiber which is the insoluble fraction of cereals may be associated with binding trace metals as reported in previous study (Ou et al. 1999). Both chitosan and activated charcoal in the insoluble fraction showed 80-85% and 100% of the binding capacity of Pb and Cd, respectively (Table 2). This study indicates that prosomillet has a potential function to bind trace metals and thereby eliminate them in the body without digestion. In contrast, cellulose in the insoluble fraction showed low binding capacities of 65.6% and 28.5% to Pb and Cd, respectively. This data showed good agreement with the result of Claye et al. (1996), who reported that the binding capacity of cellulose *in vitro* was less than other dietary fibers such as hemicellulose and lignin. Different amounts of barely were assessed to determine the effect of amounts of barley on the ability to bind Pb and Cd (Figure 1). The amounts of barley present in both the soluble and insoluble fractions had no effect on Pb adsorption. On the contrary, Cd adsorption was slightly enhanced in the insoluble fraction as the amounts of barley was increased, which was comparable to previous studies that binding capacity to heavy metals was directly proportional to the amount of dietary fiber present *in vitro* (Okieimen et al. 1985; Rose and Quarterman 1987).

The concentration of heavy metal residues in various cereals from Korea was found to be relatively low. However, the increased consumption of some cereals such as rice and wheat may enhance the exposure to heavy metals. Among the cereals tested, prosomillet showed the highest binding capacity to Pb and Cd in the insoluble fraction. This study suggests that a certain type of cereals including prosomillet can be developed for functional foods, since the cereals have a strong binding capacity to trace heavy metals so that they may reduce the exposure to heavy metals through consuming foods.

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