Trace nutrients

2.* Manganese in British food

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1. The amount of manganese in nationally-representative samples of prepared and cooked groups of foods, and in a wide variety of individual foods, was determined by atomic absorption spectroscopy.

2. The average British diet was calculated to provide 4.6 mg Mn/d of which half was derived from tea and other beverages, 30 % from cereals, and 15 % from vegetables and fruit. Animal products provided little Mn. 3. Individual foods other than tea which were particularly rich in Mn in Britain were unrefined and partially-refined cereals, and some spices and herbs. Some vegetables and fruit, coffee, wine, chocolate and brown sugar also contained significant amounts of Mn.

Manganese is one of the most abundant elements in the earth's crust (Goldschmidt, 1958) and is present in all animal and plant tissues, in fresh and salt water (Schroeder *et al.* 1966), in rain and in dust in the atmosphere (Peirson *et al.* 1974). It has also been detected in all human tissues examined (Schroeder *et al.* 1966; Hamilton *et al.* 1972).

Mn is known to be a co-factor in a number of human enzyme systems (US National Academy of Sciences, 1973), but no correlation between dietary intakes and the activity of any of these enzymes has been demonstrated. It has been suggested that Mn might be replaced by other metal ions which act as activators when Mn availability is low (Burch et al. 1975), but these mechanisms have not been investigated in vivo. Mn is especially associated with the synthesis of protein, DNA and RNA, and particularly with cartilage mucopolysaccharide synthesis (Underwood, 1977). Human requirements for this element are not known (WHO, 1973), and there was even doubt that a deficiency could occur in man until Doisy (1973) recognized the first case in a volunteer undergoing a study of vitamin K deficiency in a metabolic ward. An inadvertent failure to add Mn to a purified diet mixture resulted in weight loss, transient dermatitis, nausea and slow growth of hair and beard with changes in hair colour, and biochemically there was striking hypocholesterolaemia. In animals, the most common signs of deficiency include shortening of the limbs and abnormal fat deposits (Underwood, 1977). Toxic reactions to Mn in man have only been reported in miners exposed to very high concentrations of Mn ores (Borg & Cotzias, 1958; Cotzias 1958) but these were attributed to continuous absorption from dust in the lungs rather than from the intestine. High dietary intakes are, however, deleterious to very young rats (Chandra & Shukla, 1978), but human infants normally receive very little Mn (McLeod & Robinson, 1972b). There have been many studies of Mn in food and in selected diets in other countries, and more recent examples than those reviewed by Schlettwein-Gsell & Mommsen-Straub, 1971) are summarized in Table 1. The Mn content of most foods does not normally appear to be subject to wide variation, but total intakes are very dependent upon the kinds of cereal products eaten and the amount of tea drunk because wheat germ,

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Table 1. Studies of manganese intakes during the past 10 years

bran and tea are particularly rich in this element. The importance of these items in the British diet was one of the reasons which led to the inclusion of Mn in evaluations of the intakes of trace nutrients and other minor constituents of food in this country by the Ministry of Agriculture, Fisheries and Food. The only previous studies of Mn in Britain were by Monier-Williams (1949) who reported the daily intake of one married couple in 1937 to be 7 mg, of which almost half came from tea, and by Hamilton & Minski (1972) who found that samples of the 'total diet' from England and Wales in 1966–7 indicated an average intake of approximately 2.7 mg/d; the latter study, however, included no tea. Preliminary results from our work have been published (Ministry of Agriculture, Fisheries and Food, 1978) and the information is now reported in detail.

Intoka

METHODS

Food samples

The average daily intake of Mn was estimated by means of the food samples collected for the Ministry of Agriculture, Fisheries and Food's 'total-diet' study during 1976. The organization of this study and the foods included have been described elsewhere (Buss & Lindsay, 1978) but, in brief, selected colleges throughout Great Britain and Northern Ireland buy specified amounts of some seventy major foods in local shops and prepare and cook them as for eating; the foods are then combined into groups for analytical convenience. The study differs in detail from that described by Harries *et al.* (1969); of particular relevance for estimating Mn intakes is the inclusion of a 'beverages' group containing an infusion from a representative quantity of tea.

Fourteen colleges provided twenty-five sets of samples during the course of the year, with three to eleven participating in each quarter. These colleges were in Aberdeen, Edinburgh, Glasgow, Newcastle, Ilkley, Sheffield, Liverpool, Shrewsbury, Leicester, Brighton, Torquay, Jersey, Cardiff and Cookstown (Northern Ireland), and were thus as representative of the United Kingdom as possible.

In addition, a range of individual British foods was analysed. Most had been obtained during studies of lead and cadmium intakes (Ministry of Agriculture, Fisheries and Food, 1972, 1973), while others obtained for studies of other dietary constituents were also analysed for Mn while the samples were available. Finally, samples of food which had not otherwise been covered but which are major items in the diet or were expected to contain significantly large or small amounts of Mn, were bought in the London area to complete the study. Tea, however, was not included as it has already been studied in detail by Michie & Dixon (1977).

Analytical methods

For 'total-diet' samples and for moist foods 10 g from a representative sample were analysed, for wet foods 15-20 g were used, and for dry foods, such as powders, 2 g were taken. Most foods were digested with sulphuric acid and nitric acid; when no further charring occurred the excess of nitric acid was boiled off with two additions of water followed by heating until fumes of sulphur trioxide appeared. After dilution to 100 ml, Mn was estimated by atomic absorption spectrophotometry (Perkin Elmer model 403; Perkin Elmer, Post Office Lane, Beaconsfield, Bucks.) at 279.5 nm using a 100 mm burner. Alternatively, some samples were dry-ashed in silica crucibles at 500° overnight and the residue was taken up in 6 M-hydrochloric acid (5 ml) and evaporated to dryness. A further 5 ml HCl was added and the solution was transferred and diluted to 100 ml with water. In either instance standards containing the appropriate amount of acid were used. Full details of this method will be published elsewhere.

With this procedure recoveries are quantitative within ± 5 %: determination of the Mn content of National Bureau of Standards reference material NBS 1571 (orchard leaves) gave $89 \pm 1 \text{ mg/kg}$ (certificate 91 ± 4), while the determination of the Mn content of NBS 1577 (bovine liver) gave $12 \cdot 5 \pm 0.6$ (certificate $10 \cdot 3 \pm 1.0$). All analyses were carried out at the Laboratory of the Government Chemist, London.

RESULTS

'Total-diet' study

The results are summarized in Table 2. Values for individual colleges in different geographical areas are not presented because any variations were as likely to reflect individual differences in sampling, washing, preparing and cooking the components (which the study

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	Mn conte	Mn content (mg/kg)		Estimated intake of Mn (mg/person
Food group	Mean	Range	food eaten* (kg/d)	per d)
Cereals	6.77	2.4–14.0	0.53	1.26
Meat	0.20	0.32-1.1	0.12	0.09
Fish	0.85	0.42-1.3	0.05	0.02
Milk	< 0.10		0.40	< 0.04
Fats	< 0.30		0.08	< 0.02
Root vegetables	1.34	0.2-5-5-5	0.18	0.24
Other vegetables	1.51	I .0-2.2	0.11	0.17
Fruit and sugars	1.67	0.4-3.6	0.12	0.28
Beverages†	18.67	7.1-38.0	0.15	2.24
				approximately
			1.46	4.6

Table 2. Manganese content of 'total-diet' samples and estimated average daily intake,1976

* From Buss & Lindsay (1978)

 \dagger Each beverage sample contained 2 g coffee, 20 g concentrated soft drinks and 71 g 'ready-to-drink' soft drinks, plus the strained infusion from 7 g tea leaves (i.e. a total of 100 g as purchased). The volume of the tea infusion, which was recorded, ranged from 140-1000 ml and the concentration of Mn in the samples as received varied from 1.97-7.4 mg/kg. The Mn contents quoted have, however, been expressed per kg beverage 'as purchased'.

was designed to include) as they were to reflect real regional variations in Mn intake. Nevertheless, some colleges which provided more than one sample in the year showed consistently lower or higher amounts of Mn than the other colleges, although there was no consistent regional pattern. There was also no significant seasonal variation beyond that explicable from the different amounts of fruits and 'other vegetables' purchased. Only the mean Mn content for each food group for the whole year is therefore presented. These mean values were also used to calculate the national average intakes of Mn from different food groups, and the total intake of 4.6 mg Mn/person per d.

On average, nearly half the Mn in the United Kingdom was derived from beverages, including tea infusions as commonly consumed. Apart from this the only major source was cereals and cereal products including bread, flour, rice and breakfast cereals, which provided a further 30 % of the intake. Animal products (meat, fish and milk) and all fats together provided insignificant quantities, and fruits and vegetables provided the balance of the average intake (15 %). As these milk and fats samples contained Mn at levels below the limits of detection (0·1 and 0·2 mg/kg respectively) no further samples of these foods were taken for separate analysis.

Individual foods

The results of nearly 450 analyses of the raw edible portion of a wide variety of foods are summarized in Table 3. They are consistent with the patterns shown by the total diet samples.

Besides tea (Michie & Dixon, 1977), the richest sources of Mn among the foods commonly eaten in Britain were herbs and spices, notably sage (*Salvia officinalis*), mint (*Mentha spicata*), thyme (*Thymus vulgaris*), pepper (*Piper nigrum*), ginger (*Zingibner officinale*) and curry powder. Unrefined and partially-refined cereals were also rich, with brown and wholemeal flour, wheat germ, unpolished rice and oats all containing more than 25 mg/kg. Corn flakes, in contrast, contained very little Mn. Most animal products (meat and meat products, cheese and eggs) contained less than 0.5 mg/kg, although a few including fish

Table 3. Manganese content (mg/kg) of selected foods in Britain

(Individual values are given for up to three samples of the same kind of food; otherwise the mean and range are presented, with the number of samples in parentheses)

and range are presented, with the number of sumpted in parentitieses,	
	Mn content
Cereals:	
Flour:	
White, bread-making (twenty-four mills; bulked)	6.7
Brown, bread-making (twelve mills; bulked)	27, 28
Wholemeal, bread-making (eight mills, bulked)	28, 35
White, domestic	5.3
Wholemeal, retail	22, 25, 26
Bread:	
White (6)	4.1 (3.1–5.6)
Brown (4)	17.1 (13.7–21.2)
Wheat germ	110, 110, 150
Rice:	
Long grain, unpolished	40
Short grain, white	8.7
Oatmeal	34
Rolled oats	37
Rye flour	6.8
Corn flakes (5)	0.8 (0.7–0.9)
Breakfast cereals, assorted (8)	18
Meat:	
Beef (seven cuts, home-produced and imported)	0.6 (0.4–0.8)
Pork (three cuts)	0.3, 0.5, 0.6
Lamb (three cuts, home-produced and imported)	0.3, 0.4, 0.4
Chicken	0.3
Liver:	•
Ox	2.8, 3.6, 4.7
Lamb (4)	3.1 (2.5-4.0)
Pig	2.8, 3.0, 4.9
Chicken	1.7
Kidney:	
Ox	1.6, 2.3
Lamb (4)	1.8 (1.5-2.4)
Pig	1.7, 1.7
Sweetbread (lamb); melts (pig)	0.4; 0.4
Meat products:	
Stewing steak, canned	0.8, 0.8
Beefburger	1.6
Faggots	1.6
Steak and kidney pie	0.8, 1.9
Bacon	0.4
Luncheon meat, pork	0.7, 1.0, 1.1
Ham and pork, chopped	0.2
Lamb's tongue	0.7
Salami	0.6
Black pudding; blutwurst	2.1; 2.3
Fish:	
	0.6 1.1
Cod Plaice	0·5, 1·1 1·8
Haddock	0.8
Haddock	1.1
	I I I·3
Kipper Fich forgers	0.9
Fish fingers	v y
Dairy products:	(
Cheese, Cheddar (5)	0.3 (0.2-0.3)
Egg: White (5)	< 0.1 (< 0.1)
Yolk (5)	0.5 (0.4-0.8)

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Table 3 (cont.)

		Mn content
Vegetables:		
Fresh: Potato (5)		1.2 (0.7–1.9)
Cabbage (5)		2.2(1.8-2.9)
Cauliflower (5)		2.7 (2.0-3.1)
Spinach (4)		5.8 (2.0-13)
Carrots (5)		0.8 (0.4–1.1)
Frozen:		
Peas (5)		2.6 (1.6-4.9)
Runner beans (5)		2·2 (1·9–2·6)
Canned: Peas		1.6, 1.9, 1.9
Beans, various		1.0, 1.4, 2.4
Sweetcorn		0.4
Tomatoes		0.9
Tomato juice (4)		1.0 (0.2–1.6)
Asparagus		2.9
Mushrooms		0.3, 0.7
Celery hearts		0.8
Mixed vegetables		1.2
Fruit: Fresh:		
Apples		1.0
Oranges (10)		0.3 (0.2-0.2)
Bananas (5)		10.2 (1.9-19)
Canned:	Fruit	Syrup
Apricots, cherries (red and black), gooseberries,	0.9	0.6
grapefruit, mandarin oranges, peaches, pears,	(0.2-1.9)	(0·2–0·9)
plums, redcurrants (19)		
Blackberries	5.4, 10.1	3.2, 5.4
Blackcurrants (4)	5.1 (1.9-8)	5·0 (0·9–6·8) 1·6
Figs Pineapple	2·3 3·5, 3·5	3.3, 2.7
Raspberries	2.9, 3.2	2.2, 2.5
Rhubarb	0.5, 1.8	2.2
Pineapple juice (8)	0,	7.8 (5.3–13.9)
Nuts:		
Almonds (5)		17 (11–26)
Brazil nuts (5)		10.7 (6.6–18)
Sugar and Confectionery:		
Sugar:		
White		< 0.2, 0.2, 0.4
Demerara		0 [.] 6, 2.6 8.4, 10
Brown Chocolate (23)		4·8 (1·3–16)
Beverages:		40(1310)
Beer (20)		0.1 (0.1-0.2)
Wine:		
White (15)		8.8 (0.3-23.4)
Red (5)		14·4 (5·3–19·5)
Coffee:		
Instant (12)		20 (13-39)
Ground		15, 24, 29 1
Essence with chicory Tea:		I
Dry (14)		610 (350-900)
Baby foods:		
Infant milk, dried (4)		2·3 (1·4-3·9)
Dried foods, assorted (16)		6.0 (2.1-9.7)
Miscellaneous, canned or bottled (4)		1.5 (1.0-2.3)
X.		

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Table 3	(cont.)
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	Mn content
Pickles and spices:	
Chutney	1.3, 1.5
Soup, tinned	7.1, 7.3, 8.5
Tomato:	
Ketchup	I·9, 2·2
Paste, puree and sauce (9)	3.4 (2.2-6.1)
Curry powder	42, 45, 54
Garlic powder (Allium sativum)	IO
Ginger, ground (Zingibner officinale)	280
Mace (Myristica fragrans)	23
Mustard (7)	6.6 (5.2-7.9)
Mustard powder	17
Pepper:	
White (Piper nigrum)	45
Black (Piper nigrum)	39, 90
Cayenne (Capiscum frutescens)	23
Pimento (Pimenta dioica)	17
Salt (sodium chloride), seasoned	15
Turmeric (Curcuma longa)	32, 41
Mint (Mentha spicata)	92
Oregano (Lipia berlandieria)	14
Rosemary (Rosmarinus officinalis)	5
Sage (Salvia officinalis)	250
Thyme (Thymus vulgaris)	76

contained over 1 mg/kg and liver as much as 5 mg/kg. Most vegetables and canned fruit contained between 1 and 5 mg Mn/kg, although bananas and nuts were richer. Brown sugar, chocolate, wine and coffee were also significant sources of Mn.

DISCUSSION

The 'total-diet' study indicates that the average intake of Mn in the United Kingdom is approximately 4.6 mg/d, and that nearly half this amount is derived from tea. Individuals who do not drink tea are unlikely to make up this amount from other beverages, for it would take an additional 4 oz (100 g) of instant coffee or three glasses of wine (approximately)/d to contribute the same amount of Mn. Intakes in most other developed countries where meat, milk, refined cereals and sugar are also dietary staples are slightly lower than this country (Table 1), presumably because less tea is drunk, and cereals become the main source of Mn. Individuals who eat unrefined or partially-refined cereals could, however, obtain substantially more Mn than those who prefer the refined cereals, although Cresta (1976) predicted that intakes in Benin and Zaire would still be lower than we have found.

It should also be noted that half of the Mn in cereals is in the aleurone layer where the dietary fibre and phytic acid predominate (O'Dell *et al.* 1972) and it may therefore not be readily absorbed. Although phytases could release Mn during dough fermentation and digestion as with calcium, iron and zinc (Reinhold *et al.* 1975), it may nevertheless then be re-bound by fibre fractions in diets rich in wholemeal cereals. In contrast, the Mn in tea infusions is all in a soluble form and is therefore more likely to be physiologically available. This contrasts with Fe, where not only is almost none extracted from the leaves but the tannins present also form insoluble complexes with other dietary sources of the element (Disler *et al.* 1975; Michie & Dixon, 1977).

The concentrations of Mn in our samples of individual British foods (including milk and fats from the 'total-diet' samples) were generally well within the ranges for similar foods where these have been determined elsewhere (Schlettwein-Gsell & Mommsen-Straub, 1971;

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Guthrie, 1975), but there were some exceptions. In particular, previous estimates of Mn in wholemeal flour in Germany (Schweigart, 1962) and New Zealand (Guthrie, 1975) were higher than in this country. This could have been due to different milling practices, for there are wide variations in Mn content in different parts of the grain, or possibly to the different 'hardnesses' of the wheat. All twenty-three chocolate samples contained less than half the Mn of other studies (Schlettwein-Gsell & Mommsen-Straub, 1971), while our brown sugar contained approximately ten times the Mn of the only other published analysis (Guthrie, 1975). Brown sugar is, however, like the wines and certain other manufactured foods, an extremely variable product.

A number of foods, including the meat products, kippers, fish fingers and most of the canned vegetables and fruits had not previously been analysed for Mn, but none of these proved to be a significant source except for the tinned soups which contained $7 \cdot I - 8 \cdot 5 \text{ mg/kg}$ and curry powder which contained 42-45 mg/kg.

The amounts of Mn in the UK diet are unlikely to be too low for health, for Schroeder (1965) concluded that intakes of 2 mg/d are adequate, and Guthrie & Robinson (1977) reported recently that thirty-nine of 179 apparently-healthy women in New Zealand were consuming less than 2 mg/d. Intakes as low as 0.71 mg/d, however, lead to negative Mn balance (De, 1949), and infants whose intakes may be as low as 10 μ g/d are normally in negative balance until their diets are supplemented by cereals (WHO, 1973). Neither will these intakes be too high for health, for Mn is one of the least toxic of all elements and intakes as high as 500-2000 mg/kg food appear necessary even to retard growth in farm and experimental animals. Absorption is very low and that which is absorbed is efficiently excreted through the bile and appears in the faeces (Underwood, 1977). Further interpretation of these results must, however, await more information about the relative absorption of Mn from tea and from cereals (particularly wholegrain cereals) in the the context of the mixed diet of this country.

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