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ORIGINAL ARTICLE

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Environmental and occupational exposure to manganese: a multimedia assessment

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Abstract Methylcyclopentadienyl manganese tricarbonyl (MMT) is an organic additive used in Canada since 1976 as an anti-knock agent in unleaded gasoline. Its combustion leads to the emission of Mn oxides, especially Mn_3O_4. Since no study has assessed the potential risk of chronic exposure to low concentrations resulting from these emissions, the present investigation was undertaken to assess the level of environmental and occupational exposure of the human population. The multimedia exposure of two groups of workers (garage mechanics and blue-collar workers) potentially exposed to different levels of Mn from the combustion of MMT was assessed using personal air samplers, a dietary compilation, water samples at their places of residence, an epidemiological questionnaire and blood and hair samples. Results show that garage mechanics were exposed on average to higher atmospheric Mn at work (0.42 $\mu g/m^3$) than the blue-collar workers (0.04 $\mu g/m^3$). However, the contribution of atmospheric Mn to the total absorbed dose was less than 1%, and well below the standards estabished for occupational or environmental exposure; food contributes more than 95% of the multimedia dose. The average whole blood Mn concentrations were similar for the two groups (0.67–0.76 $\mu g/100$ ml) and fall within the normal adult range. The average hair Mn concentrations were significantly higher for the garage mechanics (0.66 $\mu g/g$) than for the blue-collar workers (0.39 $\mu g/g$). The contribution of exogenous Mn versus endogenous Mn is questioned. As judged by the governmental standards or criteria for occupational and non-occupational environments, the current Mn levels in food, water and air may not cause any problems for the workers.

Key words Biomarker · Human exposure · Manganese · Methylcyclopentadienyl manganese tricarbonyl · Multimedia

Introduction

Methylcyclopentadienyl manganese tricarbonyl (MMT: $C_9H_7MnO_3$) is an organic derivative of manganese used as an anti-knock agent in unleaded gasoline (Abbott 1987; Cooper 1984). Used in Canada since 1976 (Environment Canada 1987), MMT has seen a substantial increase in its utilization over the last few years, in particular since it replaced lead in gasoline (Royal Society of Canada 1986). The combustion of MMT leads to the formation of Mn oxides, mainly tetraoxide or hausmannite (Mn_3O_4) (Ter Harr et al. 1975). The percent of Mn emitted from the tailpipe varies and is influenced by many factors, including the condition of the vehicle and the driving cycle. According to the U.S. EPA (1990), an average tailpipe Mn emission rate of 30% appears to be a reasonable estimate. Particles of Mn_3O_4 emitted into the atmosphere have a mass median diameter of less than 0.4 µm (Mena 1980).

It has been suggested that one of the principal sources of environmental contamination and exposure to inorganic Mn in the urban area may be the combustion of MMT in gasoline (Davis et al. 1988; Environment Canada 1987; Joselow et al. 1978). The potential health risk to human populations and to the environment associated with the use of MMT in gasoline nevertheless remains poorly characterized. The lack of toxicological data about the long-term effects of chronic exposure to Mn from the combustion of MMT has considerably limited its use throughout the world (U.S. EPA 1990). However, in Canada, Health and Welfare Canada stated in 1978 that there was no evidence that the combustion of MMT would constitute a hazard to human health. On the other hand, many studies in

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occupational environments have shown that high atmospheric Mn concentrations have significant effects on human health (Organisation Mondiale de la Santé 1981; U. S. DHHS 1992; U. S. EPA 1984). Most of the results have focussed on the relationship between Mn exposure by inhalation and neurological signs and symptoms among active working populations (Hua and Huang 1991; Iregren 1990; Mergler et al. 1994; Roels et al. 1987a; Wang et al. 1989; Wennberg et al. 1992). Moreover, many neurodegenerative disorders similar to Parkinson's disease have been related to occupational exposure to Mn (Barbeau 1984; Calne 1991; Zayed et al. 1990).

Recent research efforts have attempted to assess the environmental Mn contamination arising from the combustion of MMT in abiotic (Loranger et al. 1994c; Loranger and Zayed 1994, 1995) and biotic (Brault et al. 1994; Loranger et al. 1994b) systems as well as human exposure (Drolet and Zayed 1994; Loranger et al. 1994a; Sierra et al. 1995; Zayed et al. 1994). These studies are important to an understanding of the environmental fate of Mn and ultimately to the quantification of the total human exposure. The present study was thus undertaken to further document the multimedia exposure to Mn using two groups of workers potentially exposed to different levels of Mn from MMT.

Materials and methods

From June to November 1992, garage mechanics from the Montreal region and blue-collar workers from the University of Montreal were selected to assess the multimedia exposure to Mn. All participants were white males. The garage mechanics were selected since they are potentially more exposed to Mn from the combustion of MMT (Zayed et al. 1994). The blue-collar workers were selected as a control group.

The sample size of each group was calculated using the Power program (Epicenter Software, Pasedena, Calif.). The calculation was based on the variance, the sample size, and the absolute mean differences of two data sets: (1) the annual atmospheric Mn concentrations measured in 1990 in Montreal at sampling stations of high and low traffic density (Communauté Urbaine de Montréal 1991); (2) the whole blood Mn concentrations measured for workers at a ferromanganese plant (Beauharnois, 25 km south of Montréal) and for adults living in the vicinity of the plant (Mergler et al. 1994). The theoretical sample sizes were estimated respectively at 45 and 47 individuals for air and blood data sets ($1-\beta = 0.8$, $\alpha = 0.05$). It must be pointed out that logistic constraints led us to limit the number of participants depending on the media sampled (see below).

Epidemiological data

At the beginning of the study, a questionnaire was completed by an epidemiologist for each participant. This questionnaire covered the following aspects: history of residence, history of employment, food and drug consumption, living habits including tobacco, alcohol, coffee and tea consumption, and health status in relation to respiratory problems. Each participant signed a consent form (conforming to the ethical standards of the University of Montréal) and received assurance as to the confidentiality of any information given.

Air sampling

Personal breathing zone air samples were collected using a Gil-Air portable pumps. Occupational exposure for each worker was estimated over a 5-day period (Monday through Friday) during working hours. Environmental exposure was evaluated on 2 days of the same week during non-working hours. In total, 43 garage mechanics and 30 blue-collar workers participated in the air sampling. All participants were asked to carry the air sampler or place it nearby when this was not possible (i.e. at night). At the beginning of every sampling day, each pump was calibrated to maintain a constant air flow (1.5 l/min) and a new filter (Membra-Fil mixed esters of cellulose, 0.8 μm, 37 mm diameter) was inserted in a three-piece cassette. New pumps were given to the workers for the off-work sampling. All the filters were analysed by neutron activation (INAA) to estimate total Mn and Fe concentrations (Kennedy 1989). In total, 17 blank filters were analysed by INAA for metal content. The detailed methodology related to the sampling and chemical analysis has been described in two previous studies (Sierra et al. 1995; Zayed et al. 1994). We must point out that in the case of the garage mechanics the present study includes the results from both of the aforementioned studies for atmospheric Mn concentrations.

Food and water intake

Daily food intake was measured using a dietary journal completed by each participant at the workplace and at home over 3 full days, including two weekdays and a weekend day. The workers were instructed to record both qualitatively and quantitatively all the items ingested using a specific procedure (Drolet and Zayed 1994). In total, 37 garage mechanics and 28 blue-collar workers participated in this evaluation. The dietary records were analysed using the Nutrient Analysis Program (Warwick E.W., Home Economics Department, University of Prince Edward Island, 1991), the Canadian Nutrient and Condensed Files (1991) and the Michigan State University Nutrient Data Bank. Energy content, dietary fibre and several nutrient intakes were estimated for each day. Only Mn and Fe intakes have been used in the present study. All the data were expressed in mg per day and represent the 3-day average intake for each element.

During Autumn 1992, a complementary study aiming at the estimation of the metal concentrations in the tap water of each worker's residence was conducted by our research group (Loranger et al. 1994a). In total, 33 garage mechanic and 25 blue-collar residences were sampled. Two water samples were collected at each residence, one at the first jet and the second after 1 min of flow. The average Mn and Fe concentrations of the two samples (μg/l) were used to calculate the Mn and Fe water contribution to the diet.

Biological indicators

Blood samples (6 ml) were taken at the end of the last day of the working week. Whole blood and serum Mn were analysed by atomic absorption. Serum iron was measured by spectrophotometry (Sigma kit, 565-A). Hair samples (≈ 0.5 g) were collected from the occipital region with stainless steel scissors. Hair samples were washed for 15 min in an ultrasound bath with triton X-100 to remove any dust or particles at the surface of the hair. Samples were then filtered and rinsed 4 times with 50 ml of ddH_2O and twice with 10 ml of methanol. Hair samples were finally collected on paper filters and placed in decontaminated polyethylene vials with Teflon forceps. Mn concentrations in hair were determined by INAA. The detailed methodology concerning the sampling and the chemical analyses of blood and hair can be found elsewhere (Février 1994).

Exposure and absorbed doses

The exposure dose (ED) for food was calculated by dividing workers' Mn or Fe daily intake by their weight. The absorbed dose (AD) was estimated by multiplying the food ED by the assumed absorption fraction by ingestion for Mn (3%) (Davidsson et al. 1989) and Fe (5%) (Morris 1987). The Mn and Fe EDs via water consumption were calculated by multiplying the average Mn and Fe concentrations measured at each worker's residence (μg/l) by the estimated average daily volume drunk by an adult (2 l/day). This was then divided by the worker's weight. As with food, the AD for water consumption was the assumed absorption fraction multiplied by the water consumption ED.

The occupational and non-occupational EDs via ambient air were calculated by multiplying the average atmospheric concentrations of Mn and Fe (μg/m^3) at work (5-day average) and at home (2-day average) by the volume of inhaled air at each site: home = $16\ \text{h} \times 24\ \text{m}^3/24\ \text{h}$; work = $8\ \text{h} \times 20\ \text{m}^3/24\ \text{h}$. The total ED for atmospheric Mn and Fe was calculated by summing the occupational and non-occupational ED's. Since there is no study indicating the absorption rate by human or animal lungs following exposure to Mn dusts (U.S. DHHS 1992), we fixed the absorption fraction for Mn and Fe at 100%. Thus, the atmospheric Mn and Fe ADs are equal to the EDs. The multimedia ED or AD for each worker was estimated by summing his ED or AD per medium (food, water, air). All the results were expressed as μg/kg per day. It must be pointed out that all cases with at least one missing value for any variable were deleted listwise in order to calculate comparable exposure and absorbed doses for each medium. The sample size was thus reduced to 25 for blue-collar workers and 29 garage mechanics for this calculation.

Statistical analysis

Descriptive statistics were calculated for all quantitative variables. Group comparisons for these variables were made using a non-parametric test for independent samples (Mann-Whitney *U* test). Semi-quantitative variables were compared using chi-square statistics. Correlations between the media-specific AD, the multimedia AD and the biological indicators were calculated using non-parametric Kendall's τ. All the analyses were performed using SAS (SAS Institute Inc. 1985).

Results

Epidemiological data

The garage mechanics were significantly younger ($P < 0.01$) than the blue-collar workers, with average ages of 34 and 42 years respectively (Table 1). The average weights were similar, with values of 79 kg for the blue-collar workers and 77 kg for the mechanics. Heights were also almost identical, with average values around 175 cm. Each group smoked less than one packet of cigarettes per day on average (< 20 cigarettes), but showed great interindividual variation, with a standard deviation close to the average value. Alcohol consumption was similar for both groups, except for wine, of which blue-collar workers drank an average of five glasses per week compared to one for garage mechanics.

The garage mechanics had an average of 6 years of service compared to 10 years for blue-collar workers (Table 2). Garage mechanics worked almost all the time in the garage (7.5 h) during working days and were frequently in contact with gasoline or welding materials (> 70%). The blue-collar workers were usually inside

Table 1 Physical characteristics, living habits and working history of blue-collar workers and garage mechanics

Variable[a]	Blue-collar workers (n = 30)			Garage mechanics (n = 43)		
	Mean	SD	Range	Mean	SD	Range
Age	42**	11	22–63	34	10	19–57
Weight (kg)	79.0	11.7	56.8–97.6	76.7	9.8	59.0–102.1
Height (cm)	175.1	6.7	162.6–188.0	176.4	6.9	167.6–193.0
Living habits						
Cigarettes (cig./day)	15	17	0–50	9	13	0–50
Spirits (ounces/wk)[b]	3.8	15.2	0–80	0.3	1.0	0–5
Beer (bottles/wk)[c]	6	8	0–24	8	10	0–48
Wine (glasses/wk)[d]	5*	10	0–50	1	2	0–10
Coffee (cups/day)[d]	3	2	0–12	2	2	0–10
Tea (cups/day)	< 1	< 1	0–2	< 1	1	0–6

[a] Underlined means are significantly different at $P < 0.01$ (**) and $P < 0.05$ (*) (Mann-Whitney *U* test)
[b] Ounce = 28 ml
[c] Bottle = 12 ounces = 336 ml
[d] Glass or cup = 8 ounces = 224 ml

Table 2 Working history and exposure, frequency of respiratory problems and home location of blue-collar workers and garage mechanics

Variable	Blue-collar workers (n = 30)			Garage mechanics (n = 43)		
	Mean[a]	SD	Range	Mean	SD	Range
Working history (months)						
Present job	114.5**	97.3	9–286	69.8	46.8	2–225
Previous job	24.9	43.8	0–180	15.0	34.3	0–180
Working Environment (h)						
Indoor	6***	2	1–8	7.5	1.5	0–9
Outdoor	2***	2	0–8	0.5	0.5	0–2
Working exposure[b] (%)						
Garage work	37			100***		
Gasoline: direct contact	20			77***		
Welding: direct contact	27			72***		
Respiratory problems[b] (%)	13			23 NS		
Home location[b] (%)						
Urban	37			30 NS		
Suburban	63			70		

[a] Underlined means are significantly different at $P < 0.001$ (***) and $P < 0.01$ (**) (Mann-Whitney *U* test)

[b] Worker groups are significantly different at $P < 0.001$ (***) or non-significantly different at $P > 0.05$ (NS) (chi-square statistic)

a building (75%) during the working hours and were significantly less frequently in a garage than the garage mechanics (37%). Less than 20% of all the workers (14/73) showed respiratory symptoms (asthma, cough, bronchitis) over the last year and no difference was observed between the two groups ($P > 0.05$). About one-third of the workers were living in the urban area, the others in suburbs.

Mn and Fe concentrations in the different media

The average Mn daily food intakes were similar for garage mechanics and blue-collar workers ($P > 0.05$), at 2.9 and 3.7 mg/day respectively (Table 3). The average Mn daily food intake for all the workers was 3.2 mg/day. The average daily food intake of Fe was similar for the two groups, with a value of 15.6 mg/day. The average Mn concentration in water at the residence was significantly higher for the blue-collar workers ($P < 0.001$) than for the garage mechanics, at 12.5 and 6.1 μg/l respectively. The average atmospheric Mn concentration over the 5-day working period was significantly higher ($P < 0.001$) for the garage mechanics (0.423 μg/m^3) than for the blue-collar workers (0.044 μg/m^3). The average off-work atmospheric Mn concentration was similar for the two groups. The average Fe concentration at home was also similar for the garage mechanics and the blue-collar workers. At work, the average Fe concentration was significantly higher ($P < 0.001$) for the garage mechanics than for the blue-collar workers, at 49.83 and 6.99 μg/m^3 respectively.

Biological indicators

The average Mn concentrations in whole blood and serum were 0.76 (SD = 0.30) and 0.15 μg/100 ml (SD = 0.05) respectively for the garage mechanics. The corresponding values for blue-collar workers were 0.67 (SD = 0.28) and 0.12 μg/100 ml (SD = 0.07) respectively. The average Fe concentrations in serum for garage mechanics and blue-collar workers were 70.9 μg/100 ml (SD = 33.5) and 50.8 μg/100 ml (SD = 27.7) respectively. The average Mn concentration in hair was significantly higher for garage mechanics ($P < 0.05$) than for blue-collar workers, at 0.66 (SD = 0.57) and 0.39 μg/g (SD = 0.28) respectively. The average Fe concentration was 20.20 μg/g (SD = 11.47) for blue-collar workers and 32.74 μg/g (SD = 41.46) for garage mechanics.

Mn and Fe exposure and absorbed doses

The average Mn and Fe EDs calculated for blue-collar worker and garage mechanics were comparable to the average Mn and Fe concentrations measured in various media since the workers' weights were fairly constant and the volume of water consumed (2 l) and the volume of air breathed (20 m^3) per day were the same for both groups (Table 4). The total Mn EDs for blue-collar workers and garage mechanics were estimated at 50.2 and 37.0 μg/kg per day respectively. The corresponding values were 4–6 times higher for Fe. Considering the assumed absorption fraction for each media, the total AD for Mn was estimated at 1.5 μg/kg per day for blue-collar workers and 1.1 μg/kg per day for garage

Table 3 Mn and Fe concentrations in different media and biological indicators for blue-collar workers and garage mechanics

Variable[a]	Blue-collar workers				Garage mechanics			
	No.	Mean	SD	Range	No.	Mean	SD	Range
Media								
Food[b] (mg/day)								
Mn	28	3.7	2.7	0.3–14.1	37	2.9	1.4	1.0–6.6
Fe	28	15.6	4.7	5.9–26.8	37	15.6	4.1	8.2–23.9
Drinking water[c] (μg/l)								
Mn	50	12.5***	47.3	< 0.3–283.4	66	6.1	7.9	< 0.3–46.5
Fe	50	51.7	44.6	7.6–213.4	66	80.8	125.0	2.6–735.0
Ambient air[d] (μg/m^3)								
Mn: home	60	0.008	0.011	0.005–0.087	77	0.013	0.012	0.006–0.063
Mn: work	143	0.044***	0.162	0.011–1.862	210	0.423	0.773	0.010–6.673
Fe: home	60	3.92	5.63	2.53–46.80	59	4.05	3.42	3.10–27.79
Fe: work	143	6.99***	3.77	5.72–37.11	160	49.83	110.46	3.24–1064.19
Biological[e] indicators								
Blood (μg/100 ml)								
Mn: total	30	0.67	0.29	0.20–1.31	43	0.76	0.30	0.28–1.45
Mn: serum	30	0.12	0.07	0.02–0.27	43	0.15	0.05	0.08–0.31
Fe: serum	30	50.8	27.7	5.1–142.7	43	70.9	33.5	5.0–150.6
Hair (μg/g)								
Mn	30	0.39*	0.28	0.06–1.19	43	0.66	0.57	0.12–2.47
Fe	30	20.20	11.47	0.13–44.82	43	32.74	41.46	5.13–233.50

[a] Underlined means are significantly different at $P < 0.001$ (***) and $P < 0.05$ (*) (Mann-Whitney *U* test)

[b] Drolet and Zayed (1994)

[c] Blue-collar workers = 25 residences × 2 samples (1- and 3-min jets), garage mechanics = 33 residences × 2 samples, Loranger et al. (1994a)

[d] Blue-collar workers (max. sample size) = 30 ind. × 2 days (home), 30 ind. × 5 days (work), garage mechanics (max. sample size) = 43 ind. × 2 days (home), 43 ind. × 5 days (work), Zayed et al. (1994); Sierra et al. (1995)

[e] Février (1994)

Table 4 Mn and Fe exposure doses (ED) for food, water and ambient air of blue-collar workers and garage mechanics

Variable[a]	Blue-collar workers ($n = 25$)			Garage mechanics ($n = 29$)		
	Mean	SD	Range	Mean	SD	Range
Food (μg/kg per day)						
Mn	50.0	39.5	4.1–200.8	36.8	19.0	13.3– 88.0
Fe	200.3	69.2	82.6–388.5	209.2	59.1	111.9–323.6
Drinking water (μg/kg per day)						
Mn	0.28**	0.98	0.01–4.97	0.17	0.20	0.02–1.09
Fe	1.32	0.99	0.18–4.47	2.46	3.43	0.07–16.33
Ambient air[b]						
Mn: home	0.001	0.001	< 0.001–0.006	0.002	0.002	< 0.001–0.008
Mn: work	0.004***	0.007	< 0.001–0.035	0.043	0.038	0.009–0.172
Mn: total	0.005***	0.007	< 0.001–0.035	0.045	0.039	0.010–0.178
Fe: home	0.230	0.091	0.027–0.352	0.485	0.827	0.037–4.122
Fe: work	0.226***	0.157	0.058–0.710	4.738	5.597	0.665–26.582
Fe: total	0.456***	0.181	0.163–0.955	5.224	5.694	0.950–26.875
Total exposure dose (μg/kg per day)						
Mn	50.2	39.3	4.3–201.0	37.0	19.0	13.5–88.2
Fe	202.1	69.2	85.3–389.0	216.8	61.4	118.9–335.3

[a] Underlined means are significantly different at $P < 0.001$ (***) and $P < 0.01$ (**) (Mann-Whitney *U* test)

[b] Homes μg/kg per 16 h, work μg/kg per 8 h, total = μg/kg per day

Table 5 Media-specific Mn and Fe absorbed doses (AD) for blue-collar workers and garage mechanics

	Absorption fraction	Blue-collar workers ($n = 25$)		Garage mechanics ($n = 29$)	
Manganese[a]					
Food	3%	1.499	99.2%	1.103	95.7%
Water	3%	0.008	0.5%	0.005	0.5%
Air	100%	0.005	0.3%	0.045	3.9%
Total		1.512	100%	1.153	100%
Iron[a]					
Food	5%	10.017	95.1%	10.458	66.2%
Water	5%	0.066	0.6%	0.123	0.8%
Air	100%	0.456	4.3%	5.224	33.0%
Total		10.539	100%	15.805	100%

[a] µg/kg per day

[b] Underlined means are significantly different at $P < 0.001$ (***) (Mann–Whitney *U* test)

Table 6 Non-parametric correlations (Kendall's τ) between media-specific ADs and biological indicators for blue-collar workers (*upper triangle*) and garage mechanics (*lower triangle*)

	Food	Water	Air	Whole blood	Serum	Hair	Total dose
Manganese[a]				Blue-collar workers			
Food		−0.08	−0.04	−0.12	0.13	0.00	1.00***
Water	−0.10		0.03	0.08	0.11	0.18	−0.08
Air	0.12	0.01		−0.14	0.01	0.06	−0.02
Whole blood	0.04	0.27	0.07		−0.04	0.19	−0.11
Serum	−0.17	−0.11	−0.14	−0.26*		−0.01	0.11
Hair	0.15	−0.04	0.08	−0.06	0.10		0.01
Total dose	0.92***	−0.02	0.18	0.06	−0.25	0.09	
			Garage mechanics				
Iron[a]				Blue-collar workers			
Food		0.10	0.02		0.22	0.03	0.93***
Water	−0.13		0.09		0.00	0.41**	0.11
Air	0.07	−0.11			−0.06	0.15	0.04
Serum	−0.08	0.15	0.21			−0.32*	0.27
Hair	−0.08	0.08	−0.02		0.02		0.01
Total dose	0.56***	−0.03	0.51**		0.06	−0.11	
			Garage mechanics				

Underlined values are significantly correlated at $P < 0.001$ (***), $P < 0.01$ (**) and $P < 0.05$ (*)

mechanics (Table 5). The total Fe AD was significantly higher ($P < 0.001$) for the garage mechanics than for the blue-collar workers, at 15.8 and 10.5 µg/kg per day respectively. For Mn, the ingestion route contributed more than 95% of the total AD. Similarly, the proportion of the ingested Fe to the total absorbed Fe was more than 95% for blue-collar workers. For garage mechanics, however, only two-thirds of the total Fe absorption was related to food, the remainder coming essentially from the respiratory route. Moreover, the correlation between the total Fe absorbed dose and food for the latter group was only 0.56, compared to 0.93 for the blue-collar workers, the exposed by inhalation explaining 26% (τ^2, $P < 0.001$) of the variation. Finally, for Mn, no significant correlations ($P > 0.05$) were observed between biological indicators and the media-specific and multimedia ADs (Table 6).

Discussion

The living habits and working history of the blue-collar workers and garage mechanics were quite similar in spite of the fact that the blue-collar workers were on average almost 10 years older and had worked longer at their present job. The average food consumption was also almost identical for the two groups (2.9–3.7 mg/day) and fell within the range of Mn intakes of Canadian adults (3.0–3.8 mg/day) (Health and

Welfare Canada 1990) and the world population (2.0–8.8 mg Mn/day) (WHO 1973). These dietary intakes are typical for a North American diet, which includes large amounts of meat, refined foods, milk and sugar (Drolet and Zayed 1994). Similarly, the average Fe intake was identical for the two groups, and slightly above the recommended daily dietary allowances proposed by the U.S. National Academy of Sciences (10 mg/day) (NRC 1989). Moreover, the average daily Mn EDs by ingestion for blue-collar workers (50 μg/kg per day) and garage mechanics (37 μg/kg per day) were well below the no observed adverse effect level (NOAEL = 140 μg/kg per day) established by the U.S EPA (1993).

The average Mn concentrations in tap water sampled at the blue-collar workers' and mechanics' residences were almost five times below the governmental standard (50 μg/l) fixed essentially for aesthetic reasons (Santé et Bien-être Social Canada 1989). For Fe, the average values slightly exceeded the national standard (50 μg/l), also fixed to prevent undesirable taste and discoloration (McNeely et al. 1979). More recently, the U.S. EPA (1993) has proposed a reference dose (RfD) for water consumption based on the only epidemiological study on the subject (Kondakis et al. 1989). Assuming a water consumption of 2 l/day and a body weight of 70 kg, a NOAEL and a lowest observed adverse effect level (LOAEL) of, respectively, 0.005 and 0.06 mg/kg per day have been established. These values in fact correspond to a standard of 200 μg/l and are well above the present measurements.

The average off-work atmospheric Mn concentrations for the mechanics and the blue-collar workers were comparable to Montreal background concentrations measured in 1992 with Hi-Vol samplers (< 0.01–0.05 μg/m^3) (Communauté Urbaine de Montréal 1993). The average Fe concentration measured in Montréal between 1984 and 1987 at two stations located in a high traffic density area was less than 1.0 μg/m^3 (Dann 1990). Unfortunately, the sensitivity of the method used for the analysis of Fe (INAA) and the low volume of air pumped gave us a detection limit higher than this background level.

On the other hand, the average atmospheric Mn and Fe concentrations were significantly higher at work than at home for both groups. Moreover, the average air concentrations of Mn and Fe at work were more than 10 times higher for the garage mechanics than for the blue-collar workers. Since this ratio was similar for the two metals, these higher levels in the working environment may be related mainly to Mn- and Fe-enriched dusts originating from the metal components of automobiles rather than the combustion of MMT in gasoline. Additionally, in a complementary study performed by our research group to evaluate the particle sizes of garage dust using a cascade impactor, it was found that more than 90% of the particles found on the filters exceeded 0.5 μm (Sierra et al. 1994). This result reinforces the deduction that Mn oxides from the combustion of MMT, which have sizes of less than 0.5 μm (mass median diameter), may not be the primary source of Mn dust in the garage.

Although the Mn exposure from garage dusts may be significant, these values should not constitute a significant health risk according to the present respiratory limit values. The threshold limit value (TLV) established by the American Conference of Governmental Industrial Hygienists (ACGIH 1992) for Mn_3O_4 in the occupational environment is 1000 μg/m^3. This TLV is currently under revision and will likely be reduced to 200 μg/m^3. The exposure values found in this study are still orders of magnitude below the proposed new TLV. For chronic environmental exposure, the World Health Organization has proposed a guideline limit of 1 μg/m^3 for total airborne Mn (WHO 1987), while a few years ago the United States Environmental Protection Agency (U.S. EPA 1990) adopted an inhalation reference concentration (RfC) of 0.4 μg/m^3. This last limit is comparable to the average value measured at work for the garage mechanics, but this group is not exposed to this concentration over a 24-h period all year long. However, this RfC was recently re-evaluated by U.S. EPA (1993) and was fixed to 0.05 μg/m^3 for the respirable fraction (< 5μm MMD). Another recent study suggests an RfC of 3 μg/m^3 for total Mn (Crump et al. 1994).

The total Mn and Fe EDs calculated for the garage mechanics and blue-collar workers were comparable even if the occupational atmospheric concentrations were different for the two groups. In fact, media-specific daily ADs show that the food contribution was more than 95% of the total dose, with an average value ranging from 1.1 to 1.5 μg/kg per day. This last value is comparable to the average estimation of 1.6 μg/kg per day calculated by the U.S. EPA (1984) for a 70 kg adult. The average airborne Mn contribution to the total AD was relatively small compared to the ingested fraction, at 0.4% and 4% for the blue-collar workers and mechanics respectively. In the case of Fe, the atmospheric contribution for the garage mechanics exceeded 30%.

Although Mn is considered to be one of the least toxic trace elements if ingested by humans (Hurley and Keen 1987), and although the oral route is the main pathway for Mn absorption (Organisation Mondiale de la Santé 1981), the respiratory route may contribute a non-negligible portion of the body burden in some cases. In industrial environments, where the average air Mn concentration may reach 1 mg/m^3 (Mergler et al. 1994; Roels et al. 1987b) or even more (28 mg/m^3; Hua and Huang 1991), the air contribution to the total absorbed dose (based on 100% absorption by lungs and a normal diet) may exceed 95%. The human respiratory tract, with its large surface area (70 m^2), may therefore provide an important systemic point of entry for particles, bypassing the liver and the opportunity for first-pass hepatic clearance. The absorption of Mn via lungs is known to be dependent mainly on the particle size (Task Group on Lung Dynamics 1966), but the absorption rate has not yet been quantified (U.S. DHHS 1992). Mena et al. (1969) suggested, however, that more than 60% of Mn particles inhaled by humans may be transferred to the gastrointestinal tract.

Human studies have shown that it is difficult to assess past exposure to Mn by measuring it in biomarkers such as blood, urine, faeces or tissues (U.S. DHHS 1992). In the present investigation, blood and hair were used as biomarkers of the multimedia exposure to Mn. The average blood Mn concentrations for the blue-collar workers and garage mechanics were 0.67 and 0.76 μg/100 ml respectively. These values fall within the normal range for adults (0.7–1.2 μg/100 ml) (U.S. EPA 1984). Mergler et al. (1994) and Roels et al. (1987b), in their studies on workers in Mn-producing plants, found similar average concentrations for their control groups, at 0.72 and 0.57 μg/100 ml respectively. The groups of workers exposed to about 1 mg/m^3 of Mn dust showed higher values, at 1.12 and 1.36 μg/100 ml respectively. In another study, Wang et al. (1989) found average Mn blood concentrations for ferromanganese smelter workers ranging from 1.49 to 14.6 μg/100 ml for an average air concentration in the plant of 28.8 mg/m^3. However, as mentioned by Keen et al. (1983), whole blood Mn concentrations would not reflect recent exposure but rather the present Mn status of the body tissues. In the case of serum Fe, the average values for both groups of the present study were low (< 71 μg/100 ml) but in the range of human adults (Morris 1987).

In contrast to the blood measurements, where the concentrations were similar for the two groups, the average Mn concentration in hair was more than 1.7 times higher for the garage mechanics (0.66 μg/g) than for the blue-collar workers (0.39 μg/g). For Fe concentrations in hair, even if the difference between the two groups is not significant, the ratio is the same as for Mn (1.6). These results do not necessarily reflect an increased body burden due to higher exposure to Mn or Fe by inhalation. In fact, they could be explained by a direct incorporation of Mn (and Fe) in hair since metal dust may deposit or absorb on the surface of the hair (Fergusson et al. 1983) and subsequently be absorbed (Stauber and Florence 1989). Once the Mn is incorporated in the hair, it would be impossible to distinguish the relative contribution of exogenous Mn associated with direct incorporation and that of endogenous Mn resulting from body distribution in hair. On the other hand, the Mn concentrations measured in the present study are comparable to values measured in different non-worker Caucasian populations (< 1 μg/g) (Fergusson et al. 1983; Guillard et al. 1984; Stauber and Florence 1989). However, the range of variation for the world population is quite large (0.2– > 12 μg/g) (Baruthio et al. 1988), depending notably on age (Collipp et al. 1983), race (Stauber and Florence 1989), hair coloration (Eads and Lambdin 1973) and, most important of all, the level of exposure via the respiratory route (Foo et al. 1993; Sukumar and Subramanian 1992) and the oral route (Kondakis et al. 1989; Shrestha 1989). This variability may explain the difficulty of using hair as a valid and accurate biomarker of Mn exposure.

Finally, it is argued that since no correlations have been found between Mn concentrations in blood and hair, there must be little meaning in the hair concentrations. As mentioned by Laker (1982), this is a false argument because the time scales reflected by blood and hair are different. It would thus be surprising to find a clear correlation between these two biomarkers. Moreover, the lack of correlation between Mn air concentrations and the biomarkers may also be related to the time scales considering that the half-life of Mn in blood is short and the multimedia dose corresponds to a complex variable calculated on a 24-hour basis.

Conclusion

Human exposure to manganese occurs mainly by ingestion, except in an industrial environment, where the atmospheric concentrations may contribute a significant fraction of the multimedia exposure dose. Absorption via the lungs is highly dependent on the particle size, and unlike the intestine and the liver, the lungs may constitute an important site of deposition for Mn oxides. In the context of the potential risk to public health posed by Mn from MMT, the results of the present research on blue-collar workers and garage mechanics show that the current Mn levels in food and air pose no significant problem. However, future research is needed to better characterize the Mn particles released from the combustion of MMT near roadways, and to assess more accurately the environmental fate of Mn from this source and its contribution to the food chain over a longer period. The importance of metal interactions in urban dust is also to be evaluated.

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