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ORIGINAL ARTICLE

**Joseph Zayed · Adolf Vyskocil · Greg Kennedy**

# Environmental contamination and human exposure to manganese – contribution of methylcyclopentadienyl manganese tricarbonyl in unleaded gasoline

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**Abstract** The organomanganese compound MMT (methylcyclopentadienyl manganese tricarbonyl), an antiknock additive in unleaded gasoline, has been used in Canada since 1976. Indeed, Canada is the only country where MMT is almost exclusively used. In October 1995, by court decision the Environmental protection Agency (EPA) granted Ethyl's waiver for the use of MMT in the United States. Paradoxically, in 1997 the federal government of Canada adopted a law (C-29) that banned both the interprovincial trade and the importation for commercial purposes of manganese-based substances, including MMT. However, MMT is currently widely used in Canada because of substantial stockpiling, and six Canadian provinces are challenging the law in the courts. Moreover, MMT has been approved for use in Argentina, Australia, Bulgaria, Russia, and conditionally, in New Zealand. It has been suggested by some scientists that combustion of MMT may be a significant source of exposure to inorganic Mn in urban areas. The crucial question is whether Mn contamination from industrial sources combined with the additional contamination that would result from the widespread use of MMT would lead to toxic effects. Our research efforts have attempted to assess the environmental/ecosystem Mn contamination arising from the combustion of MMT in abiotic and biotic systems as well as human exposure. The experimental evidence acquired so far provides useful information on certain environmental consequences of the use of MMT as well as raising a number of questions. Our results gave evidence indicating that roadside air, soils, plants, and animals may be contaminated by Mn. As well, some specific groups of the population could have a higher level of exposure to Mn. Nevertheless, the levels of exposure remain below international guide values. Further studies and further characterization of dose-response relationships are thus needed to provide successful implementation of evidence-based risk-assessment approaches.

**Key words** Methylcyclopentadienyl manganese tricarbonyl · Unleaded gasoline · Human exposure · Environmental contamination

J. Zayed (✉) · A. Vyskocil
TOXHUM (Human Toxicology Research Group)
and Département de médecine du travail et d'hygiène du milieu,
Faculté de médecine, Université de Montréal, C.P. 6128,
Succursale Centre-ville,
Montréal, Québec H3C 3J7, Canada
Tel.: (514) 343-5912; Fax: (514) 343-2200
e-mail: zayedj@ere.umontreal.ca

G. Kennedy
Département de génie mécanique,
École polytechnique de Montréal,
Université de Montréal, C.P. 6128,
Succursale Centre-ville,
Montréal, Québec H3C 3J7, Canada

## Introduction

Methylcyclopentadienyl manganese tricarbonyl (MMT, $C_9H_7MnO_3$) is an organic derivative of manganese produced by Ethyl Corporation and marketed as AK-33X (antiknock agent-33X) or HiTec 3000 (Jaques 1987; Moore et al. 1974). From the time of its introduction in Canada in 1976 (Environment Canada 1987), the use of MMT increased substantially until it completely replaced tetraethyl lead in gasoline in 1990 (Hurley et al. 1992). Indeed, Canada is the only country where MMT is used almost exclusively. In the United States, the Environmental Protection Agency (EPA) denied Ethyl's waiver for the use of MMT until October 1995, when a court decision allowed the company to offer it for sale to refiners for use in unleaded gasoline (Wallace and Slonecker 1997). Paradoxically, in 1997 the Canadian government adopted a law (C-29) that banned both the interprovincial trade and the importation for commercial purposes of manganese-based substances, including MMT.

However, MMT is currently used in Canada because of substantial stockpiling, and six Canadian provinces are challenging the law in the courts. Considering the excepted increasing use of MMT and the realistic perspective of international use of MMT, the continuation of studies related to environmental contamination by MMT and its combustion products and the associated human exposure and public health risk remain very important.

The use of MMT has prompted numerous debates on the potential public health risk associated with manganese (Mn), which is the main substance arising from the combustion of MMT. Many studies in occupational environments have shown that high atmospheric Mn concentrations have significant effects on human health. Most of the investigations have focused on the relationship between Mn exposure by inhalation at very high concentrations and neurological signs and symptoms among working populations (Mergler et al. 1994; Roels et al. 1987; Wennberg et al. 1992). Moreover, many neurodegenerative disorders similar to Parkinson's disease have been related to occupational exposure to Mn (Barbeau 1984; Zayed et al. 1990). However, the extrapolation of these results to chronic exposure at low concentrations of Mn remains difficult. Thus, the existing scientific knowledge related to the use of MMT in gasoline has failed to provide indisputable proof of a real health risk, and a consensus appears difficult to reach. The magnitude of the risk due to Mn emitted via the combustion of MMT remains uncertain.

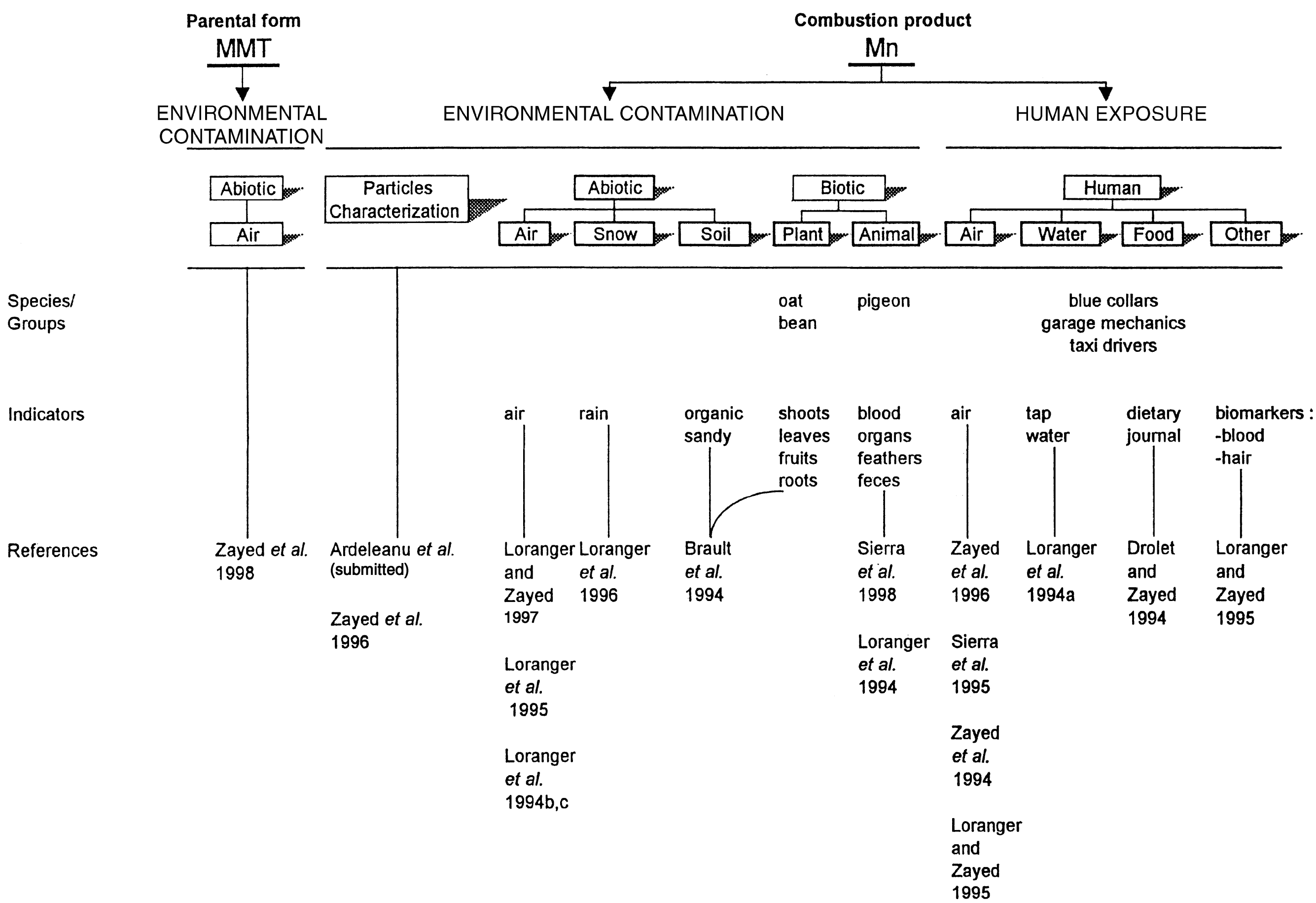
Successful implementation of an evidence-based risk-assessment approach requires the production and the accessibility of credible information that will promote and support evidence-based decision-making. Thus, for the past several years our research work has focused on the assessment of environmental contamination and human exposure to Mn arising from the use of MMT. This paper provides an overview of our research program.

## Methodology

The general approach of the research program is presented in Fig. 1. Most of our published work relates to assessments of Mn environmental contamination and human exposure to Mn. More recently we have begun to document the environmental contamination by MMT itself, and studies on personal exposure to MMT are currently under study.

Assessment of human exposure to Mn involves identification of the subgroups that might be exposed to Mn through the use of MMT and estimation of the magnitude and chronology of the doses they might receive from this exposure. We have measured the occupational and environmental exposure to airborne Mn in four different groups of workers: garage mechanics and taxi drivers, two groups that are presumed to be particularly exposed to Mn contamination from MMT in closed and open environments, respectively (Zayed et al. 1994); and office workers and blue-collar workers, two control groups (Zayed et al. 1996). The garage me-

**Fig. 1** Research program on MMT and its combustion products (Mn compounds)



chanics and blue-collar workers were used to establish the multimedia exposure dose. The precise approach and methodology of the assessment of human exposure to Mn have been described by Zayed et al. (1994) and Loranger and Zayed (1995).

The work on the assessment of Mn environmental contamination focussed on (1) characterization of Mn particulates from vehicles using MMT fuel additive; (2) assessment of the level of contamination in abiotic components (air, water, and soil); and (3) assessment of the level of contamination in biotic components (plant and animal). Since Mn from MMT can have a direct and theoretically major impact on air pollution and human exposure, specific attention was paid to this issue and the later studies focused on the particle in the respirable fraction (< 5 μm). The precise approach and methodologies used in the assessment of Mn environmental contamination have been described in the references indicated in Fig. 1.

The assessment of MMT environmental contamination is based on the methodology of the Occupational Health and Safety using Gil-Air pumps and a glass impinger containing isopropanol. The detailed methodology has been described by Zayed et al. (1998).

## Results

### Human exposure to Mn

The results of our studies in environmental and occupational settings are discussed below. Table 1 presents a summary of the Mn concentrations found. At work, the garage mechanics were exposed to a mean MMT concentration of 0.335 μg/m$^3$ ($n = 45$) and the taxi drivers, to 0.024 μg/m$^3$ ($n = 10$). Off work, the two groups were exposed to a mean concentration of 0.012 μg/m$^3$ and 0.011 μg/m$^3$, respectively. The latter concentrations are similar to the mean value of 0.012 μg/m$^3$ recorded for the office workers ($n = 20$), where about 92% of the Mn particles were found to be in respirable fraction (< 5 μm). The exposure of blue-collar workers ($n = 30$) was in the same range, with the mean value being 0.008 μg/m$^3$.

Considering multimedia exposure (Table 2), food contributes more than 95% of the absorbed dose. The average dietary consumption of Mn (evaluated using 3-day dietary records) is similar for garage mechanics and blue-collar workers, i.e., 2.9 and 3.7 mg/day, respectively, and the average level of 3.27 mg/day (Drolet and Zayed 1994) falls within the range of Mn intake published for Canadian adults (3.0–3.8 mg/day; Health and Welfare Canada 1990). As on a 70-kg body weight, the levels of exposure of the two groups of workers are 37 and 50 μg/kg per day, respectively, which are well below the no observed adverse-effect level (NOAEL = 140 μg/kg per day) established by the United States (USEPA 1993).

Exposure via water consumption contributes very little to the oral dose. The average Mn concentrations detected in tap water sampled at residences (6.1 and 12.5 μg/l for mechanics and blue-collar workers, respectively) were well below the government standard (50 μg/l; Loranger et al. 1994a; Santé et Bien-être Social Canada 1989). Thus, the corresponding exposure doses (0.17 and 0.28 μg/kg per day, respectively) can be considered negligible (< 1%) as compared with the total ingested dose (Drolet an Zayed 1994; Loranger et al. 1994a). However, this exposure source may become important for persons drinking well water [up to 17% was observed for one of the subjects, whose well water was measured to contain Mn concentrations of 190 and 283 μg/l (Loranger et al. 1994a)].

Finally, the blood Mn concentration was similar for the two groups (blue-collar workers, 6.7 μg/l; mechanics,

**Table 1** Assessment of human exposure to manganese in the urban environment ($Mn_R$ Mean respirable Mn)

| Group | Date of study | $n$ | Manganese in air (μg/m$^3$)[a] | | References |
|---|---|---|---|---|---|
| | | | Nonworking days | Working days | |
| Taxi drivers | June 1992 | 10 | 0.011 | 0.024 | Zayed et al. (1994) |
| Garage mechanics | June 1992 | 10 | 0.007 | 0.250 | Zayed et al. (1994) |
| Blue-collar workers | August–Nov. 1992 | 30 | 0.008[b] | 0.04[c] | Sierra et al. (1995), |
| Garage mechanics | August–Nov. 1992 | 35 | 0.013[b] | 0.42[c] | Loranger and Zayed (1995) |
| Office workers | January 1994 | 20 | 0.012[d] ($Mn_R$ = 0.011)[d] | | Zayed et al. (1996) |
| Taxi drivers | January 1994 | 9 | 0.028[d] ($Mn_R$ = 0.015)[d] | | Zayed et al. (1996) |

[a] Mean total concentration
[b] Nonworking hours
[c] Working hours
[d] Working + nonworking days

**Table 2** Media-specific Mn doses absorbed (μg/kg per day) as estimated for blue-collar workers and garage mechanics[a]

| | Absorption fraction (%) | Blue collars ($n$ = 25) | Garage mechanics ($n$ = 29) |
|---|---|---|---|
| Food | 3 | 1.499 (99.2 %) | 1.103 (95.7 %) |
| Water | 3 | 0.008 (0.5 %) | 0.005 (0.4 %) |
| Air | 100 | 0.005 (0.3 %) | 0.045 (3.9 %) |
| Multimedia | | 1.512 (100 %) | 1.153 (100 %) |

[a] Adapted from Loranger and Zayed (1995)

7.6 μg/l) and fell within the normal adult range (7–12 μg/l; USEPA 1984). The average hair concentration of Mn was significantly higher for the garage mechanics (0.66 μg/g) than for the blue-collar workers (0.39 μg/g).

## Environmental Mn contamination

### *Particle characterization*

A preliminary car exhaust study (Zayed et al. 1996) provided qualitative data on the chemical composition of particles collected from a tailpipe. Examination with an electron microscope revealed that most of the Mn particles were heterogeneous agglomerates varying in size from 1 to 100 μm. The Mn oxide usually appeared to be agglomerated with other exhaust particles, especially sulfur, and may thus only rarely be emitted into the environment as pure Mn oxide. In the same study, nine vehicles with different mileage and engine capacity were tested using standard procedures for urban and highway driving cycles (Ardeleanu et al., submitted for publication). One vehicle ran on gasoline without MMT and served as a control. The amount of Mn emitted from the tailpipe varied from 7% to 45% of the Mn consumed, depending on the driving cycle and the vehicle. For the urban cycle the emission rate was positively correlated with previous mileage. Particle sizes ranged from 0.2 to 50 μm. However, on average, more than 99% of the particles were in the respirable fraction (< 5 μm) and 86% measured less than 1 μm.

The first spectra produced by energy-dispersive X-ray spectrometry combined with electron microscopy seemed to show that most of the particles were Mn oxides that sometimes also contained other elements such as Al, Fe, S, and P. However, these electron microscope specimens were covered with a coating of Au and Pd to improve conductivity, and the Au and Pd may have masked some elements, especially phosphorus. Thus, a new study using carbon coating was carried out (manuscript in preparation); it showed that the frequency of Mn oxide was only 2% as opposed to 8% for Mn phosphate, 16% for Mn sulfate, and 54% for a mixture of Mn phosphate and Mn sulfate. The other 20% of the particles were Fe, Cr, and Al oxides, which also contained a small amount of Mn. In addition, analytical transmission electron microscopy characterization of the isolated particles retrieved from carbon-coated filters showed they comprised Mn-O-P-S (in order of descending peak intensity), indicating that Mn phosphate is the main constituent of the residual particles. All the particles containing Mn were amorphous.

### *Abiotic aspects*

Table 3 presents an overview of the Mn atmospheric concentrations measured in Montreal. In a preliminary study (Loranger et al. 1994c) we assessed the importance of Mn contamination on the island of Montreal in relation to other air pollutants, meteorological variables, and traffic density. Variations in Mn concentrations were significantly correlated in time with traffic density. Moreover, Mn and TSP were the best discriminators of high and low traffic density areas. No significant difference was observed between Pb, ozone, or $SO_2$ concentration in the two areas . However, it was impossible to distinguish between Mn directly emitted from automobiles, Mn-enriched road dust, and the naturally occurring Mn in crustal material.

Variations in Mn concentrations were measured in Montreal air from 1981 to 1992 (Loranger and Zayed 1994). The results indicate stable concentrations between 1981 and 1990, followed by a substantial decrease of almost 50%, in spite of annual increases of about 10% in the use of MMT since 1981. The decrease observed since 1991 is attributed to the closing of a ferromanganese plant near Montreal (located 25 km west of Montreal on the south shore of the St. Lawrence River). The average Mn concentrations calculated for the period 1981–1992 were 0.02, 0.05, and 0.06 μg/m$^3$ for stations with low, intermediate, and high traffic densities, respectively. These values may be compared with the natural background level of 0.04 μg/m$^3$ as measured in Montreal (Loranger and Zayed 1997). A decrease in atmospheric Pb concentrations was also observed after 1981; it corresponds to

**Table 3** Manganese contamination of ambient air in relation to traffic density (*Resp*. Fine particles – <5 μm, *total* total particles)

| Traffic density (vehicles/day) | Distance from the road (m) | Date of measurements | Manganese in air (μg/m$^3$) | Reference |
|---|---|---|---|---|
| <15,000 | <100 | 1990 | 50% of samples > 0.04 | Loranger et al. |
| >15,000 | <100 | 1990 | 50% of samples > 0.04 | (1994c) |
| 4,900 | 15 and 100 | March–Sep. 1992 | 0.026 | Loranger et al. |
| 75,000 | 6–275 | March–Sep. 1992 | 0.036 | (1994b) |
| <15,000 | Not reported | 1981–1992 | 0.02 | Loranger and Zayed |
| <30,000 | Not reported | 1981–1992 | 0.05 | (1994) |
| >100,000 | Not reported | 1981–1992 | 0.06 | |
| 117,585 | 25 | 1993 | 0.054 | Loranger et al. |
| | 250 | 1992 | 0.029–0.037 | (1995) |
| 10,000–15,000 | 10 | 1994 | Resp. 0.015; total 0.027 | Loranger and Zayed |
| 100,000–130,000 | 10 | 1994 | Resp. 0.024; total 0.050 | (1998) |

the decrease of about 30% per year in emissions from motor vehicles over the same period.

Modeling has also provided interesting insight into the contribution of the combustion of MMT to atmospheric Mn (Loranger et al. 1995). CALINE4 (Benson 1984) and ISCLT (USEPA 1992) were used for a study area located near a major highway (117,585 vehicles/day) in the city of Montreal. Model estimates were validated using results obtained from two sampling stations located 25 and 250 m from the road centreline. At 250 m from the highway the summer and winter average Mn concentrations measured in 1992 were 37 and 29 ng/m$^3$, respectively. At 25 m from the highway the average Mn concentration measured in autumn 1993 was 54 ng/m$^3$. It must be noted that the daily Mn concentrations varied greatly throughout the year, with the coefficient of variation (CV) being 156%. According to the model estimations, the contribution of direct emissions from motor vehicles to the atmospheric background level of Mn (as measured from sampling stations) would be about 50% at $<25$ m and less than 8% at 250 m (the total uncertainity in the model predictions was estimated at 50%). These results were confirmed in an in situ study using snow as the environmental indicator. Snow may be an interesting collection medium in winter, since particles in the air are likely to be deposited by scavenging or washout processes near the emission sources. Snow was collected at distances of 15, 25, 125, and 150 m from a highway (Montreal). The average deposition rates of Mn for the top and bottom layers ranged from 0.01 to 0.21 mg/m$^2$ per day (Loranger et al. 1996). The average concentrations of Mn decreased with distance from the road. The latter finding converges with the observation that the level of exchangeable Mn was significantly higher in an organic soil located at a site near a road with high traffic density (1.03–1.36 mg/kg) than at other sites (Brault et al. 1994).

Concerning respirable ($Mn_R$) and total manganese ($Mn_I$), a study performed in Montreal in 1994 (Loranger and Zayed 1998) provides interesting information. $Mn_R$ and $Mn_T$ concentrations were significantly higher at a site with higher traffic density (0.024 and 0.050 μg/m$^3$, respectively) than at a site with lower traffic density (0.015 and 0.027 μg/m$^3$) but did not substantially exceed the above-mentioned natural background level of 0.04 μg/m$^3$ for total Mn. The ratios of respirable to total Mn concentrations were 54% and 65% at the sites with high and low traffic density, respectively.

### *Biotic aspects*

Bioaccumulation of Mn by plants was examined using oats (*Avena nova*) and beans (*Phaseolus vulgaris*; Brault et al. 1994). These plants were grown in sandy and organic soils at a control site (greenhouse) and at two outdoor sites that were weakly (botanical garden near a road with $<20{,}000$ vehicles/day) and strongly (250 m from a road with 132,000 vehicles/day) exposed to potential Mn contamination from vehicles using MMT. Oats and green beans were chosen because both species are grown for human consumption, grow well in both types of soil, produce a large quantity of seeds, and have a relatively large root system. In addition, oats have a high tolerance to Mn and absorb less than most plants, whereas beans are much more sensitive to an excess of Mn and may develop high Mn concentrations. The highest Mn accumulation was found in the fruits and stems of oats grown in the organic and sandy soils at the highly exposed site.

In further research (Loranger et al. 1994b) we evaluated the feral pigeon (*Columba livia)* as a monitor of Mn contamination in rural (Lachute) and urban (Montreal) environments with different traffic densites (4,900 versus 75,000 cars/day). Among the characteristics that make this species appealing are its sedentary habits and diet, its long life span, and its close relationship to human activities. Atmospheric concentrations were measured over a 6-month period in two rural and four urban areas situated 6–275 m from the nearest roads. In all, 20 pigeons were captured in each area and Mn concentrations in the liver, kidney, lung, pancreas, intestine, brain, down feathers, feces, whole blood, and blood serum were measured. Air particulate data showed significantly higher Mn levels in the urban area (0.036 μg/m$^3$) relative to the rural area (0.026 μg/m$^3$). Mn concentrations were similar in the two groups of pigeons for all samples except the liver (Lachute, 2.42 mg/kg; Montreal, 3.13 mg/kg) and feces (Lachute, 32.2 mg/kg; Montreal, 46.8 mg/kg). The urban pigeons had 29% more Mn in their liver and 45% more in their feces than did the rural birds.

## Environmental contamination by MMT vapor

On the basis of methodology suggested by the Occupational Health and Safety Agency, MMT concentrations were measured in the air of five microenvironments in Montreal: a gas station, an underground car park, downtown Montreal, near an expressway, and near a refinery. The mean concentration obtained after 3 sampling days (12 consecutive h each) was 0.005 (SD 0.005) μg/m$^3$ expressed as Mn; concentrations ranged from 0.00018 to 0.025 μg/m$^3$ (Zayed et al. 1998). These concentrations are well below the ACGIH threshold limit value-time weighted average (TLV-TWA) of 200 μg/m$^3$ expressed as Mn equivalents (ACGIH 1998). The highest values obtained at the gas station (mean 0.012 μg/m$^3$) are extremely interesting in this respect since they include the residual unburned MMT emitted through the exhaust system and the MMT from evaporative emissions. However, since this mean concentration is 2–30 times higher than the concentrations measured in the other four microenvironments, it was concluded that the MMT vapor was essentially due to evaporation around the pumps. By extension, the exposure of gas pump attendants could therefore be estimated at 0.1 μg/day, assuming they work 8 h/day and that the volume of air inhaled is 1 $m^3$/h. Work is presently under way to assess personal MMT exposure.

## Discussion

The experimental evidence acquired thus far provides useful information on certain environmental consequences of the use of MMT as well as raising a number of questions. Although the results were obtained in many cases in specific microenvironments, their constancy, reproducibility, and quality lend confidence to their reliability.

The perspective of increased international use of MMT is expected to spur new interest in Mn in terms of environmental contamination and human exposure. Thus, the results provided by our research program give timely information with regard to the impact of MMT. The crucial question is whether the additional Mn contamination and population exposure that would result from the widespread use of MMT would lead to toxic effects. To answer this, we will have to know whether the increased use of MMT will bring about a significant increase in Mn atmospheric concentrations and human exposure. No study to date has provided the complete answer to this question, and this constitutes the major remaining unknown regarding the environmental significance of Mn from MMT and the resulting human exposure. Even if the available toxicological evidence does not permit firm conclusions to be drawn, it provides valuable information to those who make regulatory decisions.

Theoretically, the emission of Mn particles from the combustion of MMT leads to an increase in atmospheric concentrations, and modeling has given us an idea of this contribution: about 50% at 25 m from a highway and less than 8% at 250 m (Loranger et al. 1995). However, the in situ data cannot prove that directly emitted Mn is the primary source of Mn pollution as opposed to naturally occurring crustal material or enriched road dust. Nevertheless, the correlation between atmospheric Mn concentrations and traffic densities combined with the high percentage of fine Mn particles (< 5 μm) lead us to suspect that some selected subpopulations, such as those living near a major highway, may be highly exposed. However, the observed levels of human exposure do not constitute a significant health risk according to present respiratory limit values.

The threshold limit value (TLV) established by the American Conference of Governmental Industrial Hygienists (ACGIH 1998) in an occupational environment is 200 μg/$m^3$. The exposure values found in our study are orders of magnitude below this. For chronic environmental exposure the World Health Organization (1987) has proposed a guideline limit of 1 μg/$m^3$ for total airborne Mn, whereas the United States Environmental Protection Agency (USEPA 1990) adopted a few years ago an inhalation reference concentration (RfC) of 0.4 μg/$m^3$. The RfC value is comparable with the average ambient concentration measured at work for the garage mechanics, but this group is not exposed to this concentration over a 24-h period all year long. The RfC was reevaluated by the USEPA (1993) and was fixed at 0.05 μg/$m^3$ for the respirable fraction (< 5 μm MMD). Thus, the mean environmental concentration of MnR is almost half the RfC, with some of the higher measured concentrations reaching the RfC. That these higher concentrations were observed in an area of high traffic density supports the need for a study aiming specifically at measuring the exposure of persons living along a highway.

With regard to the oral ingestion of Mn, the daily mean intake by the mechanics and the blue-collar workers was 2.9 ± 1.4 and 3.7 ± 2.7 mg, respectively, which fell within the suggested safe range of 2.0–5.0 mg/day. Nevertheless, since we know that the accumulation of Mn in some vegetables (oats and beans) is a function of the contamination level in the urban environment (Brault et al. 1994), the impact of a proportional increase in other vegetables has to be assessed before we can quantify the increase in the oral dose. The same reasoning may be applied to meat consumption; since pigeons in a contaminated environment have higher Mn levels in the liver (Joselow et al. 1978; Loranger et al. 1994b), the consumption of bovine liver may lead to an increase in the oral dose.

Thus, the multimedia exposure dose could be increased by Mn emitted from the combustion of MMT, but there is considerable uncertainty in the amount. Models predicting the level of Mn contamination and human exposure assume that about 30% of the Mn is burned with the gasoline and emitted from the tailpipe (Ardeleanu et al. submitted for publication). This percentage is subject to considerable variation as automobile antipollution systems evolve, and an eventual increase could lead to a higher level of contamination. There is also the question of what happens to the remaining 70%. It has always been neglected in any evaluation of Mn contamination, which is correct if all residual Mn is recycled with the automobile carcass. It may thus be reasonable to neglect the Mn retained in the automobile exhaust system and to concentrate studies on the pathways that will necessarily lead to an increase in atmospheric Mn. As well, special attention should be paid to the specific combustion products. We should attempt to gain information on the toxicity of a mixture of Mn phosphate and Mn sulfate. With regard to MMT itself, the results indicate a lack of potential for exposure such that the potential risk to public health is considered to be minimal.

In the context of risk management and regulatory decision-making regarding MMT, the above-mentioned results could be helpful. Moreover, during any decision-making process the risks associated with exposure to Mn from the combustion of MMT must be weighed against those of a potential substitute. Since MMT has been approved for use in many countries, the limitations and uncertainties identified in the discussion have to be addressed. Our current research will give pertinent data regarding the quantification of Mn contamination from MMT as well as the exposure of people living near highways with a very high traffic density.

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