Particle size distribution of workplace aerosols in manganese alloy smelters applying personal sampling strategy

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Complete List of Authors:	Berlinger, Balazs; National Institute of Occupational Health, Department of Chemical and Biological Working Environment Bugge, Merete; National Institute of Occupational Health, Department of Occupational Medicine and Epidemiology Ulvestad, Bente; National Institute of Occupational Health, Department of Occupational Medicine and Epidemiology Kjuus, Helge; National Institute of Occupational Health, Department of Occupational Medicine and Epidemiology Kandler, Konrad; Technical University Darmstadt, Institute of Applied Geosciences Darmstadt, Ellingsen, Dag; National Institute of Occupational Health, Department of Chemical and Biological Working Environment

Toxicological studies have implicated particulate exposure as possibly playing a causal role in adverse cardiovascular effects. There is an opportunity to study these effects in occupational settings, but for the better understanding more information on time-specific workplace exposure to different particulate matter fractions is needed. The present work describes the results from personal size selective aerosol samplings in two manganese alloy smelters which will be later used in the epidemiological study which was initiated to examine the prevalence of early markers of cardiovascular disease with relation to exposure to different particulate matter fractions. Particle size distribution data is also essential for the better estimation of the deposited dose in the human respiratory tract as respiratory tract deposition is highly dependent on the aerosol particle size.

Particle size distribution of workplace aerosols in manganese alloy smelters applying personal sampling strategy

B. Berlinger[1], M.D. Bugge[2], B. Ulvestad[2], H. Kjuus[2], K. Kandler[3] and D. G. Ellingsen[1]

[1]Dept. of Chemical and Biological Working Environment, [2]Dept. of Occupational Medicine and Epidemiology, National Institute of Occupational Health, P.O. Box 8149 Dep. N-0033, Oslo, Norway
[3]Technical University Darmstadt, Institute of Applied Geosciences Darmstadt, Schnittspahnstr. 9, 64287 Darmstadt, Germany

Email: bbe@stami.no

Abstract

Air samples were collected by personal sampling with five stage Sioutas cascade impactors and respirable cyclones in parallel among tappers and crane operators in two manganese (Mn) alloy smelters in Norway to investigate PM fractions. The mass concentrations of PM collected by the impactors and the respirable cyclones were critically evaluated by comparing the results of the parallel measurements. The geometric mean (GM) mass concentrations of the respirable fraction and the <10 μm PM fraction were 0.18 and 0.39 mg m^{-3}, respectively. Particle size distributions were determined using the impactor data in the range from 0 to 10 μm and by stationary measurements by a Scanning Mobility Particle Sizer in the range from 10 to 487 nm. On average 50% of the particulate mass in the Mn alloy smelters was in the range from 2.5 to 10 μm, while the rest was distributed between the lower stages of the impactors. On average 15% of the particulate mass was found in the <0.25 μm PM fraction. The comparisons of the different PM fraction mass concentrations related to different work tasks or different workplaces, showed in many cases statistically significant differences, however, the particle size distribution of PM in the fraction <10 μm d_{ae} was independent of the plant, furnace or work task.

Keywords

respirable fraction, particulate matter fractions, Sioutas cascade impactor, SMPS, tappers, crane operators

Introduction

Numerous epidemiological studies have shown associations between exposure to particulate urban air pollution and increased morbidity and mortality from cardiovascular diseases.[1-6] Both short-term and long-term $PM_{2.5}$ exposures has been associated with increased incidence of cardiovascular diseases,

but the character of the exposure-response relationship is still uncertain.[7,8] Toxicological studies have implicated ultrafine particles (UFP, diameter ≤100 nm) as possibly playing a causal role in the adverse cardiovascular effects.[9,10] Limited evidence of these relationships has emerged from occupational settings.[11] Interestingly, Costello *et al.* has shown lately that recent exposure, but not cumulative exposure to $PM_{2.5}$ can be a risk factor for incident ischemic heart disease among aluminum production workers.[12] More information on time-specific workplace exposure to different PM fractions (including UFPs) is therefore needed. The manganese (Mn) alloy smelter workers participating in this study are exposed to PM with Mn content. It is well known that Mn compounds can have neurological effects,[13] therefore Mn concentration in workplace air is strictly regulated. The current exposure limit values for inhalable and respirable inorganic Mn compounds in workplace air in Norway are 1.0 and 0.1 mg m^{-3}, respectively.[14]

The health effects resulting from deposition of particulate matter (PM) in the respiratory tract depend on the dose received, the site of deposition and the body`s response to the deposited particles.[15] One important goal of workplace aerosol measurement should therefore be to ascertain the effective dose of PM delivered to the lungs. Particle deposition models show that the respiratory tract deposition is highly dependent on the aerosol particle size.[16,17] For example up to 55% of 20 nm particles with density of 1 g cm^{-3} and spherical shape can deposit in the alveolar region, while the deposition efficiency of 500 nm particles remains under 10% according to the model given by Bartley and Vincent.[17]

These models, however, are not applicable for a better dose estimation without the information on particle size distribution which is usually not available from conventional workplace aerosol measurements. Cascade impactors are able to provide sharp particle size classifications.[18] Thus, they can be useful tools when such information is required. Such equipment does have limitations in risk assessment. One of these is that the information on the collected mass of particles with different sizes is only one of the most important three metrics which might be used as relevant indicators of worker`s particle exposure, others being particle number and surface area.[19] The evaluation of particle deposition in the human respiratory tract should also consider the hygroscopic growth of aerosol particles upon inhalation which has been previously shown by a number of authors.[20-22] Size dependent chemical characterization may also give valuable information if obtained at the same time.

Cascade impactors have been used for personal and stationary sampling to measure the particle size distribution in workplace aerosols. In a study personal dust exposure levels and the dust particle size distribution was measured during various agricultural operations in California by applying four-stage Sierra Marple 294 cascade impactors.[23] Another study characterized exposures to copper and zinc oxide using single jet personal cascade impactors with five to six stages in a nonferrous foundry and compared the results with previous findings obtained using cyclones.[24] Dufresne *et al.* collected breathing zone samples with an 8-stage Sierra impactor in a magnesium foundry and three aluminium smelters to assess the distribution of the PM mass and the beryllium content between the

different size fractions.[25] Particle size distributions of oil mists in fastener manufacturing industry were determined by using a modified Marple 8-stage cascade impactor.[26] The Sioutas cascade impactor equipped with quartz-fiber substrates and after-filter was used by Birch *et al.* to collect personal samples during carbon nanofiber production for the determination of elemental carbon and organic carbon.[27] The latter model offers a good separation with its after-filter and four stages with cut points ranging from 0.25 to 10 μm aerodynamic diameter (d_{ae}) and it operates at a high flow rate, which can be maintained by a lightweight personal pump.[28]

There are also applications of stationary cascade impactors in workplace aerosol characterisation. One example is when Vincent *et al.* used a modified Andersen sampler for the particle size measurement of aerosols in primary nickel production industry workplaces.[29] Berlinger *et al.* and Chang *et al.* used a stationary 11-stage Berner cascade impactor and a compact cascade impactor (Harvard CCI) with two stages and a backup filter, respectively for the physicochemical characterization of welding fumes.[30,31]

Exposure among employees in smelters in Norway has been well assessed both quantitatively and qualitatively, however, particle size distribution by personal sampling has not yet been investigated.[32] There has also been little focus on the ultrafine size fraction of PM, although high exposure levels in the smelting industry could provide a good opportunity to investigate the association between PM exposure and established cardiovascular disease. The scientific evidence of such association in occupational exposure situations is still limited.[11]

Because of the importance of the ultrafine particles in the possible cardiovascular effects, not only personal impactors but personal nanoparticle samplers were considered to be used to assess smelter workers´ exposure to PM. Personal nanoparticle sampler (PENS) was developed in 2011 which consists of a respirable cyclone and a micro-orifice impactor with a 50% cut-off aerodynamic diameter of 4 μm and 100 nm, respectively.[33] Personal nanoparticle respiratory deposition (NRD) sampler was also developed in the same year.[34] It collects particles smaller than 300 nm similarly to their deposition in the human respiratory tract. At the end, however, personal impactors were chosen to be used at the smelters because these give information on more than only one PM size fraction.

A study in metal smelters in Norway was initiated to examine the prevalence of early markers of cardiovascular disease with relation to exposure to different PM fractions. The present work describes the results from personal aerosol samplings in two Mn alloy smelters applying Sioutas cascase impactors and respirable cyclones in parallel. The results from the epidemiological study where these exposure measurements are to be used will be published later.

Materials and methods

Plants and subjects

Air samples were collected in two Mn alloy smelters in Norway. Both plants have two smelting furnaces. Mn alloy smelter 1 is producing silicomanganese (furnace 1) and ferromanganese (furnace 2) alloys, while Mn alloy smelter 2 is producing ferromanganese only (furnace 3 and 4). Personal air samples were collected among 38 furnace workers. The main work tasks of the workers were to control the tapping process (tappers) or to operate the cranes (crane operators). Both tappers and crane operators were working between 45 and 75 minutes on the tap floor before, during and after tapping of the molten alloy which was done 3 or 4 times during an 8-hour shift. Tappers usually worked within 3-5 m from the tapping hole, but they could also sit in a pressurized cabin while following the tapping process. Crane operators performed their tasks further (5-10 m) from the tapping hole than tappers and worked mainly after the end of the tapping process. When tappers and crane operators were not working on the tap floor, they took a rest in the control area where they were not exposed to PM.

Air sampling

Each worker carried three air samplers. A 5-stage Sioutas cascade impactor (SKC, Eighty Four, PA, USA) ran in parallel with a respirable cyclone (JS Holdings, Stevenage, UK) collecting the respirable PM fraction (*parallel* respirable fraction) for 6 to 8 hours. Full-shift (approx. 8 hours) air samples were collected in the breathing zone of workers by a second respirable cyclone (*full-shift* respirable fraction).

Taking into account the benefits and disadvantages of the different impactor types, the Sioutas cascade impactor for personal sampling was chosen. The Sioutas cascade impactor equipped with 25-mm polytetrafluoroethylene (PTFE) substrates of 0.5 µm pore-size (Pall Corporation, Port Washington, NY, USA) was operated at 9 L min^{-1}. At this flow rate particles are separated and collected on the impactor stages from the top to the bottom in the following aerodynamic particle diameter ranges (in µm): 10–2.5, 2.5–1.0, 1.0–0.5, 0.5–0.25. Particles below the 0.25 µm cut-point of the last stage are collected on a 2.0 µm pore-size 37-mm PTFE after-filter (SKC, Eighty Four, PA, USA). More detailed description of the Sioutas cascade impactors have been published earlier.[28,35]

The respirable cyclones were operated at a flow rate of 2.2 L min^{-1} that results in a 50% cut-point diameter of 4.0 µm. The 37-mm plastic cassettes in the cyclones were equipped with 5.0 µm pore-size PVC membrane filters (Millipore Corp., Billerica, MA, USA).

The 2.2 L min^{-1} flow required for the respirable samplers was maintained by in-house built PS103 model personal sampling pumps (National Institute of Occupational Health, Oslo, Norway). Leland Legacy model high flow personal sampling pumps (SKC, Eighty Four, PA, USA) were applied to maintain the 9 L min^{-1} flow for the impactors. These pumps automatically cut-out at a pressure drop of approximately 500 mmH_2O, and in most cases they were unable to operate through the entire 8-hour shift, stopping after 6-7 hours. Therefore the sampling with the impactors and the cyclones running in parallel was intentionally stopped and the sampling time was recorded 6-7 hours after the start of sampling. A second cyclone was used to sample the entire work-shift. The ratio between the

PM mass concentrations obtained by the two cyclones was used to adjust data from the impactor to estimate full-shift mass concentrations. In a few cases when the PM mass concentrations were not expected to reach the level which could cause the cut-out of the impactor pump, all the three samplers were let to operate in the whole work shift.

Particle size distributions of the aerosol in the smelters were in addition examined by a scanning mobility particle sizer (SMPS) instrument (model 3034, TSI Inc., Shoreview, USA) in the range from 10 to 487 nm. The SMPS instrument was placed at 3-4 meters from the furnace and run for 6–8 hours during one day in both plants.

Analysis

The collected aerosol particulate masses were determined gravimetrically by a six-place Sartorius Micro model MC5 balance (Sartorius AG, Göttingen, Germany) in a weighing room dedicated to low filter mass measurements, under controlled relative humidity (40±2%) and temperature (20±1 °C) conditions. The balances were calibrated daily. The accuracy and precision of the mass determinations were assessed by weighing certified reference masses (19.989±0.030 and 49.953±0.040mg). The mass detection limits (DLs) calculated as 3 times standard deviation of all field blanks were below 0.01 mg for all kind of substrates and filters used in the study. Both before and after exposure the substrates and filters were stored in the weighing room for at least two days to be acclimatized prior to the weighing procedure.

Calculation of the respirable PM mass concentrations from the impactor data

In order to compare the mass concentrations obtained by the respirable cyclones and the cascade impactors directly, mass concentrations of the respirable PM fraction were calculated from the impactor data. By these calculations sampling efficiencies given by the International Organization for Standard respirable convention were used and the following equations were applied:[36,37]

$$S_{RF_i} = \frac{SE_{LL} + 4 \times SE_{MP} + SE_{UL}}{6} \times S_i \quad (1)$$

where S_{RFi} is the mass concentration of the respirable PM collected on the stage *i*; SE is the sampling efficiency according to ISO 7708 at the lower limit (LL), the midpoint size (MP) and the upper limit (UL) of the stage interval; S_i is the mass concentration of PM collected on the stage *i*. The mass concentration of the respirable PM fraction (C_{RF}) is calculated by summing up the mass concentrations of the respirable PM collected on all five stages.

$$C_{RF} = \sum_{i=1}^{5} S_{RF_i} \quad (2).$$

Statistics

Logarithmic and arc sine transformation were applied for concentrations and proportions, respectively.[38] Independent sample and paired sample t-tests were performed to compare two independent job groups (e.g., tappers and crane operators) and two dependent variables (e.g., two parallel samples), respectively. Analysis of variance (ANOVA) was used when more than two groups were compared, and the least square difference was calculated in order to assess which groups differed from each other. A two-tailed *p*-value <0.05 was considered as the level of statistical significance. IBM® SPSS® statistical programme, version 21.0 (SPSS Inc, Chicago, Illinois, United States) was used for the statistical calculations.

Results and discussion

Mass concentrations of the different PM size fractions collected by the impactors were compared to mass concentrations of the respirable fraction collected in parallel by respirable cyclones as the first step of the evaluation. Altogether nine PM size fractions were applied in these comparisons, also those (<10 μm, <2.5 μm, <1.0 μm, <0.5 μm) which were calculated from the original five fractions collected on the four impactor stages and the after filter. Pearson's correlation coefficients between the mass concentrations of these fractions and the respirable aerosol fraction collected in parallel are summarised in Table 1. There were statistically significantly high correlations ($0.61 < r < 0.88$, $p < 0.001$, $N = 37\text{-}38$) between the mass concentrations of all PM size fractions collected by the impactor and the respirable fraction in the Mn alloy smelters. The respirable fraction calculated from the impactor data was 1.3 times higher than the respirable fraction collected in parallel by the respirable cyclones (Fig. 1). This ratio is within the expectations and suggests that both sampling devices worked according to their specifications.

Workplace particulate matter mass concentrations

Mass concentrations of the different PM fractions measured in the Mn alloy smelters are summarised in Table 2. The GM mass concentrations of the respirable fraction and the <10 μm PM fraction were 0.18 and 0.39 mg m^{-3}respectively. Johnsen *et al.* found 1.6 mg m^{-3} GM dust mass concentrations in the Norwegian silicomanganese, ferromanganese and ferrochromium production group, although, they applied 'total dust' sampling cassette which has quite different particle collection characteristics compared to the samplers used in this study.[32] The mass concentrations of the *parallel* and *full-shift* respirable fractions ($N = 38$) correlated very well ($r = 0.95$, $p < 0.001$) in spite of the slightly different sampling times.

It was previously found that the GM concentration of respirable Mn was 28 μg m^{-3} in the same Mn alloy smelters which were investigated in this study.[39] Another study characterising workplace aerosols in the Norwegian Mn alloy production industry by electron microscopy reported that the

submicron size fraction is dominated by MnO and MnSi particles in FeMn and SiMn production, respectively.[40] The chemical composition of the different PM fractions in the current study will be analysed later and internationally published in detail elsewhere.

Particle mass and number size distributions

Mass concentration distributions of the PM in the first and second Mn alloy smelter and the average mass concentration distribution in both smelters are summarised in Table 3 together with the mass median diameters (MMAD) and geometric standard deviations (GSD). The MMAD and GSD values were calculated according to Christopher *et al.*[41] Values estimated under lognormal distribution assumption are given in the electronic supplement, for sake of completeness. Differential mass distribution is represented by histogram and "middle of cut-off diameters" method in Fig. 2 as it was described by Majoral *et al.*[42] On average 50% of the particulate mass in the Mn alloy smelters was in the range from 2.5 to 10 μm, the rest was distributed between the lower stages of the impactors. On average 15% of the particulate mass was found in the PM fraction <0.25 μm.

The average number and mass size distributions of the PM in the Mn alloy smelters assessed by the SMPS in the size range from 10 to 487 nm are shown in Fig. 3 and in the electronic supplement, respectively. In addition, the distribution parameters are given in table S1. The mass concentrations are not accurate as the density of the particles is not known. The distribution itself, however, is not affected by the density of the particles as long as it is not a function of particle size, which is a reasonable assumption for this size range. The particle number and mass distribution curves look more or less similar close to the different furnaces where the SMPS was running. At the same time the particle number and mass concentration levels are more different by the different furnaces.

If the particle size mass distribution in the Mn alloy smelters is compared to the particle deposition efficiency curves published by Bartley and Vincent, it can be suggested that the deposition of PM in the workers´ lungs may be relatively high compared to the total mass of the fraction <10 μm d_{ae}, because high percentage of particles can be found in those particle mass fractions which have the highest deposition efficiencies in the alveolar region.[17]

Comparisons of different workplaces and job groups

The measured mass concentrations of the five PM fractions collected by the impactor and the respirable fraction were compared between the two Mn alloy smelters. The mass concentrations of the *parallel* respirable fraction ($GM_{S1} = 0.14$ mg m^{-3}, $GM_{S2} = 0.22$ mg m^{-3}, $p = 0.024$), the 2.5–10 μm ($GM_{S1} = 0.15$ mg m^{-3}, $GM_{S2} = 0.24$ mg m^{-3}, $p = 0.035$) and <10 μm ($GM_{S1} = 0.32$ mg m^{-3}, $GM_{S2} = 0.49$ mg m^{-3}, $p = 0.050$) fractions were statistically significantly higher in Mn alloy smelter 2 compared to Mn alloy smelter 1. Otherwise the differences were not of statistical significance. The differences in the mass concentrations of the *parallel* respirable fractions might be due to the slight

differences in the duration of sampling periods in the two smeleters. The differences in the mass concentrations of the 2.5–10 μm and <10 μm fractions might be explained by the different practises for sweeping of the settled dust in the two smelters which might cause slight differences in the mass concentration of the coarse particles.

Workers at furnace 1 in Mn alloy smelter 1, the only furnace producing silicomanganese, are exposed to one third of the mass concentrations of 2.5–10 μm (GM_{F1} = 0.12 mg m^{-3}, GM_{F3} = 0.31 mg m^{-3}, p = 0.002), 1.0–2.5 μm, 0.25–1.0 μm, 0–0.25 μm (GM_{F1} = 0.027 mg m^{-3}, GM_{F3} = 0.080 mg m^{-3}, p = 0.019), <10 μm and both respirable PM fractions compared to workers at furnace 3 in Mn alloy smelter 2 producing ferromanganese. The measured mass concentrations of the *parallel* respirable fraction at furnace 1 was half of the mass concentrations at furnace 4 (GM_{F1} = 0.11 mg m^{-3}, GM_{F4} = 0.20 mg m^{-}3, p = 0.034). The differences in workers´ exposure to PM at furnace 1 and 3 might be explained by the different productions; nevertheless furnace 1 was quite similar to the other two furnaces which are also producing ferromanganese like furnace 3.

A not completely unexpected finding was that tappers are exposed to statistically significantly higher mass concentrations of the PM fractions compared to crane operators (Table 5). The 2-3 times higher mass concentrations of the different PM fractions may be due to differences in duration of work tasks and distance from the source of PM.

No statistically significant differences were found between tappers and crane operators by comparing the proportions of the five PM fractions collected by the impactor. The proportions of the PM collected by the impactors were comparable among workers exposed at different furnaces or working in different Mn alloy production plants. These findings suggest that the distribution of the particles that furnace workers are exposed to is independent of the plant, furnace or work task. On the other hand one should also take into account the uncertainty of the particle mass distribution measurements when applying cascade impactors. If the measurement uncertainty is too high, a potential difference between the distributions cannot be revealed.

Conclusions

The GM mass concentrations of the respirable fraction and the <10 μm PM fraction in the manganese alloy smelters were 0.18 and 0.39 mg m^{-3}respectively. On average 50% of the particulate(<10 μm) mass was in the range from 2.5 to 10 μm, the rest was distributed between the lower stages of the impactors. On average 15% of the particulate mass was found in the PM fraction <0.25 μm. The comparisons of the different PM fraction mass concentrations related to different work tasks or different workplaces, showed in many cases statistically significant differences, however, the particle size distribution of PM in the fraction <10 μm d_{ae} was independent of the plant, furnace or work task.

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Table 1
Associations between the mass concentrations of the PM fractions collected in parallel by impactors and respirable cyclones in the Mn alloy smelters

	Parallel respirable fraction		
	N[a]	r[b]	Equation of the line of best fit
< 10 µm	37[c]	0.88*	y = 0.04+2.02x
< 2.5 µm	37[c]	0.85*	y = -0.004+1.16x
< 1.0 µm	37[c]	0.77*	y = -0.010+0.85x
< 0.5 µm	37[c]	0.73*	y = -0.02+0.72x
< 0.25 µm	37[c]	0.61*	y = -0.02+0.50x
0.25 – 0.5 µm	38	0.85*	y = 0.003+0.23x
0.5 – 1.0 µm	38	0.71*	y = 0.009+0.13x
1.0 – 2.5 µm	38	0.85*	y = 0.005+0.31x
2.5 – 10 µm	38	0.81*	y = 0.05+0.84x

[a] Number of pairs
[b] Pearson's correlation coefficient
[c] One measurement of the < 0.25 µm fraction was excluded because of its extreme high value (10 times the mass concentration of the respirable fraction)
* $p < 0.001$

Table 2
Mass concentrations (in mg m^{-3}) of the PM fractions measured in the Mn alloy smelters

					Percentiles			
	N[a]	AM[b]	Min.	Max.	10	90	GM[c]	GSD[d]
Parallel respirable fraction[e]	38	0.219	0.046	0.654	0.075	0.469	0.175	1.98
Full-shift respirable fraction[f]	38	0.232	0.042	0.573	0.075	0.467	0.181	2.08
< 10 µm (PM_{10})[g]	37	0.488	0.116	1.50	0.170	1.10	0.390	1.96
< 0.25 µm	37	0.088	0.004	0.609	0.017	0.188	0.051	2.77
0.25 – 0.5 µm	38	0.053	0.005	0.162	0.013	0.108	0.039	2.35
0.5 – 1.0 µm	38	0.037	0.008	0.115	0.011	0.072	0.028	2.11
1.0 – 2.5 µm	38	0.074	0.009	0.239	0.019	0.166	0.055	2.24
2.5 – 10 µm	38	0.234	0.018	0.698	0.096	0.497	0.189	2.02

[a] Number of measurements
[b] Arithmetic mean
[c] Geometric mean
[d] Geometric standard deviation
[e] Respirable PM fraction sampled by the respirable cyclone which ran in parallel with impactor
[f] Respirable PM fraction sampled by the respirable cyclone collecting full-shift sample
[g] Sum of all fractions

Table 3
PM mass fractions (in %) and mass distribution parameters in the Mn alloy smelters calculated from the deposited masses on all stages of the Sioutas cascade impactors

	AM[b]	95% CI[c]	Min.	Max.
Mn alloy smelter 1 (N[a] = 19)				
< 0.25 µm	13.0	11.1 – 14.9	3.6	18.9
0.25 – 0.5 µm	12.8	10.0 – 15.7	5.2	24.1
0.5 – 1.0 µm	8.8	6.7 – 10.9	3.3	19.0
1.0 – 2.5 µm	16.3	12.5 – 20.0	5.3	37.5
2.5 – 10 µm	49.1	43.3 – 55.0	15.7	65.1
MMAD[d]	2.7 µm	2.2 – 3.1 µm	0.9 µm	4.2 µm
GSD[e]	4.5	4.2 – 4.9	3.0	5.4
Mn alloy smelter 2 (N = 18)				
< 0.25 µm	17.3	11.9 – 22.6	2.6	40.8
0.25 – 0.5 µm	10.2	7.3 – 13.0	3.1	22.2
0.5 – 1.0 µm	7.2	5.7 – 8.8	3.4	13.6
1.0 – 2.5 µm	14.9	12.8 – 16.9	8.7	22.5
2.5 – 10 µm	50.5	44.5 – 56.5	33.1	72.1
MMAD	2.6 µm	1.9 – 3.2 µm	0.5 µm	4.8 µm
GSD	4.4	3.9 – 4.9	3.2	5.6
Smelter 1+2 (N = 37)				
< 0.25 µm	15.1	12.3 – 17.8	2.6	40.8
0.25 – 0.5 µm	11.5	9.6 – 13.5	3.1	24.1
0.5 – 1.0 µm	8.0	6.7 – 9.3	3.3	19.0
1.0 – 2.5 µm	15.6	13.5 – 17.7	5.3	37.5
2.5 – 10 µm	49.8	45.8 – 53.8	15.7	72.1
MMAD	2.6 µm	2.2 – 3.0 µm	0.5 µm	4.8 µm
GSD	4.5	4.2 – 4.7	3.0	5.6

[a] Number of measurements
[b] Arithmetic mean
[c] Central 95% confidence interval
[d] Mass median aerodynamic diameter
[e] Geometric standard deviation

Table 4
Number size distribution parameters in the Mn alloy smelters calculated from the SMPS data

	AM[b]	95% CI[c]	Min.	Max.
Mn smelter 1 furnace 2 (N[a] = 187)				
CMD[d]	27 nm	25 – 28 nm	15 nm	81 nm
GSD[e]	1.94	1.90 – 1.98	1.57	3.31
Mn smelter 2 furnace 1 (N = 101)				
CMD	37 nm	34 – 39 nm	18 nm	104 nm
GSD	2.16	2.12 – 2.20	1.74	2.72
Mn smelter 2 furnace 2 (N = 104)				
CMD	38 nm	34 – 42 nm	18 nm	122 nm
GSD	2.16	2.11 – 2.21	1.67	2.99

[a] Number of size distribution scans
[b] Arithmetic mean
[c] Central 95% confidence interval
[d] Count median mobility diameter
[e] Geometric standard deviation

Table 5
Mass concentrations (in mg m^{-3}) of the PM fractions in different job groups in the Mn alloy smelters

	Job group	N[a]	GM[b]	GSD[c]	*p*-value
Parallel respirable fraction[d]	Tappers	19	0.276	1.66	<0.001
	Crane operators	19	0.110	1.67	
Full-shift respirable fraction[e]	Tappers	19	0.312	1.62	<0.001
	Crane operators	19	0.105	1.64	
< 10 µm (PM_{10})[f]	Tappers	19	0.601	1.73	<0.001
	Crane operators	18	0.247	1.58	
< 0.25 µm	Tappers	19	0.081	2.81	0.003
	Crane operators	18	0.031	2.14	
0.25 – 0.5 µm	Tappers	19	0.071	1.68	<0.001
	Crane operators	19	0.021	1.93	
0.5 – 1.0 µm	Tappers	19	0.043	1.78	<0.001
	Crane operators	19	0.019	1.92	
1.0 – 2.5 µm	Tappers	19	0.090	1.89	<0.001
	Crane operators	19	0.033	1.89	
2.5 – 10 µm	Tappers	19	0.277	1.75	<0.001
	Crane operators	19	0.128	1.86	

[a] Number of measurements
[b] Geometric mean
[c] Geometric standard deviation
[d] Respirable PM fraction sampled in parallel with impactor
[e] Respirable PM fraction sampled full-shift
[f] Sum of all fractions

Figures

Fig. 1 The association between the mass concentrations of the respirable fraction calculated from impactor data and collected by respirable cyclones in the Mn alloy smelters

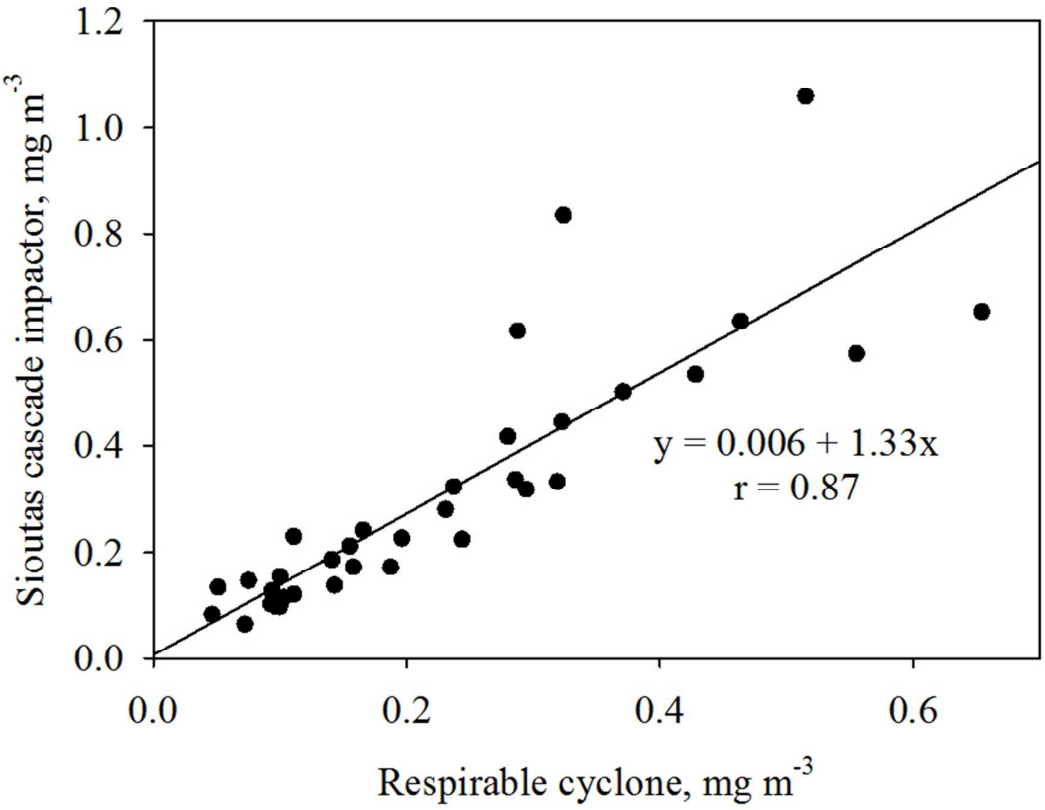

Fig. 2. Differential mass distribution of particles in the Mn alloy smelters represented by histogram (straight line) and "middle of cut-off diameters" method (dotted line)

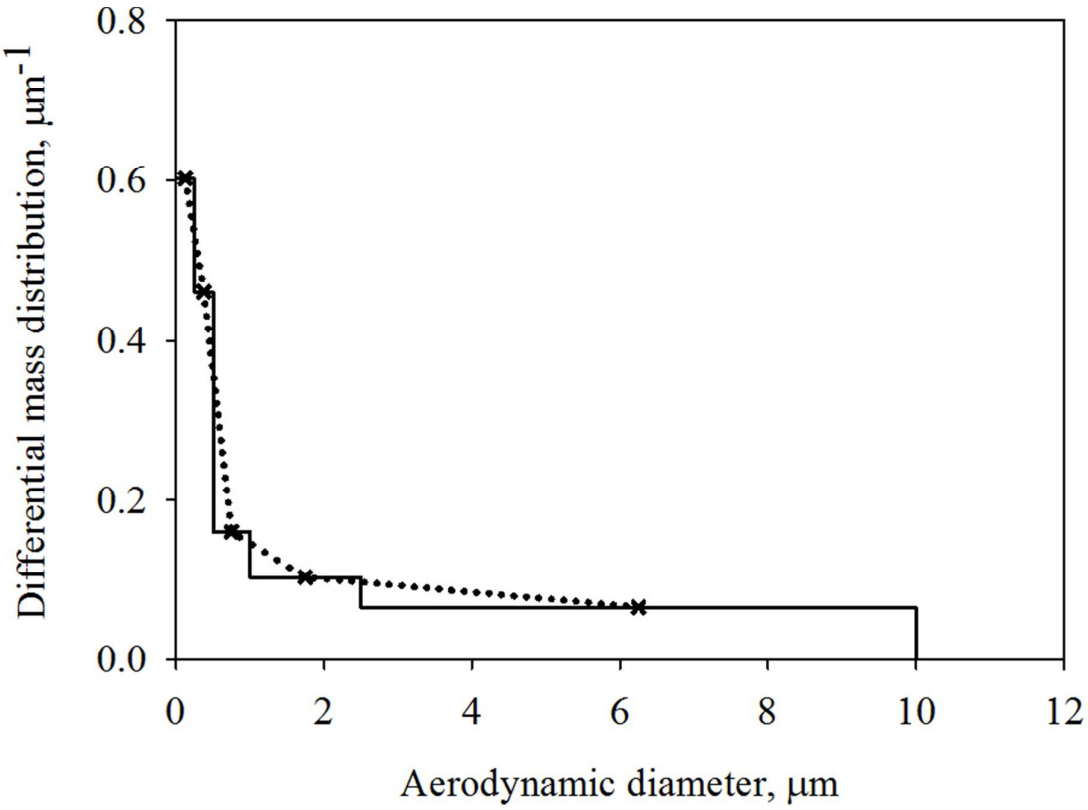

Fig. 3 Particle number concentration distributions measured by SMPS in the Mn alloy smelters