Electronic supplementary information

Sample preparation and leaching experiments

The deionised (DI) water used was prepared by a Milli Q System (18.2 MΩ cm, Millipore Corp., Billerica, USA). Nitric-, hydrofluoric- and hydrochloric acids (HNO_3, HF and HCl, respectively) were used for trace element measurements (Fluka, Buchs, Switzerland). Each inorganic salt used in the preparation of the artificial lung lining fluid simulant, D-glucose, sodium hydroxide (NaOH) and ascorbic acid were of analytical grade quality (Merck, Darmstadt, Germany). Phosphatidyl choline, α-tocopherol, uric acid, serum albumin, lysosyme, apo-transferrin and glutathione were purchased from Sigma (St. Louis, USA).

An artificial lung lining fluid simulant (Hatch´s solution) was used for leaching of the bio-accessible fraction in the collected aerosols. This solution was already applied and described in some of our previous studies.[1,2] However, the procedure used in the present contribution was slightly modified. Thus, the complete leaching procedure is described in the following. The inorganic salts and D-glucose were dissolved in DI water and the pH was adjusted to 7.4 (Gey´s solution) by using 1 M NaOH and 1 M HCl solutions. The organic compounds were dissolved in the final step to produce the Hatch´s solution. The exact composition of the solution is given elsewhere.[1] According to our experiences, the Hatch´s solution can be stored in a fridge at 2 – 8 °C for a few weeks, but the aliquot which was already heated to 37 °C or stored at room temperature more than 2-3 days cannot be used for leaching. The proteins might coagulate which prevents centrifugation of the full amount of Hatch´s solution after leaching.

Leaching of the welding aerosol filters was done in 50 mL volume VectaSpin 20™ polypropylene (PP) centrifuge tubes with 25 mL filter cup inserts equipped with 0.45 µm Nylon membranes (Whatman International Ltd., Maidstone, England, UK) with 10 mL Hatch´s solution. Each tube containing the filter and the leaching solution was placed in a laboratory oven at 37 ± 1 °C for 24 hours. The leaching solutions were then filtered by centrifugation at 2075 G with a 12 tube capacity centrifuge (Model 4K15, Sigma, Osterode am Harz, Germany). Because of the large amount of organic material in the leachates, nitric acid digestion and a 14-fold dilution had to be applied. One mL leachate was transferred to 14 mL volume PP tubes (SARSTEDT AG & Co., Nümbrecht, Germany), and 2 mL 65% nitric acid and 100 µL internal standard solution containing 1 µg mL^{-1} In, Tl, Sc, Ga, and Ge were added before heating in a laboratory oven at 90 °C for 90 minutes. After cooling, the solutions were diluted to 14 mL with DI water. A two-step acid digestion procedure was required to dissolve the non-Hatch soluble particles. 2 mL 65% nitric acid and 100 µL internal standard solution containing 140 µg L^{-1} Be were added to the filter cup inserts which were put into SV-140 Teflon autoclaves (Milestone, Sorisole, Italy). The open autoclaves were placed into a laboratory oven set to 120 °C for 120 minutes (open vessel digestion). After this step, a mixture of 2.0 mL aqua regia and 0.2 mL 40% HF was added to each autoclave which after closing were kept at 120 °C for 150 minutes in a laboratory oven (closed vessel digestion). The digested samples were diluted with DI water to 14 mL in 14 mL PP tubes.

References

1. B. Berlinger, D. G. Ellingsen, M. Naray, G. Zaray and Y. Thomassen, A study of the bio-accessibility of welding fumes, *J. Environ. Monit.*, 2008, **10**, 1448-1453.

2. D. G. Ellingsen, E. Zibarev, Z. Kusraeva, B. Berlinger, M. Chashchin, R. Bast-Pettersen, V. Chashchin and Y. Thomassen, The bioavailability of manganese in welders in relation to its solubility in welding fumes, *Environ. Sci. Process Impacts*, 2013, **15**, 357-365.

Tables

Table S1: Detection limits [µg on filter] and recoveries [%] of the Hatch soluble and non-soluble fractions in welding fume particulate matter.

Element	**Soluble fraction**	**Insoluble fraction**	**Recovery*** **(n=10)**
Al	0.19	0.64	90.9 ± 4.4
Cd	0.0010	0.048	---#
Co	0.013	0.072	---#
Cr	0.025	0.26	91.9 ± 3.8
Cu	0.34	0.71	---#
Fe	0.21	0.98	98.3 ± 4.1
Mn	0.042	0.18	99.5 ± 3.5
Mo	0.018	0.18	96.5 ± 4.1
Ni	0.018	0.29	86.7 ± 3.9
Pb	0.013	0.33	87.6 ± 4.0
Ti	0.015	0.12	88.6 ± 7.0
V	0.0051	0.18	---#
W	0.0029	0.28	---#
Zn	0.078	1.2	---#

*114 practically identical welding fume (WF) samples were collected with a multiport aerosol sampler. Ten samples were prepared and analysed with the method described in the paper. Ten samples were prepared and analysed with a reference method validated earlier (Thomassen et al., 1999). Sum of $Hatch_{souble}$ and $Hatch_{insoluble}$ fractions and the total amounts of elements measured by the reference method were compared.

#concentration below DL of one or both fractions

Table S2: P-values for overall (all three plants or all three welding techniques simultaneously) and pairwise comparisons of Hatch solubility using logrank tests.[*]

Element	Comparison of all 3 groups	Comparison of group 1 and 2[#]	Comparison of group 1 and 3[#]	Comparison of group 2 and 3[#]
Plant				
Al	0.035	0.028	0.678	0.033
Cd	0.230	not tested	not tested	not tested
Co	2.20E-9	0.095	2.57E-6	5.07E-8
Cr	< 2.20E-16	0.235	1.55E-8	< 2.20E-16
Cu	1.16E-11	0.773	1.06E-5	7.46E-11
Fe	0.020	0.716	0.030	4.91E-3
Mn	3.22E-10	0.226	3.91E-8	2.90E-11
Mo	2.19E-8	2.14E-10	0.031	5.38E-6
Ni	2.82E-5	0.490	4.35E-3	1.08E-6
Pb	3.74E-4	1.69E-4	2.99E-4	0.181
Ti	1.48E-7	0.791	1.03E-4	2.09E-7
V	1.14E-3	4.36E-3	0.324	1.65E-3
W	0.035	0.141	0.845	8.70E-3
Zn	1.63E-3	3.39E-4	0.147	0.568
Welding technique				
Al	4.15E-5	2.93E-5	0.877	3.12E-3
Cd	0.183	not tested	not tested	not tested
Co	1.03E-4	3.81E-3	0.038	3.07E-4
Cr	< 2.20E-16	< 2.20E-16	0.363	4.07E-13
Cu	1.18E-11	2.37E-7	2.82E-3	4.13E-10
Fe	0.061	not tested	not tested	not tested
Mn	3.12E-12	6.57E-11	0.722	6.22E-4
Mo	0.041	0.152	0.174	0.011
Ni	0.159	not tested	not tested	not tested
Pb	1.14E-6	0.514	5.43E-5	3.96E-7
Ti	7.77E-15	5.97E-16	0.901	1.86E-5
V	4.89E-7	7.16E-8	0.094	0.250
W	1.11E-4	3.01E-5	0.426	0.087
Zn	0.719	not tested	not tested	not tested

[*]overall and pairwise comparison based on a reduced data set of 263 samples (see main paper for details), pairwise tests were only performed when overall comparison yielded a statistically significant result (i.e., $p < 0.05$)

[#]technique 1 = manual MMA, technique 2 = semi-automatic MIG, technique 3 = automatic MIG

Table S3: P-values of two-way ANOVA using ranks.*

Element	Main effects		Interaction effect
	Plant	Technique	
Al	9.12E-3	3.93E-4	4.01E-4
Cd	0.170	0.029	0.549
Co	2.22E-9	0.999	0.020
Cr	< 2.20E-16	2.43E-12	0.036
Cu	2.57E-6	8.96E-6	7.39E-5
Fe	0.013	0.015	0.832
Mn	< 2.20E-16	5.61E-13	0.266
Mo	8.57E-7	0.269	0.311
Ni	2.81E-12	0.264	0.242
Pb	2.52E-3	7.68E-4	0.153
Ti	< 2.20E-16	1.49E-12	1.26E-3
V	1.65E-5	9.24E-6	0.398
W	8.49E-7	1.39E-5	0.216
Zn	4.93E-3	0.203	5.14E-3

*based on a reduced data set of 263 samples (see main paper for details)