Appendix. Supplementary material

Determination of airborne metal-containing nanoparticles in a historic mining area using single particle ICP-MS

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- **Collection of PM_{10} samples**

Table S1. Sampling date, location, PM_{10} mass concentration, and filtered air volume of the PM_{10} samples collected in the upper Meža Valley.

Sample	Sampling date	Sampling location	PM_{10} mass conc. (µg/m^3)	Airflow (m^3/day)
1a 1b	19.10.2018	Location 1	35	733.56
2a 2b	20.10.2018	Location 1	34	731.27
3a 3b	21.10.2018	Location 1	18	727.39
4	23.6.2021	Location 2	43	55.12
5	29.6.2021	Location 2	35	55.13
6	16.8.2021	Location 2	17	55.12
7	26.8.2021	Location 2	12	55.12

- **Schematic of the extraction optimization procedure**

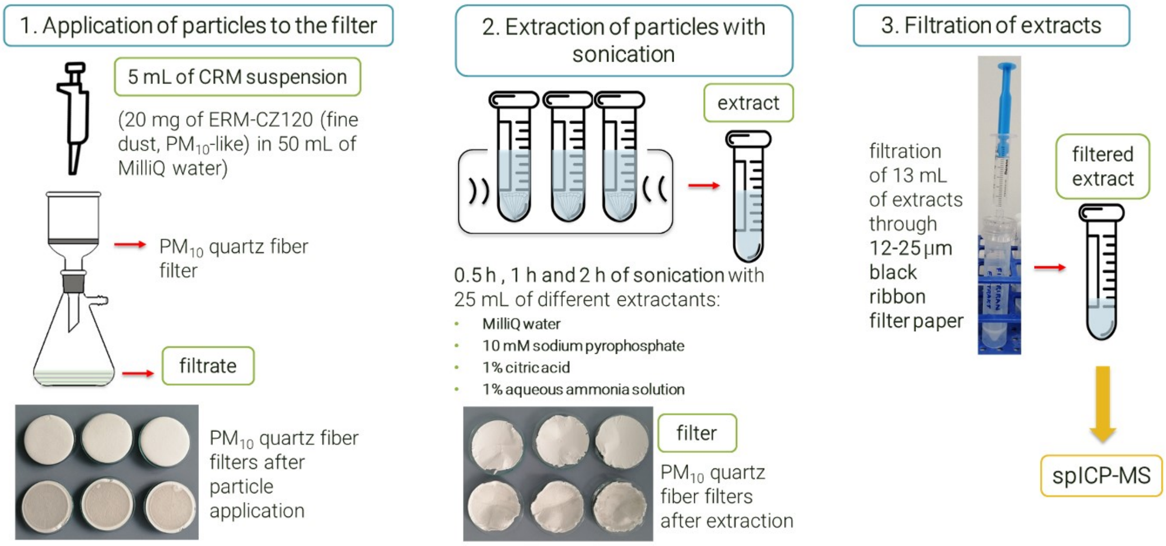


Fig. S1. Schematic of the extraction optimization procedure.

- **Microwave-assisted digestion of samples for total Zn and Pb determination**

The filter or 5 mL aliquots of liquid samples were transferred into a Teflon vessel and mixed with 2 mL of HNO_3, 1 mL of HCl, 1 mL of H_2O_2, and either 1 mL (for liquid samples) or 2 mL (for filter samples) of HF in the first step, followed by 6 mL of H_3BO_3 (4 % (*w/w*) for liquid samples or 12.5 mL for filter samples in the second step. The reagents used included hydrochloric acid (30 % (*w/w*) HCl, suprapur) and hydrofluoric acid (40 % (*w/w*) HF, suprapur) from Merck Ltd. (Darmstadt, Germany), nitric acid (67–69 % (*w/w*) HNO_3, suprapur) from Carlo Erba Reagents Srl (Milan, Italy) and boric acid (H_3BO_3, ultrapur) from Sigma-Aldrich (St. Louis, MO, USA). Digestion was carried out in a closed vessel microwave digestion system (MARS 6, CEM Corporation, Matthews, NC, USA) at the maximum power of 1600 W in two steps: ramping to T = 140 °C in 15 min, holding at T = 140 °C for 5 min, ramping to T = 200 °C in 20 min, holding at T = 200 °C for 60 min (first step), ramping to T = 140 °C in 15 min, holding at T = 140 °C for 5 min, ramping to T = 200 °C in 15 min, holding at T = 200 °C for 30 min (second step). After digestion, the clear solution was quantitatively transferred to 30 mL PP graduated tubes and made up to the mark with MilliQ water. The same procedure (acids only) was applied to a blank sample in each cycle.

- **ICP-MS operating parameters**

Table S2. Operating parameters for conventional and single particle ICP-MS measurements.

	Conventional mode	**Single particle mode**
Spray chamber	Scott double-pass	
Torch	Quartz torch with 2.5 mm injector	Quartz torch with 1.0 mm injector
Sample depth	8.0 mm	
Sampling and skimmer cones	Nickel	
Nebulizer	MiraMist, made of Teflon	MicroMist, made of glass
RF power	1550 W	
Plasma gas flow	15 L/min	
Auxiliary gas	0.90 L/min	
Nebulizer gas	1.05 L/min	0.70 L/min
Collision gas (He)	4.3 mL/min (^{66}Zn, ^{75}As), No gas (^{111}Cd, ^{208}Pb)	
Sample uptake rate	0.3 mL/min	
Dwell time	0.1 s	0.1 ms
Acquisition time	35 s	60 s (120* s)
Measured isotopes	^{66}Zn, ^{208}Pb, ^{75}As, ^{111}Cd	

* For extracts in 1 % citric acid, acquisition time was prolonged to 120 s due to the low number of Zn- and Pb-containing NPs in the samples.

- **Verification of the accuracy of the ICP-MS analysis**

Table S3. Total concentrations of selected elements determined in SPS-SW1 by conventional ICP-MS.

SPS-SW1	certified concentration (µg/L)	determined concentration (µg/L)
Zn	20*	19.9 ± 0.4
Pb	5.0 ± 0.1	5.0 ± 0.1
As	10.0 ± 0.1	9.9 ± 0.1
Cd	0.50 ± 0.01	0.51 ± 0.01

*Information value only.

- **Investigating the impact of four extraction solvents on the transport efficiency, ICP-MS response, and linearity of ionic standard calibration curves**

The first step was to evaluate whether ionic Zn and Pb standards, for the determination of the ICP-MS response, and AuNPs, for the determination of the transport efficiency, should be prepared in the extraction solvents or MilliQ water/0.1 % HNO_3. From Table S4 it can be seen that similar transport efficiencies (3.0 – 4.3 %) were determined with the particle frequency and particle size methods, independent of the matrix used. The exception was observed for the transport efficiencies determined by the particle size method in 1 mM sodium pyrophosphate (5.7 %) and 0.2 % aqueous ammonia solution (2.1 %). This was related to the 63 % higher ICP-MS response for ionic Au in 1 mM sodium pyrophosphate and 42 % lower ICP-MS response for ionic Au in 0.2 % aqueous ammonia solution compared to MilliQ water. The ICP-MS responses for ionic Zn and Pb in 0.1 % HNO_3, 1 mM sodium pyrophosphate, and 0.5 % citric acid were very similar but decreased by more than 96 % in 0.2 % aqueous ammonia solution. A reduced ICP-MS response in 0.2 % aqueous ammonia solution was most likely related to increased adhesion of ions to the surfaces of the sample container and/or the ICP-MS sample introduction system. However, this only affected the response of the ions and not the transport efficiency of the NPs (similar transport efficiencies based on the particle frequency method were observed in MilliQ water and 0.2 % aqueous ammonia solution). Therefore, for the measurements of NPs in MilliQ water, 1 mM sodium pyrophosphate, and 0.5 % citric acid, calibration curves were prepared from the matrix-matched ionic standards, whereas in the case of 0.2 % aqueous ammonia solution, ionic standards were prepared in 0.1 % aqueous HNO_3. The particle size method was selected to calculate the transport efficiency as the particle diameter of the AuNPs in the stock standard solution is less susceptible to change than the particle number concentration, which can decrease over time due to aggregation/agglomeration, particle settling, and/or particle adhesion to the container walls.

Table S4. Comparison of the transport efficiencies (calculated with particle frequency and particle size method by diluting AuNPs and ionic Au standards in relevant extraction solvents), and ICP-MS responses for ionic Au, Zn, and Pb standards with related R^2 values prepared in relevant extraction solvents. ICP-MS responses for ionic Au, Zn, and Pb standards prepared in 1 mM sodium pyrophosphate, 0.5 % citric acid, and 0.2 % aqueous ammonia solution are expressed as percentages in relation to the responses determined in MilliQ water. Results present the mean of the samples measured on two different days.

Extraction solvent	**Transport efficiency (%)**		**Ionic Au**		**Ionic Zn**		**Ionic Pb**	
	Particle frequency method	Particle size method	ICP-MS response (%)	R^2	ICP-MS response (%)	R^2	ICP-MS response (%)	R^2
MilliQ water*	3.7	3.5	100	0.9998	100	0.9998	100	0.9998
1 mM sodium pyrophosphate*	4.3	5.7	163	1	87.4	0.9999	90.8	0.9996
0.5 % citric acid	3.0	3.6	112	0.9993	126	1	103	0.9999
0.2 % aqueous ammonia solution	4.0	2.1	57.6	0.9984	3.77	0.9860	1.22	0.9986

* Ionic Zn and Pb standards were prepared in relevant matrices with the addition of 0.1 % HNO_3.

- **Summary of all calculations used in this study**

1. Total mass concentration of Zn or Pb in PM_{10} samples

$$Total\ concentration\ (mg/kg) = \frac{m_{combined}}{m_{dust\ on\ filter}} \quad \text{Eq. S1}$$

The total mass concentration of Zn or Pb on the filter was calculated by comparing the combined mass of Zn or Pb ($m_{combined}$, mg) with the mass of dust deposited on the filter ($m_{dust\ on\ filter}$, kg). The combined mass was calculated following Equation S2:

$$m_{combined}\ (mg) = m_{extract} + m_{filter} \quad \text{Eq. S2}$$

where $m_{extract}$ represents the mass of Zn or Pb in the extract (mg), and m_{filter} represents the mass of Zn or Pb left on the filter after the extraction (mg). Mass in the extract was calculated following Equation S3, while mass on the filter after extraction was calculated following Equation S4:

$$m_{extract}\ (mg) = CONC_{extract}\ x\ V_{extract} \quad \text{Eq. S3}$$

where $CONC_{extract}$ represents a concentration of Zn or Pb determined in digested extract (ng/mL), and $V_{extract}$ is a volume of extract (mL).

$$m_{filter}\ (mg) = CONC_{fiter}\ x\ V_{digested\ filter} \quad \text{Eq. S4}$$

where $CONC_{filter}$ represents a concentration of Zn or Pb determined in the solution obtained from the digested filter after extraction (ng/mL), and $V_{digested\ filter}$ is the volume of the solution obtained from the digested filter (mL).

2. Particle number concentration of Zn- or Pb-containing NPs in the PM_{10} samples

Particle number concentration in PM_{10} samples (particles/kg) was calculated following Equation S5:

$$Particle\ number\ concentration\ \left(\frac{particles}{kg}\right) = \frac{\frac{particle\ conc.}{1000} x\ V_{extract}}{m_{dust\ on\ filter}}\ x\ 1000000$$

Eq. S5

where *particle conc.* represents particle number concentration of Zn- or Pb-containing NPs determined in extracts by spICP-MS (particles/L), $V_{extract}$ is a volume of extract (mL), and $m_{dust\ on\ filter}$ is mass of dust deposited on the filter (mg).

3. Particle mass concentration of Zn- or Pb-containing NPs in the PM_{10} samples

Particle mass concentration (mg/kg) was calculated following Equation S6:

$$Particle\ mass\ concentration\ (mg/kg) = \frac{\frac{mass\ conc.}{1000} x\ V_{extract}}{m_{dust\ on\ filter}}$$

Eq. S6

where *mass conc.* represents particle mass concentration of Zn- or Pb-containing NPs determined in extracts by spICP-MS (ng/L), $V_{extract}$ is a volume of extract (mL), and $m_{dust\ on\ filter}$ is mass of dust deposited on the filter (mg).

4. Particle mass concentration of Zn- or Pb-containing NPs in ERM-CZ120

Particle mass concentration (mg/kg) in ERM-CZ120 prepared by weighing 20 mg of ERM-CZ120 powder into 50 ml of MilliQ water was calculated following Equation S7:

$$Particle\ mass\ concentration\ (mg/kg) = \frac{\frac{mass\ conc.}{1000} x\ V_{ERM-CZ120}}{m_{ERM-CZ120}}$$

Eq. S7

where *mass conc.* represents particle mass concentration of Zn- or Pb-containing NPs determined in ERM-CZ120 water suspension by spICP-MS (ng/L), $V_{ERM\text{-}CZ120}$ is a volume of ERM-CZ120 water suspension (50 mL), and $m_{ERM\text{-}CZ120}$ is the mass of ERM-CZ120 dust (20 mg).

5. Mass fraction of Zn- or Pb-containing NPs in PM_{10} samples

$$Mass\ fraction\ of\ NPs\ (\%) = \frac{particle\ mass\ concentration}{total\ concentration}\ x\ 100$$

Eq. S8

The mass fraction of NPs (%) was calculated by comparing particle mass concentration of Zn- or Pb-containing NPs determined in extracts by spICP-MS (mg/kg) with the total mass concentration of Zn or Pb determined in acid-digested PM_{10} samples by conventional ICP-MS (mg/kg).

6. Extraction recovery

$$Extraction\ recovery\ (\%) = \frac{CONC_{NPs\ in\ extract}}{CONC_{NPs\ deposited\ on\ filter}}\ x\ 100$$

Eq. S9

The extraction recovery (%) was calculated by comparing the mass concentration of Zn- and Pb-containing NPs in the extract, as determined by spICP-MS ($CONC_{NPs\ in\ extract}$, mg/kg), with their expected concentration in the ERM-CZ120 sample deposited on the quartz filter ($CONC_{NPs\ deposited\ on\ filter}$, mg/kg). The latter was calculated following the Equation S10:

$$CONC_{NPs\ deposited\ on\ filter} = CONC_{NPs\ in\ ERM-CZ120\ suspension} \times \frac{VOLUME_{deposited}\ ERM-CZ120\ suspension}{VOLUME_{extract}}$$

Eq. S10

based on the concentration of Zn- and Pb-containing NPs in the ERM-CZ120 suspended in the corresponding extraction solvent ($CONC_{NPs\ in\ ERM\text{-}CZ120\ suspension}$, mg/kg) – see Equation S7, the volume of the suspension deposited on a filter ($VOLUME_{deposited\ ERM\text{-}CZ120\ suspension}$, mL), and the volume of the extract ($VOLUME_{extract}$, mL).

- **Sample preparation and SEM-EDS analysis**

The sample droplets, prepared in MilliQ water, were deposited onto carbon tape or silicon plates and vacuum-dried. MilliQ water was chosen as the solvent for SEM-EDS analysis because drying sample droplets in sodium pyrophosphate led to the formation of a thin film that hindered particle detection. Therefore, solvent exchange was required, either by centrifuging the samples or by extracting particles from filters using MilliQ water. The uncoated samples were analyzed with a beam current of 0.8 nA, at an accelerating voltage of 20 kV and a working distance of 5 mm. Particles containing Zn and Pb were identified using the BSE mode images. Their size was determined using the measuring tool included in the Thermo Fisher Scientific SEM software, while their elemental makeup was determined using the EDS X-ray point analysis available in the AZtec software. Elemental analysis data were collected using acquisition times of 100 s, and the software was calibrated using premeasured universal standards included in the software, referenced to a Co standard.

- **Characterization of ERM-CZ120 suspended in different extraction solvents**

During the optimization of the extraction procedures, four different solvents were tested, including MilliQ water, 10 mM sodium pyrophosphate, 1% citric acid, and 1% aqueous ammonia solution. MilliQ water with a resistivity of 18.2 MΩ cm was prepared from a Direct-Q 5 system (Millipore, Watertown, MA, USA). Sodium pyrophosphate ($Na_4P_2O_7$ x $10H_2O$, pro analysis) and ammonia solution (25 % (*w/w*) NH_3, suprapur) were obtained from Merck Ltd., and citric acid ($C_6H_8O_7$, AnalaR normapur) was purchased from VWR International (Leuven, Belgium). Given that the extraction solvent may affect the properties of metal-containing NPs, for instance through their aggregation or dissolution, the influence of sodium pyrophosphate, citric acid, and aqueous ammonia solution on the particle properties was studied. For this purpose, the ERM-CZ120 material was suspended in the solutions of 1 mM sodium pyrophosphate, 0.5 % citric acid, and 0.2 % aqueous ammonia solution, representing the matrix of the corresponding extraction solvent, which was diluted 10-, 2- and 5-times in MilliQ water after extraction, respectively. Next, the particle number and mass concentrations, particle diameter, and mass fraction of Zn- and Pb-containing NPs were determined in the ERM-CZ120 suspended in the corresponding extraction solvents (Table S5). The mass fraction of Zn- and Pb-containing NPs in ERM-CZ120 suspended in 1 mM sodium pyrophosphate and 0.2 % aqueous ammonia solution was comparable to that observed in MilliQ water, while it was significantly lower in 0.5 % citric acid, indicating either the dissolution or reduced stability of the particles in citric acid. A similar trend was generally observed for the particle number and mass concentration of Zn- and Pb-containing NPs in selected extraction solvents. The dissolution of Zn- and Pb-containing NPs in the 0.5 % citric acid can be considered negligible as the baseline signals for Zn and Pb determined in the ERM-CZ120 suspension in citric acid were not significantly larger compared to those in MilliQ water (Fig. S2 and S3). Additionally, the mean particle sizes of Zn- and Pb-containing NPs in the 0. 5 % citric acid were similar to those observed in MilliQ water. From Table S5 it can be further observed that the mean particle size of Zn-containing NPs in 1 mM sodium pyrophosphate and 0.2 % aqueous ammonia solution was slightly higher than that in MilliQ water, indicating their aggregation/agglomeration. The particle size distribution (Fig. S4) further confirmed the aggregation/agglomeration of Zn-containing NPs in sodium pyrophosphate and aqueous ammonia solution.

Table S5. Particle number and mass concentration, mean particle size, and mass fraction of NPs determined for Zn- and Pb-containing NPs in ERM-CZ120 suspended in different extraction solvents and analyzed by spICP-MS. The results represent the average values with a standard deviation of six replicates.

Extraction solvent	**spICP-MS parameters**	**Zn-NPs**	**Pb-NPs**
MilliQ water	Particle number conc. (particles/kg of dust)	(1.46 ± 0.24) E+13	(2.79 ± 0.57) E+13
	Particle mass conc. (mg/kg of dust)	65.3 ± 2.1	12.8 ± 2.3
	Mean particle size (nm)	87 ± 4	32 ± 3
	Mass fraction of NPs (%)	5.26 ± 0.17	11.3 ± 2.1
1 mM sodium pyrophosphate	Particle number conc. (particles/kg of dust)	(1.54 ± 0.21) E+13	(3.81 ± 0.48) E+13
	Particle mass conc. (mg/kg of dust)	90.1 ± 5.0	15.0 ± 4.0
	Mean particle size (nm)	98 ± 2	32 ± 1
	Mass fraction of NPs (%)	7.27 ± 0.41	13.3 ± 3.5
0.5 % citric acid	Particle number conc. (particles/kg of dust)	(6.54 ± 0.63) E+12	(9.16 ± 0.33) E+12

	Particle mass conc. (mg/kg of dust)	30.9 ± 5.8	3.83 ± 0.68
	Mean particle size (nm)	90 ± 5	34 ± 1
	Mass fraction of NPs (%)	2.49 ± 0.47	3.39 ± 0.60
0.2 % aqueous ammonia solution	Particle number conc. (particles/kg of dust)	(1.73 ± 0.13) E+13	(4.82 ± 0.42) E+13
	Particle mass conc. (mg/kg of dust)	93.6 ± 30.7	15.9 ± 4.0
	Mean particle size (nm)	96 ± 2	31 ± 1
	Mass fraction of NPs (%)	7.54 ± 2.48	14.1 ± 3.5

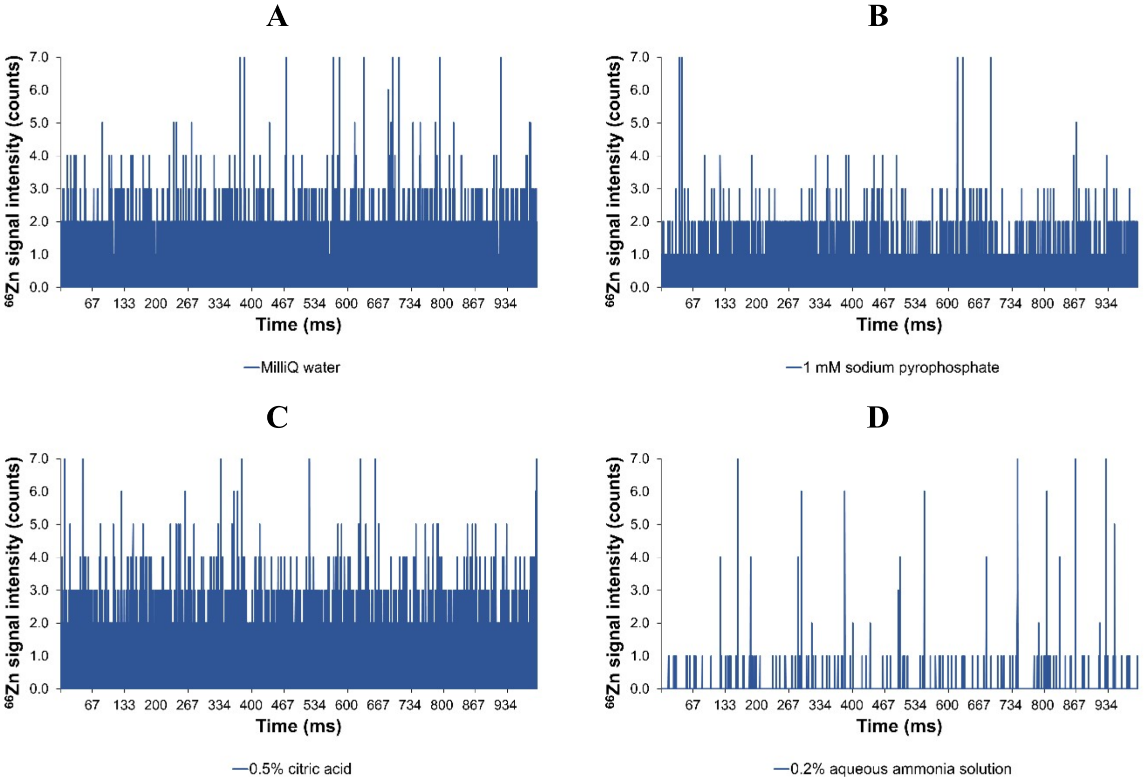


Fig. S2. Time scan for Zn signal obtained by spICP-MS in the ERM-CZ120 suspended in A) MilliQ water, B) 1 mM sodium pyrophosphate, C) 0.5 % citric acid, and D) 0.2% aqueous ammonia solution.

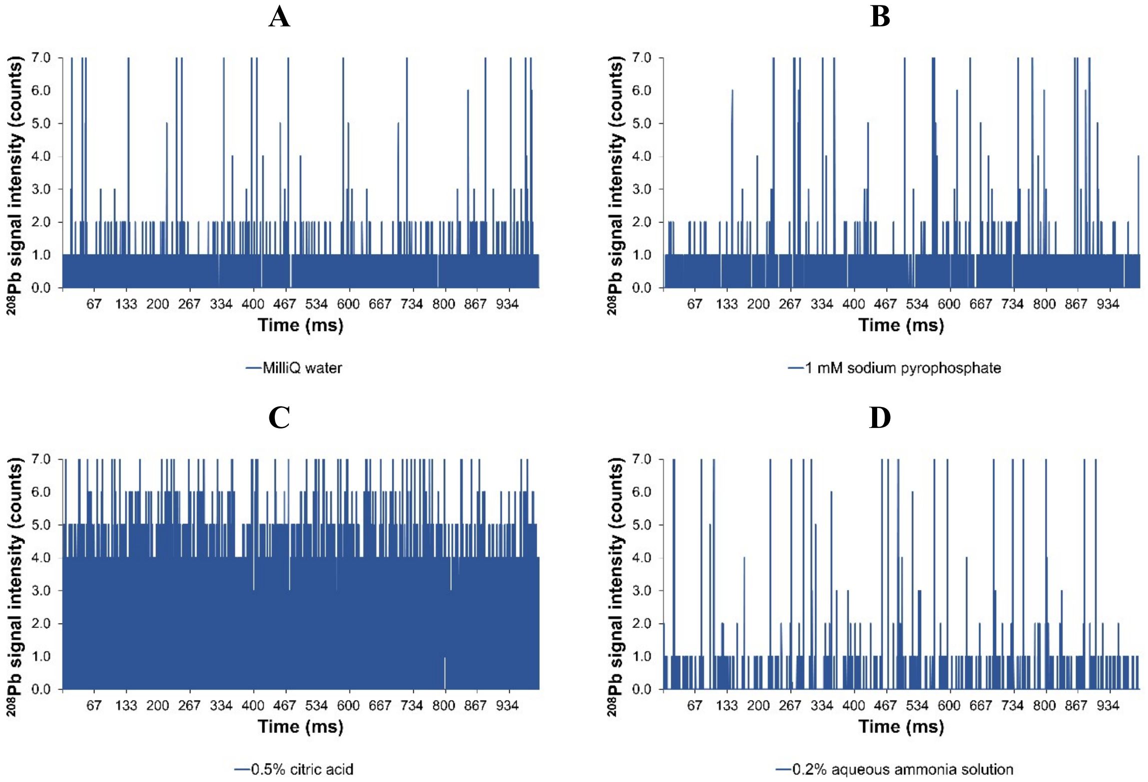
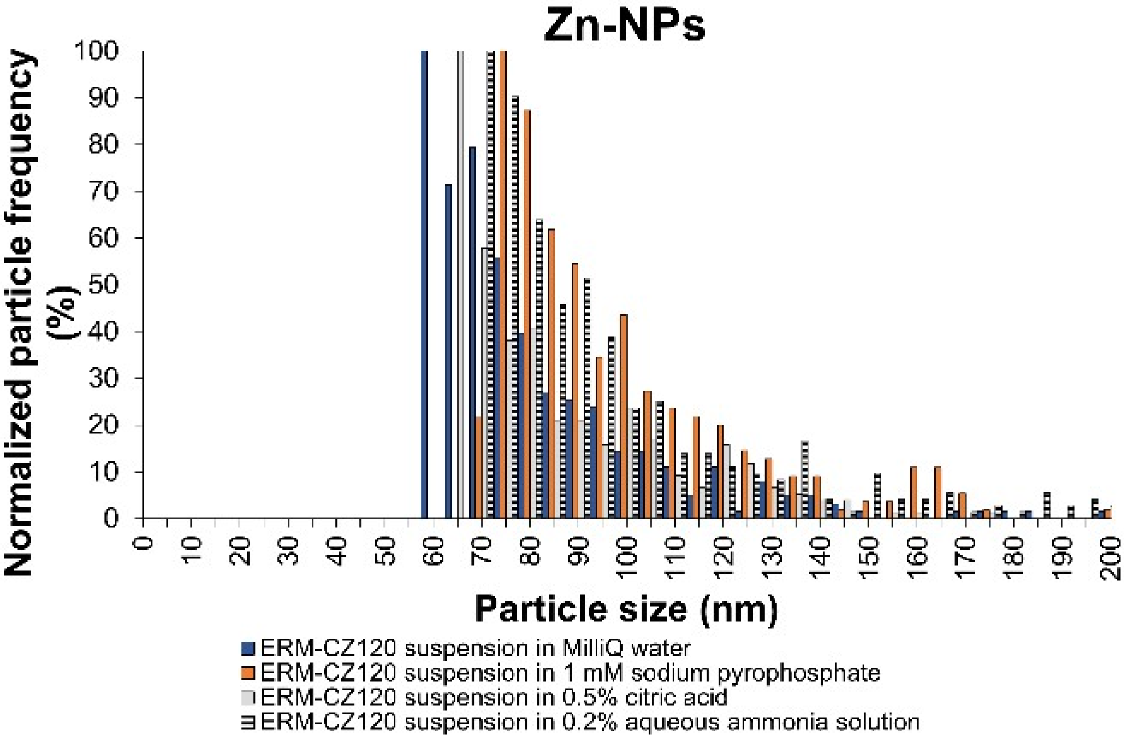


Fig. S3. Time scan for Pb signal obtained by spICP-MS in the ERM-CZ120 suspended in A) MilliQ water, B) 1 mM sodium pyrophosphate, C) 0.5 % citric acid, and D) 0.2% aqueous ammonia solution.



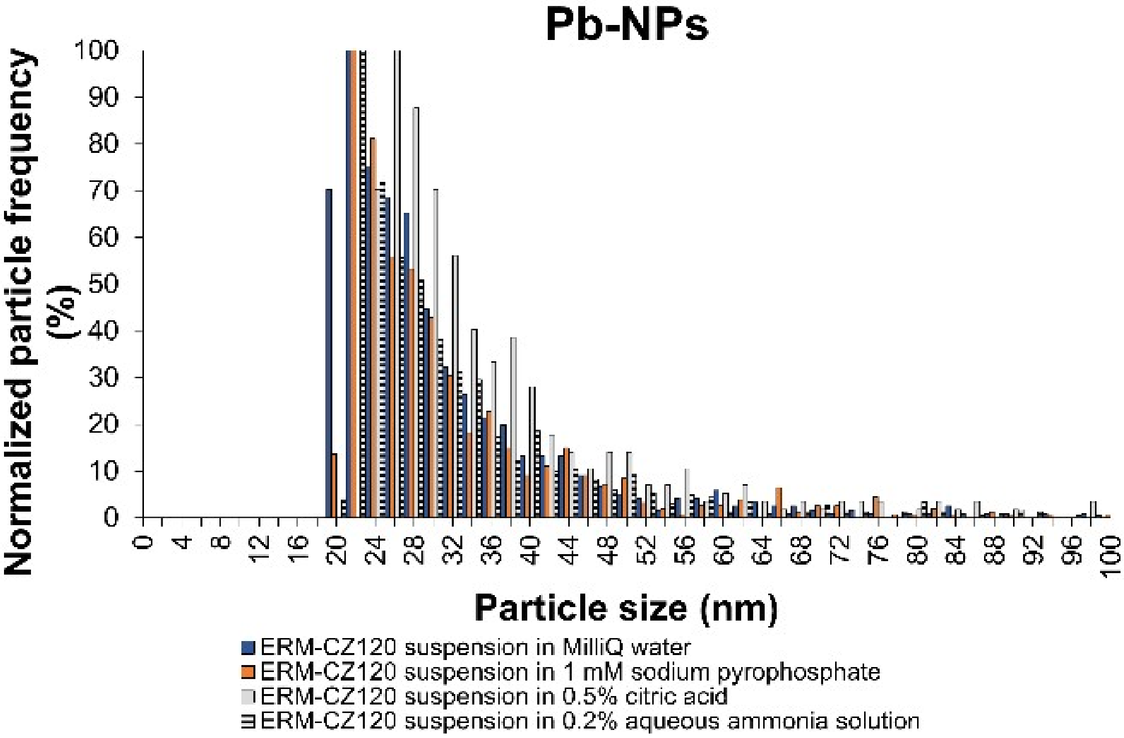


Fig. S4. Particle size distribution obtained by spICP-MS for Zn- and Pb-containing NPs in ERM-CZ120 suspended in four different extraction solvents. It should be noted that the particle size distribution plots only show a selected size range for comparison purposes, even though Zn- and Pb-containing NPs as large as 300 nm and 200 nm, respectively, were also detected.

- **Optimization of extraction duration**

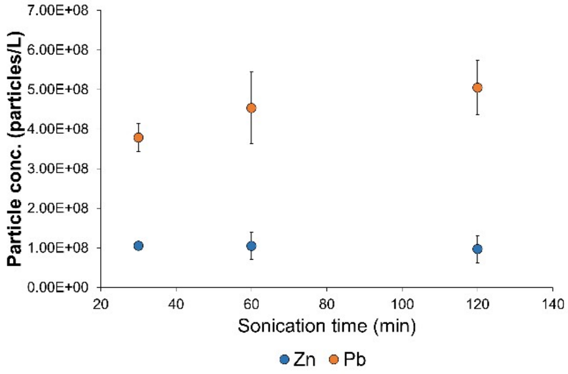


Fig. S5. The particle number concentration of Zn- and Pb-containing NPs extracted from the ERM-CZ120 deposited on PM_{10} filters was assessed as a function of sonication time, using 10 mM sodium pyrophosphate as the extraction solvent. Sodium pyrophosphate was chosen as it gave the highest particle number concentration (along with aqueous ammonia solution) when analyzing the ERM-CZ120 suspensions (Table S5). The results obtained by spICP MS represent the average values with a standard deviation of three replicates.

- **Limits of detection for ICP-MS and spICP-MS**

Table S6. Total mass concentration LOD (mg/kg) determined for Zn, Pb, As, and Cd in different extraction solvents by ICP-MS. Total mass concentration LOD was calculated as 3.3 times the standard deviation of concentrations measured in six blank samples, which consisted of corresponding extraction solvent.

Extraction solvent	Zn	Pb	As	Cd
MilliQ water	23.0	1.12	12.1	47.2
10 mM sodium pyrophosphate	22.4	1.89	9.46	28.3
1 % citric acid	4.66	3.84	36.7	8.01
1 % aqueous ammonia solution	23.9	0.823	32.6	17.5

The LOD values for the total elemental concentrations on filters were established by digesting blank quartz filters (without PM_{10}) and analyzing them using ICP-MS. The resulting LODs were 6.25 mg/kg for Zn, 0.640 mg/kg for Pb, 0.902 mg/kg for As, and 1.62 mg/kg for Cd.

Table S7. Particle size LOD, particle number concentration LOD, and particle mass concentration LOD determined for Zn- and Pb-containing NPs in different extraction solvents by spICP-MS. Particle number and mass concentration LOD were calculated as 3.3 times the standard deviation of concentrations measured in six blank samples.

Extraction solvent	Zn			Pb		
	Particle size LOD (nm)	Particle number conc. LOD (particles/kg)	Particle mass conc. LOD (mg/kg)	Particle size LOD (nm)	Particle number conc. LOD (particles/kg)	Particle mass conc. LOD (mg/kg)
MilliQ water	55 - 65	1.47 E+11	0.680	18 - 25	1.04 E+11	0.047
10 mM sodium pyrophosphate	64 - 68	1.74 E+11	1.11	20	1.64 E+11	0.054
1 % citric acid	60 – 114*	6.03 E+09	0.143	19 – 41*	4.07 E+09	0.003
1 % aqueous ammonia	65	7.95 E+11	3.75	19 - 20	3.43 E+11	0.127

solution		

*Higher size LOD values for Zn- and Pb-containing NPs in 1 % citric acid are the result of particle dissolution, which led to the elevated ionic background and consequently higher particle detection threshold.

- **Checking for unwanted retention of NPs on the 12–25 µm filter**

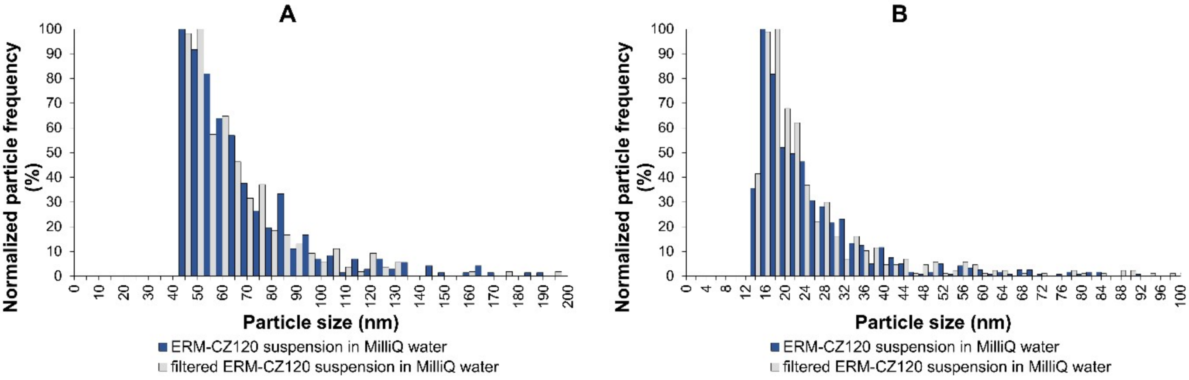


Fig. S6. Particle size distribution of A) Zn- and B) Pb-containing NPs in unfiltered and filtered (through a 12–25 µm filter) ERM-CZ120 suspension in MilliQ water.

- **Increased baseline signal in extracts with citric acid**

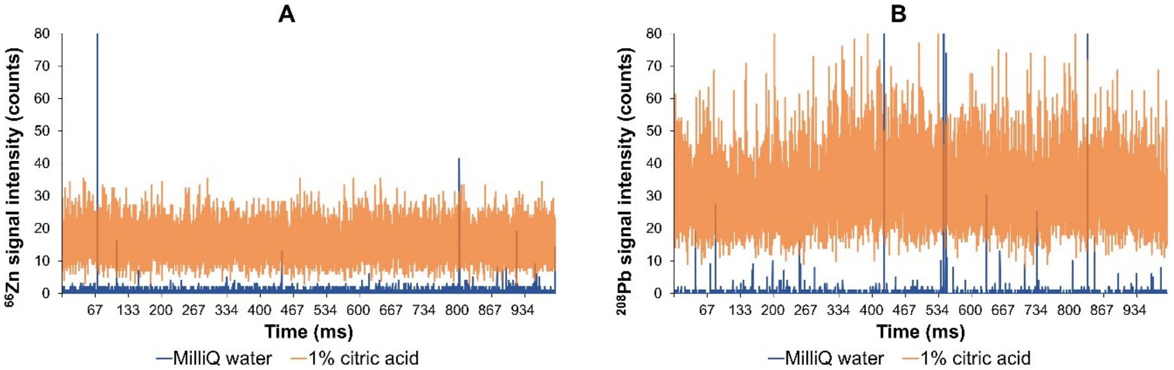


Fig. S7. Time scans for A) Zn and B) Pb signal obtained by spICP-MS in the ERM-CZ120 extracted from PM_{10} filters using MilliQ water and 1 % citric acid.

- **Zn and Pb concentrations per volume of filtered air**

Table S8. Total Zn and Pb mass concentrations, particle number, and mass concentration of Zn- and Pb-containing NPs in PM_{10} samples collected in the upper Meža Valley, calculated per volume of filtered air. Total Zn and Pb mass concentrations were determined by ICP-MS with a repeatability better than 3 %, while the other parameters were determined by spICP-MS and represent the average values with the standard deviation of two replicates.

Sample	**Zn**			**Pb**		
	Total mass conc. (ng/m^3)	**Particle number conc. (particles/m^3)**	**Particle mass conc. (ng/m^3)**	**Total mass conc. (ng/m^3)**	**Particle number conc. (particles/m^3)**	**Particle mass conc. (ng/m^3)**
1a	30.0 ± 0.9	(8.05 ± 2.84) E+04	1.04 ± 0.63	195 ± 6	(5.39 ± 0.88) E+06	1.07 ± 0.12
1b	33.7 ± 1.0	(8.09 ± 0.42) E+04	1.28 ± 0.50	206 ± 6	(6.02 ± 0.63) E+06	0.921 ± 0.217
2a	38.2 ± 1.1	(9.96 ± 0.95) E+04	0.332 ± 0.074	149 ± 4	(5.47 ± 0.20) E+06	1.09 ± 0.42
2b	31.3 ± 0.9	(9.25 ± 2.45) E+04	0.551 ± 0.041	145 ± 4	(4.96 ± 0.20) E+06	1.05 ± 0.05
3a	18.0 ± 0.5	(3.83 ± 1.46) E+04	0.148 ± 0.055	71.0 ± 2.1	(3.38 ± 0.27) E+06	0.722 ± 0.616
3b	18.5 ± 0.6	(3.37 ± 0.00) E+04	0.111 ± 0.010	68.4 ± 2.1	(3.17 ± 0.43) E+06	1.18 ± 0.67
4	63.5 ± 1.9	(3.21 ± 0.59) E+05	1.29 ± 0.07	634 ± 19	(1.44 ± 0.19) E+07	5.63 ± 0.43
5	58.7 ± 1.8	(2.21 ± 0.81) E+05	0.914 ± 0.042	660 ± 20	(1.13 ± 0.01) E+07	4.31 ± 1.72
6	22.7 ± 0.7	(8.59 ± 1.28) E+04	0.563 ± 0.061	449 ± 13	(3.47 ± 0.15) E+06	1.38 ± 0.03
7	22.2 ± 0.7	(8.00 ± 0.90) E+04	0.468 ± 0.055	275 ± 8	(2.35 ± 0.06) E+06	0.782 ± 0.269

- **Normalization of total Zn and Pb concentrations and mass concentrations of Zn- and Pb-containing NPs to total Al concentrations**

Table S9. Total Zn and Pb concentrations (Zn/Al and Pb/Al) and mass concentrations of Zn- and Pb-containing NPs (Zn NPs/Al and Pb NPs/Al) normalized to total Al concentrations, determined in each PM_{10} sample.

Sample	**Zn/Al**	**Pb/Al**	**Zn NPs/Al**	**Pb NPs/Al**
1a	0.152	0.986	0.0053	0.0054
1b	0.222	1.35	0.0084	0.0061
2a	0.204	0.793	0.0018	0.0058
2b	0.236	1.09	0.0042	0.0079
3a	0.796	3.14	0.0065	0.0320
3b	0.729	2.69	0.0044	0.0464
4	0.055	0.548	0.0011	0.0049
5	0.082	0.922	0.0013	0.0060
6	0.175	3.45	0.0043	0.0106
7	ND	ND	ND	ND

ND Not determined.

- **Recalculated particle size distribution, assuming $PbSO_4$ composition of particles**

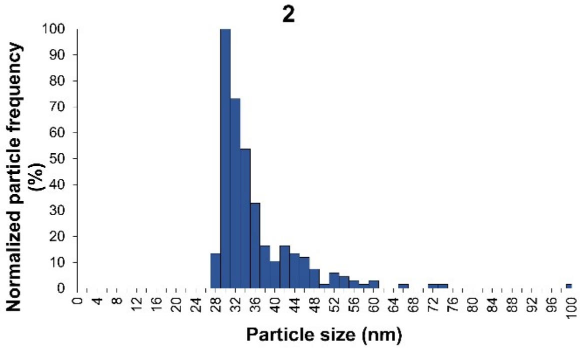
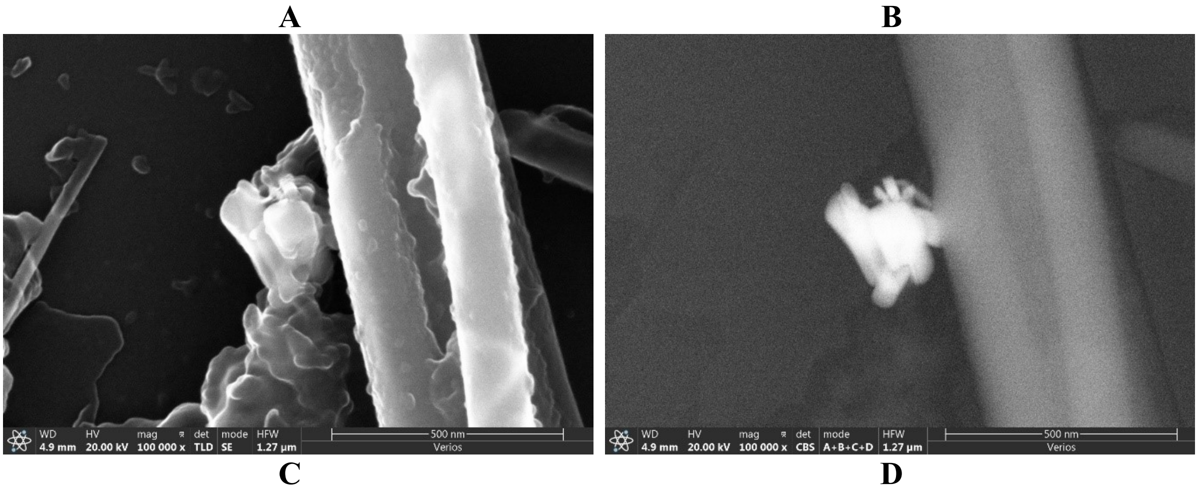


Fig. S8. Particle size distribution of Pb-containing NPs in the PM_{10} sample 2 collected in the upper Meža Valley. The particle size distribution was obtained by spICP-MS assuming the $PbSO_4$ composition of the particles.

- **Formation of a thin film after drying the samples for SEM-EDS analysis**



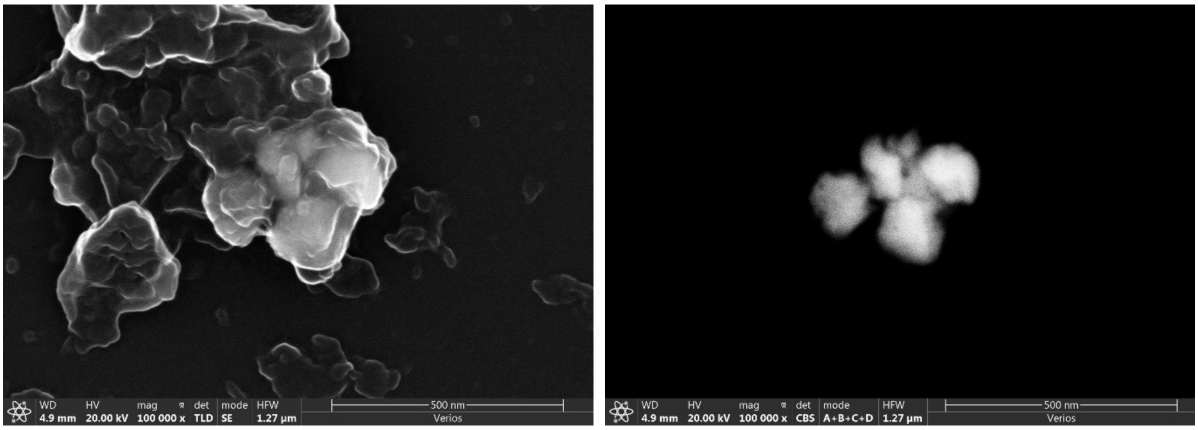


Fig. S9. Secondary electron (SE) (Figures A and C) and backscattered (BSE) (Figures B and D) SEM images of Zn- and Pb-containing (nano)particles in filtered extracts of PM_{10} samples from the upper Meža Valley, after solvent exchange. In the SE images, a layer that formed during sample drying is observed covering the particles. This exacerbated the challenge of detecting Zn- and Pb-containing (nano)particles in the BSE mode, where a combination of high contrast and low brightness was used to search the sample for particles composed of heavier elements (Figures B and D).