Appendix. Supporting Information for Reviewers

Instrument settings: digestion apparatus

Table S1. Instrument settings for the three-step pressurized digestion procedure of road dust samples performed on a

Multiwave system (Perkin Elmer, Überlingen, Germany/Anton Paar, Graz, Austria).

Step	Power (W)	Ramp Time (min)	Hold Time (min)
1	100–500	10	5
	500–1000	15	25
2	500–1000	5	25
3	500–1000	5	15

Linear correlation between RhNP concentration and the signal intensity
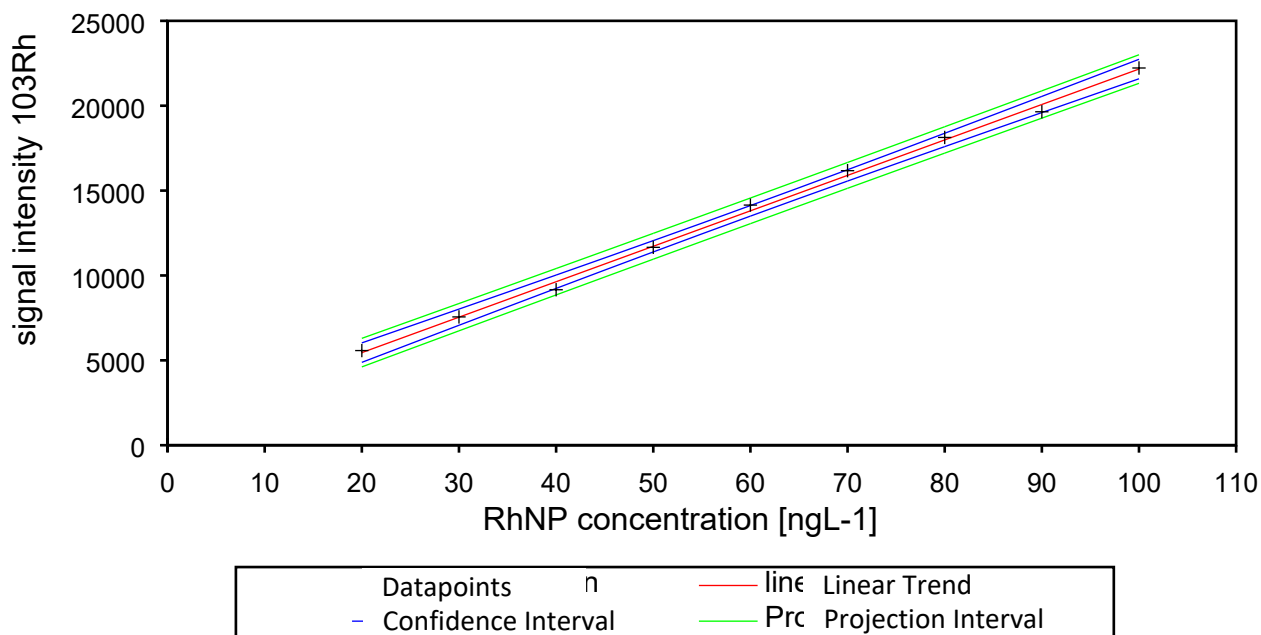

Figure S1. Linear correlation between RhNP concentration (20–100 ngL^{-1}) and the signal intensity of the CPE–ICP-MS

analysis. Coefficient of determination: 0.997.

Influence of EDTA on separation efficiency of dissolved Rh^{III}

The efficiency of the separation of dissolved rhodium from the surfactant-containing phase was optimized by the addition of EDTA.
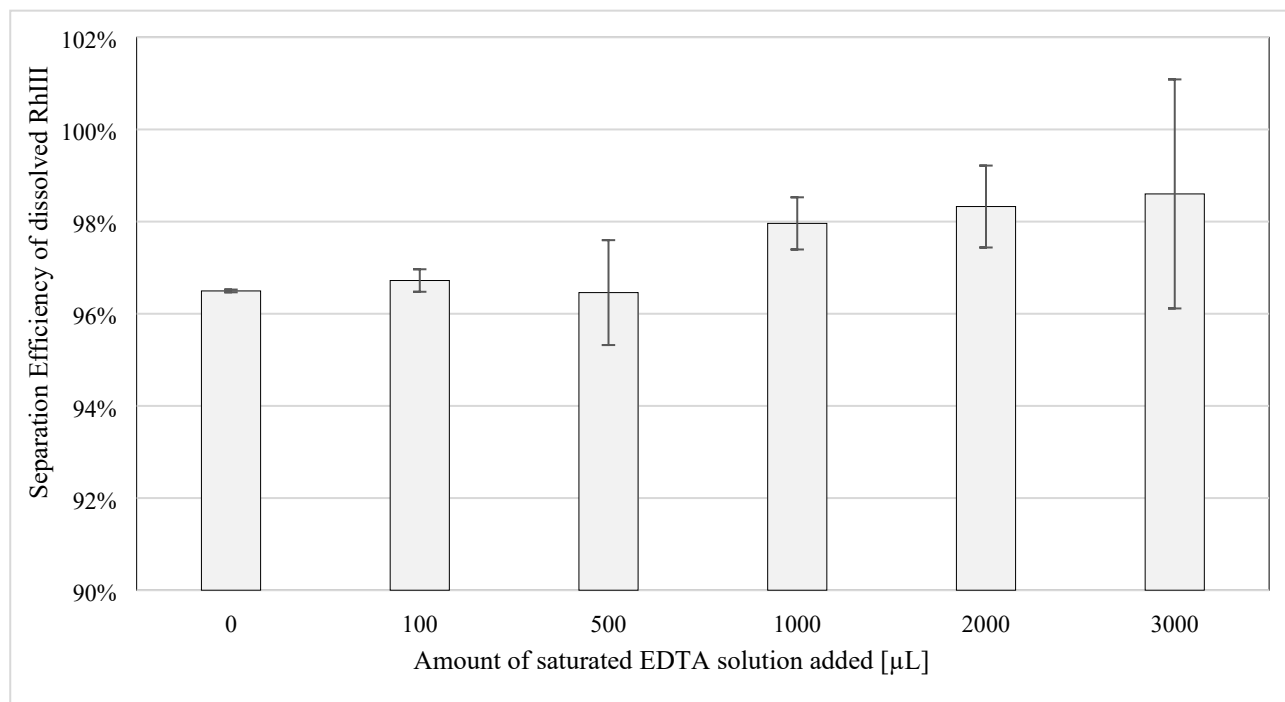

Figure S 2. Saturated EDTA was added together with the additives described in the Experimental Section. The efficiency of separation of Rh from the surfactant rich phase was determined in a 10 μgL^{-1} Rh^{III} solution by comparing the Rh content before and after performing CPE.

Calculation of the size detection limit

The diameter of a particle D can be calculated, assuming that the particle is spherical with a constant particle mass density:

$$D = \sqrt[3]{\frac{6 \cdot M_{NP}}{\rho \cdot \pi}} = \qquad \text{(Equation S1)}$$

where M_{NP} is the elemental mass of a nanoparticle and ρ is the particle mass density.

Time-resolved ICP-MS analysis gives a signal, which may allow the calculation of the particle diameter. The signal intensity I is the sum of the signal intensity of the background I_{Bkg} and the nanoparticle signal I_{NP}.

$$I = I_{Bkg} + I_{NP} \qquad \text{(Equation S2)}$$

On the basis of the computational strategy of Lee et al.[1] for converting spICP-MS data into nanoparticle sizes, the particle mass M_{NP} can be calculated from the signal intensity:

$$M_{NP} = \frac{I_{NP}}{R_i \cdot f_{NP}} \qquad \text{(Equation S3)}$$

where f_{NP} is the mass fraction of the analyzed metallic element in the nanoparticle. The elemental sensitivity R_i is derived from an external calibration curve of the desired element i:

$$R_i = \frac{k_i}{\eta} \qquad \text{(Equation S4)}$$

k_i is the slope of the obtained calibration curve and η the nebulization efficiency of the system. The nebulization efficiency η is calculated on the basis of the number of detected particle events of an Au nanoparticle suspension (30 nm size and 50 ngL^{-1} concentration).

Finally, the particle size can be calculated using the following relationship:

$$D = \sqrt[3]{\frac{6 \cdot \eta \cdot I_{NP}}{K \cdot f_a \cdot \rho \cdot \pi}} \qquad \text{(Equation S5)}$$

The nanoparticulate signal I_{NP} must be clearly distinguishable from signals of dissolved species. The

SDL is dependent on the limit of detection of I_{NP} of each desired measurement. Therefore, the limit of detection of a particle signal I_{LOD} is set to be

$$I_{LOD} = 3 \cdot I_{median}$$
(Equation S6)

with I_{median} being the median of all the signal intensities throughout the entire measurement.

The size detection limit *SDL* results from a combination of Equation S6 and Equation S5:

$$SDL = \sqrt[3]{\frac{6 \cdot \eta \cdot I_{LOD}}{K \cdot f_a \cdot \rho \cdot \pi}}$$
(Equation S7)

Sample preparation: road dust

Rainwater was collected in PP sample containers on 02.11.2017 at TUM Campus, Garching, Germany, then pooled in one PP sample container and filtered with 0.45 PES filter on the same day. After filtration a pH of 5.3 was determined for the rainwater.

The residual moisture of the road dust sample used was determined in order to relate the element concentration in the sample to the dry mass of the road dust. 1.819 g of the untreated road dust was dried to constant weight (1.717 g) at 105 °C, giving a moisture content of 5.6% for this sample. The total Rh content was determined by three individual determinations, details listed in Table S2 and Table S3.

The leachate of the road dust was extracted from untreated sample material. 50 mL of the rainwater was added to 558 mg of untreated and unground road dust, which corresponds to a dry mass of 527 mg road dust. After treating the mixture three times with ultrasound (each for 5 min) and shaking in between, the sample was placed for 16 h on a shaker with protection from light at room temperature. To settle the coarse solid material, the sample was centrifuged gently (20 min, rcf: 20 ×g) three times. After each centrifugation step, the supernatant was decanted into a fresh 50 mL tapered polypropylene sample tube. The total Rh content and the nanoparticulate content were determined in the leachate by ICP-MS and CPE—ICP-MS analysis, respectively (Table S3).

Table S2. Rhodium concentrations in the digests of a road dust sample collected in Munich, Germany. The digests of the road dust were diluted to a total volume of 250 mL and analyzed by ICP-MS (Agilent 7900 ICP-MS). Standard deviation of each analysis is based on six replicates (N = 6) and calculated according to German DIN 32645[2]. Reference material recovery was calculated based on the certificate of BCR-723.

	road dust [mg]	concentration [ng L^{-1}]	limit of detection [ng L^{-1}]	calibration range [ng L^{-1}]	reference material recovery
^{103}Rh	278	69.3 ± 0.8	2.3	50–150	98%
	300	75.4 ± 0.8			
	288	71.7 ± 0.8			

Table S3. Overview of Rhodium content in the road dust sample: the digested road dust (soil) was analyzed by ICP-MS. The leachate was generated by leaching an aliquot of the road dust with rainwater which was then analyzed by ICP-MS. The nanoparticulate fraction was investigated by CPE–ICP-MS measurements of the same leachate. All concentrations refer to the dry matter of the same road dust sample.

sample / fraction	rhodium content
soil	62.5 µg kg^{-1}
leachate of the road dust	670 ng kg^{-1}
nanoparticulate fraction in the leachate	92 ng kg^{-1}

Separation of lead by CPE

The separation of lead by CPE was investigated by spiking experiments. For this purpose, RhNP suspensions (50 ng L^{-1} CA@RhNP$_{[40nm]}$) were spiked with increasing lead concentrations and the signal intensity for Pb^{206} was evaluated by CPE-ICP-MS.

Table S4. Signal intensities of ICP-MS measurements are shown as counts per second (CPS) before and after performing the CPE. The lead concentration was determined from the isotope Pb^{206}.

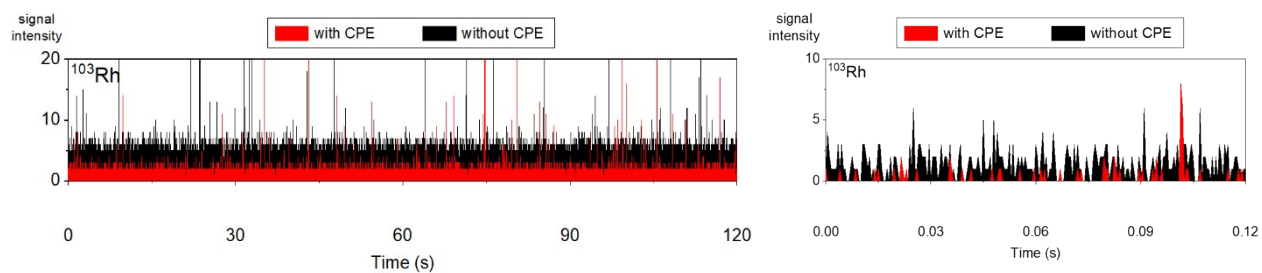| spiked lead concentration to the sample (μgL^{-1})	signal intensity (CPS) of Pb^{206}		
	before CPE	after CPE	
		Determination 1	Determination 2
0.1	1 605	53	55
0.25	4 199	27	16
0.5	9 299	54	52
0.75	14 213	66	61
1	18 919	60	81
10	200 117	51	40

Effect of CPE on spICP-MS measurement

Figure S 3. Signal intensities of single-particle ICP-MS measurement of road dust leachates with and without prior cloud point extraction. The figures on the left shows the time-resolved signal of ^{103}Rh. The figure on the right is an enlarged view of the time-resolved signals with an enlargement factor of 2 (y-axis) and 1000 (x-axis), respectively.

References

1. S. Lee, X. Bi, R. B. Reed, J. F. Ranville, P. Herckes and P. Westerhoff, *Environmental Science & Technology*, 2014, **48**, 10291-10300.

2. *Chemische Analytik - Nachweis-, Erfassungs- und Bestimmungsgrenze unter Wiederholbedingungen - Begriffe, Verfahren, Auswertung*, DIN 32 645, 2008.