

Modelling the transport of engineered metallic nanoparticles in the river Rhine – Supporting information

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Abstract

This document contains the following supporting information: details on the derivation of the emissions into the Rhine, based on the database of wastewater treatment plants, examination of the influence of the frequency of the time series on the model results, comparison with measurements, details on the mathematical modelling and results for titanium and silver.

1. Wastewater treatment plants in the Rhine basin

The discharges of nanoparticles along the river Rhine were estimated using the results from Markus et al. (2013) for the emissions per inhabitant and using a database supplied by the International Commission for the Rhine (ICPR) in Germany (ICPR, 2014). This database contains some properties of the several thousands of wastewater treatment plants (WWTPs) along the Rhine and its tributaries: name, country, receiving stream, design capacity. To aggregate these WWTP data into a shorter and more manageable table, the following rules were used:

- WWTPs located in France or Luxembourg were assigned to the Mosel, unless they discharged on the river Ill or were located in Strasbourg. Then they were assigned to a discharge "Strasbourg", as the river Ill passes through Strasbourg.
- WWTPs located in Switzerland or Austria were all assigned to a discharge "Basel", as they are upstream of the upstream boundary of the model.

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- WWTPs located in the Netherlands were all assigned to Lobith, though in this study the stretch of river downstream of the German-Dutch border was not investigated in much detail.
- Most WWTPs are actually located in Germany and there the bundesland and the tributary were used for the assignment:
 - WWTPs in Bayern were assigned to the Main.
 - WWTPs in Schleswig-Holstein were either assigned to the Mosel, unless they discharge on the Ill, in which case they were assigned to the discharge "Strasbourg".
 - WWTPs in Hessen were assigned to the Main, if they discharge on the Main and to the discharge Mainz, if they were located in the city agglomerate of Wiesbaden. If neither is the case, then they were assigned to the Neckar.
 - WWTPs in Rheinland-Paltz (Rhineland-Palatinate) were assigned to the Lahn, if they discharge on the Lahn, otherwise they were assigned to Mainz or Koblenz if they were located in either of these cities. All other WWTPs were assigned to the Mosel.
 - WWTPs from Baden-Württemberg were assigned to the discharge "Karlsruhe", "Mannheim" or if not located in either of these cities, to the Neckar.
 - Finally, WWTPs from Nordrhein-Westfalen (North Rhine-Westphalia) were assigned to discharges at Cologne, Bonn, Leverkusen, Wesel and Düsseldorf, if they were located in one of these cities and otherwise to one of the tributaries Ruhr, Lahn or Lippe, if they discharge on these rivers.
 WWTPs that discharge on the smaller rivers Sieg, Wupper, Em-scher or Erft were assigned to the discharges "Bonn", "Leverkusen", "Duisburg", "Lahn" and "Düsseldorf" respectively.

This procedure left 23 WWTPs unassigned with a total capacity of 140,000 i.e., but on the total this was negligible, certainly in view of the uncertainties that still exist despite the detailed information: only the design capacities were given, not the actual capacity or the use and it is unknown how many households and industries are not connected to the sewer system.

The resulting emissions, grouped according to the above procedure are shown in Table S1.

2. Estimation of the net emissions

Because the total number of inhabitants in the Rhine basin is roughly 50 million (Water Policy International Ltd., 2015) and the total capacity of the treatment plants is 86 million i.e. (inhabitant equivalents), the potential load was

Table S1: Estimated emissions of nanoparticles. The population data were based on the design capacity of the WWTPs in the Rhine basin (ICPR, 2015).

River	Inhabitant equivalents (in millions)	Titanium dioxide t/y	Zinc oxide t/y	Silver kg/y
Basel	8.52	31.5	42.6	392
Strasbourg	1.05	3.9	5.25	48
Karlsruhe	0.44	1.6	2.2	20
Mannheim	0.55	2.0	2.75	25
Neckar	20.0	74	100	920
Mainz	0.86	3.2	4.3	40
Main	11.0	41	55	506
Koblenz	0.32	1.2	1.6	15
Mosel	13.9	51.4	69.5	639
Lahn	0.07	0.26	0.35	3
Bonn	1.22	4.5	6.1	56
Cologne	1.82	6.7	9.1	84
Leverkusen	1.14	4.2	5.7	52
Dusseldorf	2.21	8.2	11.1	102
Ruhr	1.63	6.0	8.2	75
Duisburg	4.37	16.2	21.8	201
Wesel	0.099	0.4	0.5	4.5
Lippe	1.17	4.3	5.85	54
Lobith	15.3	56.6	76.5	704
<i>Total</i>	85.7	317	428	3941

Table S2: Flow rate and average concentration and load of suspended particulate matter of the at various locations in the river Rhine for the years 2007–2009.

Source	Flow rate m ³ /s	Concentration SPM mg/l	Load SPM kt/y
Inflow at Maxau	1025	16.0	517.2
Neckar	160	17.7	89.3
Main	250	15.0	118.3
Mosel	321	13.3	134.6
Total inflow	1756		859.4
Outflow at Bimmen	2085	18.2	1196.7
Difference	329		337.3

Table S3: Flow rate and average concentration and load of total zinc at various locations in the river Rhine for the years 2007–2009.

Source	Flow rate m^3/s	Concentration Zinc $\mu\text{g}/\text{l}$	Load Zinc t/y
Inflow at Maxau	1025	2.2	71.1
Neckar	160	10.4	52.5
Main	250	23.4	184.5
Mosel	321	19.1	193.3
Total inflow	1756		501.4
Outflow at Bimmen	2085	13.2	867.9
Difference	329		366.5

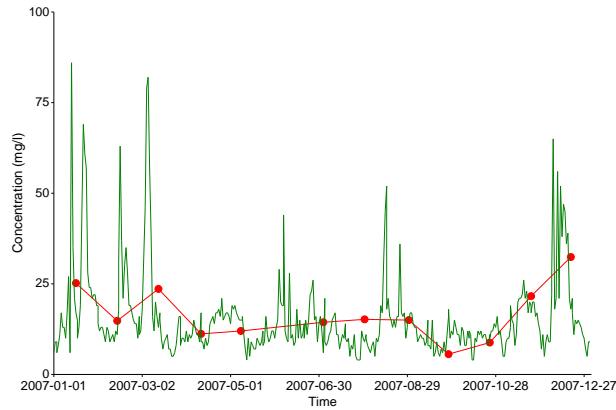


Figure S1: Comparison of the measured SPM concentrations at Bimmen and Lobith, showing the high frequency variations in the concentration. To highlight the details, the displayed period has been limited to the year 2007 instead of the full simulation period. The green line represents the daily measurements at Lobith on the Dutch side of the Dutch-German border and the red connected dots represent the two-weekly measurements at Bimmen on the German side.

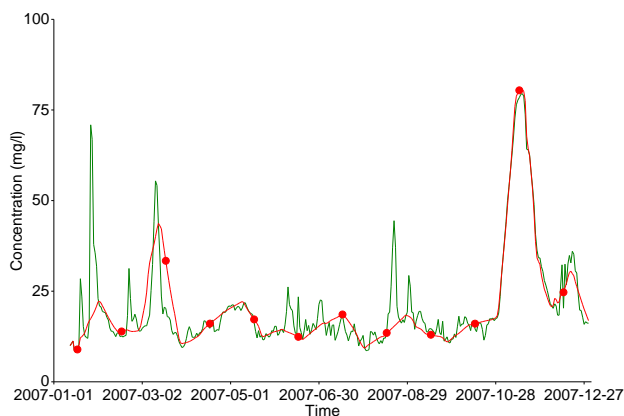


Figure S2: Comparison of the calculated SPM concentrations at Bimmen, using an original high-frequency timeseries as the upstream boundary conditions and a thinned version of that timeseries. The green line without dots represents the results with the high-frequency series and the red line with the dots represents the results with the thinned series.

corrected with a factor $50/86 = 0.58$ to account for the actual amount of wastewater being treated. This factor was equally applied to the WWTPs present in the catchment area.

Since WWTPs that use activated sludge as one of the treatment steps are capable of retaining 95% or more of the nanoparticles (Barton et al., 2015; Kaegi et al., 2011), in the model the loads from the WWTPs are reduced by a factor 20. However, it is well known that not all households are connected to the treatment plants and furthermore stormwater overflows must be taken into account. According to the European Environment Agency (EEA), 80% of the households in Europe are connected to a sewerage system ((Agency, 2015), data from 2007–2009). In some countries, notably Germany and the Netherlands, more than 90% are connected. To remain on the conservative side, in the model a fraction of 0.1 has been used to account for the households that are not connected and for the effect of storm overflows. Hence the estimates of the total loads were multiplied by a factor $0.1 + 0.9 \cdot 0.05 \approx 0.15$ to arrive at the model waste loads.

3. Influence of the measurement frequency

Since the daily measurements of suspended particulate matter at Lobith show much more variation than the two-weekly measurements at Bimmen, the question arises whether the use of two-weekly measurements leads to noticeable deviations (see Fig. S1). To this end both a detailed and a thinned-out artificial timeseries were used as the upstream boundary condition at Maxau near Karlsruhe, with all other timeseries in the input equal to the most detailed

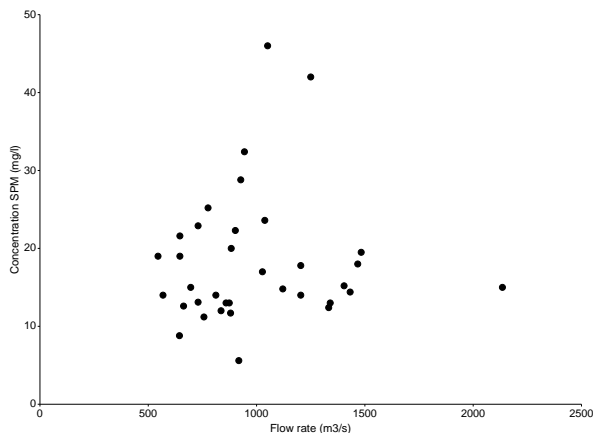


Figure S3: Correlation of the observed SPM concentrations at Bimmen and the measured flow rate in the Rhine at the same date.

available. The thinned-out timeseries was obtained by sampling the original timeseries with a frequency of once every 14 days. Then the results for Bimmen were compared, both visually and via standard statistics (see Fig. S2).

As can be seen the frequency of the timeseries has very little effect on the result. A number of short peaks are missed, but the overall pattern is the same for both series and is in fact surprisingly similar. This is reflected in the statistical parameters:

Mean for daily timeseries:	20.9 mg/l
Mean for biweekly timeseries:	20.2 mg/l
90% percentile for daily timeseries:	35.2 mg/l
90% percentile for biweekly timeseries:	33.2 mg/l
Correlation coefficient:	0.895

Missing such peaks could have a noticeable influence on the yearly transport in the case of rain-dominated rivers, as the sediment peak and the flow rate are then correlated (De Vries and Klavers, 1994). From an examination of the available data, however, no clear correlation is evident (see Fig. S3).

It was therefore concluded that the two-weekly measurements available for the German monitoring points and for all measured substances were frequent enough for the envisaged model calculations.

4. Mass balance for the Rhine

Using the measurements of the flow rate and the concentrations at the upstream and downstream boundaries as well as in the tributaries the mass balance per substance can be investigated. The individual contributions were determined by separately averaging the flow rate and the concentration over the

period 2007–2009. This method is documented to be accurate enough (De Vries and Klavers, 1994).

The result is shown in Tables S2 and S3. Here all the available data have been used. Tributaries for which no data are available are the Ruhr, the Emscher, the Lippe and the Lahn. While these are not expected to constitute major contributions, the volume balance still lacks roughly $330 \text{ m}^3/\text{s}$, some 15%. The long-term flow rates for these rivers amount to a total of around $230 \text{ (m}^3/\text{s)}$ – assuming the Lippe has roughly the same mean flow as the Ruhr, since there appears to be no information on its flow rate.

The mass balance for suspended particulate matter in the modelled area shows a surplus of about 30%, whereas for total zinc the surplus is about 40%, that is, more is flowing out at Bimmen than can be accounted for by the inflow at Maxau and the major tributaries. Unfortunately data for the other tributaries are lacking, so that only very rough estimates can be made for their contribution to the mass balance.

Besides unknown contributions from the mentioned tributaries another source can be the erosion or the runoff of particulate matter and the atmospheric deposition of zinc, which may be caused by traffic, agricultural sources and industrial activities (Fuchs et al., 2010). To begin with particulate matter: according to the ICPR the gross erosion may be up to 1.5 Mt per year (ICPR, 2015). Given that the source to make the mass balance closed is about 300 kt/y, this is five times more than is needed. The figure reported by the ICPR refers to all sediment, not just the silt and clay particles, which make up the suspended particulate matter that is of importance in this study.

For zinc, another source of information is the Dutch emission registration database (Dutch national government, 2015). This database shows a load via the atmosphere of 73 t/y for the whole of the Netherlands. Since the area of the catchment is roughly 42000 km^2 , this means an atmospheric deposition of $1.74 \mu\text{g}/\text{m}^2 \cdot \text{y}$. If this deposition holds for the German part of the Rhine basin (185000 km^2), then the total load would be: 324 t/y. As mentioned in the main text, Fuchs et al. find a contribution of 600 t/y (Fuchs et al., 2010).

As discussed in the main text, the model results for both suspended particulate matter and for total zinc turned out to be systematically lower than the measurements, when only the concentrations at the inflows were used (see Figs. S6, S8 and S10). By adding the diffuse sources discussed above the model results are much more comparable to the measurements. (see Figs. S7, S9 and S11).

5. Mathematical formulation of the processes

The processes that nanoparticles are subject to have been modelled based on several prior publications (Markus et al., 2015; Krone, 1962; Partheniades, 1962). Here the equations are collected.

The sedimentation of free nanoparticles, SPM and of both homoaggregates and heteroaggregates was modelled via a constant sedimentation velocity:

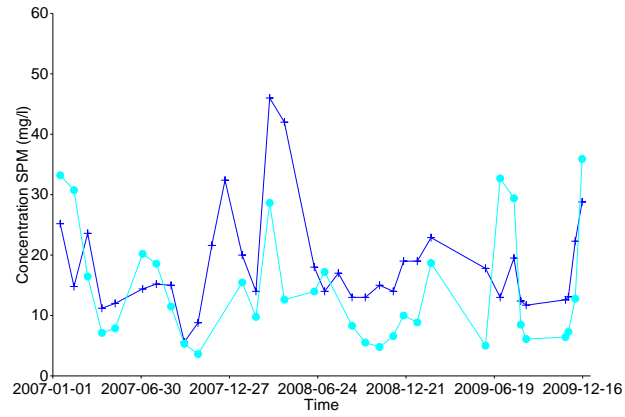


Figure S4: Measured (+) and calculated (o) concentration of suspended particulate matter at Bimmen (mg/l), without resuspension.

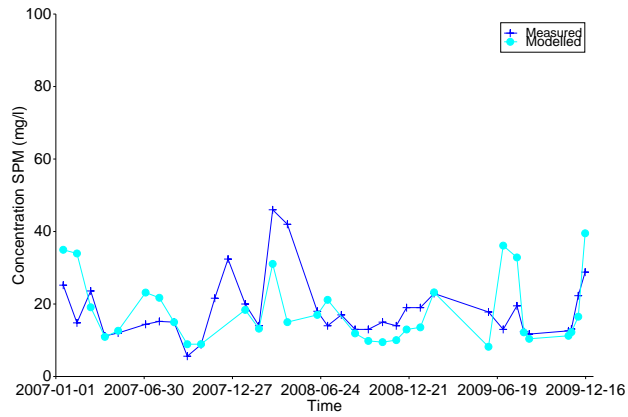


Figure S5: Measured (+) and calculated (o) concentration of suspended particulate matter at Bimmen (mg/l). In the calculation an extra source of 0.37 Mt/y was included to represent erosion.

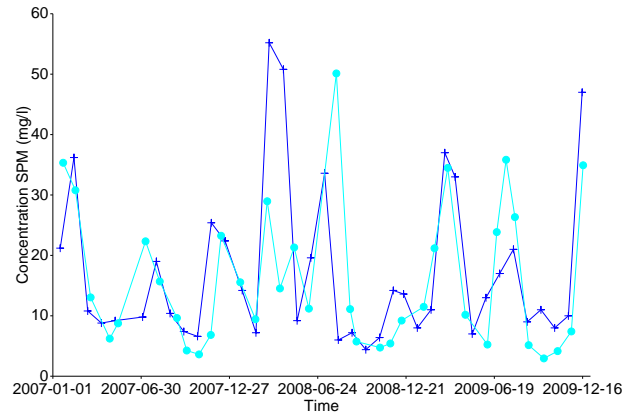


Figure S6: Measured (+) and calculated (o) concentration of suspended particulate matter at Bad Honnef, without resuspension.

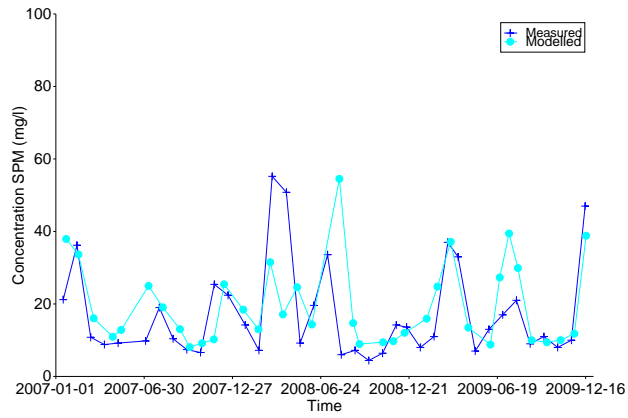


Figure S7: Measured (+) and calculated (o) concentration of suspended particulate matter at Bad Honnef. In the calculation an extra source was included to represent erosion.

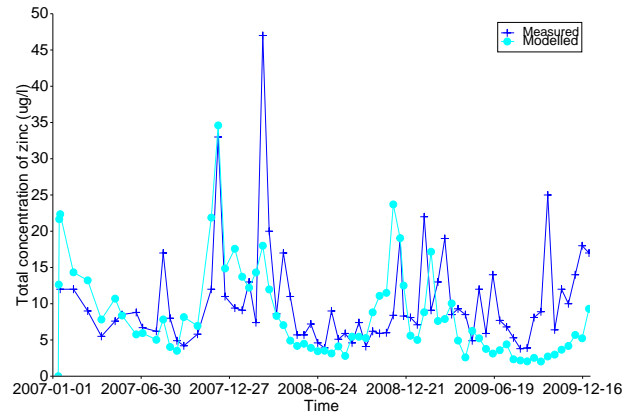


Figure S8: Measured (+) and calculated (o) total concentration of zinc at Bad Honnef, without the diffuse source.

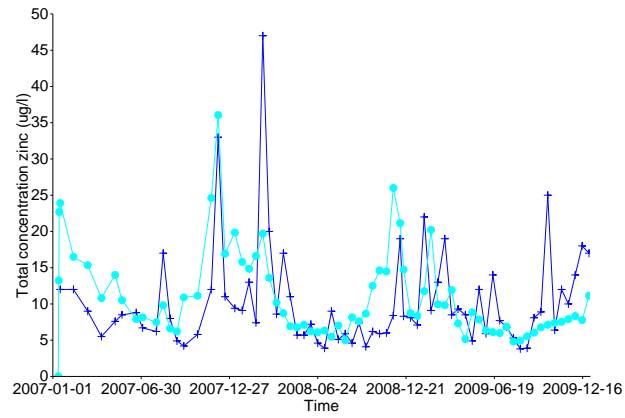


Figure S9: Measured (+) and calculated (o) total concentration of zinc at Bad Honnef, including the diffuse source.

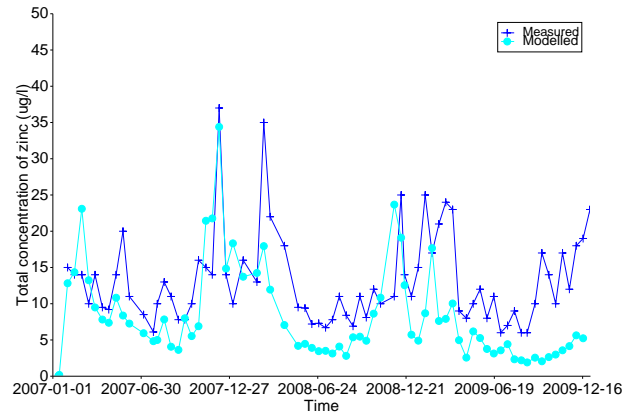


Figure S10: Measured (+) and calculated (o) total concentration of zinc at Bimmen, without the diffuse source.

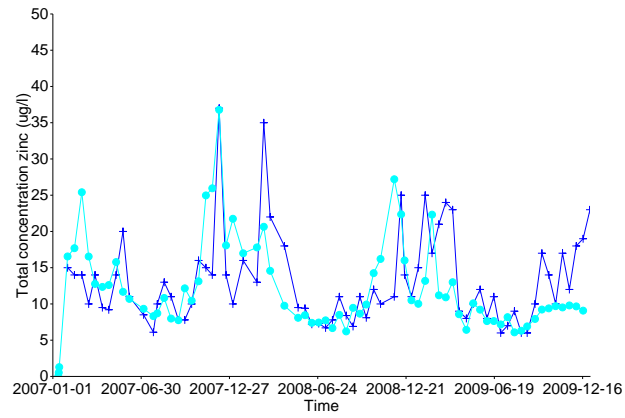


Figure S11: Measured (+) and calculated (o) total concentration of zinc at Bimmen, including the diffuse source.

Table S4: Comparison of the average concentration and the standard deviation of the model results for suspended particulate matter with the measurements for the monitoring points along the Rhine. All values in mg/l.

Monitoring location	Average (model)	Average (measurements)	Standard deviation (model)	Standard deviation (measurements)
Karlsruhe	19.3	7.6	14.0	4.2
Mainz	17.7	15.8	8.9	12.8
Koblenz	18.1	21.1	13.0	21.1
Bad-Honnef	18.7	17.4	10.4	13.3
Bimmen	17.2	18.2	8.4	8.5

Table S5: Comparison of the average concentration and the standard deviation of the model results for total zinc with the measurements for the monitoring points along the Rhine. All values in $\mu\text{g/l}$.

Monitoring location	Average (model)	Average (measurements)	Standard deviation (model)	Standard deviation (measurements)
Karlsruhe	5.2	7.6	3.6	4.2
Mainz	7.3	12.9	3.1	5.2
Koblenz	8.6	7.5	5.1	6.2
Bad-Honnef	10.9	10.3	6.1	7.0
Bimmen	11.9	13.2	6.4	6.3

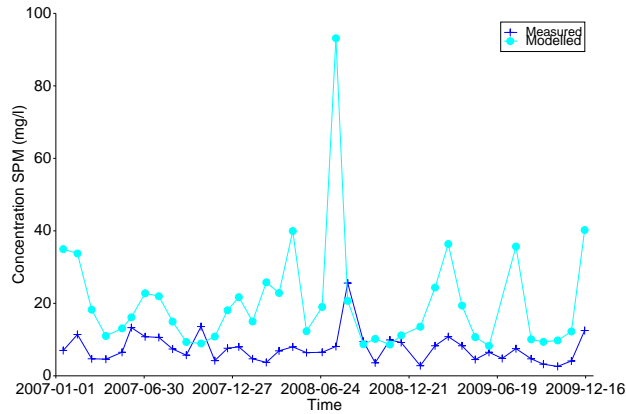


Figure S12: Measured (+) and calculated (o) concentration of SPM at Karlsruhe.

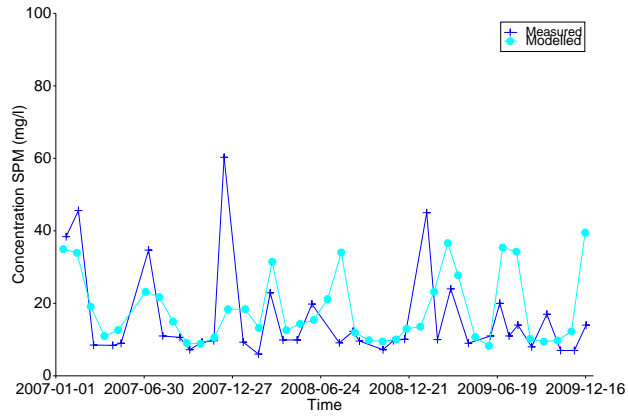


Figure S13: Measured (+) and calculated (o) concentration of SPM at Mainz.

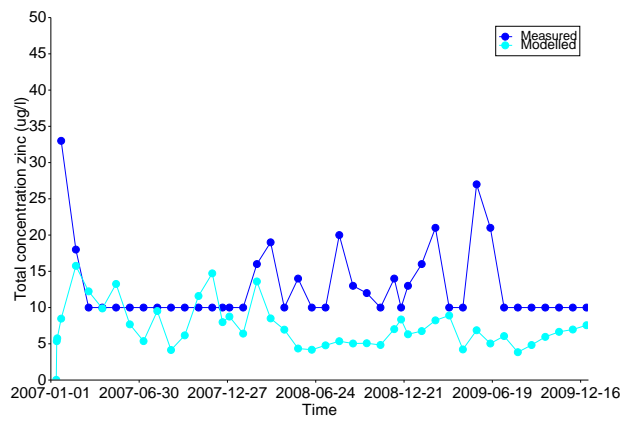


Figure S14: Measured (+) and calculated (o) total concentration of zinc at Mainz.

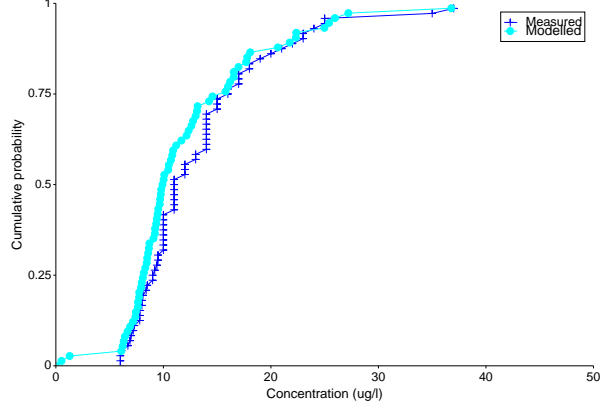


Figure S15: Cumulative probability distribution of the total concentration of zinc at Bimmen. (+) measured, (o) calculated.

$$\frac{dC}{dt} = -\frac{w_s}{H} \cdot C \quad (1)$$

where:

w_s is the sedimentation velocity (m/d)

H is depth of the water column (m)

C is the concentration of the nanoparticle fraction $\mu\text{g/l}$ or of SPM (mg/l)

The resuspension is modelled as a constant flux:

$$\frac{dC}{dt} = +\frac{M}{H} \quad (2)$$

where:

M is the resuspension rate coefficient (mg/m².d)

Homoaggregation is modelled via the following equations:

$$\frac{dC_{free}}{dt} = -k_{homoagg} \cdot C_{free}^2 - k_{sec_agg} \cdot C_{free}C_{agg} \quad (3)$$

$$\frac{dC_{agg}}{dt} = +k_{homoagg} \cdot C_{free}^2 + k_{sec_agg} \cdot C_{free}C_{agg} \quad (4)$$

where:

C_{free} is the concentration of free, that is non-adsorbed and non-aggregated, nanoparticles ($\mu\text{g/l}$).

C_{agg} is the concentration of aggregations of nanoparticles ($\mu\text{g/l}$).

$k_{homoagg}$ is the rate coefficient for the homoaggregation process (1/ $\mu\text{g}\cdot\text{d}$).

k_{sec_agg} is the rate coefficient for the aggregation of nanoparticles to existing aggregates of nanoparticles (secondary homoaggregation; 1/ $\mu\text{g}\cdot\text{d}$).

Table S6: Values of the process coefficients as used in the model calculations.

Parameter	Value
Rate coefficient of homoaggregation	0.00177 (1/ $\mu\text{g}\cdot\text{d}$)
Rate coefficient of secondary homoaggregation	0.00228 (1/ $\mu\text{g}\cdot\text{d}$)
Rate coefficient of heteroaggregation	0.0073 (1/ $\text{g}\cdot\text{d}$)
Sedimentation velocity SPM and nanoparticles	0.1 (m/d)

Heteroaggregation is modelled via the following equations:

$$\frac{dC_{free}}{dt} = -k_{agg} \cdot C_{sed} \cdot C_{free} \quad (5)$$

$$\frac{dC_{ads}}{dt} = +k_{agg} \cdot C_{sed} \cdot C_{free} \quad (6)$$

where:

k_{agg} is the rate coefficient of heteroaggregation (1/ $\text{g}\cdot\text{d}$).

C_{free} is the concentration of free nanoparticles ($\mu\text{g}/\text{l}$).

C_{ads} is the concentration of adsorbed nanoparticles (either adsorbed to inorganic or organic) ($\mu\text{g}/\text{l}$).

C_{sed} is the concentration of suspended particulate matter (either inorganic or organic; mg/l).

The coefficients were set according to Table S6 (Markus et al., 2015). The actual sedimentation rate and the resuspension rates were modelled using the classical formulations by Krone and Partheniades (Krone, 1962; Partheniades, 1962).

6. Comparison with measurements

In order to quantify the accuracy of the model results in relation to the available measurements, the concentration for suspended particulate matter (SPM) and the total concentration of zinc was averaged over time and the standard deviation was determined for both the model results and the measurements. For the model results the values at the same times as the measurements were selected (see Tables S4 and S5). The average concentrations differ 10 to 15% for the majority of the locations, but for SPM at Karlsruhe and total zinc at Mainz the model result differs substantially from the measured concentration.

An examination of the data reveals that the model results at Karlsruhe have higher peaks and a higher average (see Fig. S12). Such high peaks are, however, present at the monitoring location Mainz, downstream of Karlsruhe (see Fig. S13) and other downstream locations.

For the zinc concentration at Mainz the situation is completely different: the measurements show very little variation (see Fig. S14). In fact, closer examination of the original data base reveals that most measured values are below the detection limit of 10 $\mu\text{g}/\text{l}$ for this location. Still, the model does not reproduce the values above the limit.

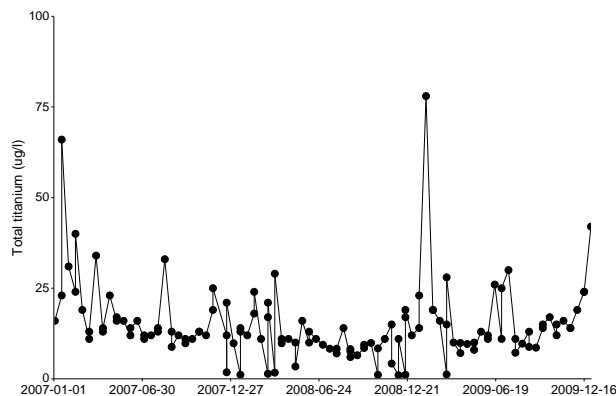


Figure S16: Measured concentration of titanium at Lobith.

The average and the standard deviation only give limited information. The so-called empirical probability distribution makes a more detailed comparison possible (see Fig. S15): on the whole the model concentration is slightly lower than the measurements, but the form of the distribution is quite similar. Even the peak values show a similar distribution. For other locations the same conclusion can be drawn, though some are less satisfactory as was also concluded from the average concentrations (these are not shown). This indicates that the model is sufficiently capable of capturing the dynamics of the system.

6.1. Measurements at Lobith for total titanium and total silver

For both titanium and silver there are few measurement data available. The only such data relevant for the chosen period are shown in Figs. S16 and S17, as collected by the Dutch Water Authorities (Dutch national government, 2015). There is a gap in the time series for silver, so that the years 2010–2011 had to be chosen instead.

The measurements show an average concentration of 10 to 15 $\mu\text{g}/\text{l}$ for titanium and of approximately 0.2 $\mu\text{g}/\text{l}$ for silver.

6.2. Titanium dioxide and silver nanoparticles

Results for titanium dioxide nanoparticles and silver nanoparticles are shown in Figs. S18 and S19, as based on the first scenario. A comparison of the calculated nanoparticle concentration and the measured concentration of total titanium and silver indicates that these nanoparticles also constitute a relatively small fraction of the total. For silver the nanoparticles contribute about 5% to the total concentration and for titanium they contribute no more than 10%. In fact, these levels are comparable to what was found for zinc oxide nanoparticles.

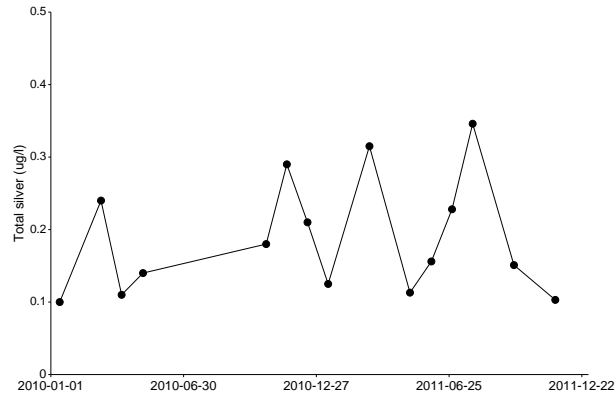


Figure S17: Measured concentration of silver at Lobith.

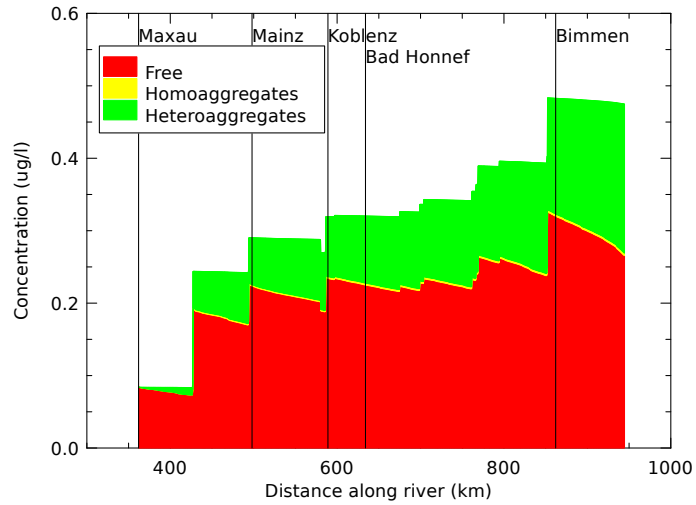


Figure S18: Calculated concentration of TiO₂ nanoparticles along the Rhine, averaged over the simulation period 2007-2009 ($\mu\text{g/l}$). The fractions are shown as cumulative. The vertical lines indicate the location of the monitoring stations. First scenario: the emissions are assumed higher in summer time.

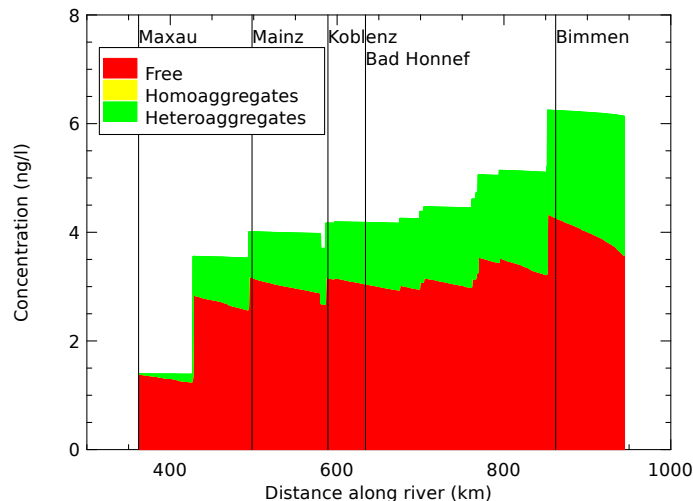


Figure S19: Calculated concentration of Ag nanoparticles along the Rhine, averaged over the simulation period 2007-2009 (ng/l). The fractions are shown as cumulative. The vertical lines indicate the location of the monitoring stations. First scenario: the emissions are assumed higher in summer time.

The aggregation processes were assumed to take place at the same rate as those for zinc oxide, as any specific information on these processes is lacking. Therefore the distribution of the nanoparticles over the various fractions is comparable to that for zinc oxide. Because the concentration of silver nanoparticles is much lower than the concentration of zinc oxide nanoparticles, the homoaggregation process is considerably slower, producing almost no homoaggregates.

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