Environmental Risk Assessment of Silver Nanoparticles in Aquatic Ecosystems Using Fuzzy Logic

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Section S1. Transport Models of AgNPs in The River

In this section, the analytical models used to determine AgNPs concentrations along the river for the continuous discharge and the accidental spill scenarios are presented.

S1.1. Continuous Discharge

A perfect mixed model is assumed in the discharge point (WWTP output). An instant mass balance model was developed to calculate the AgNPs concentration along the river, considering the outflow from the source, the river, and the AgNPs concentration at the source to yield:

$$C_0 = \frac{C_R^{''} \cdot Q_R^{''} + Q_S \cdot C_S}{Q_R} \tag{S1}$$

where C_0 is the AgNPs concentration along the river, downstream from the source and after complete mixing (ng L^{-1}), $C_R^{''}$ is the AgNPs concentration upstream from the source (ng L^{-1}), $Q_R^{''}$ is the river flow rate upstream from the source (m^3 s^{-1}), Q_S is the outflow rate from the source (m^3 s^{-1}), C_S is the contaminant concentration at the source (ng L^{-1}), and Q_R is the river flow rate downstream from the source (m^3 s^{-1}).

It was assumed that mitigation mechanisms (sedimentation, adsorption) are negligible and hence C_0 is constant between the source and the river mouth. An additional assumption considered is that there are no AgNPs upstream from the source, i.e., $C_R^{''} = 0$, then equation S1 becomes:

$$C_0 = \frac{Q_S \cdot C_S}{Q_R} = F_R \cdot C_S \tag{S2}$$

where the flow ratio, F_R, is defined as:

$$F_R = \frac{Q_S}{Q_R} \tag{S3}$$

S1.2. Accidental Spill

An advection-dispersion analytical model was used to calculate the AgNPs concentration at any downstream distance (x) from the source at a given time (t). The accidental spill is modelled as a discharge of a suspension of AgNPs of volume V_0 from a point source during time t_0 [1].

$$C_{(x,t)} = \begin{cases} C_0 \cdot B_{(x,t)} & \text{for } 0 < t < t_0 \\ C_0 \cdot B_{(x,t)} - C_0 \cdot B_{(x,t-t_0)} & \text{for } t > t_0 \end{cases} \tag{S4}$$

C_0 is determined from equation S1. For an accidental spill, Q_S from Equation S1 becomes:

$$Q_S = \frac{V_O}{t_0} \tag{S5}$$

where V_0 is the volume of the spill (m^3) and t_0 is the time during which the volume V_0 is released (s).

Based on a model for degrading organic pollutants described in [1], a simplified version of the model has been formulated. This version is based on the assumptions that particles are neither eliminated nor degraded and that $\frac{v \cdot x}{D_L} \le 500$, which yields [2]:

$$B_{(x,t)} = 0.5 \cdot erfc\left[\frac{(x - vt)}{\sqrt{4 \cdot D_L \cdot t}}\right] \tag{S6}$$

where v is the average flow velocity of the river (m s⁻¹), D_L is the longitudinal dispersion (m² s⁻¹), x the downstream distance (m), and t is time (s).

D_L can be estimated from the empirical expression [3]:

$$D_L = 0.11 \frac{W^2 \cdot v^2}{h \cdot v^*} \tag{S7}$$

where W is the average width of the river (m), h the river average depth (m), and v^* the shear velocity (assumed as $0.1 \cdot v$).

Section S2. Justification of Input Parameters for The Besòs River Model

S2.1. Continuous Montcada WWTP Discharge Case Study and Results

The analytical model depends on C_s, the concentration of AgNPs at the WWTP source (see above), from which C_0, the concentration downstream is calculated (Equation S2). In the present study, an experimental C_0 concentration value of 0.9 ng L⁻¹ AgNPs measured in July 2018 downstream from the WWTP [4] was used to calculate C_s. The effluent flow data for Montcada WWTP [5] and the monthly average river flow [6] to obtain $F_R = 0.237$, which indicates a high Flow ratio. From Equation S2 the source term, C_s, was calculated to be 3.8 ng L⁻¹ which is in agreement with source concentration ranges published elsewhere [7–9]

By using C_s as a constant input, the monthly flow rates from WWTP [5], and daily flow rates [6], we could calculate daily values for F_R and AgNPs concentrations along the river (Equation S1) for 2018 (Figure S1).
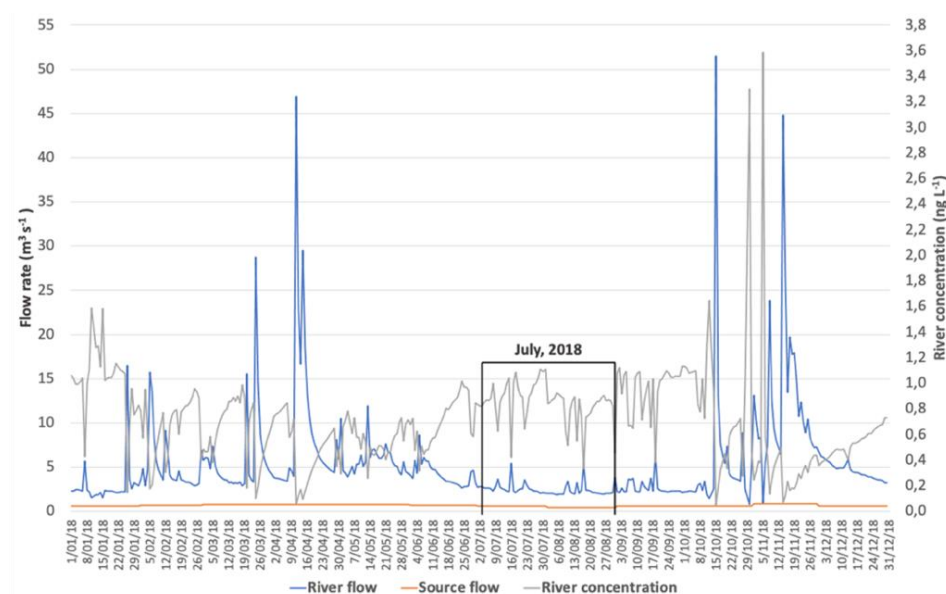

Figure S1. River flow and AgNPs concentration in Besòs river between the source and 5 km downstream from the discharge point.

The river flow is highly variable, with peaks in spring and autumn associated with seasonal rains, and low and more stable flow during the drier summer and winter months (Figure S1). The AgNPs concentration in the river peaks around October–November when the dilution of WWTP effluent is less than 50%, reaching a maximum of about 3.6 ng L⁻¹

(Figure S1). An increase in the river flow usually results in a higher dilution and thus a lower AgNPs concentration. The average value of C_0 during July is 0.9 ng L^{-1} while the annual average is 0.71 ng L^{-1}. Based on these simulations, we used a concentration range of 0–3.7 ng L^{-1} in the fuzzy logic model.

S2.2. Accidental Spill Case Study

For this scenario, we assume that the accident occurred on 13 March 2021 because for that date we have aerial photographs indicating the width (*W*) of the Besòs river at the Santa Coloma gauging station, river depth data (*h*) from the same station [10] and river flow data (Q_R) [6]. From *W* and Q_R, we can calculate the average flow velocity v. Using Equation S7 this yielded D_L = 402 m^2 s^{-1}, which indicates a high dispersion. At 5 km downstream from the spill, the inequality vx/D_L < 500 was met.

Equations S2 to S6 were used to determine the AgNPs concentration and assess the impact of the accidental spill. The AgNPs concentration at the discharge point (C_0) was calculated using Equation S2. From the spill volume (V_0) and the release duration (t_0), Q_S could be calculated from Equation S4. From C_S and V_0, the mass (*M*) of the released AgNPs could be calculated.
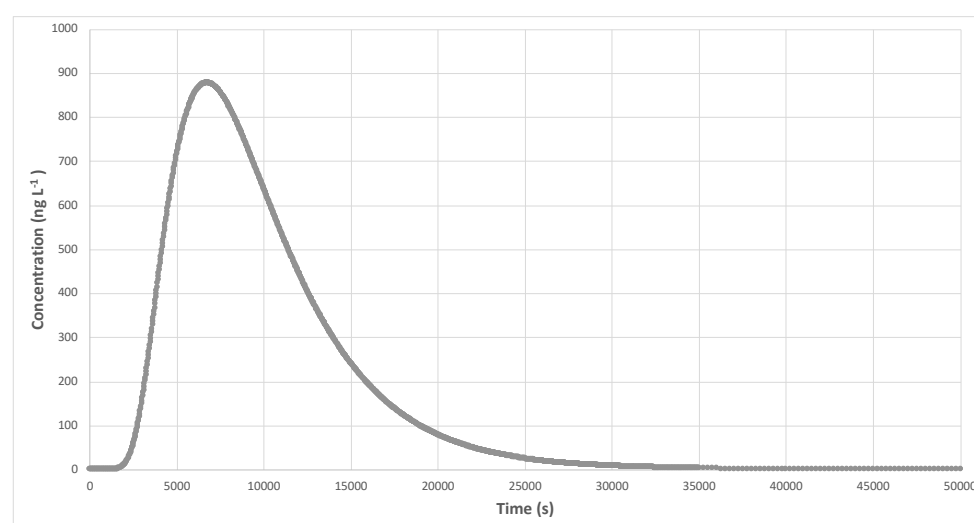

Figure S2. AgNPs concentration over time, 5 km downstream from the accidental spill.

AgNPs concentrations 5 km downstream from the spill reached a maximum of 876.34 ng L^{-1} after 1.9 hours, followed by a slow decrease in concentration. This positive skewness is caused by the high dispersion.

Section S3. Sensitivity Analysis

In this section, the sensitivity of the model is studied for the two study cases: WWTP and accident.

S3.1. WWTP Sensitivity Analysis

Tables S1 and S2 calculate the toxicity and risk as a function of input ranges of the size and concentration for the three studied AgNPs, to then obtain SR. Table S2 showed the same values of risk for concentrations range from 0.25–4.75 ng·L^{-1} and size combinations with a 50% variation.

Table S1. Sensitivity analysis for Toxicity (WWTP).

Size (nm)	Spheres-Citrate	Plates-BPEI	Wires-PVP
8	0.515	0.857	0.145

16	0.515	0.855	0.145
32	0.515	0.849	0.145
SR	0	−0.0047	0

Table S2. Sensitivity analysis for Risk (WWTP) for the range of concentration 0.25–4.75 ng·L^{-1}.

Size (nm)	Spheres-Citrate	Plates-BPEI	Wires-PVP
8	0.251	0.5	0.0734
16	0.251	0.5	0.0734
32	0.251	0.5	0.0734
SR	0	0	0

As it could be seen (Table S1), toxicity is insensitive to size for Spheres-Citrate and Wires-PVP and has a low sensitivity for Plates-BPEI. Risk values (Table S2) are insensitive to all the inputs in the studied range. This behavior is linked to the chosen fuzzy model (Spline-based S-shaped function) that uses intervals with a constant value of risk for the low range of concentrations linked to WWTP.

As mentioned before, there is a big uncertainty about the type of AgNPs that can be found in the WWTP effluents and in the river. The results from table S1 and S2 for the three types of AgNPs with a size of 16 nm could be used for sensitivity analysis of the inputs shape and coating. Shape and coating quantitative values used in the fuzzy model are 0, 5 and 10 for Wires/PVP, Spheres/Citrate and Plates/BPEI respectively. Taking as a reference the case Spheres/Citrate, it could be seen that SR for toxicity is 0.66 for the variation from reference case to Plates/BPEI and 0.72 for the variation from reference case to Wires/PVP. The SR for risk is 0.99 for Plates/BPEI and 0.71 for Wires/PVP. All these SR results show a Very High sensitivity when different shape and coating are modified.

S3.2. Accident Sensitivity Analysis

In the case of the accident, two type of AgNPs with sizes of 10 nm are used. Toxicity as a function of the range of sizes with 50% variability is shown in Table S3.

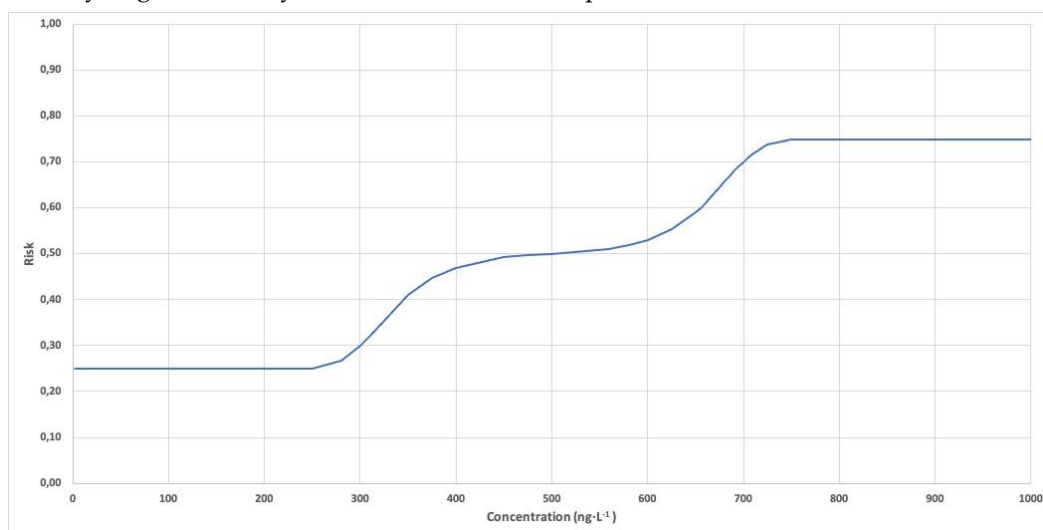**Table S3.** Sensitivity analysis for Toxicity (Accident release).

Size (nm)	Spheres-Citrate	Plates-BPEI
5	0.515	0.857
10	0.515	0.855
15	0.515	0.855
SR	0	−0.0024

Results show again insensitivity for Spheres-Citrate and Low sensitivity for Plates-BPEI.
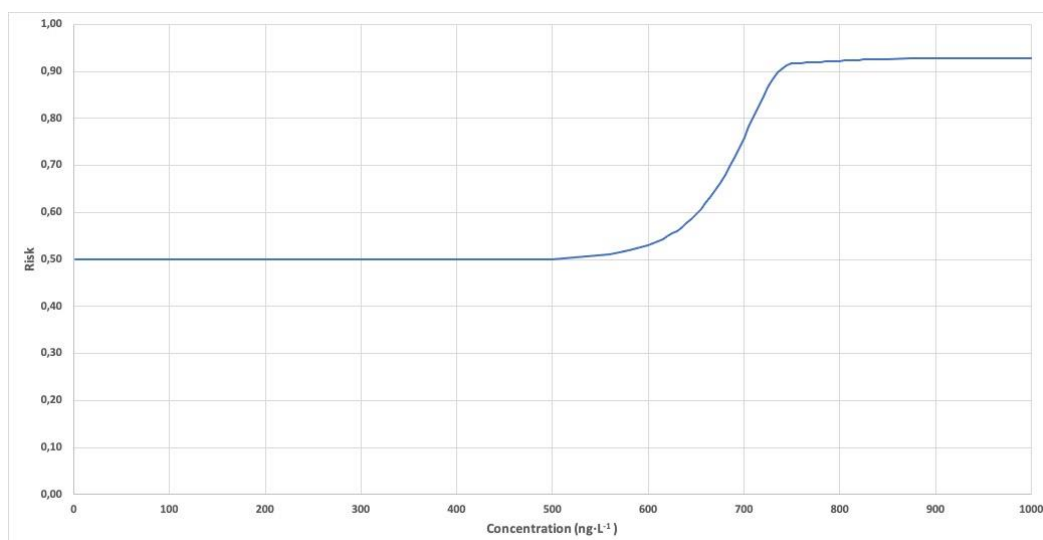
Unlike WWTP case, is assumed that the characterization of AgNPs from the accident is well known and thus uncertainty of toxicity linked to shape and coating is Low. As a consequence, the SR of risk linked to toxicity is Low or zero.

The slopes of the Figures S3 (a) and (b) were used to calculate the sensitivity of risk as a function of concentration. Figure S3 (a) shows the change in Risk to the change in AgNPs concentration for spheres citrate. The shape of this figure is linked to the fuzzy model used (Spline-based S-shaped), with slopes from zero to a maximum. In this figure, the concentration from 0 to 250 ng·L^{-1}, the concentration at 500 ng·L^{-1} and concentrations higher than 750 ng·L^{-1} shows a zero slope while the concentrations at 375 ng·L^{-1} and 625 ng·L^{-1} shows the maximum slope.

Figure S3 (b) shows a similar graph with zero slope from 0 to 500 ng·L^{-1} and for concentrations higher than 800 ng·L^{-1}. The maximum slope is centered at 700 ng·L^{-1}. The maximum slopes measured in Figure S3 (a) are 2.0×10^{-3} and 2.3×10^{-3} risk units·L·ng^{-1}, that correspond to SR of 2 and 2.3 respectively for the concentration and risk points. Figure S3 (b) shows the maximum slope of 4.1×10^{-3} risk units·L·ng^{-1} or SR = 3.71. All these SR show a Very High sensitivity values concentrated in specific concentrations.

(a)

(b)

Figure S3. Accidental Risk as a function of concentration. **(a)** Spheres Citrate **(b)** Plates BPEI.

The transition of risk sensitivities from Low to Very High or vice versa in the case of Spheres-Citrate will be produced from 250 to 300, from 400 to 450, from 500 to 600 and from 700 to 750 ng·L^{-1} and in the case of Wires-BPEI from 500 to 600 and from 730 to 750 ng·L^{-1}. Table S4 summarizes the sensitivity analysis of the present work

Table S4. Summary of Sensitivity Analysis**.**

X-Y	ΔX/X	WWTP	Accident Spheres/Citrate	Accident Plates/BPEI
Size-T	0.5	Insensitive-Low	Insensitive	Low
Size-R	0.5	Insensitive	-	-
Shape-coating-T	1.0	Very High[a]	Low[b]	Low[b]

Shape-coating-R	1.0	Very High[a]	Low[b]	Low[b]
Concentration-R	0.25	Insensitive	See text	See text

[a] Comparing with Spheres-Citrate as a reference case, [b] Assumed in a known accident.

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