Supporting Information "Removal of nanoparticles in drinking water treatment –
coagulation/flocculation/sedimentation, and sand/granular activated carbon filtration"

Tracer experiments

Tracer experiments were carried out to determine the dispersion coefficient and the porosity, and to
check that no short circuit currents occurred. A NaCl solution (10g/L) was added to the column until
the influent and effluent concentrations became identical, which was checked by measuring the
conductivity of the water). Breakthrough curves were fitted with the advection-dispersion equation
(Eq. 1) [1].

$$R\frac{\partial c_r}{\partial t} = D\frac{\partial^2 c_r}{\partial x^2} - v\frac{\partial c_r}{\partial x} - \mu c_r$$

eq.1

Here R = retardation factor, c_r = resident concentration of the liquid phase (kg/m³), t = time (min.), D =
dispersion coefficient (m²/min), x transport distance of tracer (m), v = average pore velocity (m/min),
µ = first order degradation coefficient (min⁻¹).

Colloidal filtration theory

Attachment of particles to filter material can be approximated by a modified version of the advection-
dispersion equation, shown as eq. 2 [2, 3].

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} - v\frac{\partial C}{\partial x} - k_d C \quad with\ k_d = \lambda v$$

eq. 2

In which C is the concentration of particles in the aqueous phase (kg⁻¹), t is time (s), x is distance (m)

v   =   interstitial velocity of colloidal particles (m min⁻¹)

D   =   hydrodynamic dispersion coefficient (m² min⁻¹)

k_d =   particle deposition rate coefficient (min⁻¹)

k can be determined from the experimental breakthrough curves of nanoparticles in the columns filled
with GAC or sand. The velocity is known, and thus λ can be determined. The porosity (n) can be
measured by means of tracer experiments.

The "overall single-collector efficiency" (η_0) can be calculated from equation 3 [4].

$$\eta_0 = 2.4\ A_S^{1/3} N_R^{-0.081} N_{Pe}^{-0.715} N_{vdW}^{0.052} + 0.55 A_S N_R^{1.675} N_A^{0.125} + 0.22 N_R^{-0.24} N_G^{1.11} N_{vdW}^{0.053}$$

eq.3

In which:

$$A_S = \frac{2(1-\gamma^5)}{2 - 3\gamma + 3\gamma^5 - 2\gamma^6}$$

eq. 4

In which $\gamma = (1-f)^{1/3}$

eq. 5

$$N_R = \frac{d_p}{d_c}$$

eq. 6

$$N_{Pe} = \frac{U d_c}{D_\infty}$$

eq. 7

$$N_{vdW} = \frac{A}{kT}$$

eq. 8

$$N_{gr} = \frac{4}{3} \frac{\pi \alpha_p^4 (\rho_p - \rho_f) g}{kT}$$

eq. 9

$$N_A = \frac{A}{12\pi\mu\alpha_p^2 U}$$

eq. 10

$$N_G = \frac{2}{9} \frac{\alpha_p^2 (\rho_p - \rho_f) g}{\mu U}$$

eq. 11

In these equations

η_0	=	single-collector contact efficiency [-]
A_s	=	porosity dependent diameter [-]
N_R	=	aspect ratio [-]
N_{Pe}	=	Peclet number [-]
N_{vdW}	=	Van der Waals number [-]
N_{gr}	=	gravitational number [-]
N_A	=	attraction number [-]
N_G	=	gravity number [-]
f	=	porosity [-]
d_p	=	particle diameter [m]
d_c	=	collector diameter [m]
U	=	fluid approach velocity [m s^{-1}]
D_∞	=	bulk diffusion coefficient (described by the Stokes-Einstein equation)[m^2 s^{-1}]
A	=	Hamaker constant = $3,0 \cdot 10^{-19}$ J for nAu in water [5] [J]
k	=	Boltzmann constant = $1,380\ 6485 \cdot 10^{-23}$ [J K^{-1}]
T	=	fluid absolute temperature [K]
a_p	=	particle radius [m]
ρ_p	=	particle density [kg/m^3]
ρ_f	=	fluid density [kg/m^3]
μ	=	absolute fluid viscosity [kg m^{-1}s^{-1}]
g	=	gravitational acceleration [m s^{-2}]

λ is defined as the filtration coefficient and it is assumed that this coefficient is constant in time and space.

$$\lambda = \frac{3}{2}(1-n)\frac{L}{d_C} \propto {}_C\eta_0$$

<div align="right">eq. 11</div>

In this formula n is the porosity of the filter medium. The only unknown now is the attachment efficiency (α_C), which can be calculated from the other parameters according to equation 11 [3]. This collision efficiency reflects the number of collisions between a nanoparticle and a filter medium particle, that results in deposition of the nanoparticle. The higher α_C, the higher the removal of nanoparticles by the filter material.

The contact efficiency η_0 is calculated as the sum of the individual transport mechanisms:

$$\eta_0 = \eta_D + \eta_I + \eta_G$$

<div align="right">eq. 12</div>

η_D = transport by diffusion

η_I = transport by interception

η_G = transport due to gravity

Finally, the collector removal efficiency η can be calculated from eq. 12.

$$\eta = \alpha * \eta 0$$

<div align="right">eq. 13</div>
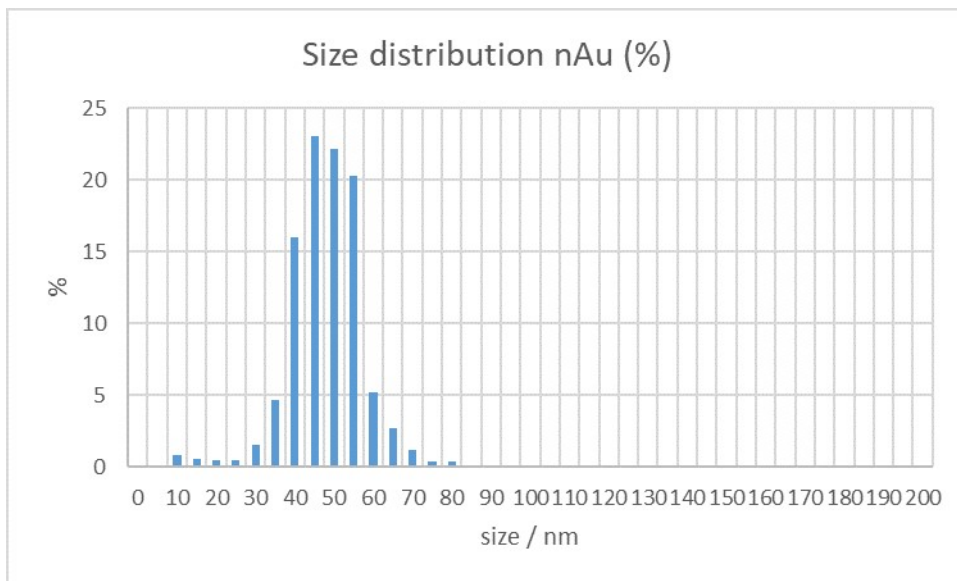
nAg and nAu analyses

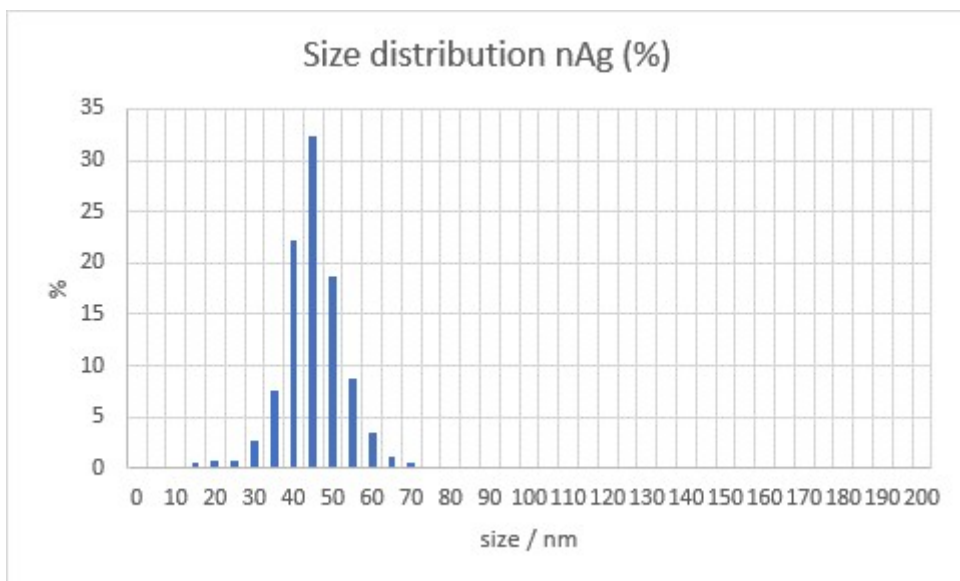Figure SI 1: Size distribution of nAu (%)

Figure SI 2: Size distribution of nAg (%)
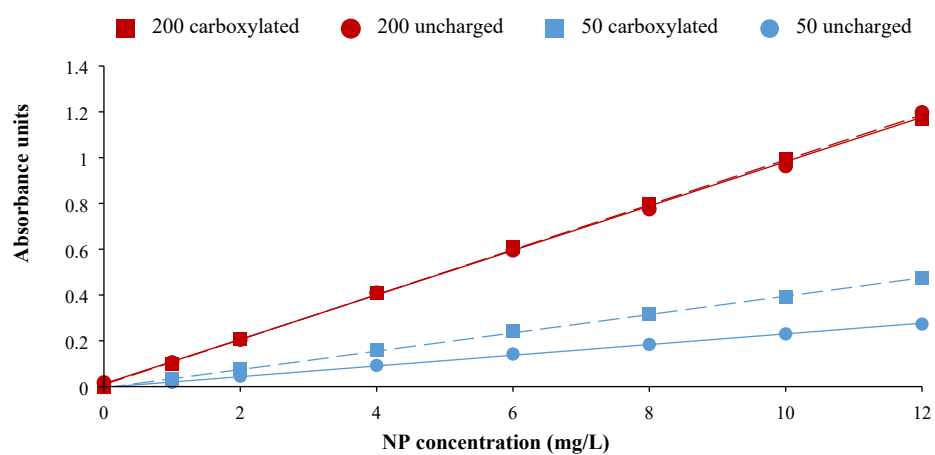
Nanoplastics analyses

Figure SI 3: Calibration curve produced using UV-VIS spectrophotometry to quantify different NP (polystyrene spheres) spiked into riverine surface water based on the UV absorption at 229 nm
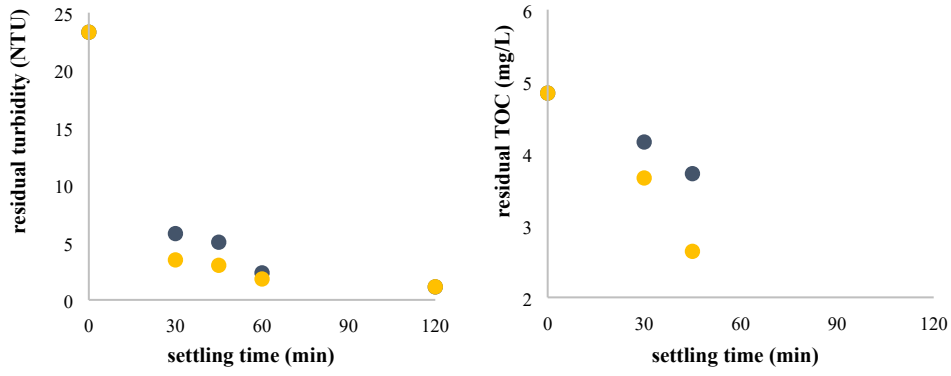
CSF Experiments

Figure SI 4: Pre-tests conducted to determine the reduction of residual turbidity and TOC when simulating coagulation-flocculation- sedimentation (CFS) using two concentrations of iron chloride as coagulant (12 (blue) and 18 (yellow) mg FeCl$_3$/L, and different settling times. Tests carried out water from the Lek canal.

Filter materials

Table SI 1: : size characterization of filter media sand and GAC for experiments with inorganic NPs

Filter medium	d10 (µm)	d50 (µm)
Clean sand	681	929
Loaded sand	717	932
Virgin GAC	578	885
Loaded GAC	504	587

Table SI 2: characteristics of the columns used for filtrations experiments with nanoplastics

		Sand filtration	GAC filtration
Column characteristics	porosity (n) [*]	0.405	0.22
	median grain size filter - d50 (µm)	1016	925
	bed height (m)	0.70	0.80
	column diameter (m)	0.035	0.035
	bed volume (ml)	673.48	769.69
	contact time (h)	0.102	0.169
	discharge Q (m3 s-1)	$1.84E^{-06}$	$1.27E^{-06}$
	column area A (m2)	$9.62E^{-04}$	$9.62E^{-04}$
	A, corrected for porosity (m2)	$3.90E^{-04}$	$4.31E^{-04}$
	flow through pores (m s^{-1})	$4.72E^{-03}$	$2.94E^{-03}$
Water matrix	Influent:		
	initial NP concentration (mg L^{-1})	2.0	
	duration NP injection phase (pore volumes)	65	104
	duration elution phase (pore volumes)	15	27
	temperature (°C)	20.1 (SD 0.2)	
	pH [**]	8.06 (SD 0.08); 8.13 (SD 0.16)	7.99 (SD 0.2); 7.77 (SD 0.2)
	conductivity (µS cm^{-1}) [**]	611 (SD 14); 608 (SD 14)	588 (SD 6); 591 (SD 20)
	UV 254 nm a	0.61 (SD 0.1); 0.59 (SD 0.09)	0.56 (SD 0.08); 0.37 (SD 0.04)
	Tracer 1 (Ceff/Cinf=50%, in s)	357	765
	Tracer 2 (Ceff/Cinf=50%, in s)	366	757

[*] The porosity was determined experimentally for the sand filter by adding water to a packed column. The porosity (n) was calculated by dividing the volume of water in the pores by the volume of the filter material. This approach was not applicable to the GAC. Therefore the porosity of the GAC filter was determined by mercury intrusion porosimetry, helium pycnometry and nitrogen adsorption. These calculations were done by Delft Solids Solutions, and subsequently by KWR Water Research Institute. The first three techniques applied differentiated the total porosity (V_{tot} = 1.50 cm^3 g^{-1}) and the internal porosity (V_{tot} = 1.06 cm^3 g^{-1}) of the GAC. The pores accessible for the NP can thus be estimated as: V_{inter} = 0.49 cm^3 g^{-1}. Using also the density of the GAC itself (2.2 cm^3 g^{-1}), the porosity of the GAC was calculated: 0.49 cm^3 g^{-1} x 2.2 cm^3 g^{-1} = 0.22.

[**] The first value corresponds to the influent measured, the second to the effluent respectively.

Water quality measurements during filtration experiments

Table SI 3: water quality parameters for clean and loaded sand in experiments with high doses of nAg and nAu. Water from the Lek Canal.

Parameter	Influent (average (± st. dev.))	Clean sand effluent (average (± st. dev.))	Loaded sand effluent (average (± st. dev.))
UV254 [cm-1]	$7,04 \cdot 10^{-2}$ ($8,49 \cdot 10^{-4}$)	$6,26 \cdot 10^{-2}$ ($\pm 7,07 \cdot 10^{-4}$)	$5,16 \cdot 10^{-2}$ ($\pm 2,05 \cdot 10^{-3}$)
Calcium [mg/L]	63 (± 0)	60,5 (± 0,71)	59,5 (± 0,71)
Magnesium [mg/L]	11 (± 0)	11 (±0)	11 (± 0)
DOC [mg C/L]	2,60 (± 0,14)	2,5 (±0,0)	2,1 (± 0,0)
Turbidity [FNE]	0,83 (± 0,04)	0,68 (±0,19)	0,41 (± 0,06)
Nitrate [mg N/L]	1,00 (± 0,01)	0,96 (±0,01)	1,09 (± 0,04)
Suspended solids	<1,0 (± 0)	<1,0 (± 0)	<1,0 (± 0)
pH	7,84 (± 0,09)	7,77 (± 0,12)	7,67 (± 0,30)
Temperature [$^\mathrm{o}$C]	19,7 (± 0,2)	20,5 (± 0,1)	19,7 (± 0,0)
Conductivity [mS/cm]	0,61 (± 0,00)	0,59 (±0,00)	0,57 (± 0,01)

Table SI 4: water quality parameters for clean and loaded sand in experiments with low doses of nAg and nAu. Water from the Lek canal.

Parameter	Influent (average (± st. dev.))	Clean sand effluent (average (± st. dev.))	Loaded sand effluent (average (± st. dev.))
UV254 [cm-1]	4,7 (± 0,3)	5,0 (± 0,1)	3,8 (± 0,1)
Calcium [mg/L]	57,5 (± 0,7)	58 (± 0)	56,5 (± 0,7)
Magnesium [mg/L]	11 (±0)	11 (±0)	11 (± 0)
DOC [mg C/L]	1,9 (±0)	2,0 (± 0,1)	1,8 (± 0,1)
Turbidity [FNE]	0,27 (±0,05)	0,28 (± 0,03)	0,32 (± 0,01)
Nitrate [mg N/L]	1,56 (± 0,01)	1,61 (± 0,04)	1,61 (± 0,01)
Suspended solids	<1,0 (± 0)	<1,0 (± 0)	<1,0 (± 0)
pH	7,53 (± 0,06)	7,74 (± 0,01)	7,45 (± 0,06)
Temperature [$^\mathrm{o}$C]	19,6 (± 0,3)	20,0 (± 0,4)	20,4 (± 0,3)
Conductivity [mS/cm]	0,62 (± 0,03)	0,63 (± 0,00)	0,64[*]

*) measured once

Table SI 5: water quality parameters for virgin activated carbon in experiments with high doses of nAg and nAu. Pre-treated drinking water from Leiduin.

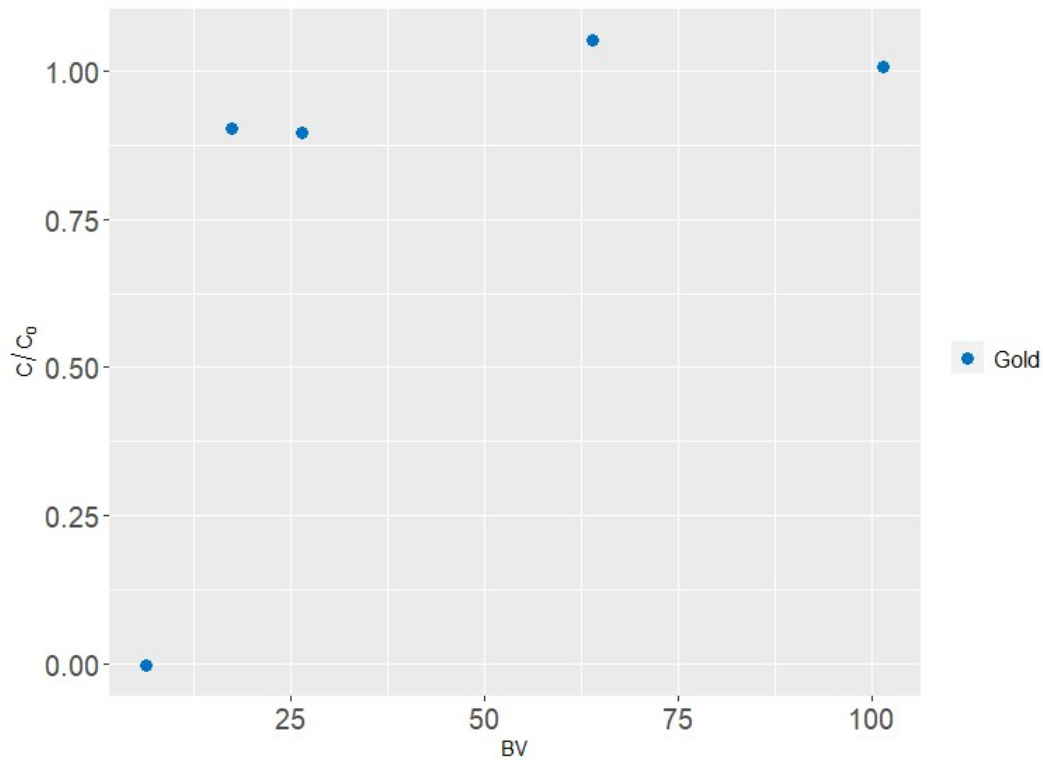| Parameter	Influent (average (± st. dev.))	Clean GAC effluent (average (± st. dev.))
UV254 [cm-1]	<0,3	<0,3 (± 0,0)
Calcium [mg/L]	<1,0	4 (± 0,6)
Magnesium [mg/L]	<1,0	<1,0 (± 0,0)
DOC [mg C/L]	<0,20	0,25 (± 0,06)
Turbidity [FNE]	0,14	0,11 (± 0,01)
Nitrate [mg N/L]	<1,0	<1,0 (± 0,0)
Suspended solids	<1,0	<1,0 (± 0,0)
pH	8,16	8,09 (± 0,85)
Temperature [^{o}C]	20,4	20,5 (± 0,3)
Conductivity [mS/cm]	0,00	0,03 (± 0,0)

Table SI 6: water quality parameters for virgin and loaded activated carbon in experiments with low doses of nAg and nAu. Pre-treated drinking water from Leiduin.

Parameter	Influent (average (± st. dev.))	Virgin GAC effluent (average (± st. dev.))	Loaded GAC effluent (average (± st. dev.))
UV254 [cm-1]	4,0 (±0,0)	< 0.3 (± 0,0)	3,4 (± 0,0)
Calcium [mg/L]	42,5 (±0,7)	39 (± 0,0)	39 (± 0,0)
Magnesium [mg/L]	9,8 (± 0,1)	9,4 (±0,1)	9,5 (± 0,1)
DOC [mg C/L]	1,95 (± 0,07)	0,26 (± 0,08)	1,80 (± 0,14)
Turbidity [FNE]	0,16 (± 0,00)	0,15 (± 0,03)	0,18 (± 0,06)
Nitrate [mg N/L]	2,43 (± 0,05)	1,31 (± 0,43)	2,58 (± 0,06)
Suspended solids	<1,0 (± 0)	<1,0 (± 0)	<1,0 (± 0)
pH	7,09 (± 0,11)	7,56 (± 0,74)	7,06 (± 0,10)
Temperature [^{o}C]	20,2 (± 0,2)	20,2 (± 0,1)	20,2 (± 0,1)
Conductivity [mS/cm]	0,56 (± 0,01)	0,51 (± 0,02)	0,53 (± 0,00)

ATP measurements were carried out according to the procedure described by Timmers et al. [6].

Table SI 7: cellular ATP measurements in column experiments with high and low doses of nanoparticles (nAg and nAu)

Experiment	Average cellular ATP (± st. dev.) [pg/g dry sand or carbon]		
	Start experiment	End experiment	Difference (%)
Clean sand WRK water, high dose	2797 (± 419)	992 (± 21)	-65
Loaded sand WRK water, high dose	173800 (± 18668)	100300 (± 8627)	-42
Clean sand WRK water, low dose	711 (± 155)	777 (± 78)	≈
Loaded sand WRK water, low dose	265000 (± 97581)	224200 (± 14991)	≈
Virgin GAC demi water 19.5 cm, high dose	Indicatively low	Indicatively low	≈
Virgin GAC Leiduin water, 20 cm, high dose	Indicatively low	325 (± 64)	increase
Loaded GAC Leiduin water, 20 cm, high dose	1425000 (± 120208)	880000 (± 127279)	-38

Figure SI 5: Breakthrough curve for nAu in clean sand with Milli-Q water

Figure SI 6: breakthrough curves for nAu, nAg and a tracer (NaCl) in clean sand with Lek water with a high dose of NPs
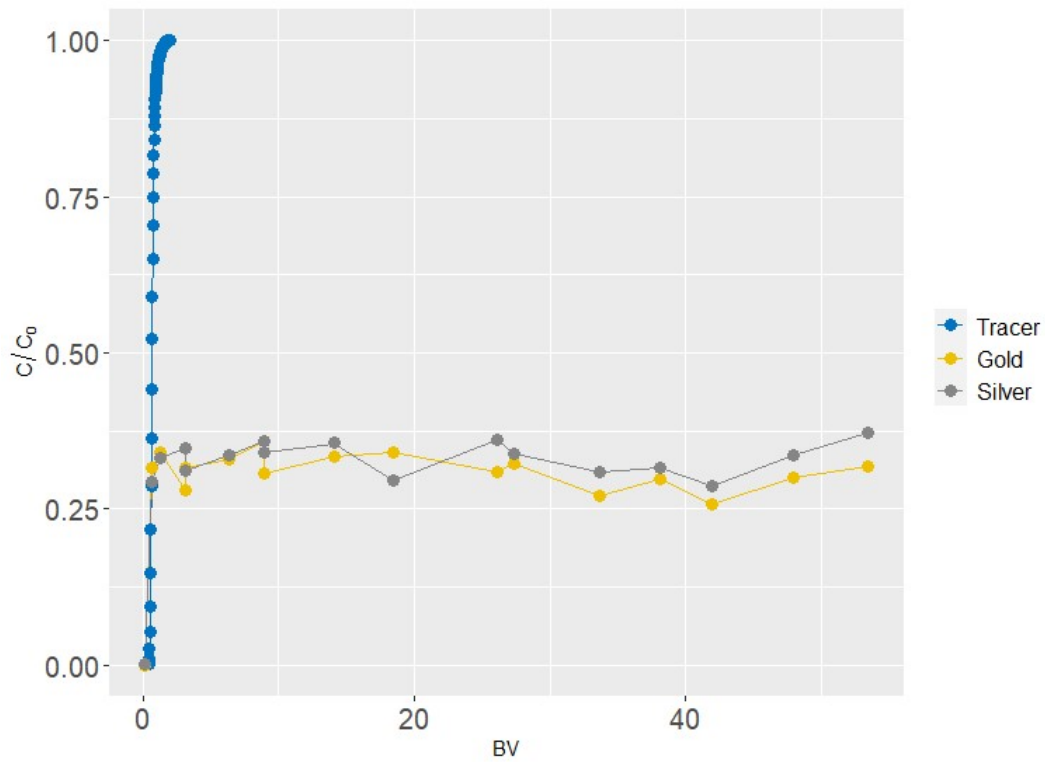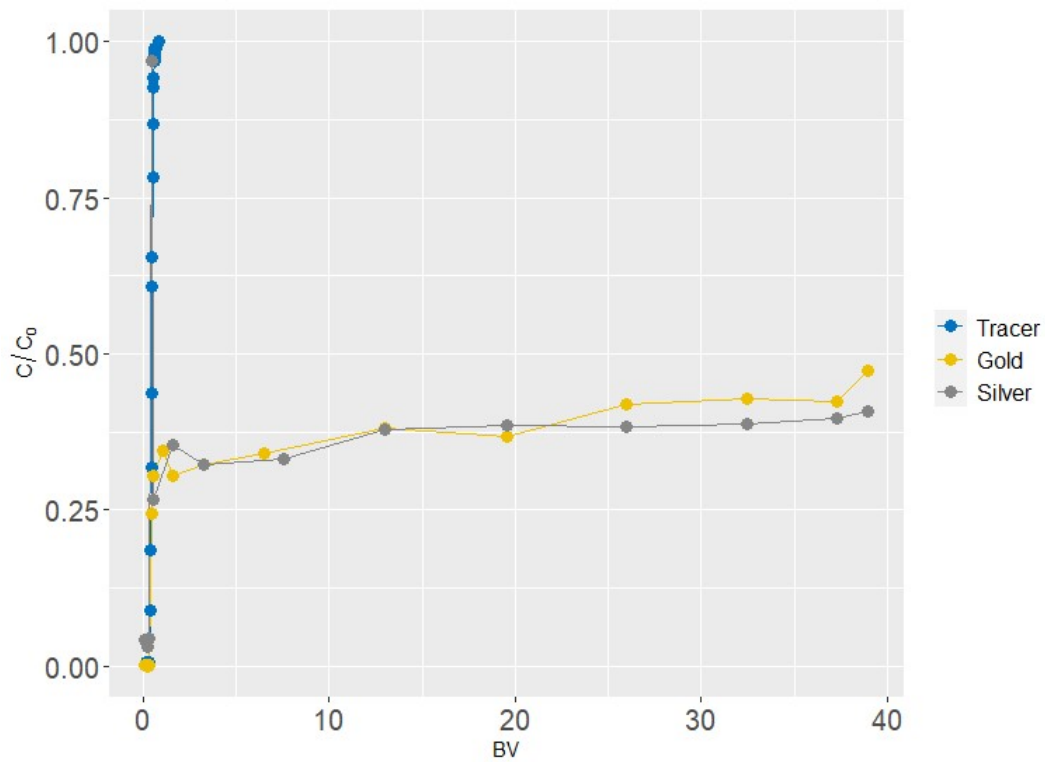
Figure SI 7: breakthrough curves for nAu, nAg and a tracer (NaCl) in loaded sand with Lek water with a high dose of NPs

Figure SI 8: breakthrough curves for nAu, nAg and a tracer (NaCl) in clean sand with Lek water with a low dose of NPs
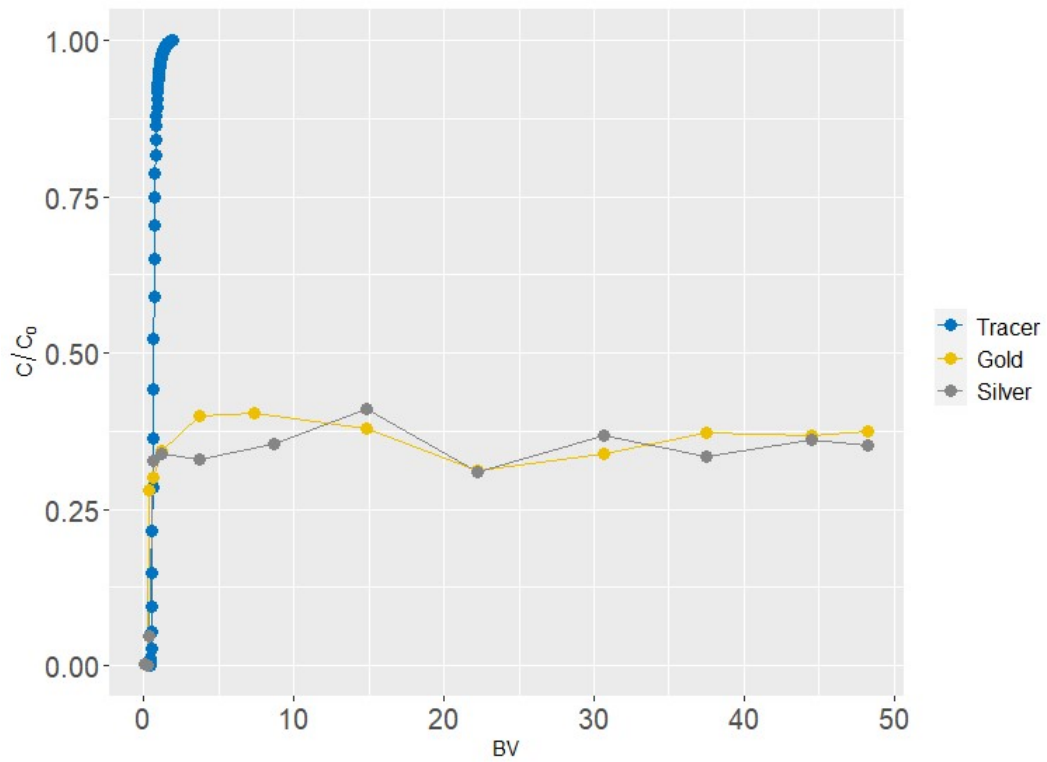
Figure SI 9: breakthrough curves for nAu, nAg and a tracer (NaCl) in loaded sand with Lek water with a low dose of NPs
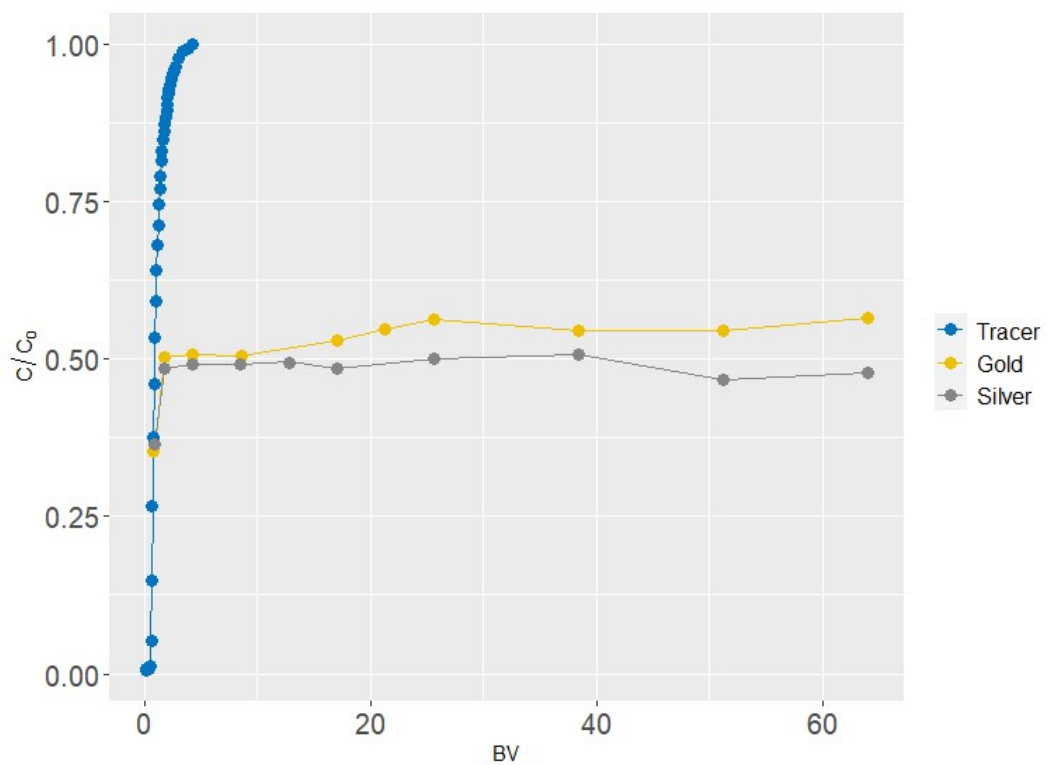

Figure SI 10: breakthrough curves for nAu, nAg and a tracer (NaCl) in virgin GAC (bed height 19.5 cm) with Milli-Q water
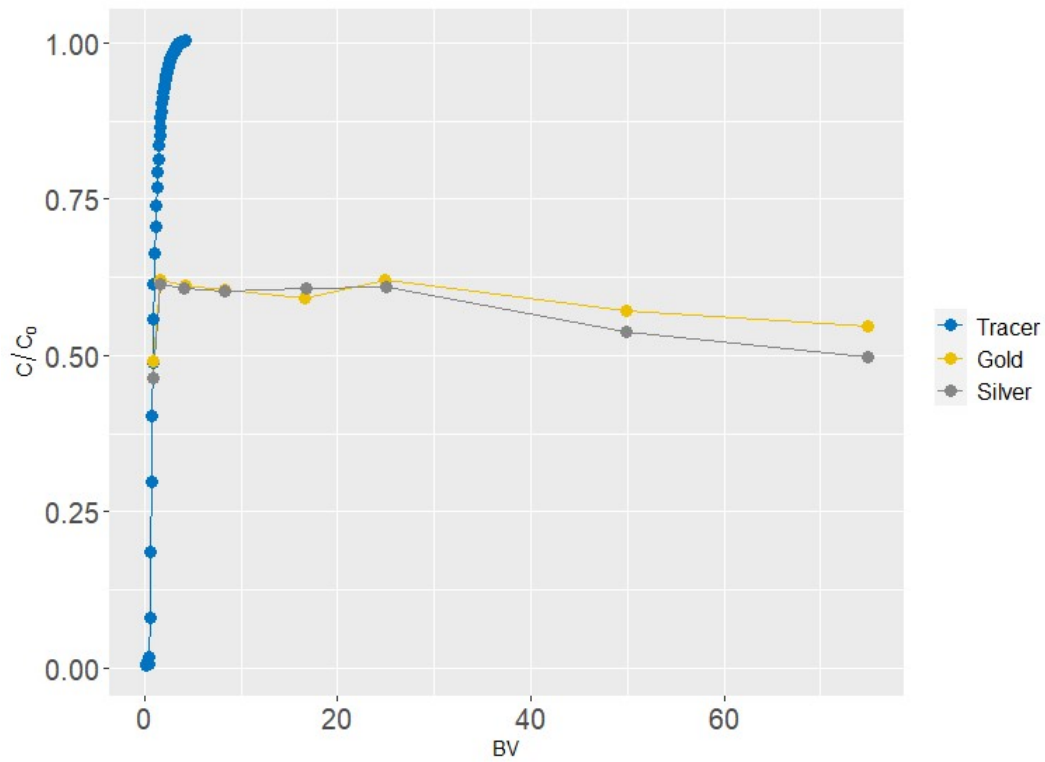
Figure SI 11: breakthrough curves for nAu, nAg and a tracer (NaCl) in virgin GAC (bed height 20 cm) with Lek water with Leiduin water
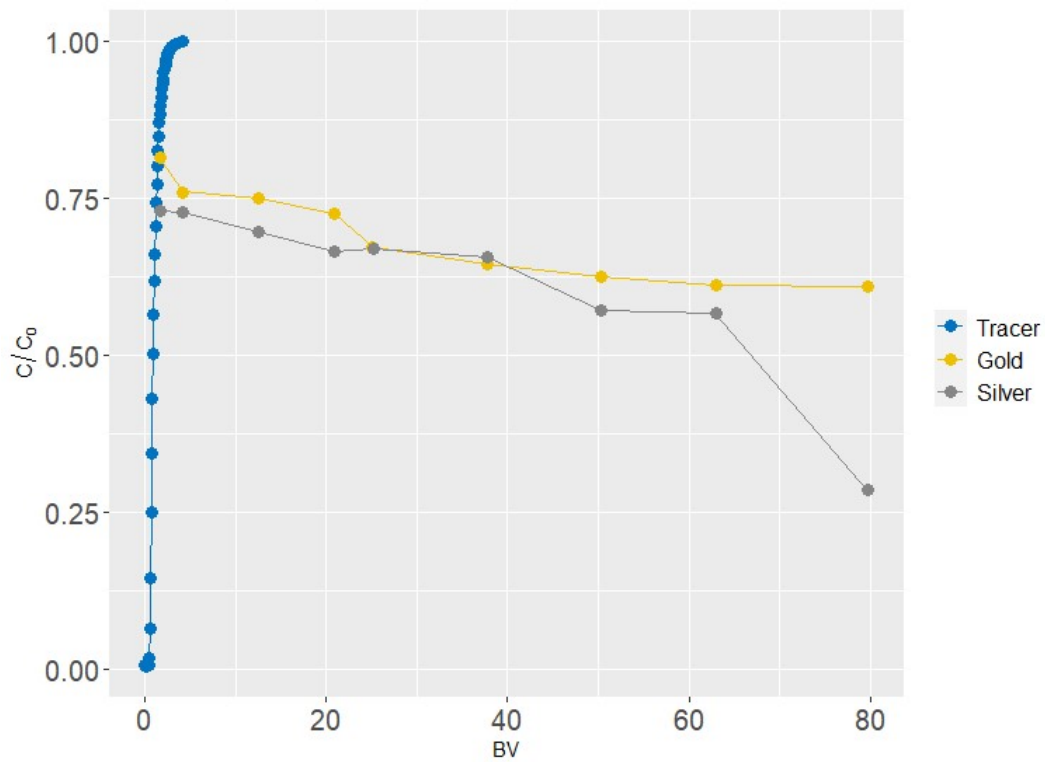

Figure SI 12: breakthrough curves for nAu, nAg and a tracer (NaCl) in loaded GAC (bed height 20 cm) with Leiduin water
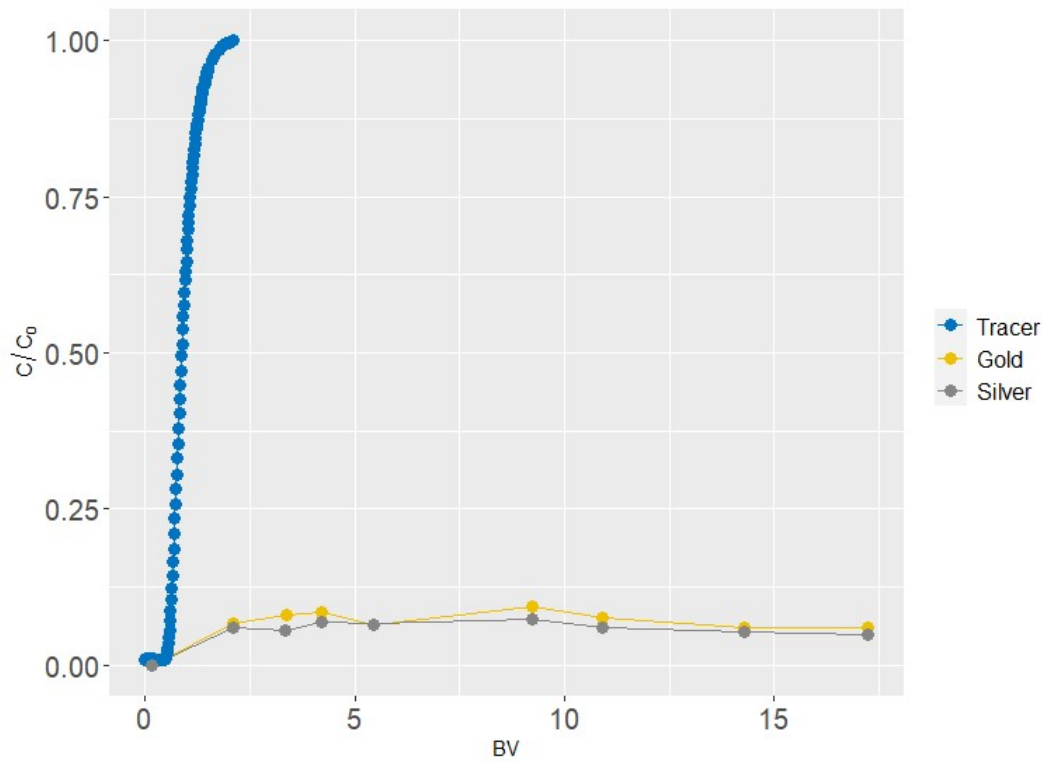
Figure SI 13: breakthrough curves for nAu, nAg and a tracer (NaCl) in virgin GAC (bed height 99 cm) with Milli-Q water
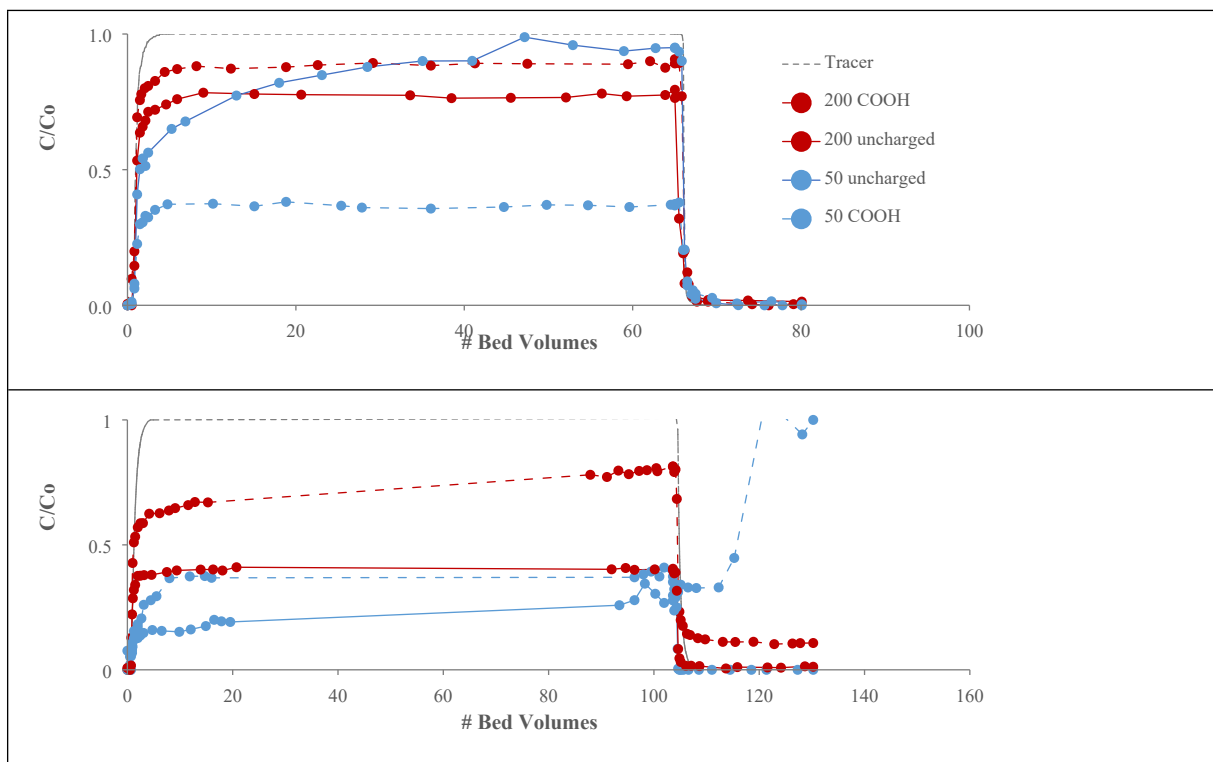

Figure SI 14: nanoplastics breakthrough curves during sand filtration (upper plot) and during GAC filtration (lower plot). Nanoplastics in the effluent are presented in relation to the constant inlet concentration (c_0 = 2 mg/L). Elution phase: surface water from the Lek canal (Nieuwegein, the Netherlands).

Table SI 8: experimentally determined nanoplastics breakthrough during column rapid sand and GAC filtration. For these experiments the individual transport mechanisms (diffusion, interception and gravity) were assessed following Tufenkji and Elimelech [4].

	Sand filtration			GAC filtration		
	η_D	η_I	η_G	η_D	η_I	η_G
200 COOH	8.7E-04	6.6E-06	1.5E-07	3.2E-03	3.6E-05	5.0E-07
200 uncharged	8.7E-04	6.6E-06	1.5E-07	3.2E-03	3.6E-05	5.0E-07
50 COOH	2.6E-03	9.1E-07	9.9E-09	9.7E-03	5.0E-06	3.2E-08
50 uncharged	2.6E-03	9.1E-07	9.9E-09	9.7E-03	5.0E-06	3.2E-08

Table SI 9: Results of column experiments with nAu and nAg based on two size characteristics of the filter medium. Unless stated otherwise, pretreated surface water was used.

Sample	particle	α_c		η		K_d
		d_{10}	d_{50}	d10	d50	d10 and d50
Clean sand, HD	nAu	0.14	0.23	5.72E-04	7.81E-04	3.15E-03
	nAg	0.16	0.27	7.03E-04	9.58E-04	3.86E-03
Loaded sand, HD	nAu	0.36	0.55	1.29E-03	1.67E-03	5.91E-03
	nAg	0.32	0.50	1.22E-03	1.58E-03	5.59E-03
Clean sand, LD	nAu	0.21	0.36	8.98E-04	1.23E-03	4.85E-03
	nAg	0.20	0.34	8.98E-04	1.23E-03	4.85E-03
Loaded sand, LD	nAu	0.31	0.48	1.10E-03	1.43E-03	5.15E-03
	nAg	0.30	0.46	1.10E-03	1.43E-03	5.15E-03
Virgin GAC	nAu	0.15	0.31	1.23E-03	1.88E-03	1.77E-02
	nAg	0.16	0.31	1.31E-03	2.01E-03	1.89E-02
Loaded GAC	nAu	0.09	0.11	7.79E-04	9.08E-04	1.30E-02
	nAg	0.10	0.12	8.73E-04	1.02E-03	1.45E-02
Virgin GAC. Milli-Q water, 20 cm column	nAu	0.19	0.39	1.57E-03	2.40E-03	2.26E-02
	nAg	0.21	0.42	1.76E-03	2.70E-03	2.54E-02
Virgin GAC. Milli-Q water, 99 cm column	nAu	0.16	0.32	1.29E-03	1.98E-03	1.86E-02
	nAg	0.16	0.32	1.29E-03	1.98E-03	2.10E-02

Literature

1.	Toride, N., F.J. Leij, and M.T. van Genuchten, *The CXTFIT Code for Estimating Transport Parameters from Laboratory or Field Tracer Experiments; version 2.0.* 1995, Salinity Laboratory: Riverside CA, USA.
2.	Yao, K.M., M.T. Habibian, and C.R. O'Melia, *Water and Waste Water Filtration: Concepts and Applications.* Environmental Science and Technology, 1971. **5**(11): p. 1105-1112.
3.	Berkowitz, B., I. Dror, and B. Yaron, *Contaminant geochemistry: Interactions and transport in the subsurface environment: Second edition*. Contaminant Geochemistry: Interactions and Transport in the Subsurface Environment: Second Edition. Vol. 9783642547775. 2014. 1-577.

4. Tufenkji, N. and M. Elimelech, *Correlation Equation for Predicting Single-Collector Efficiency in Physicochemical Filtration in Saturated Porous Media.* Environmental Science and Technology, 2004. **38**(2): p. 529-536.

5. Tsai, D.H., L.F. Pease Iii, R.A. Zangmeister, M.J. Tarlov, and M.R. Zachariah, *Aggregation kinetics of colloidal particles measured by gas-phase differential mobility analysis.* Langmuir, 2009. **25**(1): p. 140-146.

6. Timmers, P.H.A., T. Slootweg, A. Knezev, M. van der Schans, L. Zandvliet, A. Reus, D. Vughs, L. Heijnen, T. Knol, J. El Majjaoui, P. van der Wielen, P.J. Stuyfzand, and K. Lekkerkerker-Teunissen, *Improved drinking water quality after adding advanced oxidation for organic micropollutant removal to pretreatment of river water undergoing dune infiltration near The Hague, Netherlands.* Journal of Hazardous Materials, 2022. **429**.