



HAL
open science

Modelling of solid / liquid fractionation of trace metals for suspended sediments according to the hydro-sedimentary conditions of rivers - Application to ¹³⁷Cs in the Rhône River (France)

Wirginia Tomczak, Patrick Boyer, Frederique Eyrolle, Olivier Radakovitch, Mohamed Krimissa, Hugo Lepage, Muriel Amielh, Fabien Anselmet

► To cite this version:

Wirginia Tomczak, Patrick Boyer, Frederique Eyrolle, Olivier Radakovitch, Mohamed Krimissa, et al.. Modelling of solid / liquid fractionation of trace metals for suspended sediments according to the hydro-sedimentary conditions of rivers - Application to ¹³⁷Cs in the Rhône River (France). Environmental Modelling and Software, 2021, 145, pp.105211. 10.1016/j.envsoft.2021.105211 . hal-03364886

HAL Id: hal-03364886

<https://hal.science/hal-03364886>

Submitted on 3 May 2022

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Distributed under a Creative Commons Attribution - NonCommercial - NoDerivatives 4.0 International License

1 **Modelling of solid / liquid fractionation of trace metals for suspended sediments**
2 **according to the hydro-sedimentary conditions of rivers**
3 **- Application to ¹³⁷Cs in the Rhône River (France) -**

4
5 Wirginia Tomczak¹, Patrick Boyer¹, Frederique Eyrolle¹, Olivier Radakovitch¹, Mohamed
6 Krimissa², Hugo Lepage¹, Muriel Amielh³, Fabien Anselmet³

7
8 1 - Institut de Radioprotection et de Sûreté Nucléaire (IRSN), PSE-SRTE-LRTA, Cadarache,
9 France

10 2 - Electricité de France (EDF), Recherches & Développements, Chatou, France.

11 3 - Aix Marseille Université, CNRS, Centrale Marseille, IRPHE U.M.R.7342, Marseille,
12 France.

13
14 *Corresponding author:

15 *E-mail address:* patrick.boyer@irsn.fr (Patrick Boyer)

16
17 **Highlights:**

- 18 • Modelling of K_d according to hydro-sedimentary conditions
19 • Particle size effect on K_d
20 • Geochemical background effect on K_d
21 • Colloidal pumping effect on K_d .

22
23 **Abstract**

24 The behavior and impact of trace metals discharged into rivers depend on their solid/liquid
25 fractionation and the fate of these two phases according to hydro-sedimentary processes. The
26 solid/liquid fractionation depends on many environmental factors which imply uncertainties of
27 several orders of magnitude in the evaluation of the partition coefficients, whether by
28 geochemical modelling, in situ measurements or sorption-desorption experiments. In this
29 context, this paper presents a model of solid/liquid fractionation of trace metals with suspended
30 sediments in rivers which integrates the hydro-sedimentary conditions and the properties of the
31 watershed. Its comparison with the ¹³⁷Cs concentrations measured in the Rhône River (France)
32 shows that the solid/liquid fractionation of ¹³⁷Cs with suspended sediments in rivers depends
33 on chemical processes but also and above all on variations in water flow rate, size and load of
34 suspended sediments and the balance between anthropogenic discharges and the average trace
35 metal content of soils in the watershed.

36 **Keywords:** K_d modelling; river systems; suspended sediments; particle size; trace metal;
37 colloidal pumping.

38 Published as : Tomczak et al., Environmental Modelling and Software, 2021

39 doi : 10.1016/j.envsoft.2021.105211

40 **1 Introduction**

41 Within the framework of environmental and human health risk assessment; transport
42 and bioavailability of trace metals (TMs) in aquatic environments were thoroughly investigated.
43 Most TMs from anthropogenic origins such as industrial/urban wastewaters or agricultural uses
44 are delivered to aquatic systems as inorganic complexes or hydrated ions, which are more or
45 less adsorbed onto sediment particles (Vuković *et al.*, 2011). Consequently, their behavior in
46 aquatic systems strongly depends on their solid/liquid fractionation which governs their
47 mobility, bioavailability, transport and residence time.

48 In rivers, suspended sediments (SS) play a major role on such distribution because they
49 constitute important TMs carriers due to their high capacity of adsorption (Xia et al., 2004). SS
50 behavior and fate are governed by various hydro-sedimentary processes including particle
51 transport/dispersion, sedimentation, early diagenesis and erosion (Walling and Moorehead,
52 1989).

53 Among the various SS properties, the particle size is widely known as an important parameter
54 involved in the sorption of TMs because it directly defines the solid surface exchange
55 availability. Most generally, exchange surface availability increases with the decreasing size of
56 particles and the coarser particles adsorb less TMs than the smaller ones (Town and Filella,
57 2002; Payne et al., 2011). This has been thoroughly demonstrated for various TMs such as Cd
58 (Fan et al., 2017), Hg (Boszke et al., 2004), ^{110m}Ag , $^{58,60}\text{Co}$ and ^{54}Mn (Ciffroy *et al.*, 1995) and
59 ^{137}Cs and ^{210}Pb (He and Walling, 1996).

60 Furthermore, it is well established that the transport modes of SS (Crosby and Whipple, 2004)
61 and the processes of sedimentation (Gibbs *et al.*, 1971; Abarca *et al.*, 2017) and erosion (Xia *et*
62 *al.*, 2004) are particle size dependent. Particles smaller than 200 μm are generally suspended
63 and easily transferred by water flows unlike coarser particles (Palmateer *et al.*, 1993; Fan *et al.*,
64 2017).

65 Due to these mechanisms, the particle size of SS explains most of TMs contents and fluxes
66 within the water column (Sigg *et al.*, 2000; Turner *et al.*, 2002; Reynolds *et al.*, 2010; Boyer *et*

67 *al.*, 2018). It is therefore a fundamental parameter for the modelling of the solid/liquid
68 partitioning of TMs in rivers. In addition, this fractionation is also time dependent so that
69 equilibrium is not instantaneous but reached after several hours or days depending on the metal
70 and the environmental conditions. Although kinetic models exist (Cameron and Klute, 1977;
71 Garcia-Sanchez *et al.*, 2014), their parameters are poorly documented and the K_d approach
72 remains the most common operational means to assess solid / liquid fractionation of TMs
73 assuming instantaneous equilibrium and reversibility:

$$74 \quad K_d = \frac{C_s}{C_l} \quad [\text{m}^3 \cdot \text{kg}^{-1}] \quad (\text{Eq. 1})$$

75
76 Where C_s [$\text{xx} \cdot \text{kg}_{\text{dry}}^{-1}$] and C_l [$\text{xx} \cdot \text{m}^{-3}$] are the TMs contents of the solid and liquid phases, with
77 $\text{xx} = \text{kg}, \text{mol}$ or Bq .

78
79 Due to the kinetic effects, a K_d is nothing more than the ratio of the sorption and desorption
80 kinetics and it must be kept in mind that the equilibrium assumption limits its application
81 domain to contact times sufficiently long to reach these conditions. Because sorption kinetics
82 are generally faster than desorption kinetics (Pèrez *et al.*, 2015), two types of K_d have been
83 introduced for operational applications (Ciffroy *et al.*, 2009; Boyer *et al.*, 2018): a K_d sorption
84 to represent the rapid equilibrium reached when sorption processes are dominant, as in a
85 sorption experiments and downstream of a point of discharge, and a K_d desorption to represent
86 situations dominated by desorption processes such as in a desorption experiments and the long-
87 term behaviour of watersheds and bottom sediments contamination. Anyway, the K_d approach
88 remains a black box that aggregates physicochemical processes such as hydrogen bonding,
89 electrostatic and van der Waals forces, surface precipitation and surface co-precipitation
90 (Heling *et al.*, 1999; Durrieu *et al.*, 2006), as well as biochemical processes such as microbial
91 alkylation and volatilization that can change, independently of solid-liquid exchanges, the
92 solution concentrations of elements such as selenium, arsenic and mercury (Peitzsch *et al.*,
93 2010). At the same time, these processes are dependent on the chemical speciation of TMs and
94 numerous environmental factors: pH (Lu and Allen, 2001; Wang *et al.*, 2017), nature and load
95 of SS (Apte *et al.*, 1995; Dominik *et al.*, 2007; Jweda *et al.*, 2008; Boyer *et al.*, 2018), dissolved
96 organic carbon content (Barreto *et al.*, 2011; Zhang *et al.*, 2013), temperature (Warren and
97 Zimmerman, 1994), ionic strength (Duc *et al.*, 2013). As a consequence of this complexity, the
98 K_d values vary over several orders of magnitude even for a single TM and a single river as has

99 been shown by different K_d values compilations (Allison and Allison, 2005; Durrieu *et al.*,
100 2006; Ciffroy *et al.*, 2009; Boyer *et al.*, 2018; Tomczak *et al.*, 2019).

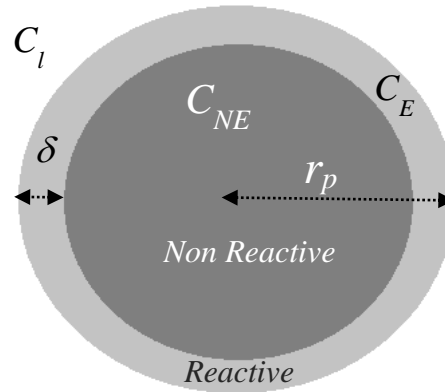
101
102 In practice, K_d values are determined by in situ measurements, sorption-desorption experiments
103 in laboratories and different modelling approaches such as parametric models (Sheppard *et al.*,
104 2009; Sheppard, 2011), dynamic models (Garcia-Sanchez *et al.*, 2014) and mass-action based
105 on thermodynamic models (Tipping, 1994; Goldberg *et al.*, 2007).

106
107 However, these different approaches are mainly based on geochemical concepts and remain
108 difficult to apply at the temporal and spatial scales of a river for those they require to be coupled
109 to hydro-sedimentary models (Garneau *et al.*, 2017) and to measure or assess a number of
110 environmental variables (Ilina *et al.*, 2020). Moreover, and despite the central role of particle
111 sizes in the solid/liquid fractionation of TMs with SS, this parameter is poorly considered by
112 these models while, at the same time, it is little documented by the scientific literature related
113 to K_d values for river systems. Thus, the effect of particle size in the models of transfer of TMs
114 in rivers is generally overlooked and, to our knowledge, the only K_d models including
115 specifically the particle sizes are those proposed by He and Walling (1996) and Abril and Fraga
116 (1996).

117
118 He and Walling (1996) performed sorption experiments on various size fractionated samples of
119 soils and sediments and showed that K_d values for ^{137}Cs and ^{210}Pb are closely correlated to the
120 specific surface area, SSA [$\text{m}^2 \cdot \text{kg}^{-1}$], through an empirical power function:

$$121 \quad K_d = a \cdot \text{SSA}^b \quad (\text{Eq. 2})$$

122 Abril and Fraga (1996) and Abril (1998a) proposed a more mechanistic approach that
123 reproduces this empirical relation by considering spherical particles and assuming that only a
124 fine external layer of thickness δ participates to the ionic exchanges within the surrounding
125 water medium, instead of the whole solid particle. Compared to the approach of He and Walling
126 (1996), based only on the raw SSA, the thickness δ can be considered as a correction factor
127 which completes the exchange surface with the porous surface layer of the particles at the inside
128 in which TMs can diffuse according to their properties. Thus, they considered that only the TMs
129 associated with this reactive external layer are exchangeable with the solution while those in
130 the non-reactive internal part are not exchangeable (Figure 1).



131

132 Figure 1: Abril and Fraga (1996) theoretical modelling concepts for spherical particles.

133 C_l: liquid concentration; C_{NE}: non-exchangeable concentration; C_E: exchangeable concentration; r_p: radius; δ:
 134 thickness of the exchange layer

135 Additionally, they assumed equilibrium between the TMs contents in the reactive layer and in
 136 the solution such as:

137
$$K_{d\delta} = \frac{C_E}{C_l} \quad (\text{Eq. 3})$$

138 Where K_{dδ} is the K_d for the TMs in the reactive layer of thickness δ [μm] and C_l [xx.l⁻¹] and C_E
 139 [xx.kg_{dry}⁻¹] are the concentrations in the liquid phase and in the exchangeable part of particles,
 140 respectively.

141 Based on these theoretical concepts, the K_d of a particle can be expressed as a function of its
 142 radius r_p [μm]:

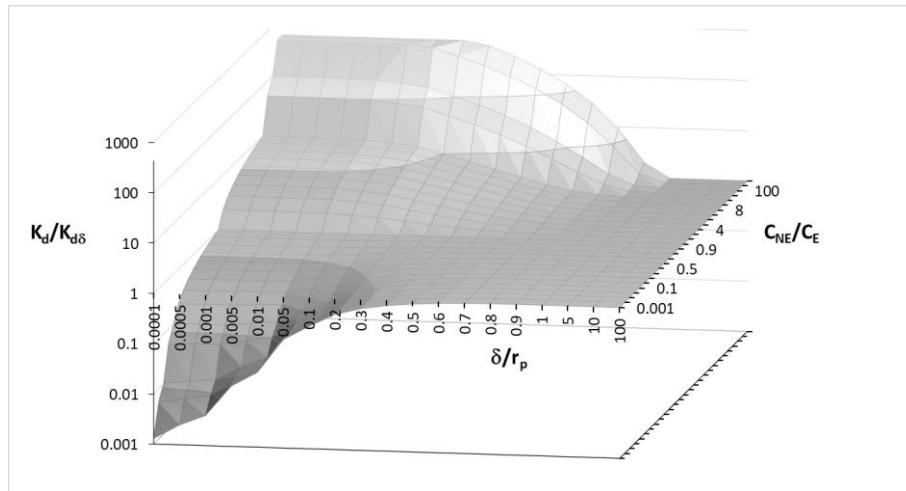
143 • if r_p > δ ⇒
$$K_d = K_{d\delta} \cdot \left(1 - \left(1 - \frac{\delta}{r_p}\right)^3\right) + K_{d\delta} \cdot \frac{C_{NE}}{C_E} \cdot \left(1 - \frac{\delta}{r_p}\right)^3 \quad (\text{Eq. 4})$$

144 • if r_p ≤ δ ⇒
$$K_d = K_{d\delta} \quad (\text{Eq. 5})$$

145

146 In these relationships, r_p is specific to particles, δ and K_{dδ} are specific to geochemical
 147 conditions and C_{NE} [xx· kg_{dry}⁻¹] is specific to the environmental context.

148 Figure 2 presents the evolution of K_d/K_{dδ} as a function of C_{NE}/C_E and δ/r_p according to this
 149 model.



150

151 Figure 2: $K_d/K_{d\delta}$ ratios as a function of C_{NE}/C_E and δ/r_p ratios according to the Abril and
 152 Fraga Model

153

154 According to the Abril and Fraga Model (labelled AFM), K_d is equal to $K_{d\delta}$ when particle sizes
 155 are smaller than the reactive layer thickness δ and when the ratio C_{NE}/C_E is close to one (Figure
 156 2). For particle sizes greater than δ , K_d decreases with r_p rising and C_{NE}/C_E decreasing, which
 157 corresponds to situations where the concentrations of anthropogenic TMs onto the surface of
 158 particles are clearly above those within the mineral. In contrast, K_d increases when r_p is high
 159 and C_{NE}/C_E is high, corresponding to situations dominated by the geochemical background of
 160 TMs.

161 This modelling approach highlights that changes in C_E , C_{NE} and r_p are sufficient to induce a
 162 variation of the K_d over several orders of magnitude, as is the case in most rivers (Tomczak *et*
 163 *al.*, 2019). In this context, we propose an adaptation of the AFM in order to determine the K_d
 164 of the TMs for SS in rivers according to the particle sizes, the hydro-sedimentary properties of
 165 the river and the geochemical context of the watershed. This adaptation was tested on a ^{137}Cs
 166 dataset acquired in the Rhône River (France) from long term monitoring. The results highlight
 167 its relevance to explain the variations of the K_d values which were observed over several years
 168 according to the water flow rate.

169

170

171 2 Method

172 For situations dominated by anthropogenic TMs ($C_{NE}/C_E < 1$), several field studies
173 (Honeyman and Santschi, 1988; Benoit and Rozan, 1999; Eyrolle *et al.*, 2006) and data
174 compilations (Boyer *et al.*, 2018; Tomczak *et al.*, 2019) show that K_d tends to decrease when
175 the load of suspended sediments, labelled [SS], increases. This trend is explained by three major
176 mechanisms which are: 1) particle size effect, 2) mass/volume ratio effect and 3) colloidal
177 pumping.

178 1) The effect of particle size reflects that [SS] and the mean radius of suspended particles both
179 tend to increase with increasing water flow rate. Observed in most cases (Müller and Förstener,
180 1968; Metha, 2014) but not all (Walling *et al.*, 2000), this tendency leads to a decrease in the
181 mean specific surface area of SS when [SS] increases and therefore to lower K_d values.

182 2) The mass/volume effect (Abril, 1998b) concerns particle sizes larger than δ and depends on
183 the balance between the total concentrations added to the rivers by the anthropogenic discharges
184 (C_D [$xx.m^{-3}$]) and the background of the TMs contents in the watershed (C_{soil} [$xx.kg^{-1}$]) which
185 can be assimilated to C_{NE} . This background is related to the presence of natural TMs and/or
186 non-reversible solid fractions of anthropogenic TMs due to industrial and agricultural uses or
187 past atmospheric fallouts and which have “migrated” within the non-reactive crystalline
188 structure of the minerals. In the case where C_D is negligible, an increase of [SS] changes the
189 solid concentrations little at the same time that it increases the liquid concentrations, resulting
190 in a decrease of K_d . The AFM indicates that this trend is reversed when C_D is sufficiently strong
191 compared to C_{soil} with a theoretical limit given by $C_D > C_{soil}/K_d\delta$.

192 3) Finally, colloidal pumping also explains the decrease of K_d together with the rise in [SS]
193 because the concentration of colloidal compounds increases mechanically at the same time as
194 [SS] when the water flow rate increases. These sub-micro particles are poorly retained by
195 filtration and it has been widely demonstrated that they are the most efficient particles to adsorb
196 TMs (Li *et al.*, 1984). Consequently, an increase in their concentrations enriches the TMs
197 contents of the filtered water (Honeyman and Santschi, 1988; Benoit and Rozan, 1999) and
198 reduces the K_d values.

199 The AFM integrates the effects of points 1 and 2 by the first and second terms in equation 4,
200 respectively. In order to integrate the colloidal pumping effect, let us consider that the liquid
201 phase is composed of the dissolved and colloidal fractions:

202 $C_l = C_d + C_c \cdot [SC]$ (Eq. 6)

203 Where C_c [$xx \cdot kg^{-1}$] is the TM concentration within the colloidal phase, $[SC]$ [$kg \cdot m^{-3}$] is the
 204 concentration of colloids, C_d [$xx \cdot m^{-3}$] is the dissolved TM concentration and C_l [$xx \cdot m^{-3}$] is the
 205 TM concentration in the total liquid phase.

206 In this case, $K_{d\delta}$ is replaced by $K_{d\delta}^*$ which is given by:

207
 208
$$K_{d\delta}^* = \frac{C_{SS,E}}{C_l} = \frac{C_{SS,E}}{C_d \cdot (1 + K_{dc} \cdot [SC])} = \frac{K_{d\delta}}{1 + K_{dc} \cdot [SC]}$$
 (Eq. 7)

209
 210 Where $C_{SS,E}$ [$xx \cdot kg^{-1}$] is the exchangeable concentration of TMs inside the reactive fraction of
 211 SS and K_{dc} [$l \cdot kg^{-1}$] is the K_d of colloids.

212
 213 The δ values obtained by Abril et Fraga (1996) for Pu, Cs and Zn are 0.78, 1.96 and 5.17 μm
 214 respectively. These values are all greater than the size of colloidal particles ($< 0.45 \mu m$) which
 215 allows us, according to the AFM theory, to assume $K_{dc} \approx K_{d\delta}$.

216
 217 With these considerations, the adaptation of the AFM to SS in rivers leads to:

218 • if $r_p > \delta \Rightarrow K_d = \frac{K_{d\delta}}{1 + K_{dc} \cdot [SC]} \cdot \left(1 - \left(1 - \frac{C_{SS,NE}}{C_{SS,E}} \right) \cdot \left(1 - \frac{\delta}{r_p} \right)^3 \right)$ (Eq. 8)

219 • if $r_p \leq \delta \Rightarrow K_d = \frac{K_{d\delta}}{1 + K_{dc} \cdot [SC]}$ (Eq. 9)

220 Where:

221 • $C_{SS,NE}$ [$xx \cdot kg^{-1}$] is the non-exchangeable concentration of TMs inside the non-reactive
 222 fraction of SS. It is a specific property of the catchment which depends on the geochemical
 223 background for naturally occurring TMs and/or on the anthropogenic background produced
 224 by non-reversible fractions generated in the long term by industrial and agricultural uses and
 225 atmospheric fallouts. Thus, this concentration can be assimilated to C_{soil} [$xx \cdot kg^{-1}$], the mean
 226 TMs concentrations in the soils of the catchment : $C_{SS,NE} = C_{soil}$

227
 228 • $C_{SS,E}$ [$xx \cdot kg^{-1}$], the exchangeable concentration of TMs inside the reactive fraction of SS,
 229 depends on the solid/liquid fractionation of C_E [$xx \cdot l^{-1}$] which is the total exchangeable
 230 concentration of TMs in the water volume. This concentration is constituted of C_{EB} [$xx \cdot l^{-1}$],
 231 the total exchangeable concentrations originated from the background concentration of TMs

232 in the watershed and C_D [xx.l^{-1}], the total concentration of TMs added by industrial liquid
233 discharges:

234

$$235 \quad C_E = C_{EB} + C_D \quad (\text{Eq. 10})$$

236

237 The total exchangeable concentrations originated from the background concentration of TMs
238 in the watershed is:

239

$$240 \quad C_{EB} = C_{\text{soil}} \cdot [\text{SS}]_R \quad (\text{Eq. 11})$$

241

242 Where $[\text{SS}]_R$ [$\text{kg}\cdot\text{m}^{-3}$] is the suspended load of reactive SS given by:

$$243 \quad \bullet \quad \text{If } (r_p > \delta) \Rightarrow [\text{SS}]_R = [\text{SS}] \cdot \left(1 - \left(1 - \frac{\delta}{r_p}\right)^3\right) \quad (\text{Eq. 12})$$

$$244 \quad \bullet \quad \text{If } (r_p \leq \delta) \Rightarrow [\text{SS}]_R = [\text{SS}] \quad (\text{Eq. 13})$$

245

246 In complement, we deduce the concentration of non-reactive SS by:

247

$$248 \quad [\text{SS}]_{NR} = [\text{SS}] - [\text{SS}]_R \quad (\text{Eq. 14})$$

249

250 The total concentration of TMs added by industrial liquid discharges can be easily assessed
251 in case of complete mixing conditions:

$$252 \quad C_D = \frac{q_D}{Q_{\text{river}}} \quad (\text{Eq. 15})$$

253 Where q_D [$\text{xx}\cdot\text{s}^{-1}$] is the flux of the anthropogenic discharges within the river and
254 Q_{river} [$\text{m}^3\cdot\text{s}^{-1}$] is the river water flow rate.

255 With this relationship, the model should be applied in a zone of complete mixing and by
256 assuming that the TMs fractions removed from the water column by solid phase
257 sedimentation are negligible, which is generally the case in rivers where the MTs are mainly
258 fixed on the finest particles which have the lowest sedimentation rates.

259 Finally, the total (T), dissolved (d), colloidal (c), liquid (l) and particulate (SS) concentrations
260 of TMs are given by:

261

$$262 \quad C_T = C_d + C_c \cdot [\text{SC}] + C_{\text{SS,E}} \cdot [\text{SS}]_R + C_{\text{Soil}} \cdot [\text{SS}]_{NR} \quad (\text{Eq. 16})$$

263
$$C_d = \frac{C_T - C_{soil} \cdot [SS]_{NR}}{1 + K_{dc} \cdot [SC] + K_{d\delta} \cdot [SS]_R} = \frac{C_E}{1 + K_{dc} \cdot [SC] + K_{d\delta} \cdot [SS]_R}$$
 (Eq. 17)

264
$$C_c = K_{dc} \cdot C_d \cdot [SC]$$
 (Eq. 18)

265
$$C_l = C_d + C_c$$
 (Eq. 19)

266
$$C_{SS,E} = K_{d\delta} \cdot C_d$$
 (Eq. 20)

267
$$C_{SS} = \frac{C_{SS,E} \cdot [SS]_R + C_{soil} \cdot [SS]_{NR}}{[SS]}$$
 (Eq. 21)

268

269 Furthermore, these concentrations can be decomposed according to the contributions of the

270 anthropogenic discharges (D) and the catchment background (B) with $f_D = \frac{C_D}{C_E}$:

271 • $C_{d,D} = f_D \cdot C_d$ and $C_{d,B} = (1 - f_D) \cdot C_d$ (Eq. 22)

272 • $C_{c,D} = f_D \cdot C_c$ and $C_{c,B} = (1 - f_D) \cdot C_c$ (Eq. 23)

273 • $C_{l,D} = f_D \cdot C_l$ and $C_{l,B} = (1 - f_D) \cdot C_l$ (Eq. 24)

274 • $C_{SS,D} = \frac{K_{d\delta} \cdot C_{d,D} \cdot [SS]_R}{[SS]}$ and $C_{SS,B} = \frac{K_{d\delta} \cdot C_{d,B} \cdot [SS]_R + C_{soil} \cdot [SS]_{NR}}{[SS]}$ (Eq. 25)

275

276 We can then define the K_d specifically to the anthropogenic discharges and to the catchment

277 background by:

278
$$K_{d,D} = \frac{C_{SS,D}}{C_{l,D}}$$
 and $K_{d,B} = \frac{C_{SS,B}}{C_{l,B}}$ (Eq. 26)

279

280 These different calculation steps are summarized in Table 1.

281

282 Table 1: Summary description of the model

283 (See text for the description of parameters)

Input parameters	
$\delta, K_{d\delta}, K_{dc} (\sim K_{d\delta}), Q_{river}, [SS], [SC], r_p, C_{soil}, q_D$ (or $C_D = \frac{q_D}{Q_{river}}$)	
1 - Calculation of the reactive and non-reactive loads of SS	
<ul style="list-style-type: none"> • If ($r_{50} > \delta$) $\Rightarrow [SS]_R = [SS] \cdot \left(1 - \left(1 - \frac{\delta}{r_p}\right)^3\right)$ • If ($r_{50} \leq \delta$) $\Rightarrow [SS]_R = [SS]$ • $[SS]_{NR} = [SS] - [SS]_R$ 	
2 - Calculation of the total exchangeable and non exchangeable TMs concentrations	
• $C_{EB} = C_{soil} \cdot [SS]_R$	• $C_E = C_D + C_{EB}$

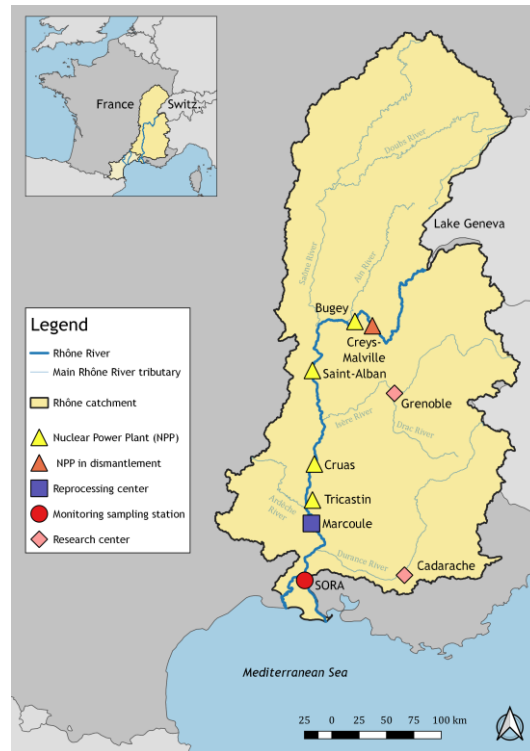
<ul style="list-style-type: none"> • $C_D = \frac{q_D}{Q_{river}}$ 	<ul style="list-style-type: none"> • $f_D = \frac{C_D}{C_E}$
4 - Calculation of the dissolved, colloidal and liquid TMs concentrations	
<ul style="list-style-type: none"> • $C_d = \frac{C_E}{1+K_{dc} \cdot [SC] + K_{d\delta} \cdot [SS]_R}$ • $C_c = K_{dc} \cdot [SC] \cdot C_d$ • $C_l = C_d + C_c$ 	<ul style="list-style-type: none"> • $C_{d,D} = f_D \cdot C_d ; C_{d,B} = C_d - C_{d,D}$ • $C_{c,D} = f_D \cdot C_c ; C_{c,B} = C_c - C_{c,D}$ • $C_{l,D} = f_D \cdot C_l ; C_{l,B} = C_l - C_{l,D}$
3 - Calculation of the particulate TMs concentrations	
<ul style="list-style-type: none"> • $C_{SS,E} = K_{d\delta} \cdot C_d$ • $C_{SS} = \frac{C_{SS,E} \cdot [SS]_R + C_{soil} \cdot [SS]_{NR}}{[SS]}$ 	<ul style="list-style-type: none"> • $C_{SS,D} = \frac{K_{d\delta} \cdot C_{d,D} \cdot [SS]_R}{[SS]}$ • $C_{SS,B} = \frac{K_{d\delta} \cdot C_{d,G} \cdot [SS]_R + C_{soil} \cdot [SS]_{NR}}{[SS]}$
5 - Calculation of the K_d	
$K_d = \frac{C_{SS}}{C_l} ; K_{d,D} = \frac{C_{SS,D}}{C_{l,D}} ; K_{d,B} = \frac{C_{SS,B}}{C_{l,B}}$	

284

285 3 Material

286 The model was applied to determine the variability depending on the river discharge of the
287 K_d of ^{137}Cs in the SS of the downstream part of the Rhône River (south of France). Its results
288 were compared to time-series of liquid and particulate ^{137}Cs concentrations and their
289 corresponding ratio measured between 2005 and 2018 at the IRSN monitoring station, SORA,
290 which is located on the Rhône downstream of all the nuclear facilities (Figure 3).

291



292

Figure 3: Rhône River and IRSN monitoring station SORA

293

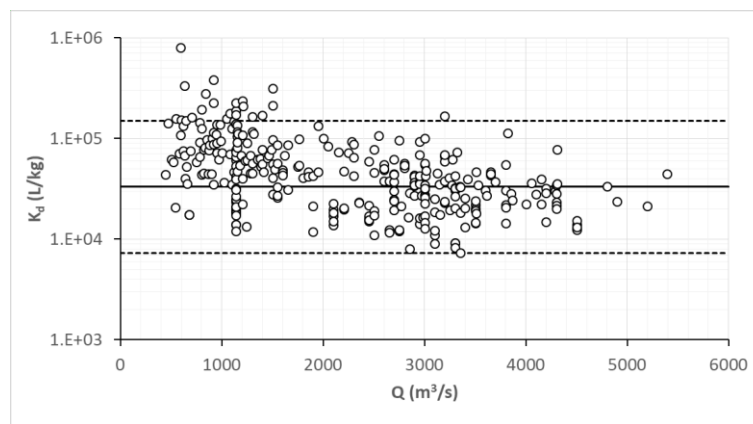
294 The IRSN monitoring station SORA and its sampling protocol for SS and filtered water are
295 detailed in Antonelli *et al.* (2008), Eyrolle *et al.* (2012) and Eyrolle *et al.* (2020). Outside flood
296 periods, a composite sample resulting from samples taken every 80 minutes is collected over a
297 period of about one month. During flood periods ($> 3\,000\text{ m}^3\cdot\text{s}^{-1}$), the composite sample is
298 produced using samples taken every 60 minutes over 8 hours. Radionuclide analyses are
299 performed on the particulate fraction (suspended sediments, SS) and on the dissolved fraction
300 (fraction less than $0.5\ \mu\text{m}$, filtered waters, FW).

301

302 The representativeness of these data in terms of K_d depends on the validity or otherwise of the
303 equilibrium of the solid / liquid fractionation of the ^{137}Cs contained in these samples according
304 to its origin, its transit time in the river and the delay between the sampling and the filtration.

305 At the SORA station, the main sources of ^{137}Cs are the contamination of the soils of the
306 watershed (cf. 3.4) and the discharges of the Marcoule Center (cf. 3.5). While the contamination
307 of the watershed is old enough to assume a complete equilibrium and consequently a real K_d ,
308 the interpretation is less obvious for the discharges of the Marcoule Center which is located 65
309 km upstream from the SORA station for a transit time close to one day. During this transit time,
310 it can be considered that the processes of solid/liquid fractionation is dominated by the sorption

311 processes, for which equilibrium conditions are reached after one or two hours (Pérez, 2015).
 312 Consequently, it can be assumed that the solid/liquid ratios of ^{137}Cs in the Rhône at the level of
 313 the SORA station are a combination between the sorption K_d (cf. 1) of the Marcoule discharges
 314 and the real K_d of the watershed. However, it must also be considered that these conditions are
 315 not exactly those measured by the SORA station in reason of the sampling procedure which
 316 increases the contact time over a period of one month allowing to reach a quasi-equilibrium for
 317 the solid/liquid ^{137}Cs concentrations in the samples. This is partially demonstrated by the good
 318 agreement between the solid/liquid ratio measured at the SORA station and the distribution of
 319 the desorption K_d compiled in the framework of the AMORAD program of the International
 320 Agency of Energy Atomic (IAEA) (Boyer *et al.*, 2018; Tomczak *et al.*, 2019).



321
 322 Figure 4: ^{137}Cs solid/liquid ratio measured at the SORA station vs IAEA distribution of SS
 323 desorption K_d .

324 (Dataset (points), IAEA conditional geometric mean (full line) and IAEA 5th and 95th
 325 percentiles (dotted lines))

326
 327
 328 Consequently, it can be assumed that the solid / liquid ratios determined from the data of the
 329 SORA station are probably representative of the K_d of ^{137}Cs in the Rhône at this station but not
 330 necessarily of the state of the solid / liquid fractionation which crosses the section of sampling.

331
 332 In complement, the distance and the transfer time between the Marcoule Center and the SORA
 333 station permit also to assume as correct the assumption of complete mixing and the use of
 334 Equation 12 (cf. Section 2).

335

3.1 Calculation procedure

As the ^{137}Cs concentrations and the model input parameters (Table 1) were not all available at the same time, the variabilities of the solid and liquid concentrations and K_d were modeled by considering the conditional statistical distribution of [SS] and r according to the river discharge and the statistical distributions, over the period 2005-2018, of C_{soil} and C_D . The range of river discharges was scanned between Q_{MIN} ($400 \text{ m}^3 \cdot \text{s}^{-1}$) and Q_{MAX} ($6000 \text{ m}^3 \cdot \text{s}^{-1}$). For each water flow rate, several sets of input parameters were determined with a weighted Latin hypercube method which consisted of four imbricated loops scanning between their 2nd and 98th percentiles the conditional distributions of [SS] and r according to Q and the distributions of C_{soil} and C_D . The result associated to each set of input parameters was weighted by the product of the probability densities of the different parameters. Finally, the geometric means and the minimal and maximal values of the modelled solid and liquid concentrations and K_d obtained at the different water flow rates were compared with the conditional statistical distributions of the dataset.

The calculation procedure was developed as an Excel macro written in Visual Basic Application language. For information, the calculation times on a laptop computer and with the parameters specified in Table 2 are approximately 15 seconds.

It was not possible to determine statistical distributions for the specific parameters of ^{137}Cs , δ and $K_{d\delta}$, because only the values published by Abril and Fraga (1996) were available:

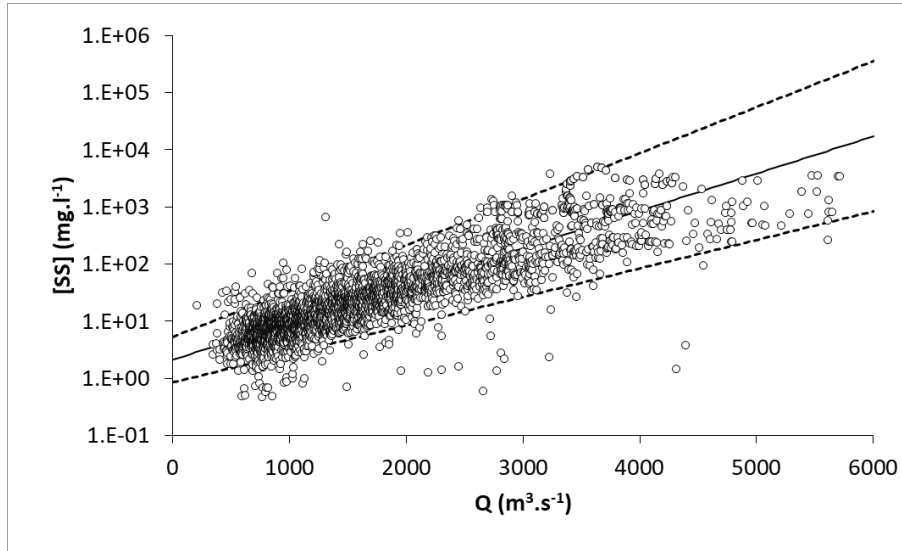
$$\delta = 1.96 \text{ } \mu\text{m} \text{ and } K_{d\delta} = 68 \cdot 10^3 \text{ l} \cdot \text{kg}^{-1}$$

Therefore, these two values were directly applied and used in the discussion. In the meantime, the statistical distributions of the other input parameters are detailed below.

358

3.2 Conditional statistical distribution of [SS] as a function of the river discharge

The conditional log-normal distribution of [SS] as a function of the river discharge was determined from data acquired between March 2001 and April 2008 at the SORA monitoring station (Eyrolle *et al.*, 2012). The conditional geometric means ($\text{GM}([\text{SS}]|Q)$), geometric standard deviations ($\text{GSD}([\text{SS}]|Q)$) and second and ninety-eighth percentiles ($2^{\text{th}}([\text{SS}]|Q)$ and $98^{\text{th}}([\text{SS}]|Q)$) were determined using a sliding window method (Tomszak *et al.*, 2018) applied to this dataset classified according to the increasing water flow rates (Figure 5).



366

367 Figure 5: Suspended sediment concentrations versus Rhône River discharge at SORA station
 368 (Q, [SS]) dataset (points), conditional geometric mean (full line) and 2th and 98th
 369 percentiles (dotted lines)
 370

371 The mean relationships obtained for GM([SS]|Q) and GSD([SS]|Q) are:

372 $GM([SS]|Q) = 2.13 \cdot e^{0.0015 \cdot Q} \text{ [mg.l}^{-1}\text{]}$ with $R^2 = 0.98$ (Eq. 27)

373 $GSD([SS]|Q) = 1.56 \cdot e^{0.0002 \cdot Q}$ with $R^2 = 0.54$ (Eq. 28)

374

375 3.3 Conditional log-normal distribution of r as a function of the river discharge

376 The distributions of the radius r of SS as a function of the river discharge were
 377 determined from data of suspended sediments sizes distributions acquired with an hourly time
 378 step between December 2011 and August 2012 at the SORA station (Adell, 2013). In practice,
 379 one of the operational parameters to represent these distributions as a function of the water flow
 380 is r_{50} , i.e. the fiftieth percentile of the particle volume distribution. For the AFM, the
 381 consequences consecutive to the use of this parameter in place of the particle size distribution
 382 depend on the difference between $\left(1 - \frac{\delta}{r_{50}}\right)^3$ and $\sum_{r_i > \delta} f_i \cdot \left(1 - \frac{\delta}{r_i}\right)^3$ (see Eq. 8 and 9) where
 383 f_i is the frequency of the radius r_i .

384 Over the range of water flow rates covered by our particle size data, these two expressions differ
 385 by less than 20% at the same time that the variability of r_{50} is extended over a range greater than
 386 a factor 2 (ten times more) for each water flow condition (Figure 6). Therefore, and for this
 387 application case, using the variability of r_{50} instead of the particle size distributions enhances

388 the operational capabilities of the model without affecting the accuracy of the results. However,
 389 if this simplification is without consequences here, it is less suitable when applying the model
 390 to a specific suspension or in view to assess the transfers of TMs to deposited sediments for
 391 which the sedimentation / erosion processes increase the sorting of the particles according to
 392 their size and the hydraulic conditions

393

394 For water flow rates between 400 and 3000 m³.s⁻¹, the data show that r₅₀ vary between 3 and 10
 395 μm (Figure 6) which is consistent with other results obtained on the Rhône River (Slomberg *et*
 396 *al.*, 2016) and rivers from the Humber and Tweed catchments (Walling *et al.*, 2000). For this
 397 range of water flow, the conditional log-normal distributions of r₅₀ as a function of the river
 398 discharge were determined in the same way as for [SS]. Thus, the variability of r₅₀ for water
 399 flow rates between 400 and 3000 m³.s⁻¹ is covered by a conditional geometric mean
 400 (GM(r₅₀|Q)) represented by an equation of the second order (Eq. 29) and a constant conditional
 401 standard deviation (GSD(r₅₀|Q)) equal to 1.2 (Figure 6).

402 • If (Q ≤ 3000 m³.s⁻¹) ⇒

403
$$GM(r_{50}|Q) = 2.12 \cdot 10^{-6} \cdot Q^2 - 7.96 \cdot 10^{-3} \cdot Q + 13 \text{ [}\mu\text{m]} \text{ (R}^2=0.65) \text{ (Eq. 29)}$$

404
$$GSD(r_{50}|Q) = 1.2 \text{ (Eq. 30)}$$

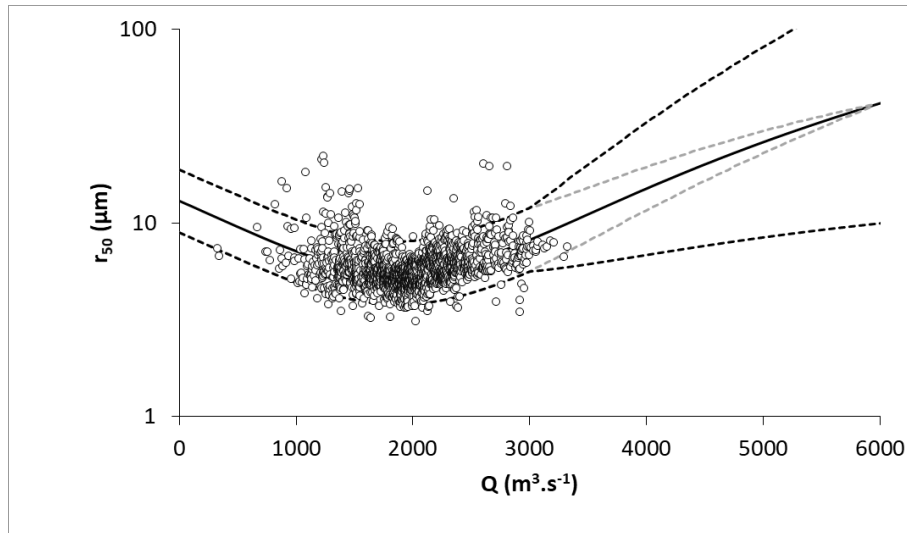
405 • If (Q > 3000 m³.s⁻¹) ⇒

406 Beyond water flow rates of 3000 m³.s⁻¹, the lack of data does not allow a detailed assessment
 407 of the variability of r₅₀. As a first approximation, this variability is extrapolated by considering
 408 Eq. 29 for GM(r₅₀|Q) and by increasing GSD(r₅₀|Q) from 1.2 for Q = 3000 m³.s⁻¹ to 2 for Q =
 409 6000 m³.s⁻¹ (Figure 6):

410
$$GSD(r_{50}|Q) = (Q - 3000) \cdot \frac{2-1.2}{6000-3000} \text{ (Eq. 31)}$$

411 To assess the sensitivity of the model, the results obtained with this assumption are compared
 412 in the discussion (cf. Section 5) with those given by a reduced variability defined by a
 413 GSD(r₅₀|Q) which decreases from 1.2 for Q = 3000 m³.s⁻¹ to 1 for Q = 6000 m³.s⁻¹.

414



415

416 Figure 6: Mean radius r_{50} of suspended sediments vs Rhône River discharge at station SORA
 417 (Q, r_{50}) dataset (points) and conditional geometric mean (full line) and 2th and 98th
 418 percentiles (dotted lines) – Black for $GSD(r_{50}|6000) = 2$ and Grey for $GSD(r_{50}|6000) = 1$
 419

420 3.4 Statistical distribution of the mean ^{137}Cs concentrations in the soils of the catchment

421 The background of the ^{137}Cs concentrations in the soils of the Rhône watershed is related
 422 to the atmospheric fallout from past nuclear tests and the Chernobyl accident (Perkins and
 423 Thomas, 1980; Duffa, 2001; Zebracki *et al.*, 2013a,b). This background was estimated between
 424 11 and 19 $\text{Bq}\cdot\text{kg}^{-1}$ for the year 2003 (Antonelli *et al.*, 2008; Eyrolle *et al.*, 2012) and between 3
 425 and 11 $\text{Bq}\cdot\text{kg}^{-1}$ for the year 2018 (Thollet *et al.*, 2018). Consequently, the variations of the
 426 minimal and maximal values of C_{soil} for the period 2003 to 2018 can be described by two
 427 exponential relations with an effective decay period of 7 years for the minimal values
 428 ($C_{\text{soil,MIN}}(y) = 11 \cdot e^{-0.1 \cdot (y-2003)}$) and of 16 years for the maximal values ($C_{\text{soil,MAX}}(y) = 19 \cdot$
 429 $e^{-0.042 \cdot (y-2003)}$) with y the considered year. These values are within the range of the values
 430 published in the scientific literature (Garcia-Sanchez, 2008). They are faster than the radioactive
 431 decay period of ^{137}Cs (30.2 years) because they aggregate the radioactive decay with several
 432 transfer processes such as wash-off, erosion, infiltration, etc...

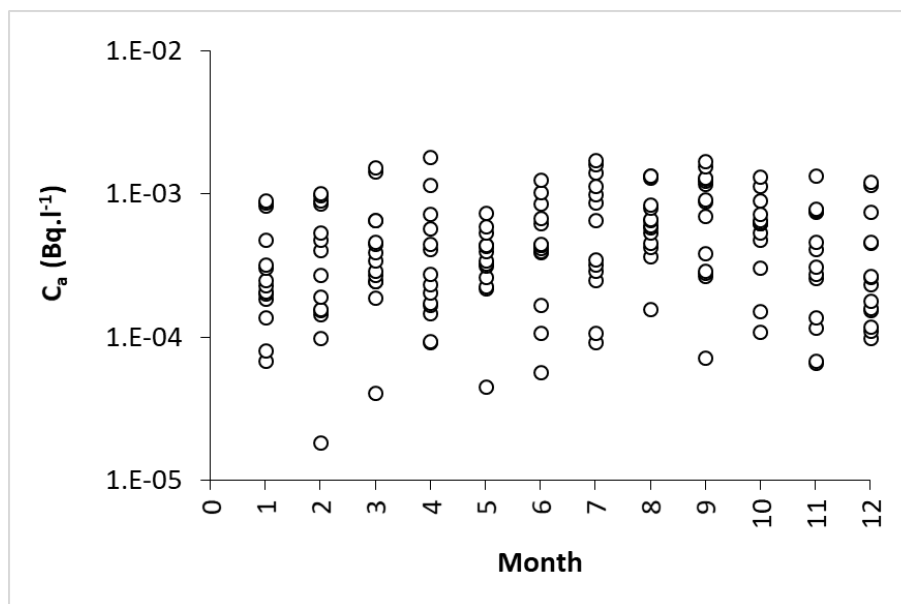
433 The statistical distribution of C_{soil} between 2015 and 2018 was determined by discretizing these
 434 two curves with a yearly time step. For each year, the interval between the minimal and maximal
 435 values was discretized into 20 intervals with the assumption of uniform distribution. These steps
 436 provided a dataset of 260 soil activities which was statistically described by a log-normal
 437 distribution with $GM(C_{\text{soil}}) = 9.8 \text{ Bq}\cdot\text{kg}^{-1}$ and $GSD(C_{\text{soil}}) = 1.46$ ($R^2 = 0.99$).

438 For each water flow rate, the distribution of C_{soil} was scanned between its 2th and 98th percentiles
439 which were 4.5 and 21.3 Bq.kg⁻¹.

440

441 3.5 Statistical distribution of the industrial liquid discharges of ¹³⁷Cs

442 The main anthropogenic source of ¹³⁷Cs liquid discharges into the Rhône is the Marcoule
443 spent nuclear fuel reprocessing plant which discharges one order of magnitude more than the
444 other nuclear facilities along the Rhône River (Charmasson, 1998; Rolland, 2006). For the
445 period 2005 to 2018, the fluxes of ¹³⁷Cs monthly discharged by the Marcoule center ranged
446 from 10² to 10⁴ MBq.month⁻¹. Considering the average monthly water flow rates and noting
447 that the Marcoule center is not authorized to discharge when the water flow rate of the Rhône
448 exceeds 4000 m³.s⁻¹ at its lower part (Zebracki *et al.*, 2015), these releases lead to added
449 monthly activities ranging between 2·10⁻⁴ and 2·10⁻³ Bq.l⁻¹ over the period 2005-2019 (Figure
450 7).



451

452 Figure 7 : Theoretical average monthly concentrations of ¹³⁷Cs added by the liquid discharges
453 of the Marcoule Center

454 Figure 7 shows that the variability of the added concentrations from industries does not depend
455 on the month that is suggested to consider the entire variability whatever the river discharge.
456 This variability is represented by a log-normal law defined by $GM(C_D) = 3.9 \cdot 10^{-4}$ Bq.l⁻¹ and
457 $GSD(C_D) = 2.43$ ($R^2 = 0.99$).

458 For each water flow rate, the distribution of C_D was scanned between the 2th and the 98th
 459 percentiles which are $6.23 \cdot 10^{-5}$ and $2.40 \cdot 10^{-3} \text{ Bq.l}^{-1}$.

460

461 4 Results

462

Table 2: Summary of the input parameters

Parameter	Law	Range	N ^(*)
δ	n.r	1.96 μm	n.r
$K_{a\delta}$	n.r	$68 \cdot 10^4 \text{ l.kg}^{-1}$	n.r
Q	n.r	0 – 6000 $\text{m}^3 \cdot \text{s}^{-1}$	40
[SS]	Conditional log-normal as a function of Q $GM([SS] Q) = 2.13 \cdot e^{1.5 \cdot 10^{-3} \cdot Q}$ $GSD([SS] Q) = 1.56 \cdot e^{0.0002 \cdot Q}$	2 th ([SS] Q) - 98 th ([SS] Q)	10
f_c	Discussed in results section	See results section	n.r
r_{50}	Conditional log-normal as a function of Q $GM(r_{50} Q) = 2.12 \cdot 10^{-6} \cdot Q^2 - 7.96 \cdot 10^{-3} \cdot Q + 13$ If ($Q \leq 3000$) $\Rightarrow GSD(r_{50} Q) = 1.2$ If ($Q > 3000$) $\Rightarrow GSD(r_{50} Q) = (Q - 3000) \cdot \frac{0.8}{3000}$	2 th ($r_{50} Q$) - 98 th ($r_{50} Q$)	10
C_{soil}	Log-normal $GM(C_{soil}) = 9.8 \text{ Bq.kg}^{-1}$ $GSD(C_{soil}) = 1.46$	4.5 – 21.3 Bq.kg^{-1}	10
Ca	Log-normal if $Q < 4000 \text{ m}^3 \cdot \text{s}^{-1}$ $GM(Ca) = 3.9 \cdot 10^{-4} \text{ Bq.l}^{-1}$ $GSD(Ca) = 2.43$ if $Q > 4000 \text{ m}^3 \cdot \text{s}^{-1}$ then $C_a = 0 \text{ Bq.l}^{-1}$	$6.2 \cdot 10^{-5} - 2.4 \cdot 10^{-3}$ Bq.l^{-1}	10

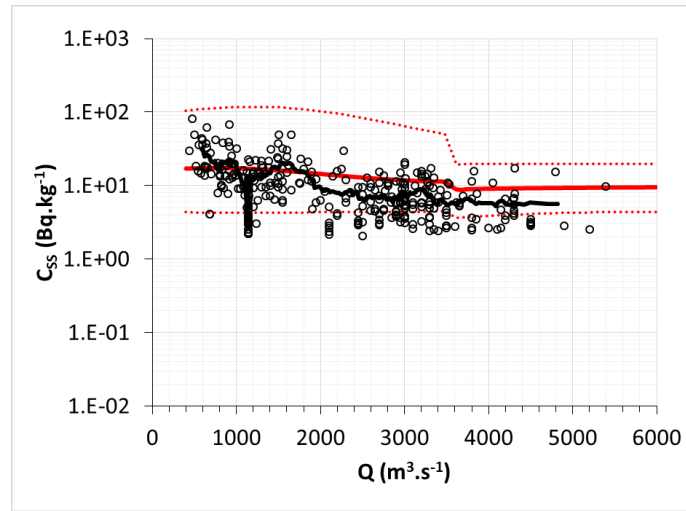
463 ^(*)N is the number of intervals for scanning the statistical distributions between their 2th and 98th
 464 percentiles. For each distribution, N was determined incrementally until no significant change was
 465 observed.

466 n.r: non relevant

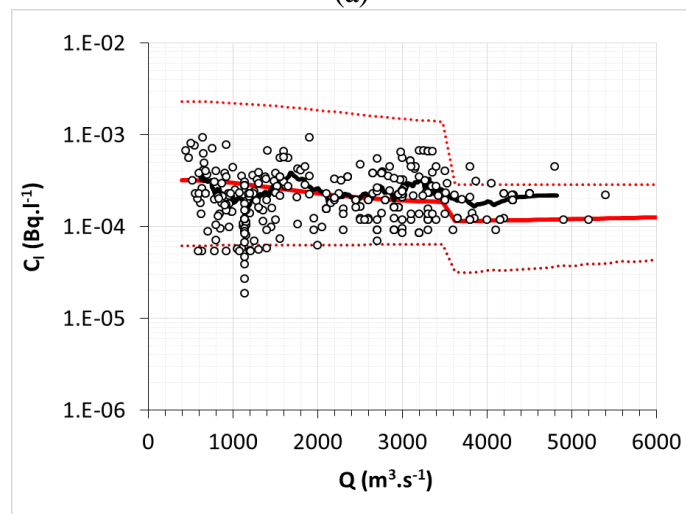
467

468 Table 2 summarizes the input parameters applied for the calculations and Figure 8 compares,
 469 as a function of the river discharge, the raw values (points) and sliding geometric means (black
 470 lines) of the particulate and dissolved concentrations and K_d of ^{137}Cs to their modelled
 471 conditional geometric means (red lines) and modelled conditional minimum and maximum
 472 values (dashed red lines).

473
474

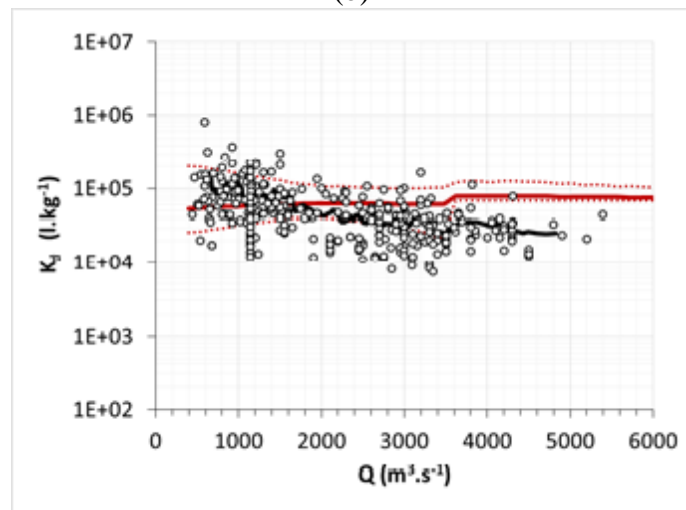


(a)



(b)

475
476



(c)

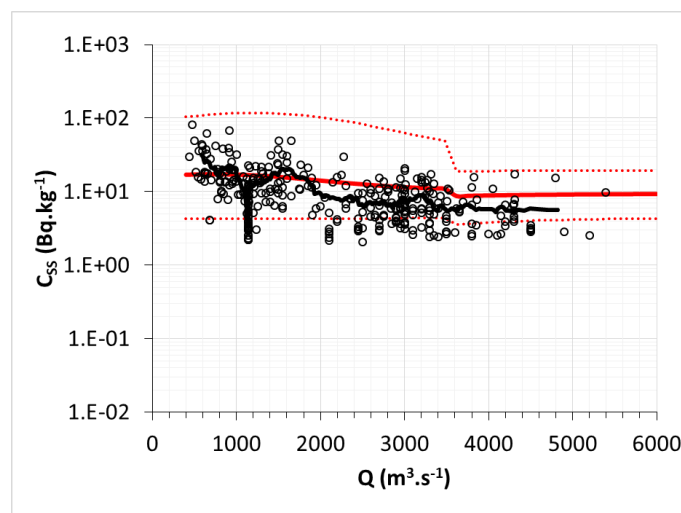
477
478
479
480
481
482
483
484

Figure 8: C_{SS} , C_I and K_d of ¹³⁷Cs: raw values (open circles) and sliding geometric means (black full lines) measured at the SORA station from 2005 to 2018 vs conditional geometric means (red full lines) and conditional minimum and maximum values (red dashed lines) modelled with the parameters of Table 2

485 Figure 8 (a) and (b) show that, without any calibration, the variabilities and the mean values
 486 given by the model for the particulate and liquid concentrations are very close to those
 487 measured: less than a factor of 2 on average. The modelled variability of K_d (Figure 8c) is in
 488 the same range as those measured when the water flow rates are less than $2000 \text{ m}^3 \cdot \text{s}^{-1}$. Beyond
 489 that, the model underestimates the variability and overestimates the mean values of K_d and the
 490 first idea that comes to mind to improve the modelling is to reduce $K_{d\delta}$ which seems closer to
 491 $20\text{-}30 \cdot 10^3 \text{ l} \cdot \text{kg}^{-1}$ than to $68 \cdot 10^3 \text{ l} \cdot \text{kg}^{-1}$. If this change effectively improves the modelling of K_d
 492 for water flow rates greater than $2000 \text{ m}^3 \cdot \text{s}^{-1}$, it induces also an underestimation of the
 493 particulate activities and K_d at lower water flow rates.

494 Therefore, reducing $K_{d\delta}$ is not the right way to improve the modelling of K_d over the entire
 495 range of water flow rates because this improvement requires increasing the dissolved activities
 496 without modifying the particulate ones. In practice, the only way to obtain this result is to
 497 introduce a colloidal pumping. Indeed, the modelling of the mean and the variability of K_d
 498 becomes correct over the entire range of water flows by applying $[\text{SC}] = \frac{f_c}{100} \cdot [\text{SS}]$ with $f_c \approx 3\%$
 499 (Figure 9).

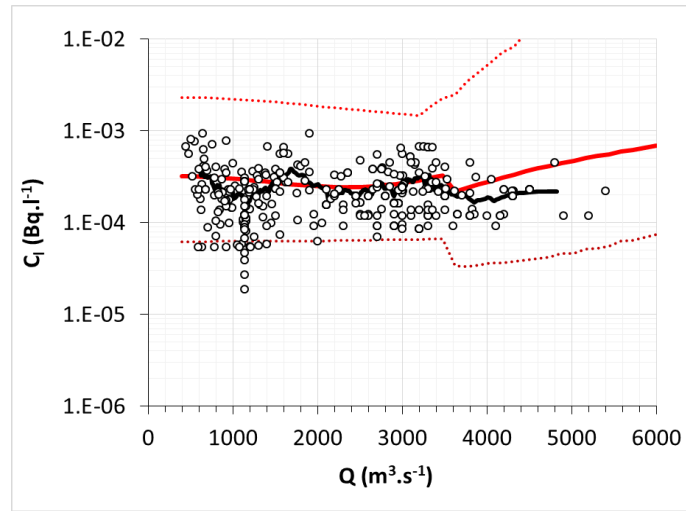
500



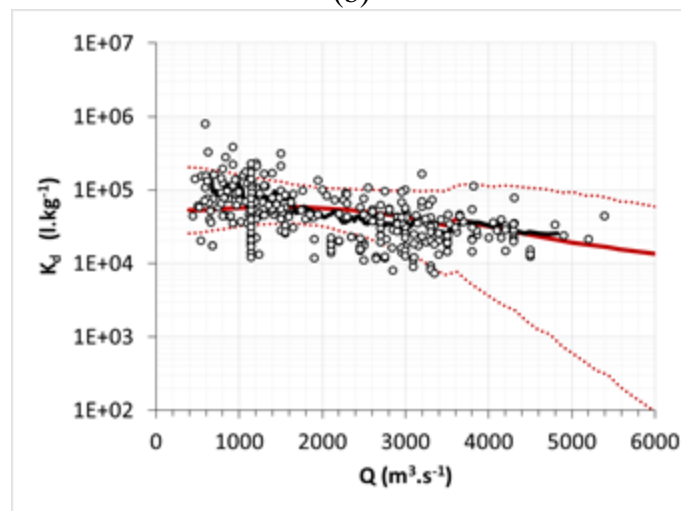
(a)

501
 502

503
504



(b)

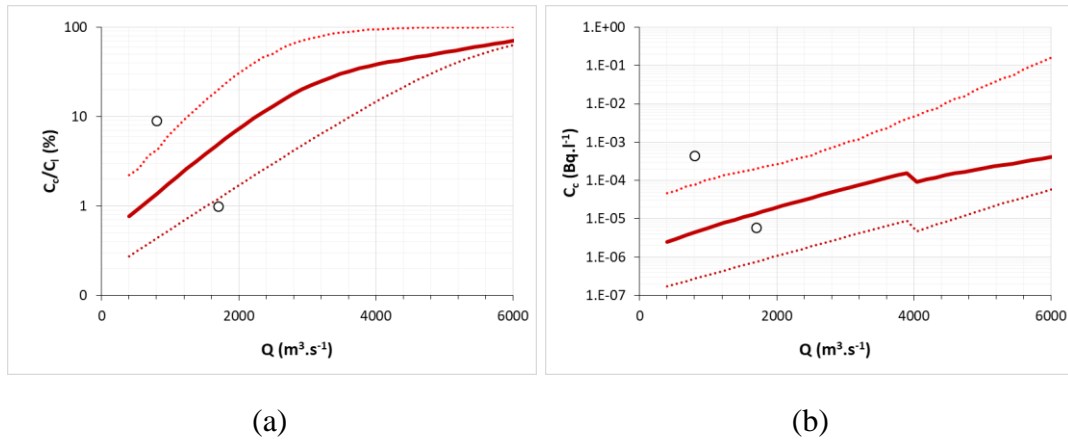


(c)

505
506
507
508
509
510
511
512

Figure 9 : C_{SS} , C_I and K_d of ^{137}Cs : raw values (open circles) and sliding geometric means (black full lines) measured at the SORA station from 2005 to 2018 vs conditional geometric means (red full lines) and conditional minimum and maximum values (red dashed lines) modelled with the parameters of Table 2 and $[\text{SC}] = 0.03 \cdot [\text{SS}]$

513 The small amount of data available on the Rhône colloids contents are consistent with $f_c \approx 3\%$
514 and support the hypothesis of a colloidal pumping effect. Slomberg *et al.* (2016) measured a
515 colloidal content of 1% for a suspended load of 50 mg.l^{-1} and the modelled ^{137}Cs concentrations
516 in colloids (C_c , Eq. 18) are in agreement with measurements performed at the SORA station
517 by Eyrolle and Charmasson (2004) (Figure 10).



518

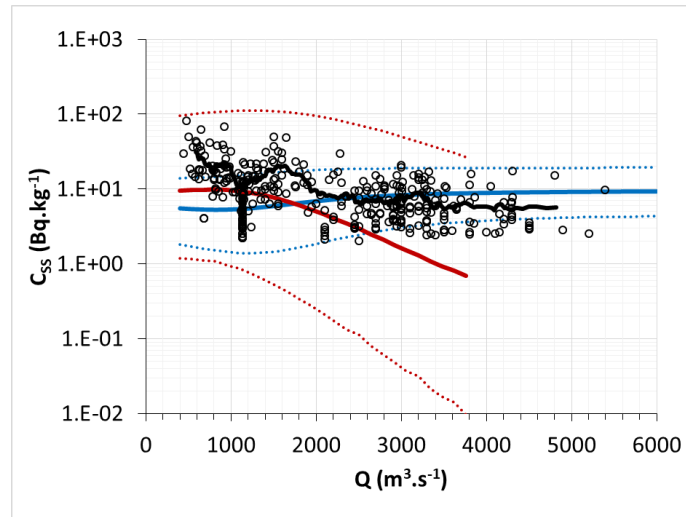
519

520 Figure 10 : C_c/C_1 and C_c : data measured at the SORA station by Eyrolle and Charmasson
 521 (2004) (open circles) vs conditional geometric means (red full lines) and conditional
 522 minimum and maximum values (dashed red lines) modelled with the parameters of Table 2
 523 and $[SC] = 0.03 \cdot [SS]$
 524

525 Figure 10 shows that the contribution of the colloidal fraction to the liquid ^{137}Cs concentration
 526 becomes significant (C_c/C_1 mean $> 10\%$) when the river discharge exceeds $2000\text{ m}^3\cdot\text{s}^{-1}$ and
 527 suggests it can become dominant above $4000\text{ m}^3\cdot\text{s}^{-1}$. The threshold of $2000\text{ m}^3\cdot\text{s}^{-1}$ corresponds
 528 to a change in the hydro-sedimentary regime of the Rhône River which is illustrated by the
 529 dynamic of the r_{50} according to the water flow which increases faster above $2000\text{ m}^3\cdot\text{s}^{-1}$ (Figure
 530 6). The aim of this paper is not to discuss the origin of this change, also observed on the dynamic
 531 of $[SS]$ by Sadaoui *et al.* (2016), but it may correspond to a change in the erosion regime of the
 532 river with an erosion of the stocks of deposited sediments. In this case, two hypotheses could
 533 explain the colloidal pumping of ^{137}Cs in the Rhône River: 1) colloids mainly originate from
 534 the erosion of bottom sediments and/or river banks and they adsorb ^{137}Cs from industrial
 535 releases once they are in the water column, 2) colloidal forms of ^{137}Cs are directly produced by
 536 the erosion of ^{137}Cs sedimentary stocks accumulated since the previous erosive event. This last
 537 hypothesis is however not confirmed by the data and the model. Indeed, the remobilisation of
 538 colloidal forms of ^{137}Cs from sedimentary stocks would lead theoretically to an increase of the
 539 activities of ^{137}Cs within the filtered waters which is not supported by the measured
 540 concentrations which remain almost constant within their variability range, whatever the water
 541 flow rate (Figure 9b). Besides, this hypothesis would require introducing into the model a
 542 secondary source term which does not seem necessary here.

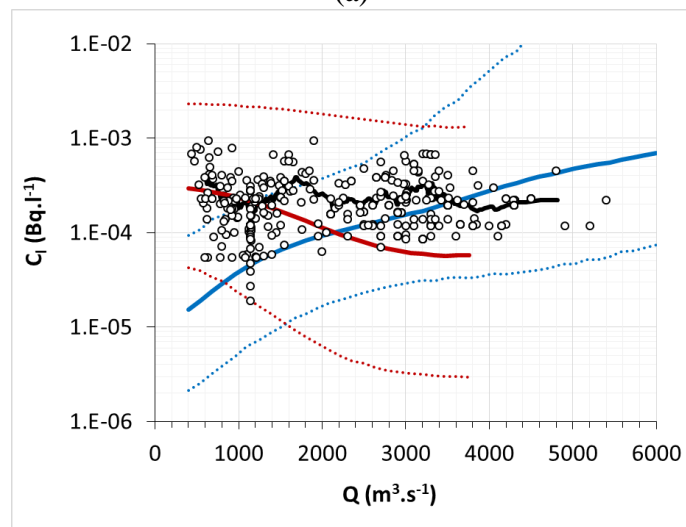
543 On another hand, the importance to consider the catchment background is well demonstrated
 544 by comparing the variabilities of the solid and liquid ^{137}Cs concentrations and of the K_d
 545 specifically to the background of the watershed and the industrial discharges (Eq. 26)
 546 respectively represented on Figure 11 by the blue and red lines.

547
548



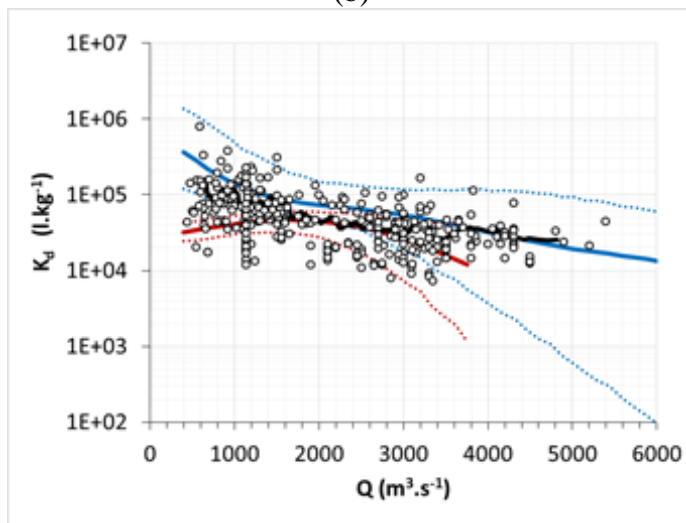
(a)

549
550



(b)

551
552



(c)

Figure 11 : C_{SS} , C_l and K_d of ^{137}Cs : raw values (open circles) and sliding geometric means (black full lines) measured at the SORA station from 2005 to 2018 vs conditional geometric means (full lines) and conditional minimum and maximum values (dashed lines) modelled with the parameters of Table 2 and $[\text{SC}] = 0.03 \cdot [\text{SS}]$ for the contributions of the background of the watershed (blue lines) and the industrial discharges (red lines)

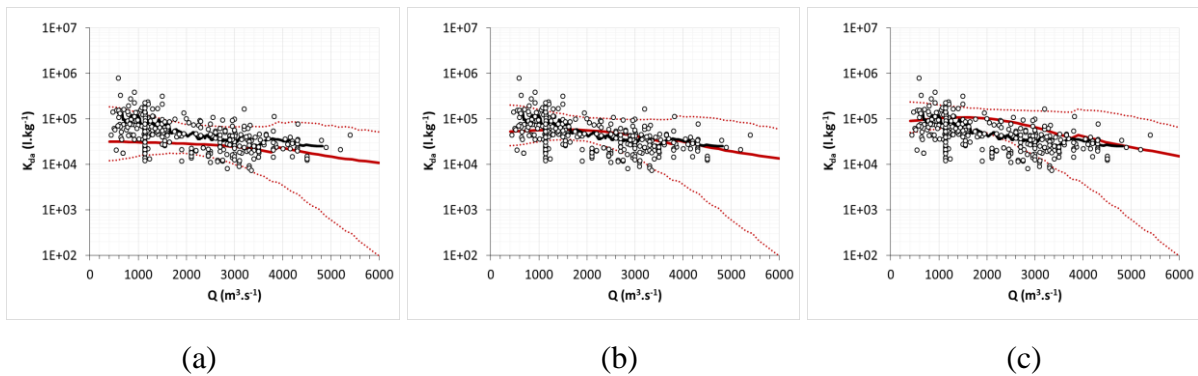
558 For C_{SS} , (Figure 11a) the industrial discharges and background contributions are close below
 559 $2000 \text{ m}^3 \cdot \text{s}^{-1}$. Above this water flow rate, the background contribution becomes more and more
 560 dominant because of the increase in $[SS]$ and r_{50} . Figure 11b shows that C_I is essentially linked
 561 to the anthropogenic discharges at low water flow rates and to the catchment background after
 562 $2000 \text{ m}^3 \cdot \text{s}^{-1}$. Figure 11c shows that the K_d of the anthropogenic releases is lower than the K_d of
 563 the geochemical background regardless of the river discharge. Above $4000 \text{ m}^3 \cdot \text{s}^{-1}$, where there
 564 are no anthropogenic discharges (see 3.4), the model reproduces correctly the mean K_d that
 565 translates the strong dependence of this variable to the catchment background.

566

567 5 Discussion

568 At this stage, one must remember that the model very faithfully reproduces the average
 569 trends and variabilities of C_{SS} , C_I and K_d of ^{137}Cs as a function of the water flow rate of the
 570 Rhône and without requiring an additional calibration than that of the colloidal fraction in the
 571 suspension. This result is all the most surprising since no variabilities were considered for the
 572 chemical parameters of ^{137}Cs , δ and $K_{d\delta}$, for which we directly considered the values obtained
 573 by Abril (1998b) from the laboratory experiments of He and Walling (1996) on soil and
 574 sediment particles totally independent from the Rhône.

575 To better appreciate the representativeness of these two parameters, Figure 12 presents the
 576 changes in K_d depending on whether $K_{d\delta} = 30 \cdot 10^3$, $68 \cdot 10^3$ and $140 \cdot 10^3 \text{ l} \cdot \text{kg}^{-1}$.



577

578

579 Figure 12 : Variabilities of K_d as a function of the river discharge for $\delta = 1.96 \mu\text{m}$ and $K_{d\delta} =$
 580 $30 \cdot 10^3$ (a), $68 \cdot 10^3$ (b) and $140 \cdot 10^3$ (c) $\text{l} \cdot \text{kg}^{-1}$.

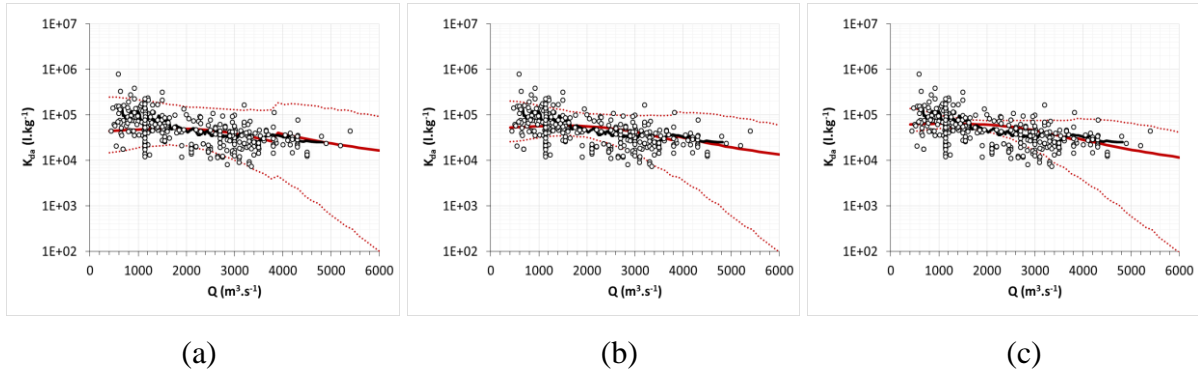
581 (Open circles: data measured at the SORA station from 2005 to 2018; Black full line: sliding
 582 geometric mean of raw data; Red full line: modelled geometric means; Red dashed lines: modelled
 583 minimal and maximal values)

584

585 $K_{d\delta}$ moves the geometric means vertically without significantly affecting the amplitude of the
 586 variability. The best results are obtained with the $K_{d\delta}$ value of Abril (1998b) which highlights

587 its strong representativeness, especially since a change less than a factor of two is enough to
 588 reduce the accuracy of the modelled mean curve.

589 Figure 13 presents the changes in K_d depending on whether $\delta = 1, 1.96$ and $4 \mu\text{m}$.



590

591

592 Figure 13: Variabilities of K_d as a function of the river discharge for $\delta = 1$ (a), 1.96 (b) and 4
 593 (c) μm and $K_{d\delta} = 68 \cdot 10^3 \text{ l.kg}^{-1}$.

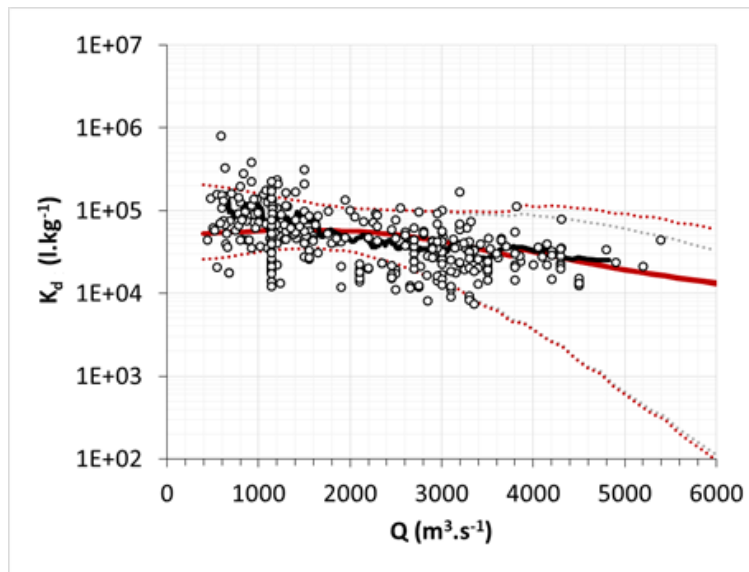
594 (Open circles: data measured at the SORA station from 2005 to 2018; Black full line: sliding
 595 geometric mean of raw data; Red full line: modelled geometric means; Red dashed lines: modelled
 596 minimal and maximal values)

597

598 Compared to $K_{d\delta}$, Figure 13 shows that the variations of δ affect the amplitude of the variability
 599 of K_d without significantly modifying the geometric means. The lower δ is, the greater is the
 600 variability of K_d because the contribution of the non-exchangeable fractions (representative of
 601 the geochemical background of the watershed) decreases at the same time as δ .

602 Comparison between the modelled variability and the dataset shows that δ cannot be greater
 603 than the value given by Abril (1998b) and suggests that the variability of the dataset is better
 604 represented by $\delta = 1 \mu\text{m}$. Consequently, an uncertainty can be assumed for δ ($1 < \delta < 2 \mu\text{m}$) but
 605 it remains limited to a factor of 2, which once again confirms the strong representativeness of
 606 the value published by Abril (1998b).

607 For water flow rates greater than $3000 \text{ m}^3 \cdot \text{s}^{-1}$ the main uncertainty is linked to the lack of data
 608 for r_{50} (cf. 3.5). If the right agreement between the modelled and measured geometric means
 609 allows to consider as acceptable the Equation 29 for the evolution of $\text{GM}(r_{50}|Q)$, it remains an
 610 uncertainty about the effect of the strong variability associated to r_{50} for this range of water flow
 611 rates (cf. 3.5). To assess this effect, Figure 14 compares the results obtained with this variability
 612 to those obtained with the reduced variability of r_{50} defined by a $\text{GSD}(r_{50}|Q)$ decreasing from
 613 1.2 for $Q = 3000 \text{ m}^3 \cdot \text{s}^{-1}$ to 1 for $Q = 6000 \text{ m}^3 \cdot \text{s}^{-1}$ (Figure 6).



614 Figure 14 : K_d of ^{137}Cs modelled with a high variability of r_{50} (red lines) vs modelling with a
 615 low variability of r_{50} (grey lines)
 616 (Open circles: data measured at the SORA station from 2005 to 2018; Black full line: sliding
 617 geometric mean of raw data; Red full line: modelled geometric means; Red and Grey dashed lines:
 618 modelled minimal and maximal values)
 619
 620

621 This figure shows few effects of the variability of r_{50} on the modelling of the K_d distributions
 622 for water flow rates larger than $3000 \text{ m}^3 \cdot \text{s}^{-1}$. Just appears a light decreasing of the maximal K_d
 623 values explained by the greater minimal particle sizes induced by the lower variability.
 624 However, the effects are limited and quasi-invisible for the minimal K_d values. For water flow
 625 rates larger than $3000 \text{ m}^3 \cdot \text{s}^{-1}$, this behaviour of the model is essentially explained by the
 626 colloidal loads which increases at the same time that the suspended load. When the water flow
 627 rate increases, the modelled K_d values are thus more and more controlled by the colloidal
 628 pumping and less and less by the particle size as it is shown by comparison of Figure 8c (without
 629 colloidal pumping) and Figure 9c (with colloidal pumping). From an operational point of view
 630 this result suggests that the attention payed to the colloidal phases of TMs is all the more
 631 important that the water flow rate is strong.

632 These results highlight both the correct behaviour of the model and its robustness. They
 633 motivate to extend its application to other TMs than ^{137}Cs and to rivers other than the Rhône,
 634 the input data being the average concentrations of TMs in the soils of the watershed, the
 635 anthropogenic discharges and the load and the average size of the SS as well as the colloidal
 636 load as a function of the water flow. Under the present form of the model, the main constraints
 637 are the checking of the mixing conditions and the transit time since the anthropogenic
 638 discharges and, probably the most important, the knowledge for each TM of δ , the thickness of
 639 the exchange layer and $K_{d\delta}$, its specific K_d . The results obtained here suggest that these two
 640 parameters could have a generic representativeness if they are determined independently of the

641 hydro-sedimentary conditions, which would be possible from laboratory experiments, by
642 adjustment with *in-situ* data and/or with geochemical models.
643

644 From a general point of view, this work demonstrated that the variability of the K_d of SS in
645 rivers does not only depend on the chemical conditions but also and rather on the hydro-
646 sedimentary conditions as previously shown by Cho et al. (2016), the discharges and the context
647 of the watershed. These considerations suggest that this modelling approach could contribute
648 to the prediction of the impact of changes in erosion regimes of rivers and watersheds on the
649 TMs transfers in rivers, for example in a context of climate change. In this case, the model will
650 have to be coupled with hydro-sedimentary models capable of predicting the impact of these
651 changes on the hydro-sedimentary properties of the river.
652

653 **6 Conclusions**

654 This paper reports an adaptation of the model of Abril and Fraga (1996) to model the K_d of
655 trace metals in suspended sediments of rivers as a function of the river discharge, the load and
656 the mean particle size of suspended sediments, the colloidal pumping effect, the geochemical
657 and anthropogenic backgrounds of the watershed and the industrial discharges. The application
658 to the case of ^{137}Cs in the Rhône River highlights the fact that the variability of the ^{137}Cs K_d is
659 essentially explained by the geochemical and anthropogenic backgrounds of the catchment, the
660 industrial discharges and the changes, as a function of the river discharge, of the load and mean
661 size of suspended sediments. This illustrates how much the variability of K_d of suspended
662 sediments is not dependent only on chemical processes and must be considered from a larger
663 point of view, that include the hydro-sedimentary processes and the catchment context. This is
664 not very surprising considering that the non-exchangeable fractions of trace metals are poorly
665 reactive to changes in chemical conditions and that, at the temporal and spatial scales of a river,
666 the impact of these changes remains limited compared to the hydro-sedimentary forcing. These
667 results highlight also the strong representativeness of the specific chemical parameters such as
668 the parameters δ and $K_{d\delta}$ of the Abril and Fraga Model and lead us to suggest focalizing the
669 geochemical models of K_d on the determination of this kind of parameters or equivalent ones.

670 **Acknowledgements**

671 The present work was carried out within the framework of the GGP collaboration
672 program between EDF and IRSN and the authors thank these institutions for their support and
673 funding.
674

675 **References**

- 676 Abarca M., Guerra P., Arce G., Montecinos M., Escauriaza C., Coquery M., Pastén P. (2017).
677 Response of suspended sediment particle size distributions to changes in water chemistry at
678 an Andean mountain stream confluence receiving arsenic rich acid drainage. *Hydrological*
679 *Processes*, 31, pp. 296-307.
680
- 681 Abril J.M., Fraga E. (1996). Some physical and chemical features of the variability of K_d
682 distribution coefficients for radionuclides. *J. Environ. Radioactivity* 30(3), pp. 253-270.
683
- 684 Abril J.M. (1998)a. Basic Microscopic Theory of the Distribution, Transfer and Uptake Kinetics
685 of Dissolved Radionuclides by Suspended Particulate Matter - Part I: Theory Development.
686 *J. Environ. Radioactivity*, 41(3), pp. 307-324.
687
- 688 Abril J.M. (1998)b. Basic Microscopic Theory of the Distribution, Transfer and Uptake
689 Kinetics of Dissolved Radionuclides by Suspended Particulate Matter — Part II:
690 Applications. *J. Environ. Radioactivity*, 41(3), pp. 325-342.
691
- 692 Adell W. (2013). Caractérisation de la distribution granulométrique des particules en transit
693 dans le Rhône aval au cours du temps et des conditions hydrologiques. Rapport stage Master
694 Sciences de l'Eau et de l'Environnement - Hydrosystèmes et Bassins Versants : diagnostic
695 et risque environnemental. 51 pp.
696
- 697 Allison J.D., Allison T.L. (2005). Partition coefficient for metals in surface water, soil, and
698 waste. EPA/600/R-05/074 Washington, DC, United States.
699
- 700 Antonelli C., Eyrolle F., Rolland B., Provansal M., Sabatier F. (2008). Suspended sediment and
701 ¹³⁷Cs fluxes during the exceptional December 2003 flood in the Rhône River, southeast
702 France. *Geomorphology*, 95, pp. 350-360.
703
- 704 Apte S.C., Benko W.I., Day G.M. (1995). Partitioning and complexation of copper in the Fly
705 River, Papua New Guinea. *Journal of Geochemical Exploration* 52(1-2), pp. 67-79.
706
- 707 Barreto S.R.G., Barreto W.J., Deduch E.M. (2011). Determination of partition coefficients of
708 metals in natural tropical water. *Clean Soil, Air, Water*, 39(4), pp. 362-367.
709
- 710 Benoit G., Rozan T.F. (1999). The influence of size distribution on the particle concentration
711 effect and trace metal partitioning in rivers. *Geochimica et Cosmochimica Acta*, 63(1), pp.
712 113-127.
713
- 714 Boszke L., Kowalski A., Siepak J. (2004). Grain size partitioning of mercury in sediments of
715 the middle Odra River (Germany/Poland). *Water Air and Soil Pollution*, 159, pp. 125-138.
716
- 717 Boyer P., Wells C., Howard B. (2018). Extended K_d distributions for freshwater environment.
718 *J. Environ. Radioactivity*, 192, pp. 128-142.
719
- 720 Cameron, D. A., Klute, A. (1977). Convective-dispersive transport with a combined kinetic and
721 equilibrium model, *Water Resour. Res.*, 13, pp. 183-188.
722

- 723 Charmasson, S. (1998). Cycle du combustible nucléaire et milieu marin – Devenir des effluents
724 rhodaniens en Méditerranée et des déchets immergés en Atlantique nord-est. Thèse de
725 doctorat d'état, Université Aix-Marseille II, 365 pp.
726
- 727 Cho E., Arhonditsis G.B., Khim J., Chung S., Heo T.Y. (2016). Modelling metal-sediment
728 interaction processes: Parameter sensitivity assessment and uncertainty analysis.
729 Environmental Modelling & Software, 80, pp. 159-174.
730
- 731 Ciffroy P., Siclet F., Humbert B. (1995). In situ determination of 110m-Ag, 58-Co, 60-Co and
732 54-Mn distribution between freshwater and suspended matter. International Symposium on
733 Environmental Impact of Radioactive Releases, IAEA-SM-339/90, pp. 299-309.
734
- 735 Ciffroy P., Durrieu G., Garnier J-M. (2009). Probabilistic distribution coefficients (Kds) in
736 freshwater for radioisotopes of Ag, Am, Ba, Be, Ce, Co, Cs, I, Mn, Pu Ra, Ru, Sb, Sr and
737 Th. – Implications for uncertainty analysis of models simulating the transport of
738 radionuclides in rivers, J. Environ. Radioactivity, 100(9), pp. 785-794.
739
- 740 Crosby B., Whipple K. (2004). Surface Processes and Landscape Evolution. Massachusetts
741 Institute of Technology: MIT OpenCourseWare.
- 742 Dominik J., Vignati D.A.L., Pereira de Abreu M.-H., Kottelat R., Szalinska E., Bas B.,
743 Bobrowski A. (2007). Speciation and environmental fate of chromium in rivers
744 contaminated with tannery effluents. Engineering in Life Sciences, 7(2), pp. 155-169.
745
- 746 Duffa C. (2001). Répartition du plutonium et de l'américium dans l'environnement terrestre de
747 la basse vallée du Rhône. Thèse de doctorat, Université Aix-Marseille III, 179 pp.
748
- 749 Duc T.A., Loi V.D., Thao T.T. (2013). Partition of heavy metals in a tropical river system
750 impacted by municipal waste. Environmental Monitoring and Assessment, 185, pp. 1907-
751 1925.
752
- 753 Durrieu G., Ciffroy P., Garnier J.M. (2006). A weighted bootstrap method for the determination
754 of probability density functions of freshwater distribution coefficients (Kds) of Co, Cs, Sr
755 and I radioisotopes. Chemosphere, 65(8), pp. 1308-1320.
756
- 757 Eyrolle F., Charmasson S. (2004). Importance of colloids in the transport within the dissolved
758 phase (<450 nm) of artificial radionuclides from the Rhône river towards the Gulf of Lions
759 (Mediterranean Sea). J. Environ. Radioactivity, 72, pp. 273-286.
760
- 761 Eyrolle F., Duffa C., Antonelli C., Rolland B., Leprieur F. (2006). Radiological Consequences
762 of the extreme flooding on the lower course of the Rhône valley (December 2003, South
763 East France). Science of the Total Environment, 366, pp. 427-438.
764
- 765 Eyrolle F., Radakovitch O., Raimbault P., Charmasson S., Antonelli C., Ferrand E., Aubert D.,
766 Raccasi G., Jacquet S., Gurriaran R. (2012). Consequences of hydrological events on the
767 delivery of suspended sediment and associated radionuclides from the Rhône River to the
768 Mediterranean Sea. J Soils Sediments, 12, pp. 1479-1495.
769
- 770 Eyrolle F., Lepage H., Antonelli C., Morereau A., Cossonnet C., Boyer P., Gurriaran R. (2020).
771 Radionuclides in waters and suspended sediments in the Rhône River (France) - current

772 contents, anthropic pressures and trajectories. *Science of the Total Environment*, 723, pp.
773 137-873.

774

775 Fan J., Zhao G., Sun J. (2017). Binary component sorption of cadmium, and copper ions onto
776 Yangtze River sediments with different particle sizes. *Sustainability*, 9, 2089, 16 pp.
777

778 Garneau C., Sauvage S., Sanchez-Perez J.M., Lofts S., Brito D., Neves R., Probst A. (2017).
779 Modelling trace metal transfer in large rivers under dynamic hydrology: A coupled
780 hydrodynamic and chemical equilibrium model. *Environmental Modelling & Software*, 89,
781 pp. 77-96.

782

783 Garcia-Sanchez L. (2008). Watershed wash-off of atmospherically deposited radionuclides:
784 review of the fluxes and their evolution with time. *J. Environ. Radioactivity*, 99, pp. 563-
785 573.

786

787 Garcia-Sanchez L., Loffredo N., Mounier S., Martin-Garin A., Coppin F. (2014). Kinetics of
788 selenate sorption in soil as influenced by biotic and abiotic conditions: a stirred flow-through
789 reactor study. *J. Environ. Radioactivity*, 138, pp. 38-49.
790

791 Gibbs R.J., Matthews M.D., Link D.A. (1971). The relationship between sphere size and
792 settling velocity. *Journal of Sedimentary Petrology*, 41, pp. 7-18.
793

794 Goldberg S., Criscenti L.J., Turner D.R., Davis J.A., Cantrell K.J. (2007). Adsorption –
795 desorption processes in subsurface reactive transport Modelling. *Vadose Zone J.*, 6, pp. 407-
796 435.
797

798 He Q., Walling D.E. (1996). Interpreting particle size effects in the adsorption of ¹³⁷Cs and
799 unsupported ²¹⁰Pb by mineral soils and sediments. *J. Environ. Radioactivity*, 30(2), pp. 117-
800 137.
801

802 Heling R., Raskob W., Popov A., Zheleznyak M. (1999). Overview of hydrological dispersion
803 module - HDM of RODOS. RODOS Report Decision Support for Nuclear Emergencies.
804 RODOS-WG4-TN(99)18.
805

806 Honeyman B.D., Santschi P.H. (1988). Metals in aquatic systems - Predicting their scavenging
807 residence times from laboratory data remains a challenge. *Environ. Sci. Technol.*, 22(8), pp.
808 862-871.
809

810 Ilina S.M., Marang L., Lourino-Cabana B., Eyrolle F., Boyer P., Coppin F., Sivry Y., Gélabert
811 A., Benedetti M.F. (2020). Solid/liquid ratios of trace elements and radionuclides during a
812 Nuclear Power Plant liquid discharge in the Seine River: Field measurements vs
813 geochemical modelling. *J. Environ. Radioactivity*, 220-221, 10 pp.
814

815 Jweda J., Baskaran M., van Heed E., Schweitzer L. (2008). Short-lived radionuclides (⁷Be and
816 ²¹⁰Pb) as tracers of particle dynamics in a river system in southeast Michigan. *Limnology*
817 and *Oceanography*, 53(5), pp. 1934-1944.
818

819 Li Y.H., Burkhardt L., Buchholtz M., O'Hara P., Santschi P.H. (1984). Partition of radiotracers
820 between suspended particles and seawater. *Geochimica and Cosmochimica Acta*, 48, pp.
821 2011-2019.

822
823 Lu Y., Allen H.E. (2001). Partitioning of copper onto suspended particulate matter in river
824 waters. *Science of the Total Environment*, 277, pp. 119-132.
825

826 Müller G., Förstner U. (1968). General Relationship between Suspended Sediment
827 Concentration and Water Discharge in the Alpenrhein and some other Rivers. *Nature*, 217,
828 pp. 244-245.
829

830 Palmateer G.A., McLean D.E., Kutas W.L., Meissner S.M. (1993). Investigations of suspended
831 particulate-bacterial interaction in agricultural drains. *Particulate matter and aquatic*
832 *contaminants*. Boca Raton; CRC Press.
833

834 Payne T.E., Brendler V., Comarmond M.J., Nebelung C. (2011). Assessment of surface area
835 normalisation for interpreting distribution coefficients (K_d) for uranium sorption. *J. Environ.*
836 *Radioactivity*, 102, pp. 888-895.
837

838 Peitzsch M., Kremer D., Kersten M. (2010). Microfungal alkylation and volatilization of
839 selenium adsorbed by goethite. *Environmental Science & Technology* 44(1), pp. 129-135.
840

841 Pérez, F.F., Sweeck, L., Bauwens, W., Van Hees, M., Elskens, M. (2015). Adsorption and
842 desorption kinetics of ^{60}Co and ^{137}Cs in fresh water rivers. *J. Environ. Radioactivity*, 149,
843 pp. 81-89.
844

845 Perkins R.W., Thomas C.W. (1980). Worldwide fallout. Pages 53-82 in W.C. Hanson editor,
846 “Transuranic elements in the environment”, U.S. DOE, USA.
847

848 Reynolds R.A., Stramski D., Wright V.M., Woźniak S.B. (2010). Measurements and
849 characterization of particle size distributions in coastal waters. *Journal of Geophysical*
850 *Research*, 115(8), 19 pp.
851

852 Rolland B. (2006). Transfert des radionucléides artificiels par voie fluviale: conséquences sur
853 les stocks sédimentaires rhodaniens et les exports vers la Méditerranée. Thèse de l’Université
854 Paul Cézanne d’Aix-Marseille, 243 pp.
855

856 Sadaoui M., Ludwig W., Bourrin F., Raimbault P. (2016). Controls, budgets and variability of
857 riverine sediment fluxes to the Gulf of Lions (NW Mediterranean Sea). *J. Hydrol.*, 540, pp.
858 1002-1015.
859

860 Sigg L., Xue H., Kistler D., Schönenberger R. (2000). Size fractionation (dissolved, colloidal
861 and particulate) of trace metals in the Thur River, Switzerland. *Aquatic Geochemistry*, 6, pp.
862 413-434.
863

864 Sheppard S.C., Long J., Sanipelli B., Sohlenius G. (2009). Solid/liquid partition coefficients
865 (K_d) for selected soils and sediments at Forsmark and Laxemar-Simpevarp I. R-09-27, S R
866 (Eds.), Swedish Nuclear Fuel and Waste Management Co, pp. 1402-3091.
867

868 Sheppard S.C., Sohlenius G., Omberg L.G., Borgiel M., Grolander S.N. (2011). Solid/liquid
869 partition coefficients (K_d) and plant/soil concentration ratios (CR) for selected soils, tills and
870 sediments at Forsmark. *Svensk Kärnbränslehantering AB, SKB R-11-24*. Stockholm,
871 Sweden. Report. 77 pp. ISSN 1402-3091.

872
873 Slomberg D.,L., Ollivier P., Radakovitch O., Baran N., Sani-Kast N., Miche H., Borschneck
874 D., Grauby O., Bruchet A., Scheringer M., Labille J. (2016). Characterization of suspended
875 particulate matter in the Rhône River: insights into analogue selection. *Environmental*
876 *Chemistry*, 13(5), pp. 804-815.
877
878 Thollet F., Le Bescond C., Lagouy M., Gruat A., Grisot G., Le Coz J., Coquery M., Lepage H.,
879 Gairoard S., Gattacceca J., Ambrosi J.-P., Radakovitch O. (2018). Observatoire des
880 Sédiments du Rhône. Irstea.
881
882 Tipping E. (1994). WHAMC- a chemical equilibrium model and computer code for waters,
883 sediments, and soils incorporating a discrete site/electrostatic model of ion-binding by humic
884 substances. *Journal of Compute Geoscience*, 20, pp. 973-1023.
885
886 Tomczak W., Boyer P., Krimissa M., Radakovitch O. (2019). K_d distributions in freshwater
887 systems as a function of material type, mass-volume ratio, dissolved organic carbon and pH.
888 *Applied Geochemistry*, 105, pp. 68-77.
889
890 Town R.M., Filella M. (2002). Size fractionation of trace metal species in freshwaters:
891 implications for understanding their behaviour and fate. *Re/Views in Environmental Science*
892 *& Bio/Technology*, 1(4), pp. 277-297.
893
894 Turner A., Millward G.E. (2002). Suspended particles: Their role in estuarine biogeochemical
895 cycles. *Estuarine. Coastal and Shelf Science*, 55, pp. 857-883.
896
897 Vuković Ž., Marković L., Radenković M., Vuković D., Stanković S. (2011). Heavy metal and
898 bacterial pollution of the Sava River in Serbia. *Archives of Industrial Hygiene and*
899 *Toxicology*, 62, pp. 11-16.
900
901 Walling D.E., Moorehead P.W. (1989). The particle size characteristics of fluvial suspended
902 sediment : an overview. *Hydrobiologia*, 176/177, pp. 125-149.
903
904 Walling D.E., Owens P.N., Waterfall B.D., Leeks G.L.G., Wass P.D. (2000). The particle size
905 characteristics of fluvial suspended sediment in the Humber and Tweed catchments, UK.
906 *Science of the Total Environment*, 251/252, pp. 205-222.
907
908 Wang J., Baskaran M., Niedermiller J. (2017). Mobility of ^{137}Cs in freshwater lakes: A mass
909 balance and diffusion study of Lake St. Clair, Southeast Michigan, USA. *Geochimica et*
910 *Cosmochimica Acta* 218, pp. 323-342.
911
912 Warren L.A., Zimmerman A.P. (1994). The influence of temperature and NaCl on cadmium,
913 copper and zinc partitioning among suspended particulate and dissolved phases in an urban
914 river. *Water Research*, 28(9), pp. 1921-1931.
915
916 Xia X.M., Li Y., Yang H., Wu C.Y., Sing T.H., Pong H.K. (2004). Observations on the size
917 and settling velocity distributions of suspended sediment in the Pearl River Estuary, China.
918 *Continental Shelf Research*, 24, pp. 1809-1826.
919
920 Zebracki M., Eyrolle F., Cagnat X., Antonelli C., De Vismes-Ott A., Boullier V. (2013)a.
921 Characterization of naturally occurring radionuclides in the lower part of the Rhône River

- 922 waters (France), preliminary results from suspended sediments monitoring, *Water Resources*
923 *Management VII. WIT Trans. Ecol. Environ.*, 171, pp. 235-245.
- 924
- 925 Zebracki M., Eyrolle-Boyer F., De Vismes-Ott A., Antonelli C., Cagna X., Boullier V. (2013)b.
926 Radionuclide contents in suspended sediments in relation to the flood types in the lower part
927 of the Rhône River. *Procedia Earth and Planetary Science*, 7, pp. 936-939.
- 928
- 929 Zebracki M., Eyrolle-Boyer F., Evrard O., Claval D., Mourier B., Gairoarde S., Cagnat X.,
930 Antonelli C. (2015). Tracing the origin of suspended sediment in a large Mediterranean river
931 by combining continuous river monitoring and measurement of artificial and natural
932 radionuclides. *Science of the Total Environment*, 502, pp. 122-132.
- 933
- 934 Zhang Y., Zhang Y., Yu T. (2013). Quantitative characterization of Cu binding potential of
935 dissolved organic matter (DOM) in sediment from Taihu Lake using multiple techniques.
936 *Frontiers of Environmental Science & Engineering*, 8(5), pp. 666-674.