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## **Modelling of solid / liquid fractionation of trace metals for suspended sediments according to the hydro-sedimentary conditions of rivers - Application to $^{137}\text{Cs}$ in the Rhône River (France)**

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

4  
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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 <sup>137</sup>Cs concentrations measured in the Rhône River (France)  
32       shows that the solid/liquid fractionation of <sup>137</sup>Cs 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.

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## 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),  $^{110m}\text{Ag}$ ,  $^{58,60}\text{Co}$  and  $^{54}\text{Mn}$  (Ciffroy *et al.*, 1995) and  
59  $^{137}\text{Cs}$  and  $^{210}\text{Pb}$  (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  $\mu\text{m}$  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  $\text{Bq}$ .

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).

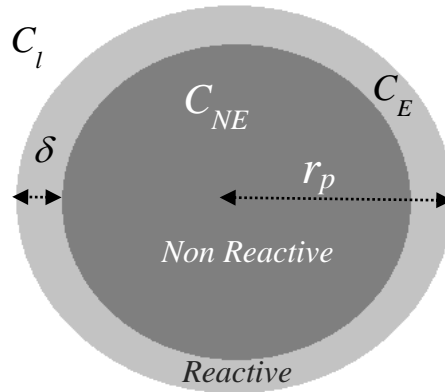
101  
102 In practice,  $K_d$  values are determined by in situ measurements, sorption-desorption experiments  
103 in laboratories and different modelling approaches such as parametric models (Sheppard *et al.*,  
104 2009; Sheppard, 2011), dynamic models (Garcia-Sanchez *et al.*, 2014) and mass-action 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  $^{137}\text{Cs}$  and  $^{210}\text{Pb}$  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  $\delta$  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  $\delta$  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<sub>l</sub>: liquid concentration; C<sub>NE</sub>: non-exchangeable concentration; C<sub>E</sub>: exchangeable concentration; r<sub>p</sub>: 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<sub>dδ</sub> is the K<sub>d</sub> for the TMs in the reactive layer of thickness δ [μm] and C<sub>l</sub> [xx.l<sup>-1</sup>] and C<sub>E</sub>  
 139 [xx.kg<sub>dry</sub><sup>-1</sup>] are the concentrations in the liquid phase and in the exchangeable part of particles,  
 140 respectively.

141 Based on these theoretical concepts, the K<sub>d</sub> of a particle can be expressed as a function of its  
 142 radius r<sub>p</sub> [μm]:

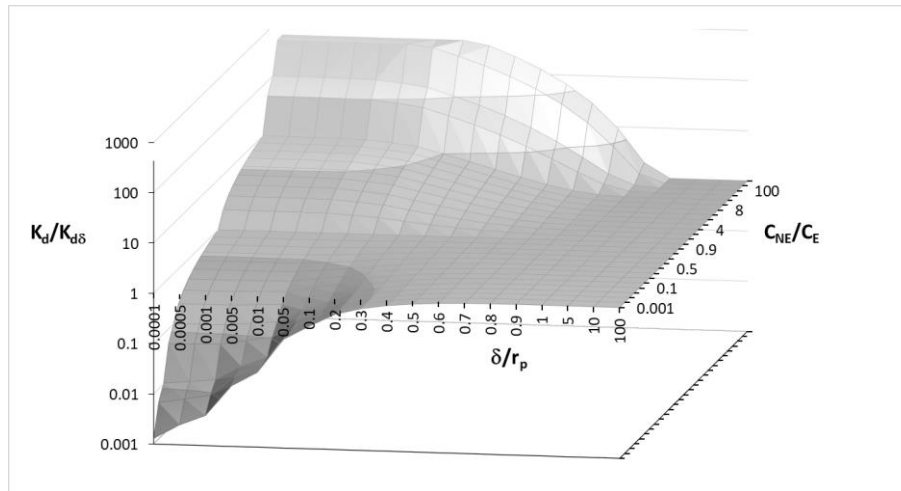
143 • if r<sub>p</sub> > δ ⇒ 
$$K_d = K_{d\delta} \cdot \left(1 - \left(1 - \frac{\delta}{r_p}\right)^3\right) + K_{d\delta} \cdot \frac{C_{NE}}{C_E} \cdot \left(1 - \frac{\delta}{r_p}\right)^3 \quad (\text{Eq. 4})$$

144 • if r<sub>p</sub> ≤ δ ⇒ 
$$K_d = K_{d\delta} \quad (\text{Eq. 5})$$

145

146 In these relationships, r<sub>p</sub> is specific to particles, δ and K<sub>dδ</sub> are specific to geochemical  
 147 conditions and C<sub>NE</sub> [xx· kg<sub>dry</sub><sup>-1</sup>] is specific to the environmental context.

148 Figure 2 presents the evolution of K<sub>d</sub>/K<sub>dδ</sub> as a function of C<sub>NE</sub>/C<sub>E</sub> and δ/r<sub>p</sub> according to this  
 149 model.



150

151 Figure 2:  $K_d/K_{d\delta}$  ratios as a function of  $C_{NE}/C_E$  and  $\delta/r_p$  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  $\delta$  and when the ratio  $C_{NE}/C_E$  is close to one (Figure  
 156 2). For particle sizes greater than  $\delta$ ,  $K_d$  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  $^{137}\text{Cs}$   
 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  $\delta$  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  $\delta$  values obtained by Abril et Fraga (1996) for Pu, Cs and Zn are 0.78, 1.96 and 5.17  $\mu m$   
 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

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

241

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

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

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

245

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

247

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

249

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

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

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

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

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)

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

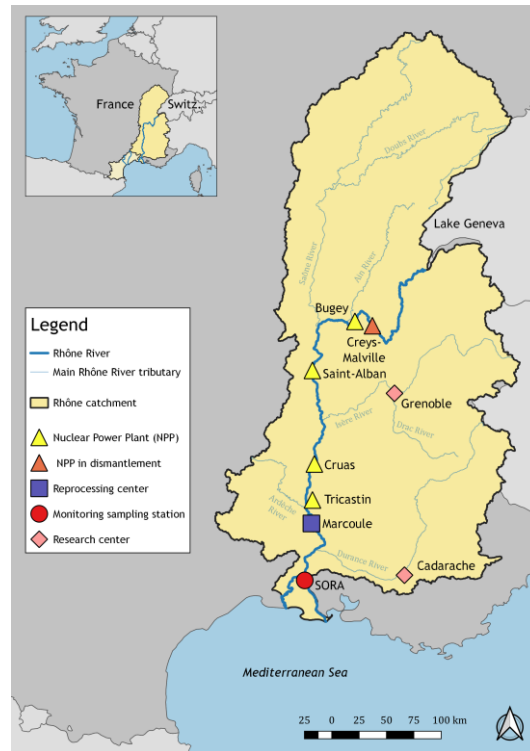
<ul style="list-style-type: none"> <li>• <math>C_D = \frac{q_D}{Q_{river}}</math></li> </ul>	<ul style="list-style-type: none"> <li>• <math>f_D = \frac{C_D}{C_E}</math></li> </ul>
<b>4 - Calculation of the dissolved, colloidal and liquid TMs concentrations</b>	
<ul style="list-style-type: none"> <li>•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

284

### 285 3 Material

286 The model was applied to determine the variability depending on the river discharge of the  
287  $K_d$  of  $^{137}\text{Cs}$  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  $^{137}\text{Cs}$  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

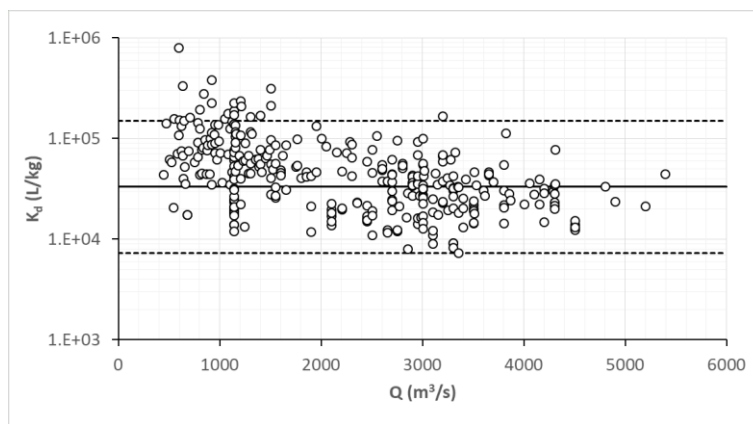
294 The IRSN monitoring station SORA and its sampling protocol for SS and filtered water are  
295 detailed in Antonelli *et al.* (2008), Eyrolle *et al.* (2012) and Eyrolle *et al.* (2020). Outside flood  
296 periods, a composite sample resulting from samples taken every 80 minutes is collected over 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  $^{137}\text{Cs}$  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  $^{137}\text{Cs}$  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  $^{137}\text{Cs}$  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  $^{137}\text{Cs}$  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:  $^{137}\text{Cs}$  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 5<sup>th</sup> and 95<sup>th</sup>  
 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  $^{137}\text{Cs}$  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  $^{137}\text{Cs}$  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  $C_{\text{soil}}$  and  $C_D$ . The range of river discharges was scanned between  $Q_{\text{MIN}}$  ( $400 \text{ m}^3 \cdot \text{s}^{-1}$ ) and  $Q_{\text{MAX}}$  ( $6000 \text{ m}^3 \cdot \text{s}^{-1}$ ). 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 2<sup>nd</sup> and 98<sup>th</sup> percentiles the conditional distributions of [SS] and  $r$  according to  $Q$  and the distributions of  $C_{\text{soil}}$  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  $^{137}\text{Cs}$ ,  $\delta$  and  $K_{d\delta}$ , because only the values published by Abril and Fraga (1996) were available:

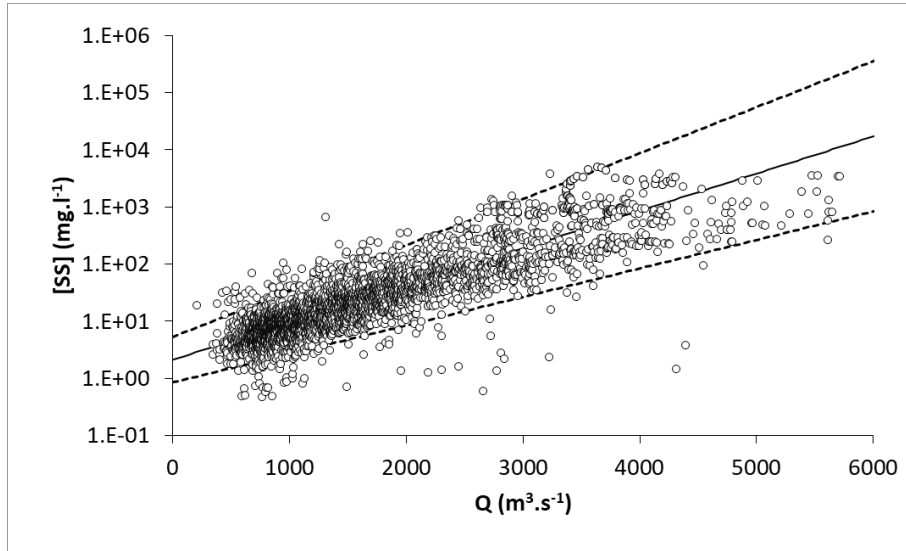
$$\delta = 1.96 \text{ } \mu\text{m} \text{ and } K_{d\delta} = 68 \cdot 10^3 \text{ l} \cdot \text{kg}^{-1}$$

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 2<sup>th</sup> and 98<sup>th</sup>  
 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 m<sup>3</sup>.s<sup>-1</sup>, the data show that r<sub>50</sub> 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 r<sub>50</sub> as a function of the river  
 398 discharge were determined in the same way as for [SS]. Thus, the variability of r<sub>50</sub> for water  
 399 flow rates between 400 and 3000 m<sup>3</sup>.s<sup>-1</sup> is covered by a conditional geometric mean  
 400 (GM(r<sub>50</sub>|Q)) represented by an equation of the second order (Eq. 29) and a constant conditional  
 401 standard deviation (GSD(r<sub>50</sub>|Q)) equal to 1.2 (Figure 6).

402 • If (Q ≤ 3000 m<sup>3</sup>.s<sup>-1</sup>) ⇒

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

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

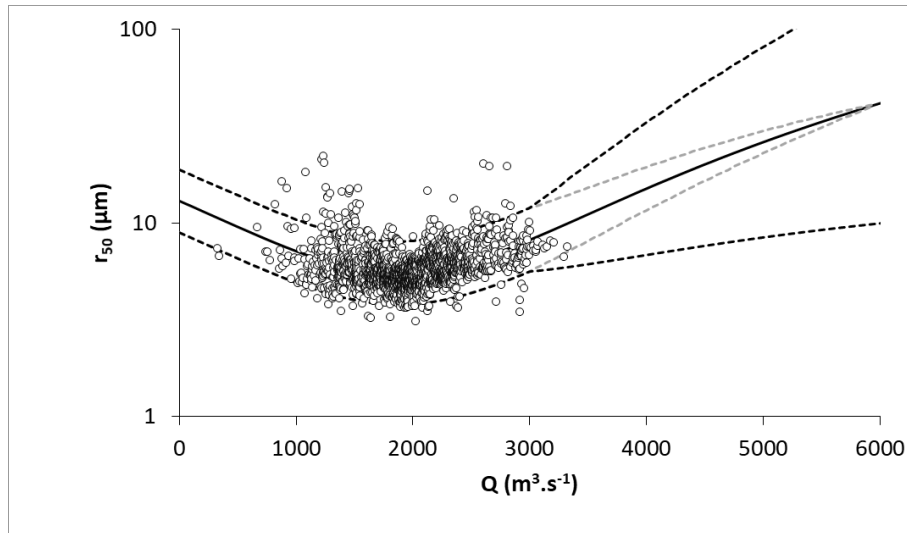
405 • If (Q > 3000 m<sup>3</sup>.s<sup>-1</sup>) ⇒

406 Beyond water flow rates of 3000 m<sup>3</sup>.s<sup>-1</sup>, the lack of data does not allow a detailed assessment  
 407 of the variability of r<sub>50</sub>. As a first approximation, this variability is extrapolated by considering  
 408 Eq. 29 for GM(r<sub>50</sub>|Q) and by increasing GSD(r<sub>50</sub>|Q) from 1.2 for Q = 3000 m<sup>3</sup>.s<sup>-1</sup> to 2 for Q =  
 409 6000 m<sup>3</sup>.s<sup>-1</sup> (Figure 6):

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

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(r<sub>50</sub>|Q) which decreases from 1.2 for Q = 3000 m<sup>3</sup>.s<sup>-1</sup> to 1 for Q = 6000 m<sup>3</sup>.s<sup>-1</sup>.

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 2<sup>th</sup> and 98<sup>th</sup>  
 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 $^{137}\text{Cs}$ concentrations in the soils of the catchment

421 The background of the  $^{137}\text{Cs}$  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  $\text{Bq.kg}^{-1}$  for the year 2003 (Antonelli *et al.*, 2008; Eyrolle *et al.*, 2012) and between 3  
 425 and 11  $\text{Bq.kg}^{-1}$  for the year 2018 (Thollet *et al.*, 2018). Consequently, the variations of the  
 426 minimal and maximal values of  $C_{\text{soil}}$  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  $^{137}\text{Cs}$  (30.2 years) because they aggregate the radioactive decay with several  
 432 transfer processes such as wash-off, erosion, infiltration, etc...

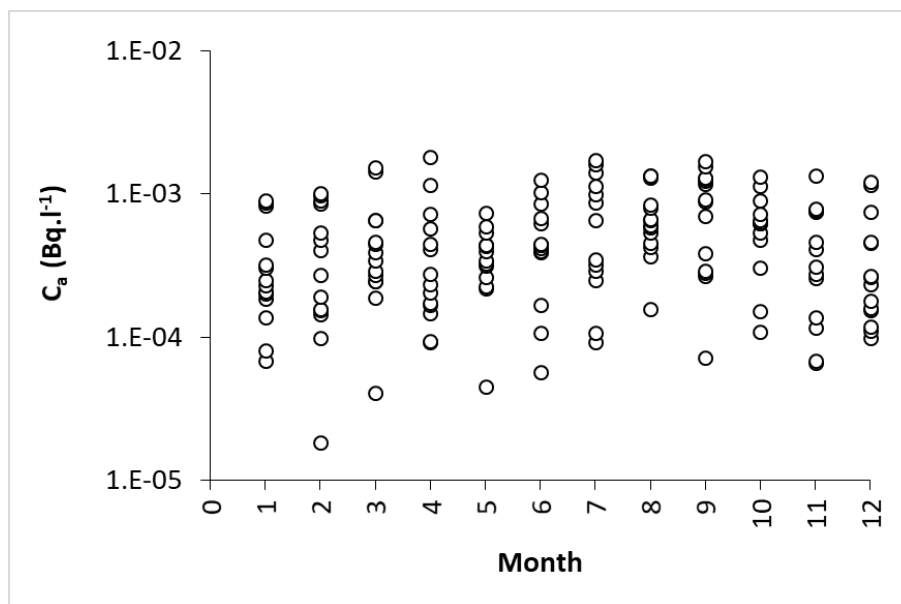
433 The statistical distribution of  $C_{\text{soil}}$  between 2015 and 2018 was determined by discretizing these  
 434 two curves with a yearly time step. For each year, the interval between the minimal and maximal  
 435 values was discretized into 20 intervals with the assumption of uniform distribution.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

438 For each water flow rate, the distribution of  $C_{\text{soil}}$  was scanned between its 2<sup>th</sup> and 98<sup>th</sup> percentiles  
439 which were 4.5 and 21.3 Bq.kg<sup>-1</sup>.

440

### 441 3.5 Statistical distribution of the industrial liquid discharges of <sup>137</sup>Cs

442 The main anthropogenic source of <sup>137</sup>Cs 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 <sup>137</sup>Cs monthly discharged by the Marcoule center ranged  
446 from 10<sup>2</sup> to 10<sup>4</sup> MBq.month<sup>-1</sup>. 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 m<sup>3</sup>.s<sup>-1</sup> at its lower part (Zebracki *et al.*, 2015), these releases lead to added  
449 monthly activities ranging between 2·10<sup>-4</sup> and 2·10<sup>-3</sup> Bq.l<sup>-1</sup> over the period 2005-2019 (Figure  
450 7).



451

452 Figure 7 : Theoretical average monthly concentrations of <sup>137</sup>Cs 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  $GM(C_D) = 3.9 \cdot 10^{-4} \text{ Bq.l}^{-1}$  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 2<sup>th</sup> and the 98<sup>th</sup>  
 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 <sup>(*)</sup>
$\delta$	n.r	1.96 $\mu\text{m}$	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]	<b>Conditional log-normal as a function of Q</b> $\text{GM}([\text{SS}] \text{Q}) = 2.13 \cdot e^{1.5 \cdot 10^{-3} \cdot \text{Q}}$ $\text{GSD}([\text{SS}] \text{Q}) = 1.56 \cdot e^{0.0002 \cdot \text{Q}}$	2 <sup>th</sup> ([SS] Q) - 98 <sup>th</sup> ([SS] Q)	10
$f_c$	Discussed in results section	See results section	n.r
$r_{50}$	<b>Conditional log-normal as a function of Q</b> $\text{GM}(r_{50} \text{Q}) = 2.12 \cdot 10^{-6} \cdot \text{Q}^2 - 7.96 \cdot 10^{-3} \cdot \text{Q} + 13$ If ( $\text{Q} \leq 3000$ ) $\Rightarrow \text{GSD}(r_{50} \text{Q}) = 1.2$ If ( $\text{Q} > 3000$ ) $\Rightarrow \text{GSD}(r_{50} \text{Q}) = (\text{Q} - 3000) \cdot \frac{0.8}{3000}$	2 <sup>th</sup> ( $r_{50} \text{Q}$ ) - 98 <sup>th</sup> ( $r_{50} \text{Q}$ )	10
$C_{\text{soil}}$	<b>Log-normal</b> $\text{GM}(C_{\text{soil}}) = 9.8 \text{ Bq.kg}^{-1}$ $\text{GSD}(C_{\text{soil}}) = 1.46$	4.5 – 21.3 $\text{Bq.kg}^{-1}$	10
Ca	<b>Log-normal if <math>\text{Q} &lt; 4000 \text{ m}^3 \cdot \text{s}^{-1}</math></b> $\text{GM}(\text{Ca}) = 3.9 \cdot 10^{-4} \text{ Bq.l}^{-1}$ $\text{GSD}(\text{Ca}) = 2.43$ if $\text{Q} > 4000 \text{ m}^3 \cdot \text{s}^{-1}$ then $C_a = 0 \text{ Bq.l}^{-1}$	$6.2 \cdot 10^{-5} - 2.4 \cdot 10^{-3}$ $\text{Bq.l}^{-1}$	10

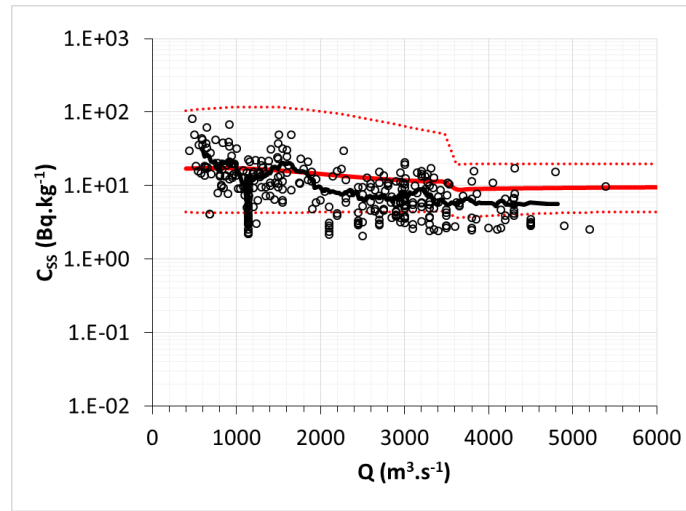
463 <sup>(\*)</sup>N is the number of intervals for scanning the statistical distributions between their 2<sup>th</sup> and 98<sup>th</sup>  
 464 percentiles. For each distribution, N was determined incrementally until no significant change was  
 465 observed.

466 n.r: non relevant

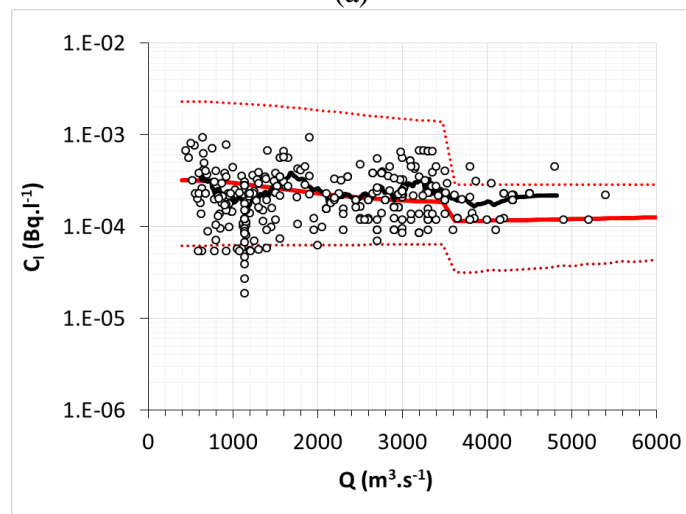
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468 Table 2 summarizes the input parameters applied for the calculations and Figure 8 compares,  
 469 as a function of the river discharge, the raw values (points) and sliding geometric means (black  
 470 lines) of the particulate and dissolved concentrations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

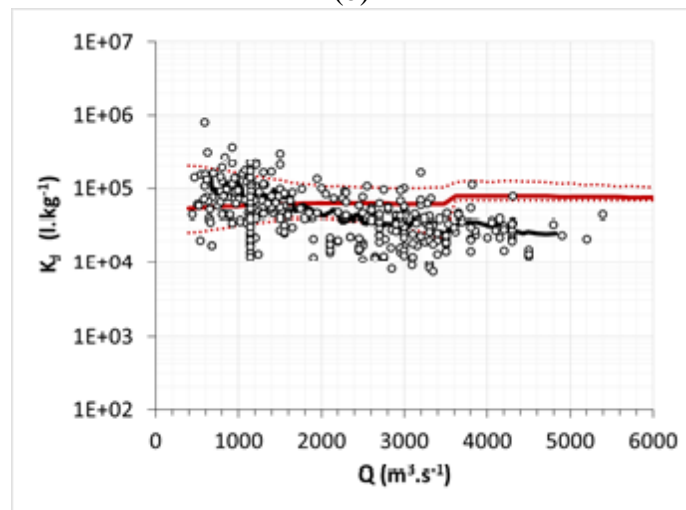
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474



(a)



(b)



(c)

475  
476

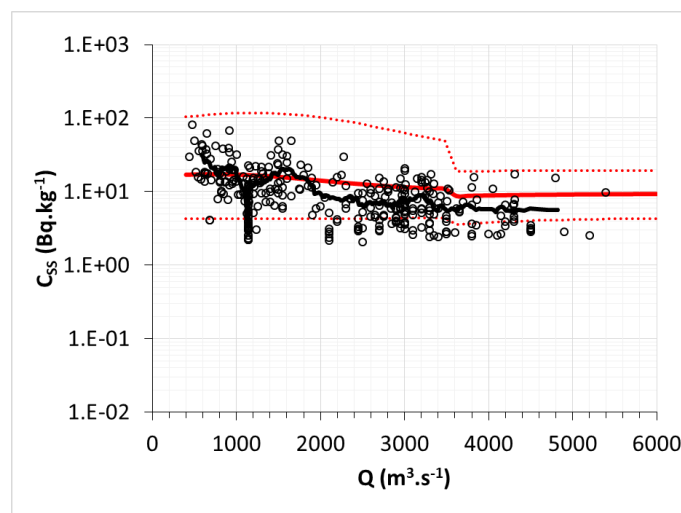
477  
478  
479

480 Figure 8:  $C_{SS}$ ,  $C_I$  and  $K_d$  of  $^{137}\text{Cs}$ : raw values (open circles) and sliding geometric means  
481 (black full lines) measured at the SORA station from 2005 to 2018 vs conditional geometric  
482 means (red full lines) and conditional minimum and maximum values (red dashed lines)  
483 modelled with the parameters of Table 2  
484

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).

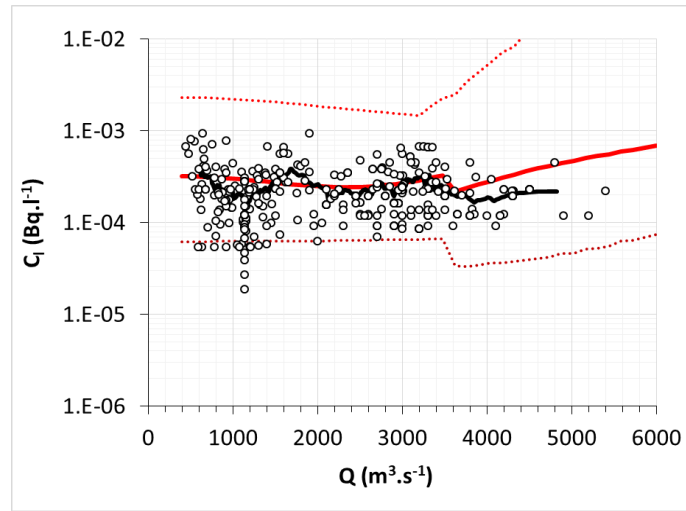
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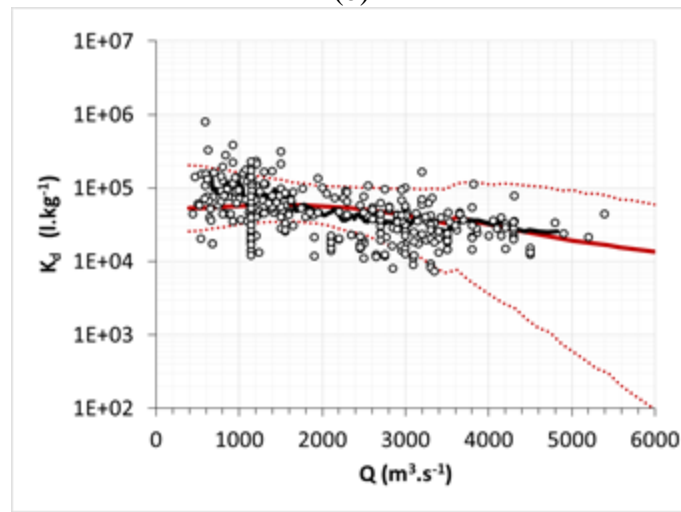
(a)

501  
502

503  
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(b)

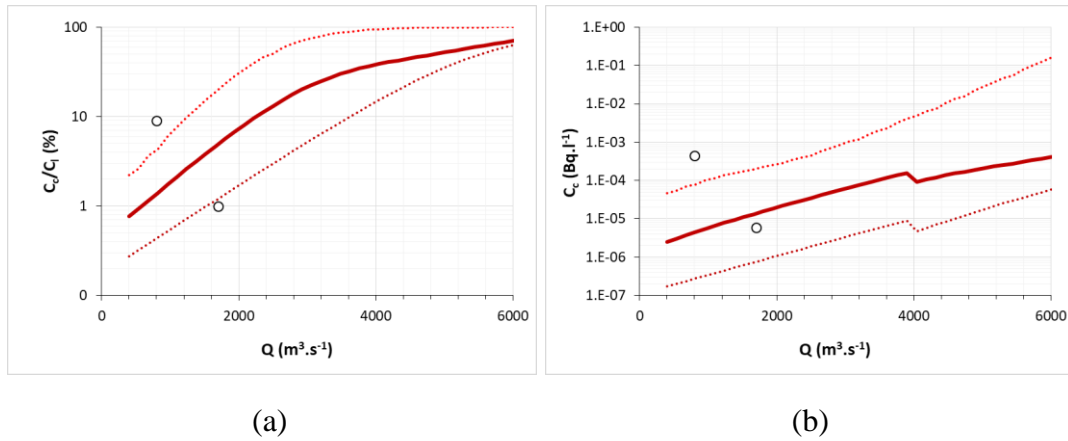


(c)

505  
506  
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508  
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512

Figure 9 :  $C_{SS}$ ,  $C_1$  and  $K_d$  of  $^{137}\text{Cs}$ : 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  $50 \text{ mg.l}^{-1}$  and the modelled  $^{137}\text{Cs}$  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

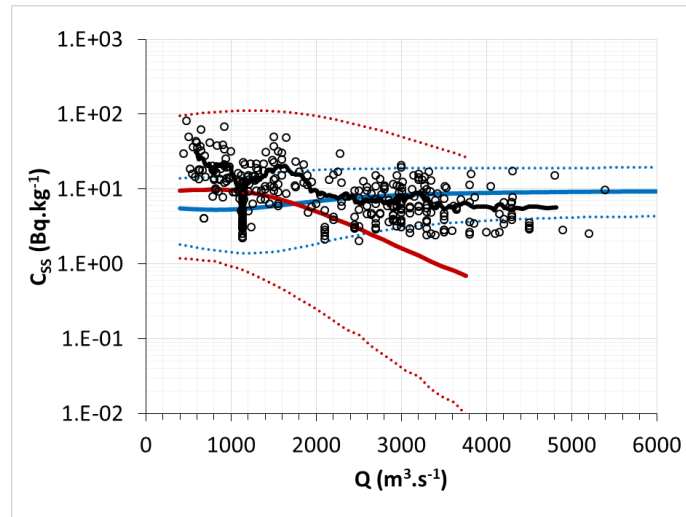
519

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  $^{137}\text{Cs}$  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  $^{137}\text{Cs}$  in the Rhône River: 1) colloids mainly originate from  
 534 the erosion of bottom sediments and/or river banks and they adsorb  $^{137}\text{Cs}$  from industrial  
 535 releases once they are in the water column, 2) colloidal forms of  $^{137}\text{Cs}$  are directly produced by  
 536 the erosion of  $^{137}\text{Cs}$  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  $^{137}\text{Cs}$  from sedimentary stocks would lead theoretically to an increase of the  
 539 activities of  $^{137}\text{Cs}$  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.

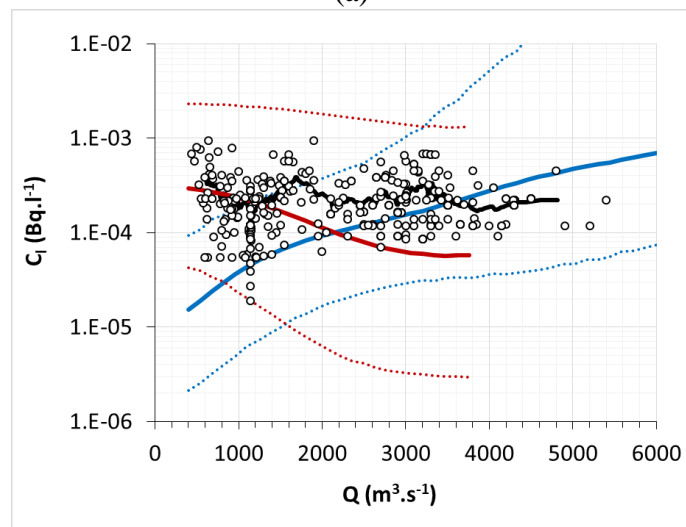
543 On another hand, the importance to consider the catchment background is well demonstrated  
 544 by comparing the variabilities of the solid and liquid  $^{137}\text{Cs}$  concentrations and of the  $K_d$   
 545 specifically to the background of the watershed and the industrial discharges (Eq. 26)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

547  
548



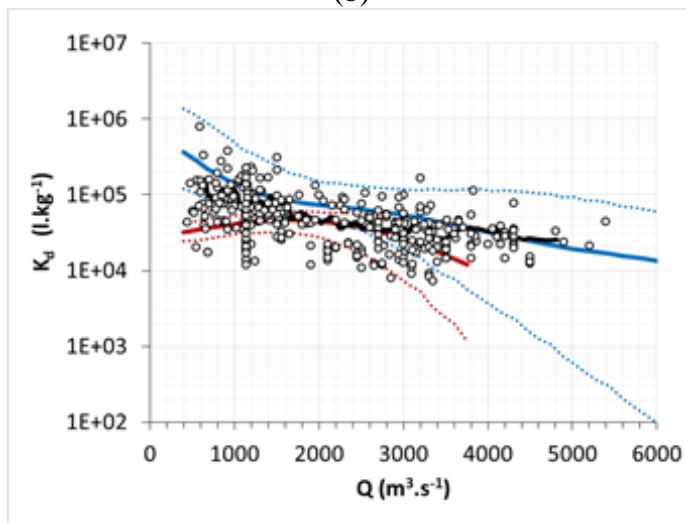
(a)

549  
550



(b)

551  
552



(c)

Figure 11 :  $C_{SS}$ ,  $C_l$  and  $K_d$  of  $^{137}\text{Cs}$ : 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)

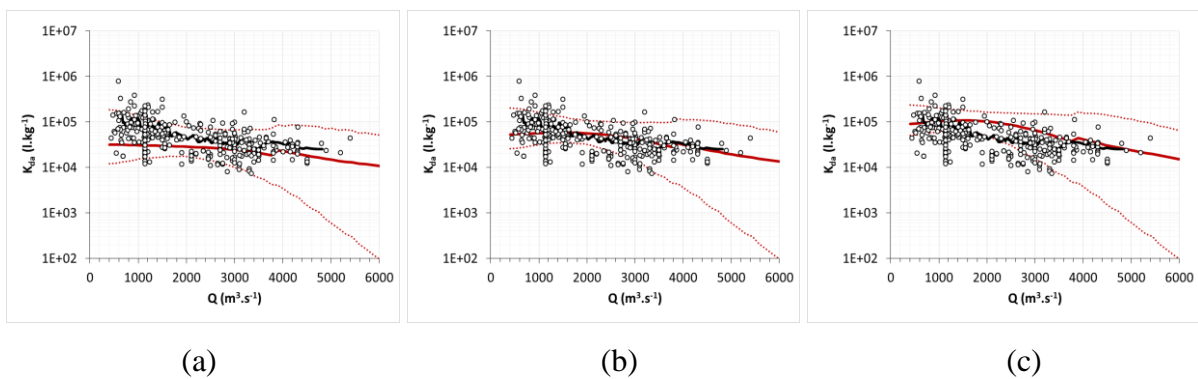
558 For  $C_{SS}$ , (Figure 11a) the industrial discharges and background contributions are close below  
 559  $2000 \text{ m}^3 \cdot \text{s}^{-1}$ . Above this water flow rate, the background contribution becomes more and more  
 560 dominant because of the increase in  $[SS]$  and  $r_{50}$ . Figure 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  $^{137}\text{Cs}$  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  $^{137}\text{Cs}$ ,  $\delta$  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  $\delta = 1.96 \text{ }\mu\text{m}$  and  $K_{d\delta} =$   
 580  $30 \cdot 10^3$  (a),  $68 \cdot 10^3$  (b) and  $140 \cdot 10^3$  (c)  $\text{l} \cdot \text{kg}^{-1}$ .

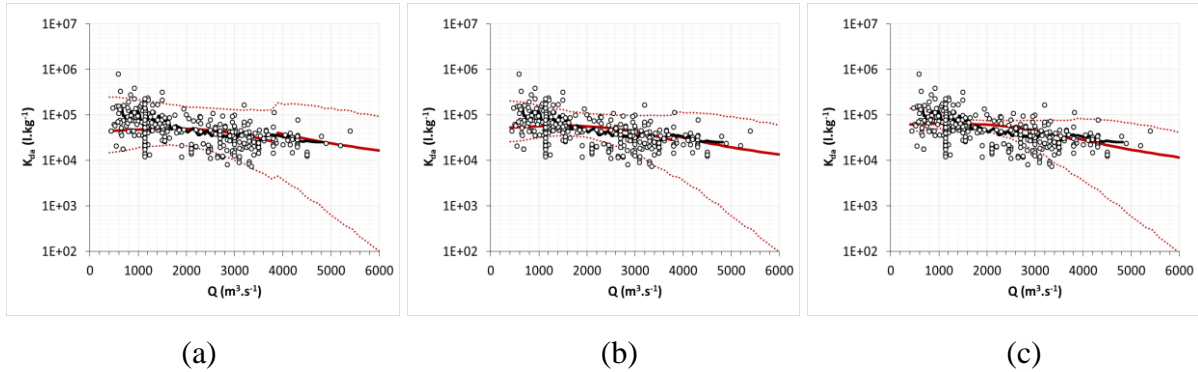
581 (Open circles: data measured at the SORA station from 2005 to 2018; Black full line: sliding  
 582 geometric mean of raw data; Red full line: modelled geometric means; Red dashed lines: modelled  
 583 minimal and maximal values)

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  $4 \mu\text{m}$ .



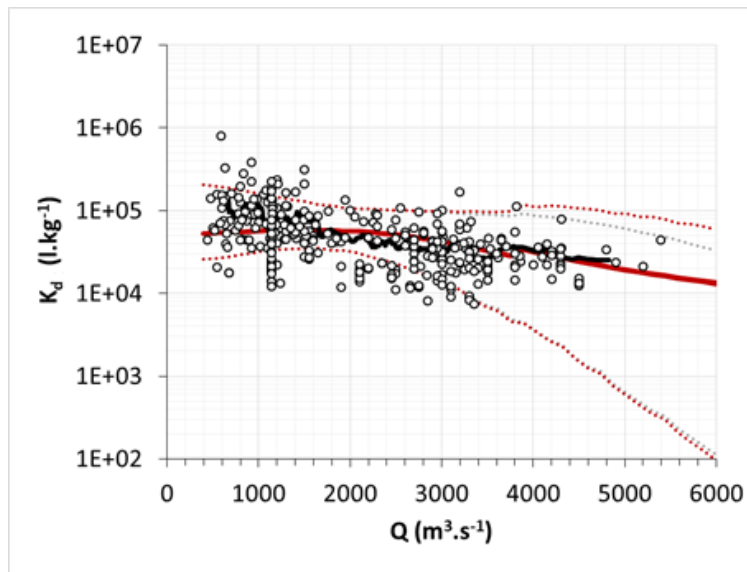
592 Figure 13: Variabilities of  $K_d$  as a function of the river discharge for  $\delta = 1$  (a),  $1.96$  (b) and  $4$   
593 (c)  $\mu\text{m}$  and  $K_{d\delta} = 68 \cdot 10^3 \text{ l.kg}^{-1}$ .

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)

598 Compared to  $K_{d\delta}$ , Figure 13 shows that the variations of  $\delta$  affect the amplitude of the variability  
599 of  $K_d$  without significantly modifying the geometric means. The lower  $\delta$  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  $\delta$ .

602 Comparison between the modelled variability and the dataset shows that  $\delta$  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  $\delta$  ( $1 < \delta < 2 \mu\text{m}$ ) 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  $^{137}\text{Cs}$  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  $^{137}\text{Cs}$  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  $\delta$ , 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  $^{137}\text{Cs}$  in the Rhône River highlights the fact that the variability of the  $^{137}\text{Cs}$   $K_d$  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  $\delta$  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.

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674

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