



HAL
open science

Modelling geochemical and kinetic processes involved in lead (Pb) remobilization during resuspension events of contaminated sediments.

Philippe Ciffroy, Lucie Monnin, Jean-Marie Garnier, Jean-Paul Ambrosi,
Olivier Radakovitch

► To cite this version:

Philippe Ciffroy, Lucie Monnin, Jean-Marie Garnier, Jean-Paul Ambrosi, Olivier Radakovitch. Modelling geochemical and kinetic processes involved in lead (Pb) remobilization during resuspension events of contaminated sediments.. *Science of the Total Environment*, 2019, 679, pp.159-171. 10.1016/j.scitotenv.2019.04.192 . hal-02500144

HAL Id: hal-02500144

<https://hal.science/hal-02500144>

Submitted on 18 Aug 2020

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

Modelling geochemical and kinetic processes involved in lead (Pb) remobilization during resuspension events of contaminated sediments

Philippe Ciffroy¹, Lucie Monnin², Jean-Marie Garnier², Jean-Paul Ambrosi², Olivier Radakovitch^{2,3}

¹ EDF, Division Recherche et Développement, Laboratoire National d'Hydraulique et Environnement (LNHE), Chatou, France.

² Aix Marseille Univ, CNRS, IRD, INRA, Coll France, CEREGE, Aix-en-Provence, France

³ Institut de Radioprotection et de Sûreté Nucléaire (IRSN), PSE-ENV/SRTE/LRTA, BP3, 13115 Saint-Paul Lez Durance, France

Abstract

2 The objective of this paper is to present a model simulating and predicting the exchange kinetics
of lead (Pb) between contaminated sediments and water during resuspension events potentially
4 occurring in reservoirs. We developed an innovative model that combines thermodynamic
speciation of particulate surfaces (oxides and POC), thermodynamic Pb speciation in water, and
6 kinetic modelling of exchanges between free Pb and particulate sites (i.e. dissolution of a
carbonate carrier phase, adsorption/coprecipitation and desorption/dissolution to/from oxides and
8 adsorption and desorption/degradation to/from particulate organic particles). We used results
from laboratory resuspension experiments performed on sediments from three contaminated dam
10 reservoirs to calibrate a new chemical speciation model.

Uptake and release processes to/from sediments were found to be controlled by at least two
12 successive reactions that can be associated to two particulate pools (here oxides and POC).

Kinetic adsorption and desorption rates were calibrated for seven experimental conditions.
14 Variability in kinetic rates allowed to evaluate the effect of solid-to-liquid ratio and sediment
origin on exchange kinetics at the water-particles interface. It was shown that the kinetic release
16 of dissolved Pb by desorption or dissolution from the oxides is reproduced almost identically
between the experiments, regardless of the solid-to-liquid ratio and sediment origin.
18 Readsorption on the long term on POC sites is more variable, even if ranges of variation in the
adsorption and desorption kinetic rates related to POC remain limited considering that tested
20 sediments are quite contrasted.

22 **Keywords**

Dam reservoir; Metal remobilization; Sediment resuspension; Speciation; Kinetics modeling

24

Capsule

26 A kinetic model simulating the dynamics of lead (Pb) during sediment resuspension was
developed and calibrated on laboratory experiments performed on three contaminated sediments.

28

1 Introduction

30 A large part of the trace metal(loid)s (TM) introduced by anthropogenic inputs in aquatic
environments are finally stored in the sediments, where they can be found in two main solid
32 forms: (co)precipitated in mineral forms like sulphides or carbonates, or adsorbed onto the
surface of reactive phases like oxyhydroxydes, organic matter or clay. This distribution
34 influences their bioavailability and toxicity, and the extent to which they can be remobilised in
the water in case of a change in physicochemical conditions. Indeed, when sediments are

36 resuspended due to natural events or anthropic activities, the particles undergo a sudden and
major change in the pH, redox, solid-to-liquid ratio and other chemical conditions. Resuspension
38 may promote the remobilization of TM from the solid to the dissolved phase (Kalnejais et al.,
2010; Superville et al., 2014), and therefore poses a risk of water quality degradation.
40 Remobilization of TM depends both on the characteristics of the sediments, on the TM
distribution, and on the physico-chemical conditions prevailing during the resuspension
42 (Cantwell et al., 2002; SedNet, 2014). Besides, TM concentrations that are measured in water
during laboratory experiments (e.g. Simpson et al., 2000; Cantwell et al., 2002; Ye et al., 2013;
44 Kalnejais et al., 2010; Hwang et al., 2011) or in-situ resuspension events (Caetano et al., 2003;
Superville et al., 2014) result from several kinetic release (desorption/dissolution) and uptake
46 (adsorption/(co)precipitation) processes from/to the suspended particles.

In the case of dams associated with hydroelectric power plants, the reservoirs sometimes need to
48 be fully drawn down for the safety inspections and maintenance tasks (Poupart and Royet, 2010).
These draining operations could be a problem in the case of contaminated reservoirs because
50 they lead to sediment resuspension. An increase of dissolved metal concentrations above water
quality standards due to remobilization is one of the risks. Being able to estimate it is an
52 important stake in order to improve the management of reservoirs.

Laboratory resuspension experiments are helpful to mimic and predict the remobilization of TM
54 occurring during *in situ* sediment resuspension and to test the influence of particles
concentrations or kinetics of chemical reactions. Results of resuspension experiments in
56 numerous works show kinetic evolutions of TM concentrations in the dissolved phase, and
competition phenomenon for the adsorption of TM on the solid suspended particles (Saulnier and
58 Mucci, 2000; Caille et al., 2003; Camino Martin-Torre et al., 2017; Monnin et al., 2018). The
evolution of TM concentrations in water are thus controlled by both rapid and slow release and
60 uptake processes. Evaluating and predicting the remobilization of TM over time appear thus

important to assess the risk of water quality degradation. These assessments and predictions can
62 be conducted using chemical modelling. Computer codes like Visual Minteq, Phreeqc or
WHAM allow to calculate speciation of dissolved TM in waters and the sorption of TM onto
64 solid phases. Most of them cannot however predict the temporal evolution of such distribution,
because all the thermodynamic processes included in the codes are assumed to be at equilibrium
66 and the reaction kinetics are not taken into account. Only PHREEQC has the capacity for kinetic
modelling using the 'kinetic' and 'rates' keywords; the Geochemist's Workbench
68 (www.gwb.com) also has kinetic capabilities for metal(loid) speciation reactions, but they need
to be defined in the software by the modeler.

70 Taking into account this background, we first developed a new chemical speciation model
combining thermodynamic and kinetic processes; this model simulates exchange reactions
72 between free dissolved TMs and solid surfaces and is theoretically applicable to all TMs. We
then used results from laboratory 'long-term' resuspension experiments performed on sediments
74 from three contaminated dam reservoirs to calibrate this model for a specific TM as an example,
i.e. lead (Pb). On a modelling point of view, Pb speciation, adsorption/precipitation and
76 desorption/dissolution is used here as a proxy for trace metals in a very general way. However, it
can obviously not be used as a proxy in a quantitative way. Moreover, it cannot be used as a
78 proxy for metalloids such as As and Se, as their behavior is very different from the divalent trace
metal cations. It should be noted here that the notions of 'short-' vs 'medium-' vs 'long term'
80 experiments are quite relative and must be put in perspective with the purpose of the study. In
our case, the purpose of the study was to investigate fate of TMs during management operations
82 on dams that occur during some hours. So, the 'long-term' terminology is consistent with the
duration of our experiments (i.e. 160 hours). Our objective was then to combine a
84 thermodynamic model with a kinetic model simulating exchange reactions between free
dissolved metal and solid surfaces. This model, coded under the Ecolego® platform (Nia et al.,

86 2011; Ciffroy et al., 2011, 2016), is based on processes similar to those included in e.g. Visual
Minteq, but it allows the user to describe sorption/desorption reactions by their kinetic rates,
88 instead than by their equilibrium affinity constants. Ecolego® was selected as the coding
platform because it is a systems oriented software program instead of geochemical modelling
90 software like PHREEQC. Moreover, it is designed for uncertainty and sensitivity analysis and
such capabilities can be of concern for future applications (Ciffroy and Benedetti, 2018). This
92 paper presents the fundamental of this model and focus on the behavior of one major TM as an
example, i.e. lead (Pb).

94

2 Material and methods

96 This section describes the experimental design used for collecting site-specific data and the
model approach developed for describing kinetics in the exchange of TM between water and
98 particles.

2.1 Study site, sampling and sediment characterization

100 Sediments were sampled from three French reservoirs, operated for hydroelectricity: Les
Mesches, Queuille and Rochebut, denoted hereafter A, B and C (Figure 1).

102 Reservoir A has a surface of 9.5 ha and is located in the south of the French Alps. High levels of
As, Cd, Pb and Zn were found in the sediments due to the presence of two ancient Pb-Zn mines
104 in the watershed. The zinc and lead sulphides ores were exploited from 1750 to 1927. The origin
of these TM is unambiguous regarding the small size of the watershed and the fact that it was not
106 occupied by humans except for the mine extraction.

Reservoir B is located in the French Massif Central, 30 km northwest of the city of Clermont-
108 Ferrand. Reservoir B has a surface of 36 ha and a maximal depth of about 30 m. A number of

former mining sites of Pb, As and F exist in the watershed, and in particular several deposits of
110 Ag and Pb were exploited in this mining zone.

Reservoir C is located in the French Massif Central. Gold was intensively mined in the area in
112 the twentieth century and the exploitation generated 300 000 m³ of tailings disposed on a 5
hectare site (rehabilitated in 2010-2011), in close proximity of the river about 12 km upstream
114 from the reservoir.

Water and sediment were collected in June 2015 in the reservoir A and in April 2016 in the
116 reservoirs B and C. Water was pumped out from the shore and passed through a ceramic filter of
0.4 µm. Sediment samples (0-10 cm surface layer) were collected with an interface UWITEC®
118 corer. The sediment was directly extracted to measure Eh and pH (by planting the electrodes in
the wet sediment), and placed into sealed glass jars to maintain their reduced state. It was
120 manually homogenized in the laboratory in a N₂ filled glove-bag, and divided into several sub-
samples that were stored in individual glass jars at 4°C in darkness. A new jar was opened for
122 each resuspension experiment, and Eh and pH were measured to check the good conservation of
the sediments. They were compared with those measured during the sampling to check the good
124 conservation of the sediments.

All the methods that were undertaken for characterizing the sediment were described in detail in
126 Monnin et al (2018).

128 **2.2 Lead (Pb) distribution in sediment**

For running the model described hereafter it is necessary to define initial conditions, i.e. the
130 concentrations of Pb in each of the particulate phases (oxides, Particulate Organic Carbon
(POC), precipitated carbonates) at the initial time of the resuspension experiments. These initial
132 conditions were determined experimentally with ascorbate and sequential extractions. The

ascorbate extractions were carried out to quantify more specifically the trace metals bound to
134 amorphous and easily reducible Fe and Mn oxides and hydroxydes. Ferrihydrite and iron
monosulfide (FeS) are considered soluble in the ascorbate solution, in contrary to pyrite,
136 hematite or goethite (Ferdelman, 1988; Kostka et Luther, 1994; Anschutz et al., 1998). The
standardized BCR 3-step extraction scheme (Rauret, 1998; Quevauviller, 2007) was slightly
138 modified in order to adapt the one of Tessier et al. (1979) to the first fraction and to separate the
"exchangeable" and "carbonate" fractions. The sequential extraction provides then four fractions:
140 exchangeable (F1a); carbonates-bound metals (F1b); reducible fraction (F2 from BCR) and the
oxidizable fraction (F3 from BCR). The detailed procedure is described in Monnin et al (2018).
142 Finally, the residual fraction is assumed to be equal to the total metal content minus the sum of
the previous four fractions. The Pb fraction that could be extracted simultaneously with Acid
144 Volatile Sulphides (AVS) was not evaluated because the redox potentials in the sediments (+245
mV for reservoir A and +270-290 mV for reservoir B and C) do not favour the occurrence of
146 AVS phases (De Jonge et al, 2012).

Procedures followed for conducting the chemical extractions are described in detail in Monnin et
148 al.(2018).

2.3 Laboratory resuspension experiments

150 Aliquots of sediments were resuspended using an Applikon® bioreactor, a 3L glass reactor in
which the sediment is stirred by both a propellers assembly and a magnetic stirrer. pH, Eh,
152 dissolved oxygen and temperature were measured continuously with four probes passed through
the head plate on the top of the reactor (Monnin et al., 2018).

154 Each resuspension experiment was performed on a new sample from a sealed jar. A mass of wet
sediment was inserted into the 3L reactor filled with filtered water collected from the respective
156 sampling site. Ambient air was continuously bubbled into the reactor to mimic the real
environmental situation of a draining operation. A total of seven experiments were conducted,

158 with sediment mass corresponding respectively (on a dry sediment to water ratios basis) to 2.7,
5.0 and 9.4 g.L⁻¹ for reservoir A, to 1.6 and 5.3 g.L⁻¹ for reservoir B and to 2.1 and 4.9 g.L⁻¹ for
160 reservoir C. This range of solid-to-liquid ratios was chosen to mimic Suspended Particulate
Matter (SPM) concentrations potentially found during draining operations. **Such values are**
162 **realistic when considering experience gained on management of reservoirs.** Since hydraulic
conditions and shear stress at the vicinity of sediments vary over time during draining operations,
164 SPM concentrations is indeed not constant and may vary at least over one order of magnitude.

The experiments were run for 120 to 160 h. During the experiment, the water was sampled
166 through a syringe inserted into the reactor. 30 mL of water samples were collected successively
at the start time (t₀) (prior to sediment addition), and again after sediment addition at 2, (5), 10,
168 20, 30 min and 1, 1.5, 2, 5, 15, 24, 48, 72, 96, 120, (160) h. The total volume collected represents
a maximum of 18% of the initial water volume in the reactor. **Corrections were applied for**
170 **taking this loss into account.** Each sample was separated into three aliquots: a) 10 mL were
filtered through 0.7 µm glass microfiber and stored frozen in glass vials until DOC analysis
172 (Shimadzu TOC-V_{CSH} ; PROTEE laboratory); b) 12 mL were filtered through 0.22 µm syringe
filters for alkalinity and major ions (Metrohm microtitrator and capillary electrophoresis
174 respectively); c) 8 mL were filtered through 0.22 µm syringe filters and acidified with ultrapur
nitric acid for major and trace elements analysis (ICP-MS). A specific resuspension experiment
176 carried out previously to determine the quantity of elements that could be adsorbed onto the glass
wall of the reactor showed that this bias is negligible (Monnin et al., 2018).

178

2.4 Conceptual model framework

180 The model developed here is theoretically applicable for all TMs, but the calibration work
presented in this paper was dedicated to a specific TM chosen as an example, i.e. lead (Pb). This
182 model is similar to those developed and tested in Ciffroy et al. (2001), Ciffroy et al. (2003) and

Garnier et al. (2006), who studied adsorption and desorption kinetics of TM to/from natural
184 particles collected in the Loire river. For some TM (e.g. Co, Mn, Cs in some conditions), they
observed similar kinetic trends as those observed here for Pb (see Results section), i.e. a
186 desorption phase followed by a readsorption phase. They interpreted such experimental results as
follows: the TM that desorbed just after mixing corresponds to the TM associated with the weak
188 and fast sites; excess TM in solution are then readsorbed on less accessible and/or more specific
sites. From these observations, the authors proposed a ‘two-successive reversible’ kinetic model
190 that was able to fit the experimental data. This model was adapted here for the purpose of our
experimental procedure and results. All the processes, assumptions and parameters involved in
192 the model are summarized in Table 1. Its main principles are described below.

Three particulate phases are here assumed to contribute to TM exchanges between water
194 (dissolved phase) and particles, i.e. oxides, POC and carbonates. The total concentrations of
oxides and POC are assumed to be constant over the duration of the experiment. However,
196 physico-chemical conditions like pH or ionic strength showed significant evolution during the
experiment (see Results section). As a consequence, speciation of oxides and the POC surface
198 may change over time and such modifications were taken into account in the model.

First, speciation of oxide surfaces (noted hereafter SOH, e.g. FeOH, AlOH and/or MnOH) were
200 modeled. Oxides exhibit an amphoteric behaviour, i.e. they may react with protons (H^+) present
in solution to form a net positively charged surface (SOH_2^+) at low pH, or a net negatively
202 charged surface (SO^-) at high pH. Only anionic forms (SO^-) are assumed to interact with cationic
free TM in solution. The SO^- fraction was then calculated by a thermodynamic speciation model
204 integrated in our modeling system. For this purpose, we coded the HFO model developed by
Dzombak and Morel (1990), which calculates the distribution between SOH, SO^- and SOH_2^+ .

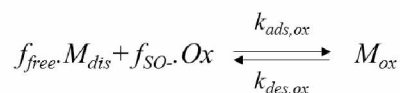
206 Secondly, speciation of the POC surface (noted hereafter *HHS* for protonated Humic Substances)
was modeled. Indeed, humic substances may be present as the protonated and deprotonated

208 species HHS and HS^- , and cationic TM are assumed to interact with anionic forms (HS^-). The
 210 HS^- fraction among the POC surface sites was then calculated by a thermodynamic speciation
 212 WHAM (Tipping, 1998) which calculates the distribution of sites among protonated and
 deprotonated species.

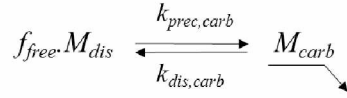
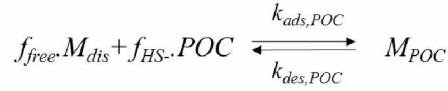
214 Finally, considering the total dissolved concentration (M_{dis}) would create a bias in the model.
 Actually, TM species that interact with oxides and POC are not the whole ‘dissolved metal’ M_{dis} ,
 216 but only its free cationic species M^{+} . As physico-chemical conditions like pH change over time,
 the fraction of free species M^{+} may show variations too. Two kinds of complexation reactions
 218 occurring in the dissolved phase were therefore incorporated in our model. On one hand,
 complexation of TM with inorganic ligands (hydroxides, nitrates, sulfates, chlorine and
 220 carbonates) was described by affinity constants at equilibrium K_{ML} . Data are taken from the
 Visual Minteq database (<https://vminteq.lwr.kth.se/>). On the other hand, complexation of TM
 222 with Dissolved Organic Carbon (DOC), i.e. dissolved humic acids and fulvic acids was
 described according to the SHM model previously mentioned. It accounts for chemical
 224 interactions between DOC and TM, as well as electrostatic interactions at the vicinity of the
 humic surface.

226 In conclusion, the thermodynamic models integrated in our tool allowed to calculate the fraction
 of interacting sites on oxides, (SO), and on POC, (HS^-), as well as the fraction of free species
 228 (f_{free}), for the duration of our experiments. These models are described in detail in Ciffroy and
 Benedetti (2018).

230 Exchanges are then described by three chemical reactions:



232



234 where M_{dis} , M_{ox} , M_{POC} and M_{carb} represent TM in water, or associated with oxides, POC and
 precipitated carbonates respectively (g.L^{-1}); Ox and POC represent oxides and POC
 236 concentrations (g.L^{-1}); $k_{ads,ox}$ and $k_{des,ox}$ are the adsorption and desorption kinetic rates (in L.g_{Ox}^{-1}
 $\cdot \text{h}^{-1}$ and h^{-1} respectively) to and from oxides; $k_{ads,POC}$ and $k_{des,POC}$ are the adsorption and
 238 desorption kinetic rates (in $\text{L.g}_{POC}^{-1} \cdot \text{h}^{-1}$ and h^{-1} respectively) to and from POC; $k_{prec,carb}$ and
 $k_{dis,carb}$ are the precipitation and dissolution kinetic rates (in h^{-1}) to and from carbonates; f_{free} is the
 240 fraction of free TM in the dissolved phase (i.e. $\frac{M^{Z+}}{M_{dis}}$); f_{SO^-} is the fraction of anionic sites on oxides
 (i.e. $\frac{SO^-}{SOH+SO^-+SOH_2^+}$); f_{HS^-} is the fraction of anionic sites on POC (i.e. $\frac{HS^-}{HHS+HS^-}$). Actually, transfer
 242 of TM from oxides to water can be due to both chemical desorption and solid dissolution.
 Similarly, transfer of TM from POC to water can be due to both chemical desorption and
 244 (a)biotic degradation of the POC. No information is available to distinguish these processes and
 then the $k_{des,ox}$ and $k_{des,POC}$ parameters implicitly incorporate both desorption and dissolution for
 246 oxides, and desorption and degradation for the POC. It will be hereafter called ‘desorption’. The
 same assumption is made for ‘adsorption’ to oxides and POC that incorporate potential solid
 248 formation.

250 2.5 Initial conditions

For calibrating the model from experimental results, it is necessary to define the initial
 252 conditions of the simulation, i.e. the concentration of Pb in each of the solid phases (i.e. oxides,
 POC and carbonates) at the start time. Major and trace element concentrations in waters used for

254 the resuspension experiments were measured and were used as initial contents in water. Methods
are presented in detail in Monnin et al. (2018) Chemical extractions provide information on
256 element distribution between different solid phases in the sediment before resuspension. The
proportion of metals extracted in the fraction F1b with acetic acid $C_2H_4O_2$, and the fraction F3
258 with H_2O_2 , in the sequential extraction scheme (Monnin et al., 2018), were respectively used to
quantify the metals bound to carbonates and to particulate organic matter. The amount of TM
260 bound to oxides were assumed to be extracted with the ascorbate reagent.

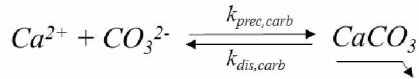
The total amount of oxides in the sediment was derived from the proportions of Fe, Mn and Al in
262 the ascorbate extraction. The proportions of Fe, which is the main component of the oxides, are
similar in the ascorbate fraction and in the reducible fraction F2 of the sequential extraction. The
264 Fe-, Mn- and Al- oxides were included in the calculation of the solid oxide phase (Table 2).

266 **2.6 Calibration of dissolution kinetic rate of carbonates**

For each model, the third reaction describes the dissolution of carbonates, leading to a
268 remobilization of associated Pb, and inversely the precipitation of carbonates, leading to a
potential co-precipitation of Pb, assuming Pb is in the carbonate fraction. X-ray diffraction
270 showed that calcite ($CaCO_3$) and dolomite ($CaMg(CO_3)_2$) are the major mineral phases the
sediments from reservoir A, but magnesian calcite may be also present (Monnin et al., 2018).
272 The proportions of these three phases and their respective contents in TM cannot be calculated.
In contrast, calcite was not evidenced in the sediments of reservoir B nor C. For sake of
274 simplicity, calcite was used as a proxy to represent all carbonates . The quantity of calcite in
sediment is estimated through the calculation of the Saturation index (SI), expressed as:

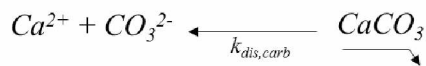
$$276 \quad (1) \quad SI = \log\left(\frac{IAP}{K_s}\right)$$

where IAP is the Ion (Ca^{2+} and CO_3^{2-}) Activity Product; K_s is the solubility product of calcite
 278 ($\log_{10}(K_s) = -8.48$). When the system is undersaturated (i.e. when $SI < 0$), calcite may dissolve
 and the concentrations of calcium and carbonates may increase. The reaction describing such a
 280 dissolution/precipitation process is the following:



282 As the carbonate concentration (CO_3^{2-}) is also driven by acid/base reactions with HCO_3^- and
 H_2CO_3 , these reactions were also implemented in our model using the pK_a of each reaction and
 284 assuming equilibrium.

In the experiments on reservoir A, a significant increase in both Ca^{2+} and CO_3^{2-} concentrations
 286 was observed and SI is negative, interpreted as a continuous dissolution of calcite. Even if
 precipitation and dissolution can simultaneously occur, we considered here due to the negative
 288 SI that the reaction is predominantly directed as:



290 For calibrating the dissolution kinetic rate $k_{dis,carb}$, we used experimental data related to Ca^{2+} and
 CO_3^{2-} , and subsequent IAP . Besides, we experimentally observed that SI follows an exponential
 292 trend, so we added an exponential correction factor $\alpha_{dis,carb}$ (unitless) describing the fact that
 dissolution decreases if SI is close to 0. Kinetic evolution of Ca^{2+} and CO_3^{2-} is then given by:

294 (2) **If $SI < 0$,** $\frac{d(Ca^{2+})}{dt} = \frac{d(CO_3^{2-})}{dt} = k_{dis,carb} \cdot e^{-\alpha_{dis,carb} \cdot SI}$

296 We then optimized parameter values to minimize the distance between calculated and measured
 values according to the procedure described in section 2.8.

298 Pb associated to calcite can be remobilized simultaneously and it is then assumed that the kinetic
 dissolution rate of calcite-associated Pb is the same as for calcite itself.

2.7 Calibration of sorption and desorption kinetic rates to/from oxides/POC

302 Kinetic trends observed for Pb in all our experiments showed two stages, i.e. a first desorption
stage followed by a readsorption stage (see Results section). As discussed in Ciffroy et al.
304 (2001), Ciffroy et al. (2003) and Garnier et al. (2006), TM desorbed just after mixing should
correspond to TM associated to weak and fast sites, and excess TM in solution are then
306 readsorbed on less accessible and/or more specific sites. From a theoretical point of view, we
could then assume that oxides correspond to weak and fast sites, while POC corresponds to
308 strong and slow sites; or vice-versa. When observing adsorption/desorption reactions on oxides
and POC, we can observe that oxides and POC play symmetric roles from a mathematical point
310 of view, and that it is mathematically impossible to decide which kind of sites are the weakest
and fastest, and which ones are the strongest and slowest.

312 Two scenarios could then be considered from a theoretical point of view. The first one assumes
that Pb is weakly associated to oxides and strongly associated to POC. In this scenario, the initial
314 increase of Pb in the solution is predominantly attributed to desorption from oxides and $k_{des,ox} >$
 $k_{des,POC}$. This scenario may be supported by a qualitative interpretation of experimental results.

316 Fe and Mn concentrations in water showed indeed a significant increase during the first
minutes/hours of the resuspension experiment, suggesting fast processes occurring at the surface
318 of oxides. Besides, Saturation indexes (SI) calculated with Visual MINTEQ indicate
undersaturation of several Fe oxides and (oxy)hydroxides (e.g. ferrihydrite, goethite, gibbsite,
320 pyrolusite and manganite) at the beginning of the resuspension experiment, suggesting possible
dissolution of oxides (we remind that dissolution and desorption of TM associated to oxides are
322 implicitly confounded in our model). The second scenario assumes that Pb is weakly associated
to POC and strongly associated to oxides. In this scenario, the initial increase of Pb in the
324 solution is predominantly attributed to desorption from POC and $k_{des,POC} > k_{des,ox}$. Note also

that potential (a)biotic degradation of POC may occur but is implicitly confounded with
326 desorption in our model.

The choice between these two scenarios was based on the qualitative arguments given above; the
328 first scenario seems reasonable in our study and it was then selected. We then calibrated the
kinetic parameters under the constraint $k_{des,ox} > k_{des,POC}$. However, we must keep in mind that
330 this is a prior assumption and not a demonstration.

332 **2.8 Fitting process**

The two parameters describing dissolution of carbonates $k_{dis,carb}$ and $\alpha_{dis,carb}$ were first fitted.
334 Then, the four parameters describing exchanges with oxides and POC (i.e. $k_{ads,ox}$, $k_{des,ox}$,
 $k_{ads,POC}$ and $k_{des,POC}$) were fitted from the experimental results. We conducted a probabilistic
336 approach to define the most probable combinations of parameters, similarly to the process
described in Ciffroy et al, 2011 (as illustrated in Figure 2). Instead of determining a single value
338 for each of the parameters, the objective was to define Probability Density Functions (PDF),
describing the range of most probable values for each parameter, as well as correlations between
340 parameters. The steps followed for deriving PDFs for each of the model parameters are the
following (see fig 1 in Ciffroy et al; 2011):

342 Step 1: each of the parameters to be fitted is described by a PDF characterizing the range of
potential values. As no previous knowledge related to the kinetic rates is available, large log-
344 uniform PDFs (over several orders of magnitude) were first selected. **Log-uniform distributions**
were chosen because they are the less informative ones, allowing to uniformly covering a range
346 **of potential values over several orders of magnitude.**

Step 2: 10000 values of each parameter were randomly sampled through a Monte Carlo
348 procedure, allowing to obtain 10000 combinations of parameters. The model was run for each of
the 10000 combinations of parameters, providing 10000 $M_{dis}=f(t)$ curves.

350 Step 3: In the experiments described above, variables (i.e. Ca^{2+} , CO_3^{2-} and M_{dis} concentrations)
were measured at different deployment times (from 2 minutes to 120 or 160 h, see 2.4). For
352 fitting the parameters related to calcite dissolution, we only used the experimental SI values as
described above. For fitting the parameters related to TM exchanges with solids, we used the
354 M_{dis} values. Let's write Y the output of interest (i.e. SI or M_{dis}). For each of the 10000
simulations previously generated, error was calculated as follows:

356
$$(3) \quad \varepsilon_p = \sum_i \left(Y_{measured}(t_i) - Y_{p,calculated}(t_i) \right)^2$$

where $Y_{measured}(t_i)$ and $Y_{p,calculated}(t_i)$ refers to the measured and calculated output at time t_i ;
358 the index p refers to the p^{th} combination of parameters (with $p=1$ to 10000).

Step 4: the 10000 simulations were then ranked according to the error ε_p . The lowest errors ε_p
360 correspond to the 'best' combinations of parameters, i.e. those minimizing the distance between
measured and calculated values. To estimate the robustness of the parameterization, it is
362 necessary to estimate the range of parameter values that may give equivalent results. Typically, a
non-sensitive parameter will give equivalent errors over a wide range of values, while a sensitive
364 parameter will give equivalent errors over a narrow range of values. To evaluate the set of
parameter values that may equivalently give good results, a statistical Wilcoxon test was
366 undertaken on the ranked combinations. Probability Density Functions (PDFs) were thus built
for each parameter.

368 Step 5: once PDFs are fitted for all the parameters, the model is run again replacing the non-
informative PDFs used at step 1 (i.e. log-uniform PDFs) by informative PDFs obtained at step 4
370 (e.g. normal PDFs). Besides, correlations identified between parameters at step 4 are also

introduced in the investigated model. When correlation(s) is(are) defined, the Iman-Conover
372 technique (Iman and Conover, 1982) was processed to generate parameter samples respecting
these correlations.

374 Step 8: calculated curves obtained from the informative PDFs were compared to experimental
data. For facilitating the interpretation, this plot is synthesized by three curves, i.e. the curve
376 obtained with the best combination of parameters, and the 5th percentile and 95th percentile
curves respectively.

378 The fitting process described above was performed for each of the seven experimental
conditions. We thus obtained parameter PDFs for each of these seven experiments and the
380 consistency of these PDFs among sites and solid-to-liquid ratios was discussed (see section 3.5).
Another approach to calibration was also tested to discuss the model's capabilities: parameter
382 PDFs were calibrated by considering all the experiments performed for site A together (site A
was chosen for this calibration exercise because three experimental conditions were available
384 while only two were available for sites B and C). The final objective is indeed to apply the
chemical model described here within larger hydrology/sedimentation model, and a single
386 parameter set for a given site is likely to be more useful in this perspective.

3 Results and discussion

388 3.1 Experimental kinetics of Pb concentrations in water

The evolution of Pb concentrations in the dissolved phase during the resuspension experiments is
390 shown in **Figure 3**. It showed two stages, whatever the sediment used and the amount of
suspended sediments: a first desorption stage, followed by a readsorption stage. The dissolved
392 concentrations increased during the first 5 hours of the experiments for sediment A, 24 h to 48 h
for site B, and 5 h to 15 h for site C, followed by a continuous decrease. The maximum
394 concentrations of Pb measured during the experiments were between $2.30 \cdot 10^{-6} \text{ g.L}^{-1}$ (site 'C- 2.1

g.L⁻¹) and 1.37 10⁻⁵ g.L⁻¹ (site 'B- 5.3 g.L⁻¹'). The concentrations of dissolved Pb represent a
396 release of 0.4 to 1.8 % of the total Pb associated to the suspended solid particles.

398 **3.2 Physico-chemical parameters in water**

The concentrations of dissolved organic carbon (DOC, not shown – see Monnin et al, 2018 and
400 Monnin 2018) in water during the resuspension experiments ranged between 1 and 5.6 mg.L⁻¹
for site A, 2.1 and 7.7 mg.L⁻¹ for site B, and 5.5 and 7.9 mg.L⁻¹ for site C, depending on the
402 experiments. These variation ranges are wide, however the DOC do not show any clear trend
over the duration of the experiments.

404 The redox potential (Eh) of the stirred and aerated water decreases immediately when sediments
are resuspended (results not shown – see Monnin et al, 201 and Monnin 2018). Eh then rises
406 sharply for a short period (up to one hour for site A; Monnin et al. 2018) and then slowly
increases up to the end of the experiments. The redox variations do not affect the dissolved
408 speciation of Pb, which is the trace element we chose to model.

The pH follows a similar pattern with an instantaneous decrease after the sediment addition
410 followed by an increase from 10 minutes of resuspension (Figure 4). A larger decline of pH is
measured during the resuspension of sediments B and C compared to the sediment A. The XRD
412 analysis of the sediments show that, unlike the sediments B and C, the sediment from site A
contains carbonate minerals (calcite and dolomite), of which dissolution have partially buffered
414 the pH decrease.

416 **3.3 Evolution of f_{SO} , f_{HS} and f_{free} during the sediment resuspension**

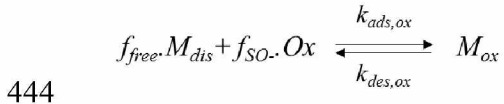
3.3.1 Speciation of the POC and oxides surfaces

418 The total concentrations of oxides and POC in the suspended particles, respectively obtained
from the ascorbate extraction and the total organic carbon analysis, are given in Table 2. The
420 sediments from sites B and C contain more POC than those from site A (4.8 to 7.9 % versus 1.6-
1.8 %). Higher amounts of Fe, Mn and Al are also extracted in the ascorbate fraction for the
422 sediments B and C, so the concentrations of oxides are higher than for sediment A.

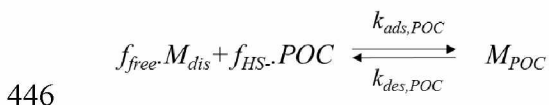
The total concentrations of POC and oxides are assumed to remain constant over the duration of
424 the resuspension experiments. However, the evolution of the physico-chemical conditions during
the experiments (ex. pH, ionic strength) may alter the speciation of oxides and POC surfaces and
426 change the concentrations of adsorption sites over time. Cappuyns et al (2014) and Camino
Martin-Torre et al (2017) for example shown that the variation of pH associated to changes in
428 oxidation processes during resuspension experiments may had an influence on TM releases. The
partition between protonated and deprotonated sites on the POC and Oxides surfaces were
430 calculated according to the models described in 2.4 and the evolution of the fraction of anionic
sites (f_{SO^-} and f_{HS^-}) are shown in **Figure 5**.

432 Both f_{SO^-} and f_{HS^-} follow the same evolution as the pH during the resuspension experiments: a
decrease during the first 10 minutes, then an increase. The highest and lowest fractions f_{SO^-} and
434 f_{HS^-} respectively correspond to the resuspension experiments of sediment 'A 5 g.L⁻¹' and
sediment 'B 5.3 g.L⁻¹', during which the highest and lowest pH values are measured. Given the
436 protonation/deprotonation of the surface sites that are considered, the fractions of anionic sites
 f_{SO^-} and f_{HS^-} are highly dependent of the pH variations. Indeed, a shift in pH influences the
438 direction of the reactions $SOH \rightleftharpoons SO^- + H^+$ and $SHH \rightleftharpoons HS^- + H^+$. According to Le
Chatelier's principle, a decrease of pH (increase of $[H^+]$) promotes the formation of SOH and
440 SHH and the decrease of the fractions of reactive sorption sites SO^- and HS^- .

Decrease (respectively increase) in pH will then decrease (respectively increase) reactive
 442 (negatively charged) sites of the oxides and POC. Thus, decrease in pH will decrease the
 variables f_{SO^-} and f_{HS^-} involved in the reactions



and



If we consider the Le Chatelier's principle, then each reaction will be directed to counteract the
 448 decrease in $f_{SO^-} \cdot Ox$ and $f_{HS^-} \cdot POC$. Each reaction will then be directed in the reverse way.

3.3.2 Speciation of dissolved Pb

450 The results of speciation calculations show that the vast majority of dissolved Pb is complexed
 with the dissolved organic matter (data not shown). The free ionic species Pb^{2+} represent only a
 452 small fraction of the total amount of dissolved Pb (Figure 5). Minimum f_{free} ($7.0 \cdot 10^{-7}$ – $3.8 \cdot 10^{-6}$)
 are obtained with the input data of resuspension 'A-2.7 g.L⁻¹'. The highest calculated f_{free} ($8.6 \cdot 10^{-6}$ – $8.4 \cdot 10^{-5}$)
 454 correspond to the resuspension 'B-5.3 g.L⁻¹'. Over the duration of resuspension, the
 f_{free} ratios increase up to their highest values during the first 10 minutes and then decrease until
 456 the end of the experiments.

During the sediment resuspension, the dissolved Pb remains mainly complexed with the
 458 dissolved organic substances but the pH decrease at the beginning of the experiments promotes
 the increase of the fraction Pb^{2+} (Figures 3 and 5).

460 The significant kinetic changes in reactive adsorption sites and free metal concentrations during
 the resuspension experiments, as shown in Figure 5, highlight the importance of taking into

462 account the speciation of Oxides and POC surfaces and the speciation of dissolved TM in the
model.

464 **3.4 Carbonate dissolution parameters**

As described in the Material and Method section, the kinetic rate describing carbonate
466 dissolution $k_{dis,carb}$ and the correction factor $\alpha_{dis,carb}$ were calibrated using kinetic evolution of
 Ca^{2+} and CO_3^{2-} , integrated in the Saturation Index of calcite SI . Parameter values obtained for the
468 three resuspension experiments with sediments from site A are reported in Table 3.

For the resuspension of the sediments from sites B and C (that do not contain carbonate minerals
470 detected by the XRD analysis), the evolution of alkalinity over time is optimally reproduced by
taking into account the pH variation over time only (data not shown). For these resuspension
472 experiments, considering carbonate dissolution did not improve the model results and no kinetic
rates of carbonate dissolution were therefore calibrated.

474 The comparison between experimental and calculated SI for the resuspension of sediment A are
reported in Figure 4. The dashed blue line represents the SI computed without calcite dissolution,
476 taking into account only pH variations that influence the concentration of CO_3^{2-} . For this site, the
pH evolution allows to explain in part the evolution of SI during the experiments, especially
478 during the first hour of resuspension. However, pH variations are not enough to explain the
increase of the calcite SI at the end of the three experiments (Figure 4). Adding the process of
480 calcite dissolution, thanks to the calibrated constants $k_{dis,carb}$ and $\alpha_{dis,carb}$, allows the calculated SI
to be well adjusted to the measured one. The TM bound to the carbonate fraction in the sediment
482 A before resuspension (deduced from sequential extraction) are then released in the dissolved
phase with the same kinetic rate that the calcite dissolution.

484

3.5 Adsorption/desorption parameters on/from oxides and POC

486 As described in the Material and Method section, the kinetic rates describing adsorption on
oxides and POC ($k_{ads,ox}$ and $k_{ads,POC}$) and desorption from oxides and POC ($k_{des,ox}$ and
488 $k_{des,POC}$) were calibrated from experimental data. Parameter values obtained for each of the
resuspension experiments are reported in Table 3.

490 The comparison between measured Pb concentrations (experimental) and calculated
concentrations is reported in Figure 3. The goodness-of-fit is in part quantified by the
492 determination coefficient R^2 that is reported in Table 3 for each condition. All the R^2 values are
high, characterizing accurate calibration. The calibration of the kinetic rates of adsorption and
494 desorption of Pb at the surface of POC and Oxides, and of the calcite dissolution for site A,
allows to faithfully reproduce the kinetic evolution of dissolved Pb during the resuspension of
496 the sediments from the three sites. Besides, uncertainty margins derived from the application of
Probability Density Functions for each parameter are narrow, showing the robustness of the
498 modeling approach (Table . The concentrations of Pb increase during the first part of the
experiments and then decrease until the end. They reach their maximum values after 5 h with the
500 sediments from site A, 24 to 48 h for site B, and 5 h à 15 h for site C. The release and uptake of
Pb over time and the maximum concentration values are well reproduced with the model.

502 The Pb evolution is successfully reproduced considering its release from one type of solid phase
(the oxides pool), added to the release from carbonates in the case of site A, followed by its
504 uptake by another type of solid particles (the organic particulate pool). The values of the
calibrated kinetic constants of Pb desorption from oxides ($k_{des,ox}$) are very similar between the
506 experiments for the three sites. The mean values (of the normal distributions indicated in Table
3) of $k_{des,ox}$ ranged from $1.4 \cdot 10^{-2} \text{ h}^{-1}$ for site 'C-4.9 g.L⁻¹' to $4.5 \cdot 10^{-2} \text{ h}^{-1}$ for site 'B-1.6 g.L⁻¹'.

508 The kinetic constant of adsorption to the oxides $k_{ads,ox}$ is not a sensitive parameter for the
modelling of the Pb partition between solid and liquid phase. This is the reason why no PDF was
510 determined for the $k_{ads,ox}$ parameter, but only an extremum value (Table 3). This may be

explained by the assumptions chosen for the model: Pb is indeed assumed to be first released
512 from weak and fast sites present on oxides, and then to be potentially uptaken to slower and
stronger POC sites. Readsorption is then dominated by the adsorption kinetic on POC sites and
514 adsorption kinetics on oxides) is then poorly sensitive on modeling results. The kinetic release of
dissolved Pb by desorption or dissolution from the oxides is therefore reproduced almost
516 identically between the experiments, while the reverse process of uptake by adsorption or co-
precipitation on the oxides is negligible.

518 The readsorption of dissolved Pb from the solution on the long term is reproduced through the
adsorption on the second type of solid phase: the organic particles (POC). The adsorption kinetic
520 rate ($k_{ads,POC}$) showed a greater variability between the three sites, and also between the
experiments with the various mass of suspended sediment from a single site (variation by one
522 order of magnitude). For the site A, the adsorption rate of Pb on the POC is similar for the 2.7
and 5.0 g.L⁻¹ experiments (respectively $3.9 \cdot 10^7$ and $2.3 \cdot 10^7$ L.g⁻¹.h⁻¹) and slightly decreases for
524 the 9.4 g.L⁻¹ experiment ($7.9 \cdot 10^6$ L.g⁻¹.h⁻¹). For the sites B and C, the values of $k_{ads,POC}$ are
higher for the experiments with 5.3 and 4.9 g.L⁻¹ of suspended sediments than with 1.6 and 2.3
526 g.L⁻¹, showing a potential effect of the solid-to-liquid ratio on adsorption kinetics on strong and
slow sites present on POC. Instead, desorption kinetic rates from POC ($k_{des,POC}$) remain quite
528 similar for a given site (range from $2.7 \cdot 10^{-3}$ to $4.7 \cdot 10^{-3}$ h⁻¹ for site A; from $9.4 \cdot 10^{-4}$ to $5.9 \cdot 10^{-3}$ h⁻¹
for site B; from $8.3 \cdot 10^{-3}$ to $1.5 \cdot 10^{-2}$ h⁻¹ for site C), with an inter-site variability over about one
530 order of magnitude. The kinetic readsorption of dissolved lead by uptake to POC sites showed
then a slight effect of the solid-to-liquid ratio and a slight inter-site variability. Ranges of
532 variation of the adsorption and desorption kinetic rates related to POC remain however relatively
limited (they do not exceed one order of magnitude), considering the fact that sediments
534 originated from quite contrasted reservoirs.

As indicated in section 2.8, a single set of parameter PDFs was also calibrated by considering the three experimental conditions tested for site A together. Parameter PDFs thus obtained are presented in Table 3, as well as the determination coefficient R^2 (indicator of the goodness-of-fit). The model goodness-of-fit thus obtained is unavoidably poorer than those obtained by separate calibration (0.78 for the ‘all-together’ calibration versus 0.97, 0.94 and 0.94 for the ‘single’ calibrations), but it remains quite acceptable, showing that a global calibration is of good value for a further incorporation within a larger hydrology/sedimentation model.

542

4 Conclusion

544 This study evidenced the interest of ‘long-term’ experiments for a better characterisation of the interactions of Pb between water and sediments in the context of resuspension events. Such experiments showed that exchanges of Pb between sediments and water can efficiently be represented by multi-compartmental kinetic model. This model is innovative since it combines thermodynamic speciation of particulate surfaces (oxides and POC), thermodynamic TM speciation in water, and kinetic modelling of exchanges between free TMs and particulate sites.

550 Uptake and release processes were found to be controlled by at least two successive (fast and slow) reactions that can be associated to two particulate pools (here oxides and POC). The relative contribution of fast and slow reactions respectively on the partitioning at the water-particles interface was quantified for different contexts (three sites and different sediment concentrations) through the calibration of kinetic adsorption and desorption rates. Variability in kinetic rates allowed to evaluate the effect of solid-to-liquid ratio and sediment origin on exchange kinetics at the water-particles interface. It was shown that the kinetic release of dissolved Pb by desorption or dissolution from the oxides is reproduced almost identically between the experiments, regardless solid-to-liquid ratio and sediment origin. Readsorption on

the long term on POC sites is more variable, even if ranges of variation in the adsorption and
560 desorption kinetic rates related to POC remain limited considering that tested sediments are quite
contrasted.

562 When simulating the behaviour of a TM like Pb in a reservoir submitted to resuspension events,
it is therefore necessary to take into account several exchange processes and the residence time
564 of the particulate phase downstream to the resuspension point. The model described in this paper
is able to simulate transient processes and modification in the speciation of particulate TMs. It
566 would be interesting to compare chemical time constants determined in this paper with the
residence time of water and particles downstream to reservoirs. Consequently, to know whether
568 chemical kinetics play a major role on the behavior of TMs during their downstream transit, it
would be useful to combine the chemical model developed in this paper with hydraulic and
570 sedimentological models.

571 **References**

572 Anschutz, P., Zhong, S., Sundby, B., Mucci, A., Gobeil, C. (1998). Burial efficiency of
573 phosphorus and the geochemistry of iron in continental margin sediments. *Limnology and*
574 *Oceanography*, 43, 53-64. <https://doi.org/10.4319/lo.1998.43.1.0053>

575 Caetano, M., Madureira, M.-J., Vale, C. (2003). Metal remobilisation during resuspension of
576 anoxic contaminated sediment: short-term laboratory study. *Water, Air and Soil Pollution* 143, 23–
577 40. <https://doi.org/10.1023/A:1022877120813>

578 Caille, N., Tiffreau, C., Leyval, C., Morel, J.L. (2003). Solubility of metals in an anoxic
579 sediment during prolonged aeration. *Science of The Total Environment* 301, 239–250.
580 [https://doi.org/10.1016/S0048-9697\(02\)00289-9](https://doi.org/10.1016/S0048-9697(02)00289-9)

581 Camino Martin-Torre M., Cifrian E., Ruiz G., Galan B., Viguri J.R. (2017). Estuarine sediment
582 resuspension and acidification : release behaviour of contaminants under different oxidation levels
583 and acid sources. *Journal of environmental Management.* 199, 211-221.
584 <http://dx.doi.org/10.1016/j.jenvman.2017.05.044>

585 Cantwell, M.G., Burgess, R.M., Kester, D.R. (2002). Release and phase partitioning of metals
586 from anoxic estuarine sediments during periods of simulated resuspension. *Environmental Science*
587 *and Technology* 36, 5328-5334. <https://doi.org/10.1021/es0115058>

588 Cappuyns, V., Alian, V., Vassilieva, E., & Swennen, R. (2014). pH dependent leaching
589 behavior of Zn, Cd, Pb, Cu and As from mining wastes and slags: kinetics and mineralogical control.
590 *Waste and Biomass Valorization*, 5(3), 355-368

591 Ciffroy, P., Garnier, J.-M., Khanh Pham, M. (2001). Kinetics of the adsorption and desorption
592 of radionuclides of Co, Mn, Cs, Fe, Ag and Cd in freshwater systems: experimental and modelling
593 approaches. *Journal of Environmental Radioactivity*, 55, 71–91. [https://doi.org/10.1016/S0265-](https://doi.org/10.1016/S0265-931X(01)00026-1)
594 [931X\(01\)00026-1](https://doi.org/10.1016/S0265-931X(01)00026-1)

595 Ciffroy, P., Garnier, J.-M., Benyahya, L. (2003). Kinetic partitioning of Co, Mn, Cs, Fe, Ag, Zn
596 and Cd in fresh waters (Loire) mixed with brackish waters (Loire estuary): experimental and
597 modelling approaches. *Marine Pollution Bulletin*, 46, 626–641. [https://doi.org/10.1016/S0025-](https://doi.org/10.1016/S0025-326X(02)00517-9)
598 326X(02)00517-9

599 Ciffroy, P., Nia, Y., Garnier, J.M. (2011). Probabilistic multicompartmental model for
600 interpreting DGT kinetics in sediments. *Environmental science and technology*, 45, 9558-9565.
601 <https://doi.org/10.1021/es104221b>

602 Ciffroy, P., Alfonso, B., Altenpohl, A., Banjac, Z., Bierkens, J., Brochot, C., Critto A, De
603 Wilde T., Fait G., Fierens T., Garratt J., Giubilato E., Grange E., Johansson E., Radomyski A.,
604 Reschwann K., Suciu N., Tanaka T., Tedoisi A., Van Holderbeke M., Verdonck F. (2016). Modelling
605 the exposure to chemicals for risk assessment: a comprehensive library of multimedia and PBPK
606 models for integration, prediction, uncertainty and sensitivity analysis—the MERLIN-Expo tool.
607 *Science of the Total Environment*, 568, 770-784. <https://doi.org/10.1016/j.scitotenv.2016.03.191>

608 Ciffroy, P., & Benedetti, M. (2018). A comprehensive probabilistic approach for integrating
609 natural variability and parametric uncertainty in the prediction of trace metals speciation in surface
610 waters. *Environmental pollution*, 242, 1087-1097

611 De Jonge, M., Teuchies, J., Meire, P., Blust, R., & Bervoets, L. (2012). The impact of increased
612 oxygen conditions on metal-contaminated sediments part I: Effects on redox status, sediment
613 geochemistry and metal bioavailability. *Water research*, 46(7), 2205-2214

614 Dzombak, D.A., Morel, F.M.M. (1990). Surface complexation modelling: hydrous ferric oxide.
615 Wiley-Interscience, New York

616 Ferdelman, T.G. (1988) The distribution of sulfur, iron, manganese, copper and uranium in salt
617 marsh sediment cores as determined by sequential extraction methods. Dissertation, University of
618 Delaware

619 Garnier, J.-M., Ciffroy, P., Benyahya, L. (2006). Implications of short and long term (30 days)
620 sorption on the desorption kinetic of trace metals (Cd, Zn, Co, Mn, Fe, Ag, Cs) associated with river
621 suspended matter. *Science of The Total Environment*, 366, 350–360.
622 <https://doi.org/10.1016/j.scitotenv.2005.07.015>

623 Gustafsson, J.P. (2001). Modeling the acid-base properties and metal complexation of humic
624 substances with the Stockholm Humic Model. *Journal of Colloid and Interface Science*, 244, 102-
625 112. <https://doi.org/10.1006/jcis.2001.7871>

626 Gustafsson, J. P., Berggren Kleja, D. (2005). Modeling salt-dependent proton binding by
627 organic soils with the NICA-Donnan and Stockholm Humic models. *Environmental Science and*
628 *Technology*, 39, 5372-5377.

629 Hwang, K.-Y., Kim, H.-S., Hwang, I. (2011). Effect of resuspension on the release of heavy
630 metals and water chemistry in anoxic and oxic sediments. *CLEAN Soil Air Water*, 39, 908–915.
631 <https://doi.org/10.1002/clen.201000417>

632 Iman, R.L., Conover, W.J. (1982). A distribution-free approach to inducing rank correlation
633 among input variables. *Community Statistical Simulation Computation*, 11, 311-334.

634 Kalnejais, L.H., Martin, W.R., Bothner, M.H. (2010). The release of dissolved nutrients and
635 metals from coastal sediments due to resuspension. *Marine Chemistry*, 121, 224–235.
636 <https://doi.org/10.1016/j.marchem.2010.05.002>

637 Kostka, J.E., Luther, G.W. (1994). Partitioning and speciation of solid phase iron in saltmarsh
638 sediments. *Geochimica Cosmochimica Acta*, 58, 1701-1710. [https://doi.org/10.1016/0016-](https://doi.org/10.1016/0016-7037(94)90531-2)
639 [7037\(94\)90531-2](https://doi.org/10.1016/0016-7037(94)90531-2)

640 MacDonald, D.D., Ingersoll, C.G., Berger, T.A. (2000) Development and evaluation of
641 consensus-based sediment quality guidelines for freshwater ecosystems. *Archives of Environmental*
642 *Contamination and Toxicology*, 39, 20-3. <https://doi.org/10.1007/s002440010075>

643 Monnin, L., Ciffroy, P., Garnier, J. M., Ambrosi, J. P., & Radakovitch, O. (2018).
644 Remobilization of trace metals during laboratory resuspension of contaminated sediments from a
645 dam reservoir. *Journal of Soils and Sediments*, 18(7), 2596-2613. [https://doi.org/10.1007/s11368-018-](https://doi.org/10.1007/s11368-018-1931-5)
646 1931-5
647 Monnin L. (2018) Changement de spéciation des éléments traces métalliques lors de la remise
648 en suspension de sédiments de barrages. PhD Aix-Marseille University, 183 pp.

648 Nia, Y., Garnier, J. M., Rigaud, S., Hanna, K., Ciffroy, P. (2011). Mobility of Cd and Cu in
649 formulated sediments coated with iron hydroxides and/or humic acids: a DGT and DGT-PROFS
650 modeling approach. *Chemosphere*, 85, 1496-1504.
651 <https://doi.org/10.1016/j.chemosphere.2011.08.045>

652 Poupart, M., Royet, P. (2001). La surveillance des grands barrages. Colloque Technique du
653 Comité Français des Barrages et Réservoirs, Aix-en-Provence.

654 Quevauviller, P. (2007). Fractionnement d'éléments pour étude dans l'environnement.
655 *Techniques de l'ingénieur*, pp 3854.

656 Rauret, G. (1998). Extraction procedures for the determination of heavy metals in contaminated
657 soil and sediment. *Talanta*, 46, 449-455. [https://doi.org/10.1016/S0039-9140\(97\)00406-2](https://doi.org/10.1016/S0039-9140(97)00406-2)

658 Saulnier, I., Mucci, A. (2000). Trace metal remobilization following the resuspension of
659 estuarine sediments: Saguenay Fjord, Canada. *Applied Geochemistry*, 15, 191–210.
660 [https://doi.org/10.1016/S0883-2927\(99\)00034-7](https://doi.org/10.1016/S0883-2927(99)00034-7)

661 SedNet, European Sediment Research Network (2004). Contaminated sediments in European
662 river basins. 69p.

663 Simpson, S.L., Apte, S.C., Batley, G.E. (2000). Effect of Short-Term Resuspension Events on
664 the Oxidation of Cadmium, Lead, and Zinc Sulfide Phases in Anoxic Estuarine Sediments. *Environ.*
665 *Sci. Technol.* 34, 4533–4537. <https://doi.org/10.1021/es991440x>

666 Superville, P.-J., Prygiel, E., Magnier, A., Lesven, L., Gao, Y., Baeyens, W., Ouddane, B.,
667 Dumoulin, D., Billon, G. (2014). Daily variations of Zn and Pb concentrations in the Deûle River in

668 relation to the resuspension of heavily polluted sediments. *Science of The Total Environment*, 470–
669 471, 600–607. <https://doi.org/10.1016/j.scitotenv.2013.10.015>

670 Tessier, A., Campbell, P.G.C., Bisson, M. (1979). Sequential extraction procedure for the
671 speciation of particulate trace metals. *Analytical Chemistry*, 51, 844–851.
672 <https://doi.org/10.1021/ac50043a017>

673 Tipping, E. (1998). Humic ion-binding model VI: an improved description of the interactions
674 of protons and metal ions with humic substances. *Aquatic geochemistry*, 4(1), 3-47

675 Ye, S., Laws, E.A., Gambrell, R. (2013). Trace element remobilization following the
676 resuspension of sediments under controlled redox conditions: City Park Lake, Baton Rouge, LA.
677 *Applied Geochemistry* 28, 91–99. <https://doi.org/10.1016/j.apgeochem.2012.09.008>

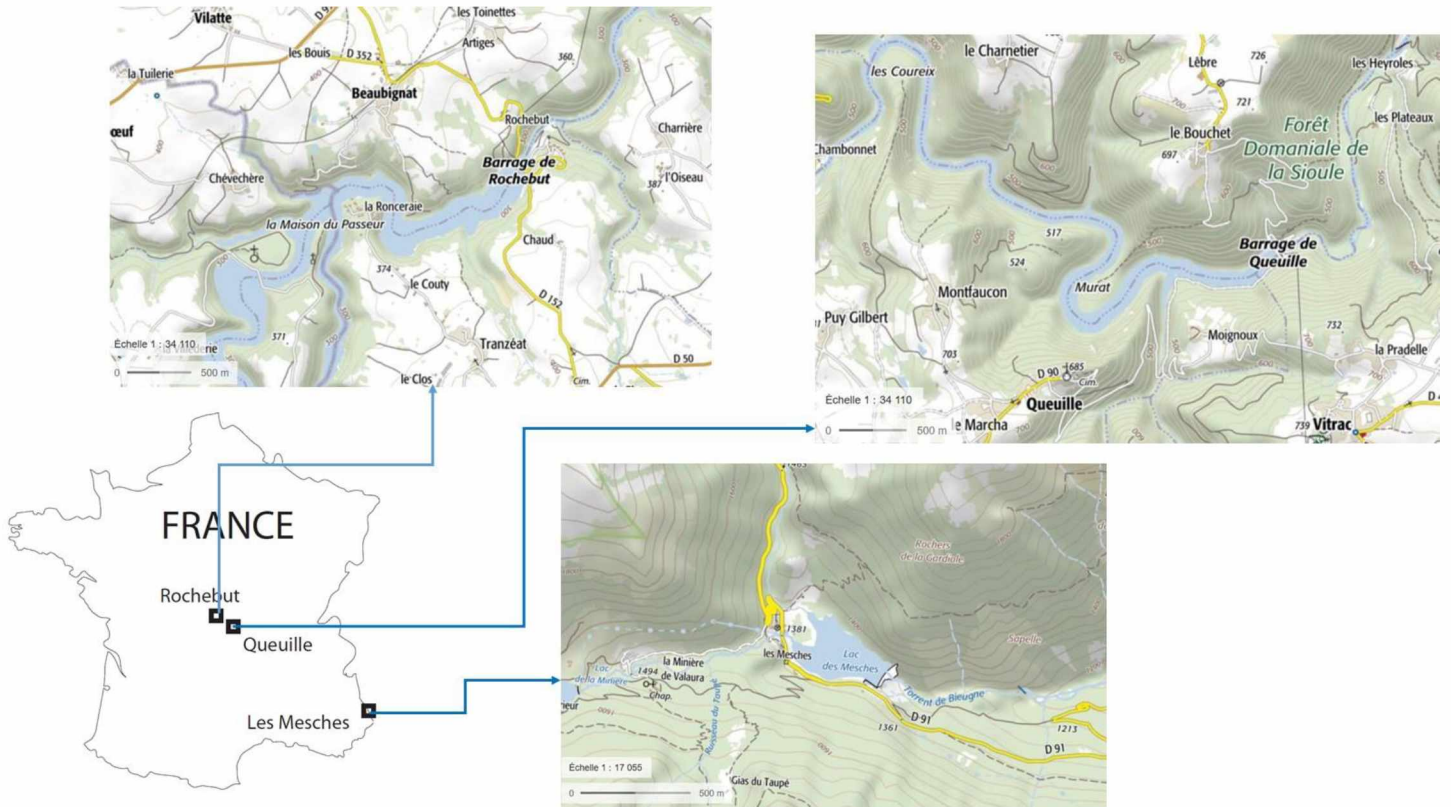


Figure 1 - Locality map showing the 3 sites in relation to France and detailed locality maps

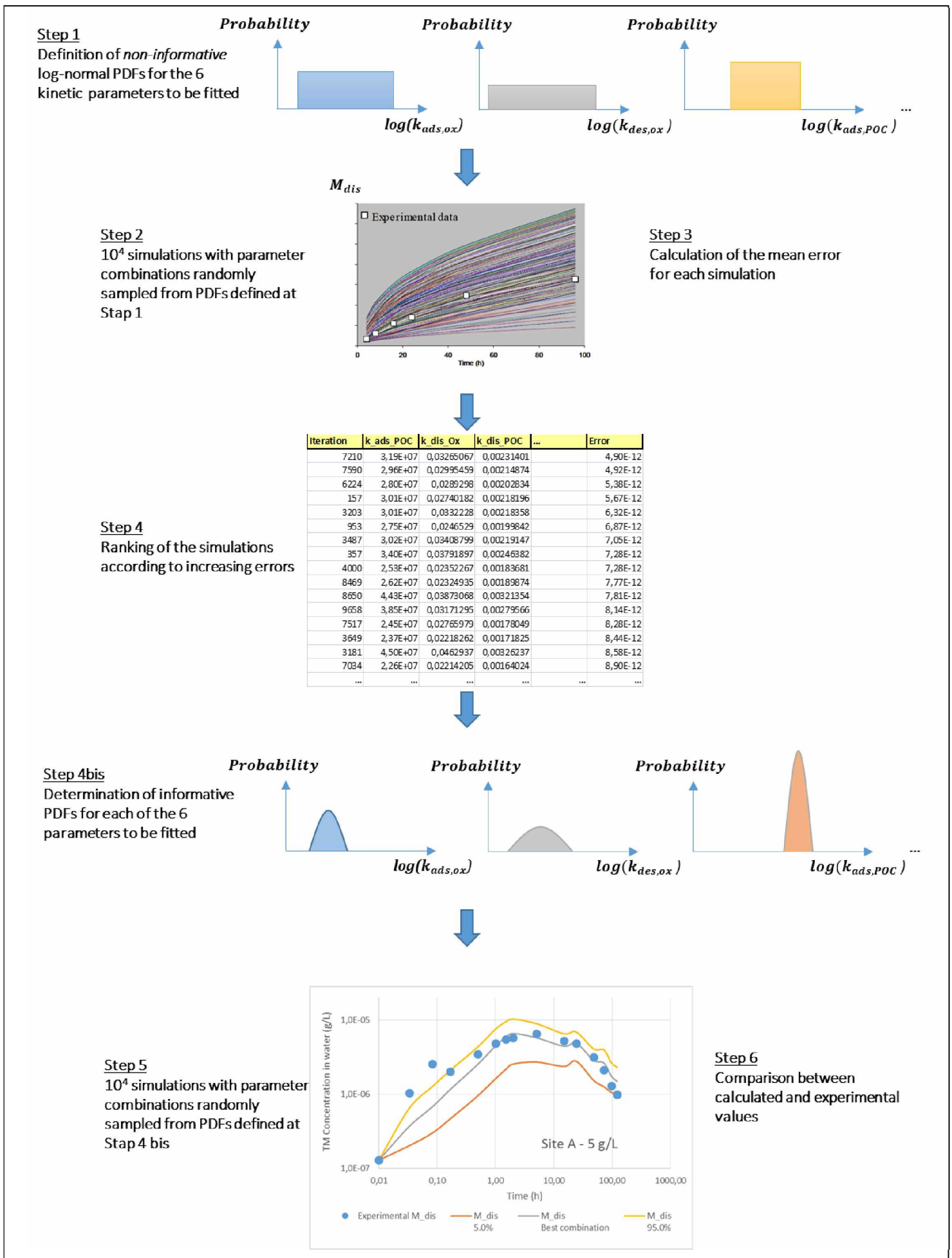


Figure 2 - Steps followed for fitting model parameters

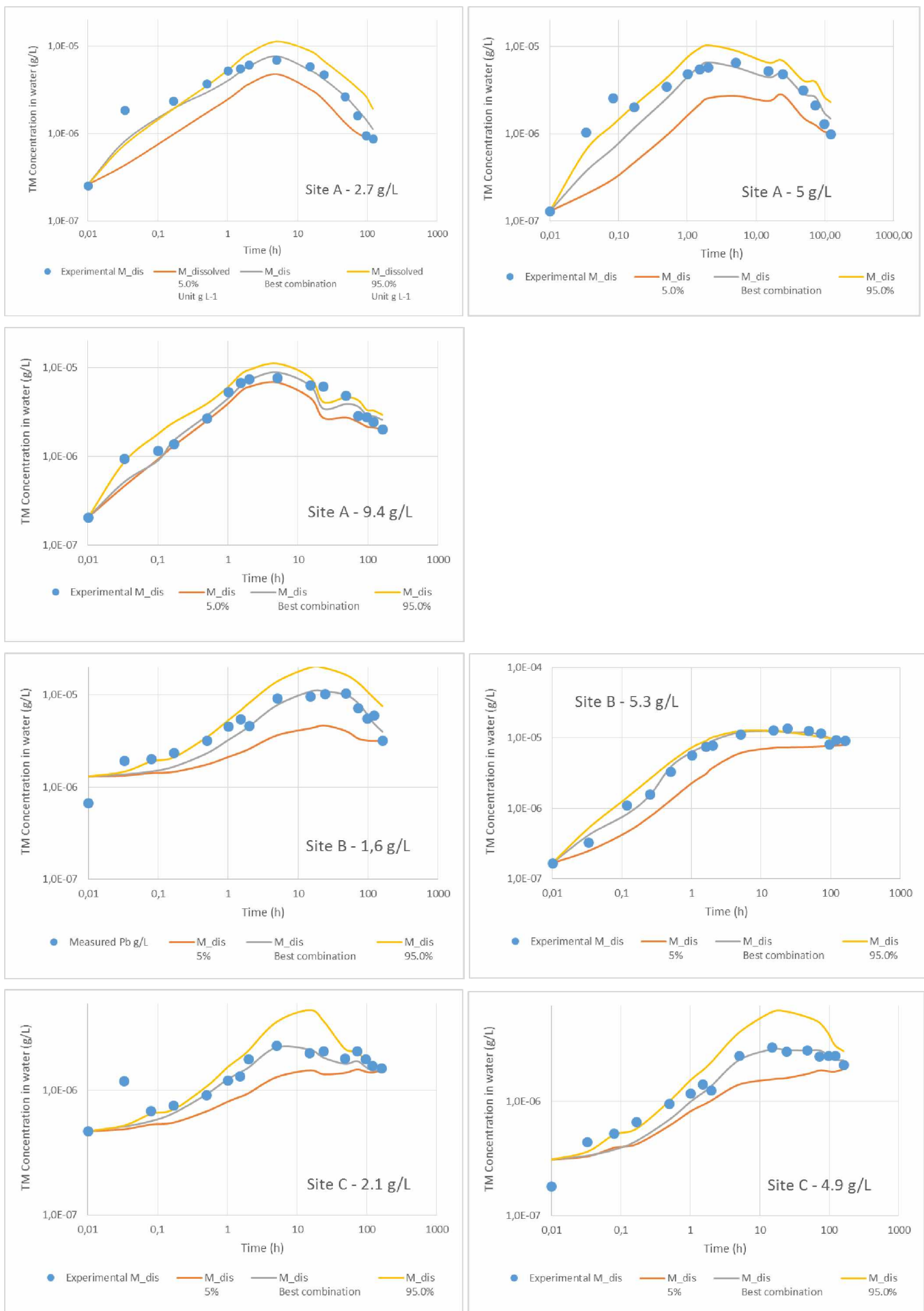


Figure 3 – Dissolved Pb concentration – Comparison between experimental (blue dots) and calculated kinetic evolutions (best combination of parameters, 5th percentile and 95th percentile of the curves generated with the PDFs obtained for each of the parameters)

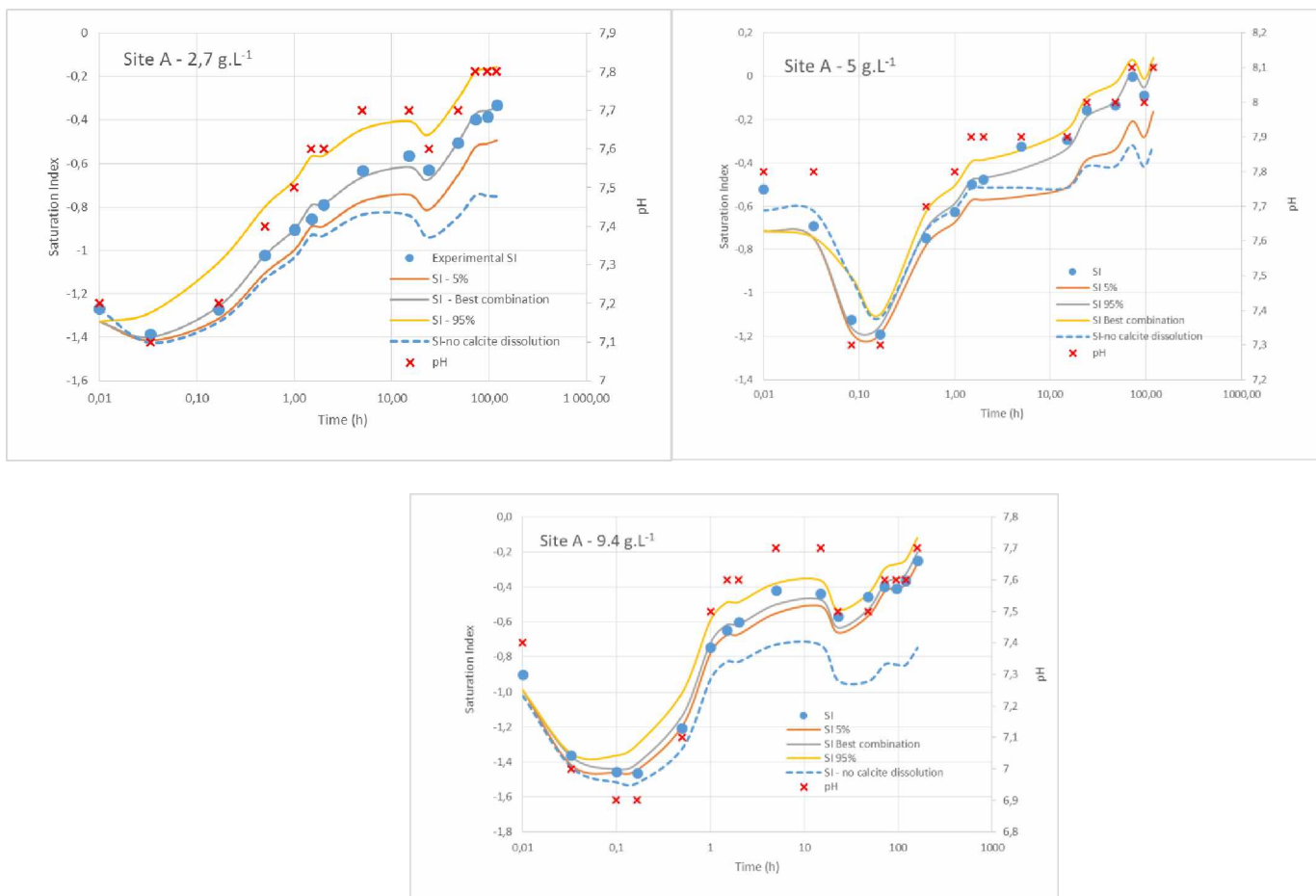


Figure 4 – Saturation index (SI) of calcite – Comparison between experimental and calculated kinetic evolutions. The dashed blue line represents the SI computed without calcite dissolution

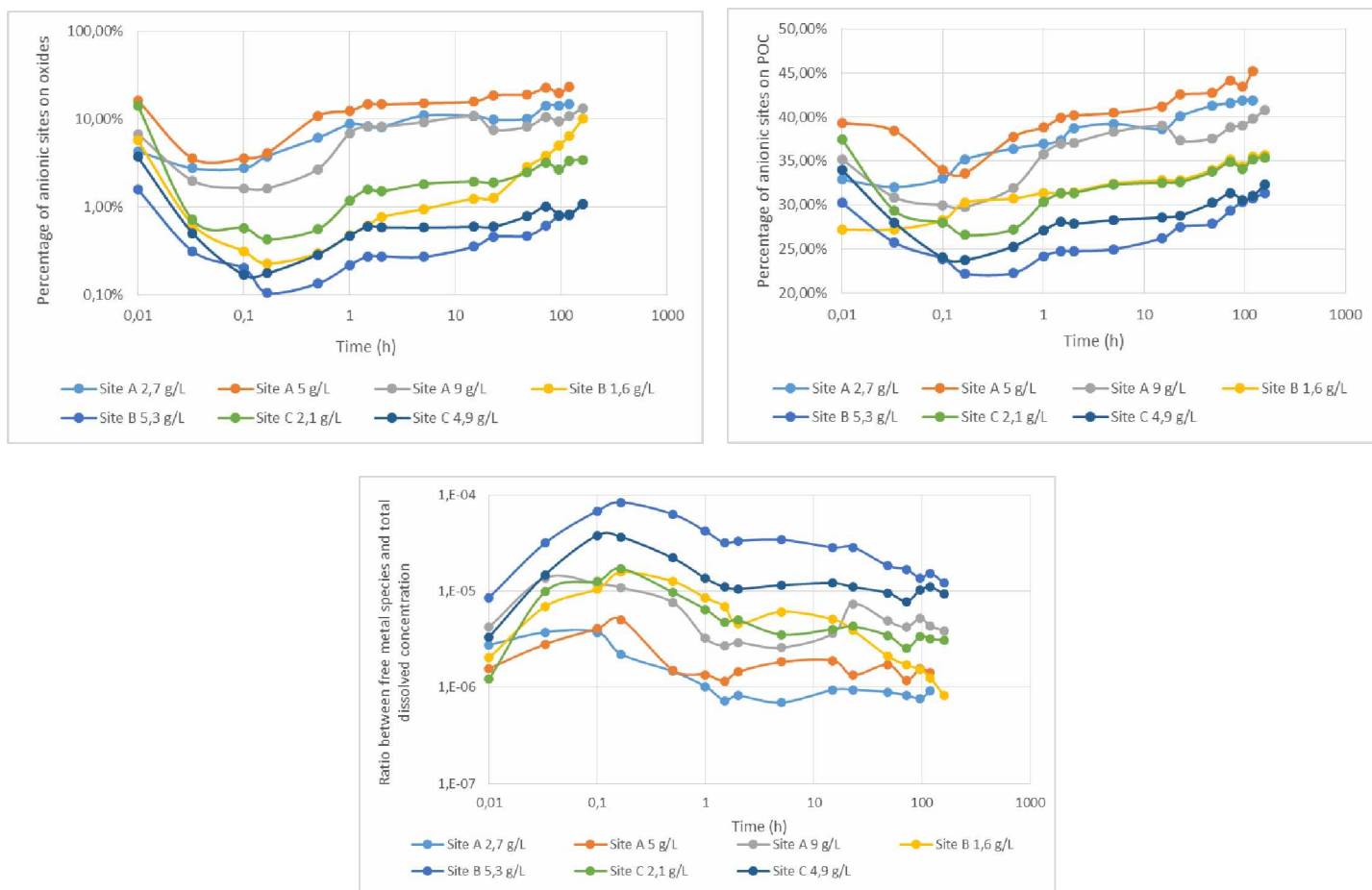


Figure 5 – Fraction of anionic sites f_{SO^-} (%), log scale) on the surface of oxides, fraction of anionic sites f_{HS^-} (%) on the surface of POC, and Ratio f_{free} between free species Pb^{2+} and the total dissolved concentration during the resuspension experiments, for the three sites and all the resuspension experiments.

Simulated process	Aim of the sub-model	Equilibrium ⁽¹⁾ vs Kinetic ⁽²⁾ assumption	Parameters involved in the model	Source and Reference
Speciation of oxide surfaces	Calculating the distribution of deprotonated (SO ⁻), neutral (SOH) and protonated species (SOH ₂ ⁺) on oxide surface	Equilibrium assumption	Physico-chemical characteristics of hydrous ferric oxides: <ul style="list-style-type: none"> • Specific Surface Area of oxide, SSA_{SOH} • Density of monodentate binding sites, $Site_density_{S1}$ • Density of multidentate binding sites, $Site_density_{S2}$ Equilibrium constant of protonation/deprotonation reactions <ul style="list-style-type: none"> • Equilibrium constant of reaction $S1OH \leftrightarrow S1O^-$, $logK_{S1O^-}$ • Equilibrium constant of reaction $S1OH \leftrightarrow S1OH_2^+$, $logK_{S1OH_2^+}$ • Equilibrium constant of reaction $S2OH \leftrightarrow S2O^-$, $logK_{S2OH_2^+}$ • Equilibrium constant of reaction $S2OH \leftrightarrow S2OH_2^+$, $logK_{S2O^-}$ 	‘HFO’ model from Dzombak and Morel (1990) Parameter values are taken from Dzombak and Morel (1990) and are synthesized in Ciffroy and Benedetti (2018)
Speciation of the POC surface	Calculating the distribution of deprotonated (HS ⁻) and neutral (HHS) species on the POC surface (Humic substances)	Equilibrium assumption	Physico-chemical characteristics of the Humic Substances (HS): <ul style="list-style-type: none"> • Site density of functional groups on HS, N_S • Percentage of active DOM that is Fulvic Acids (FA), $Ratio_FA/DM$ • Percentage of active Particulate Organic Carbon (POC) that is FA, $Ratio_FA/POC$ • Group density on FA (quantity of binding sites per unit mass of FA), $Group_density_{FA}$ • Group density on Humic Acids (HA) (quantity of binding sites per unit mass of HA), $Group_density_{HA}$ Equilibrium constant of protonation/deprotonation reactions <ul style="list-style-type: none"> • Intrinsic proton dissociation constants for carboxylic (type A) and phenolic (type B) sites on FA and HA, $logK_{FA_A}$; $logK_{FA_B}$; $logK_{HA_A}$; $logK_{HA_B}$ (four parameters) • Distribution terms modifying for types A and B of FA and HA, ΔpK_{FA_A}; ΔpK_{FA_B}; ΔpK_{HA_A}; ΔpK_{HA_B} (four parameters) • Gel fraction parameter for dissolved FA and HA, gf_{FA}; gf_{HA} • Stern layer capacitance, C 	Stockholm Humic Substances Model (SHM) from Gustafsson (2001) Parameter values are taken from Gustafsson (2001) and are synthesized in Ciffroy and Benedetti (2018)
Complexation of TM with inorganic ligands	Calculating the concentration of TM complexed with hydroxyls, nitrates, sulfates, chlorine and carbonates ions, and then calculating the distribution among free TM (M ^{z+}) and complexed species (ML) in solution	Equilibrium assumption	Affinity constants at equilibrium of the reactions between free TM (M ^{z+}) and ligand (OH ⁻ or NO ₃ ⁻ or SO ₄ ²⁻ or Cl ⁻ or CO ₃ ²⁻) to give complexed species (ML)	Parameter values are taken from Visual Minteq
Complexation of TM with Dissolved Organic Matter (DOM)	Calculating the concentration of TM complexed with DOM, and then calculating the distribution among free TM (M ^{z+}) and	Equilibrium assumption	Equilibrium constant of the reaction leading to the formation of monodentate humic substance-TM complex, $logK_{HSM_mono}$ Equilibrium constant of the reaction leading to the formation of bidentate humic	Stockholm Humic Substances Model (SHM) from Gustafsson (2001)

	complexed species (M-DOM) in solution		substance-TM complex, $\log K_{HSM, bi}$ Distribution term modifying equilibrium constants for humic substances, ΔLK_{HSM}	Parameter values are taken from Gustafsson (2001) and Tipping et al (2011), and are synthesized in Ciffroy and Benedetti (2018)
Speciation of carbonates in solution	Calculating the distribution among CO_3^{2-} , HCO_3^- and H_2CO_3	Equilibrium assumption	Equilibrium constants of the Acid/Base reactions of the $\text{HCO}_3^-/\text{CO}_3^{2-}$ and $\text{H}_2\text{CO}_3/\text{HCO}_3^-$ couples	Parameter values are taken from Visual Minteq
Dissolution/Precipitation of carbonates + Dissolution/Coprecipitation of TM from/to carbonates	Calculating the kinetics in the dissolution of calcite to carbonates in solution	Kinetic assumption	Dissolution kinetic rate, $k_{dis,carb}$ Solubility product of calcite, K_s Exponential correction factor, $\alpha_{dis,carb}$	This model Calibrated for each experimental condition
Complexation of TM with hydrous oxides	Calculating the kinetic adsorption/desorption of TM to/from oxides	Kinetic assumption	Desorption/dissolution rate constant from oxides, $k_{des,ox}$ Adsorption rate constant to oxides, $k_{ads,ox}$	This model Calibrated for each experimental condition
Complexation of TM with POC	Calculating the kinetic adsorption/desorption of TM to/from POC	Kinetic assumption	Desorption/degradation rate constant from POC, $k_{des,POC}$ Adsorption rate constant to POC, $k_{ads,POC}$	This model Calibrated for each experimental condition

Table 1 – Processes, assumptions and parameters involved in the model

- (1) ‘Equilibrium’ assumption means that all the reactions involved for simulating the targeted process are described by equilibrium constants
- (2) ‘Kinetic’ assumption means that all the reactions involved for simulating the targeted process are described by forward and reverse kinetic rate constants

Site	Sediment conc. g.L ⁻¹	Oxides concentration (g.L ⁻¹)	POC (g.L ⁻¹)	$k_{dis,carb}$ h ⁻¹	$\alpha_{dis,carb}$ unitless	$k_{ads,ox}$ L.g ⁻¹ .h ⁻¹	$k_{des,ox}$ h ⁻¹	$k_{ads,POC}$ L.g ⁻¹ .h ⁻¹	$k_{des,POC}$ h ⁻¹	R ²
A	2.7	8.31 10 ⁻³	4.32 10 ⁻²	$\mathcal{N}(1.85.10^{-5}; 1.6.10^{-5})$	$\mathcal{N}(5.94; 1.1)$	< 10 ⁶	$\mathcal{N}(3.6.10^{-2}; 1.3.10^{-2})$	$\mathcal{N}(3.9.10^7; 1.5.10^7)$	$\mathcal{N}(2.8.10^{-3}; 1.4.10^{-3})$	0.97
	5.0	1.54 10 ⁻²	8.80 10 ⁻²	$\mathcal{N}(2.2.10^{-4}; 1.3.10^{-4})$	$\mathcal{N}(4.25; 0.61)$	< 10 ⁶	$\mathcal{N}(2.7.10^{-2}; 1.5.10^{-2})$	$\mathcal{N}(2.3.10^7; 8.6.10^6)$	$\mathcal{N}(2.7.10^{-3}; 1.3.10^{-3})$	0.94
	9.4	2.89 10 ⁻²	1.65 10 ⁻¹	$\mathcal{N}(1.1.10^{-5}; 8.5.10^{-6})$	$\mathcal{N}(5.46; 0.98)$	< 10 ⁶	$\mathcal{N}(1.8.10^{-2}; 7.9.10^{-3})$	$\mathcal{N}(7.9.10^6; 3.9.10^6)$	$\mathcal{N}(4.7.10^{-3}; 2.6.10^{-3})$	0.94
	All conditions together			$\mathcal{N}(8.3.10^{-5}; 5.1.10^{-5})$	$\mathcal{N}(5.22; 0.9)$	< 10 ⁶	$\mathcal{N}(2.45.10^{-2}; 8.10^{-3})$	$\mathcal{N}(2.1.10^7; 9.10^6)$	$\mathcal{N}(1.8.10^{-3}; 1.6.10^{-3})$	0.78
B	1.6	8.50 10 ⁻²	1.02 10 ⁻¹	0	-	< 10 ⁵	$\mathcal{N}(4.5.10^{-2}; 2.1.10^{-2})$	$\mathcal{N}(1.5.10^6; 6.7.10^5)$	$\mathcal{N}(9.4.10^{-4}; 4.1.10^{-4})$	0.96
	5.3	2.82 10 ⁻¹	4.16 10 ⁻¹	0	-	< 10 ⁵	$\mathcal{N}(2.3.10^{-2}; 7.4.10^{-3})$	$\mathcal{N}(3.3.10^5; 1.3.10^5)$	$\mathcal{N}(5.9.10^{-3}; 2.3.10^{-3})$	0.98
C	2.1	8.10 10 ⁻²	1.01 10 ⁻¹	0	-	< 10 ⁵	$\mathcal{N}(3.7.10^{-2}; 1.2.10^{-2})$	$\mathcal{N}(4.10^6; 1.5.10^6)$	$\mathcal{N}(1.5.10^{-2}; 5.6.10^{-3})$	0.94
	4.9	1.89 10 ⁻¹	2.38 10 ⁻¹	0	-	< 10 ⁵	$\mathcal{N}(1.4.10^{-2}; 4.7.10^{-3})$	$\mathcal{N}(5.6.10^5; 2.4.10^5)$	$\mathcal{N}(8.3.10^{-3}; 3.5.10^{-3})$	0.99

Table 1 – Probability Density Functions (PDFs) of the parameters fitted. PDFs provided in the table are normal PDFs $\mathcal{N}(\text{mean}; \text{SD})$.