Solid/liquid ratios of trace elements and radionuclides during a Nuclear Power Plant liquid discharge in the Seine River: Field measurements vs geochemical modelling

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Abstract

This study focuses on the determination of **field solid/liquid ratios (Rd)** values of trace element (TE) and radionuclide (RN) in the Seine River (France) during a concerted low radioactivity level liquid regulatory discharge performed by a Nuclear Power Plant (NPP) and their confrontation with Kd values calculated from geochemical modeling. This research focuses on how **field Rd** measurements of TE and RN can be representative of Kd values and how Kd models should be improved.

For this purpose 5 sampling points of the Seine River during a NPP's liquid discharge were investigated: upstream from the discharge in order to assess the natural background values in the area of effluent discharge, the total river water mixing distance (with transect sampling), and 2 points downstream from this last area. The main parameters required determining **field Rd** of TE and RN and their geochemical modeling (Kd) were acquired. Filtered waters were analyzed for alkalinity, anions, cations, dissolved organic carbon (DOC), TE, and RN concentrations. Suspended particulate matter (SPM) was analyzed for particulate organic carbon (POC), TE and RN concentrations and mineralogical composition. **Field Rd** and Kd values are in good agreement for stable Cd, Cu, Ni, Pb and Zn and for ⁷Be. Conversely, measured **field Rd** for stable Ag, Ba, Sr, Co and Cs are systematically higher than modeled Kd values. Even if only the lowest possible values were obtained for ¹³⁷Cs and ⁶⁰Co Rd measurements, these estimated limits are higher than calculated Kd for ¹³⁷Cs and in good agreement for ⁶⁰Co. Finally, only two RN exhibit **field Rd** lower than calculated Kd: ²³⁴Th and ²¹⁰Pb.

Comparison of **field Rd** vs. modeled Kd values for TE and RN allows the identification, for each element, of the main involved adsorption phases and geochemical mechanisms controlling their fate and partitioning in river systems.

Keywords: radionuclides, trace elements, partition coefficient, geochemical modeling, River

Highlights:

- This research focuses on how **field solid/liquid ratios (Rd)** measurements of trace elements and radionuclides can be representative of Kd values and how Kd models should be improved.

- Field R_d measurements and modeled K_d values are in good agreement for stable Cd, Cu, Ni, Pb and Zn and for ^7Be
- Comparison of field R_d vs. modelled K_d values for trace elements and radionuclides allows the identification of the main geochemical mechanisms controlling their fate and partitioning in river systems.

1 Introduction

The distribution (or partitioning) coefficient (K_d) between soluble and particulate phases is one of the most important parameters used in estimating the mobility of trace elements or radionuclides (TE or RN) in fresh, estuarine and marine waters. Partition coefficients help to assess health and environmental risks because they allow quantifying pathways of environmental transport, spatial and temporal distributions, mobility and bioavailability of trace element and radionuclides (Sibley *et al.*, 1986; Benes *et al.*, 1992, 1994; Ciffroy *et al.*, 2001; Brach-Papa *et al.*, 2005). Trace element and radionuclide, characterized by high K_d values exhibit low mobility within water bodies and predominant transfer pathways through physical dispersion of solid particles. Those characterized by low K_d values are mainly exported within water fluxes and their concentrations in the environment fluctuate more rapidly than those of the former group (Vesely *et al.*, 2001). K_d is defined as the ratio of the trace element and radionuclides concentration sorbed onto naturally occurring solid surfaces to their corresponding concentration in the dissolved phase of the surrounding water mass. Using K_d parameter assumes that (1) only low concentration of trace element and radionuclide are both in aqueous and solid phases, (2) relationship between their concentrations in the solid and liquid phases is linear, (3) equilibrium conditions are reached, (4) similar and reversible rapid adsorption and desorption kinetics are observed, (5) it describes trace element and radionuclide partitioning between one single sorbate (TE and RN) and one unique sorbent type (soil, particular matter, sediments, etc.), and (6) all adsorption sites are accessible and have equal strength (EPA, 1999). Most K_d values used in environmental and health risks assessment originate from the literature after statistical analyses (J. Allison and T. Allison, 2005; IAEA, 2010). K_d values are usually derived from field solid/liquid ratios (R_d) obtained from laboratory or field experiments and depend on the nature of adsorbent and on the chemical conditions of the aqueous media used. However,

laboratory experiments determine R_d values for a predominant process or a single sorbent associated with a given chemical solution composition (Radovanovic and Koelmans, 1998; Tipping *et al.*, 1998; Vesely *et al.*, 2001). Thereby, K_d values are not necessarily suitable and/or available for a wide range of river systems. Most generally, they represent an integrative representation of complex processes controlling solid/liquid partitioning including various parameters such as suspended particulate matter (SPM) concentration, composition and origin (Zhao and Hou, 2012), major and trace element concentrations (Lourino-Cabana *et al.*, 2010), pH value (EPA, 1999), water temperature, redox conditions (Bird and Schwartz, 1997; Xue *et al.*, 1997), ionic strength, organic matter (OM) concentration and nature (Bryan *et al.*, 2002; Pokrovsky *et al.*, 2010) and climatic settings (O'Connor and Connolly, 1980; Garnier *et al.*, 1997; J. Allison and T. Allison, 2005). Thus, the relevance and robustness of literature-derived K_d values most generally highly depend on both the number of referenced data and physico-chemical information associated to those data. As K_d values ranging over until five orders of magnitude can be obtained from literature (EPA, 1999; IAEA, 2010; Boyer *et al.*, 2017; Tomczak *et al.*, 2019), using generic or default K_d values can result in significant uncertainties when they are used to predict the fate of trace element and radionuclide. Thereby, site-specific K_d values are required for site-specific trace element and radionuclide and risk assessment calculations. Ideally, site-specific K_d values should be deduced from field R_d measured for a huge range of biogeochemical conditions characterizing the target ecosystem, which is generally not the most common case. It is therefore crucial to link K_d values with realistic environmental physico-chemical settings before they are applied to trace element and radionuclide transport modeling in rivers submitted to discharges from Nuclear Power Plant (NPP's) (Ciffroy *et al.*, 2000, 2009).

In this frame, the main objectives of our study were (1) to acquire field R_d s for trace element and radionuclide during a NPP's liquid discharge from regulatory operations in the

Seine River; (2) to apply a geochemical speciation modeling for Kd calculation by using physico-chemical parameter values measured at the various sampling points as input data; (3) to compare calculated Kd values to the field Rds of trace element and radionuclide in order to improve and to refine the geochemical models.

2. Materials and methods

2.1. Field settings, sampling sites, sampling procedure and sample treatment

The study area is located within the Seine River upstream and downstream of La Motte-Tilly (Fig. 1). The Seine River drains a typical Mesozoic-Cenozoic sedimentary basin constituted of limestone mixed or inter bedded with terrigenous sediments derived from the paleo reliefs bordering the Mesozoic and Cenozoic seas (Roy *et al.*, 1999). The Seine Basin is characterized by a temperate and oceanic climate and is nearly uniform in terms of relief, geology and hydrology. The hydrological regime is pluvial oceanic, with mean rainfall between 500 and 1000 mm/year (Meybeck *et al.*, 2004). Detailed description of the Seine River regarding the flow rates and their seasonal variations, geological settings and climatic regime are described in details in Guérini *et al.*, 1998; Roy *et al.*, 1999; Ciffroy *et al.*, 2000; Meybeck *et al.*, 2004; Billen *et al.*, 2007; Even *et al.*, 2007.

Fig. 1 and Fig. 2 present a simplified scheme of the Seine river watershed, along with the sampling points, and the synthesis of analysis conducted and carrier phases taken into account in the Kd calculation, respectively. Sample inventory and associated characteristics are presented in Table 1. Samples were collected in august 2013 during a scheduled NPP's liquid discharge at the most upstream station as a natural background values point (COP-1), at the regulatory discharge point (i.e. discharged water COP-2), in the middle course of the stream in the zone of total mixing (COP-3) with transect samples points (COP-3.1, COP-3.2 and COP-3.3), and two points downstream (COP-4 and COP-5)

The NPP's liquid discharge started at 2.00 AM and lasted 72 hours. The samplings started 7 hours after the beginning of the discharge (Table 1) to be performed in complete mixing conditions.

SPM and filtered water sampling for radionuclides analyses

For radionuclides, large volume water samples (from 917 L to 1 313 L) were collected using a high capacity submersible pump and directly passed through 0.50 µm Millipore Milligarde® cartridge filters for particle/solution separation. Ash filters (408°C) were used for SPM radionuclide concentrations. To measure filtered water radionuclide concentration a protocol of radionuclides concentration described in Eyrolle-Boyer *et al.* (2014) that consist in evaporation of 200 L aliquots of filtered waters to dryness (40°C) was used for the Seine River samples.

Dissolved load and Suspended Particulate Matter (SPM) sampling

For major and trace elements, 2 L of grab surface water samples (i.e. depth from 0 to 0.5 meter) were sampled, filtered and treated directly in the field. For SPM, large volumes of water river samples (about 20 L of surface water samples) were collected in polyethylene shadow-proof packets for later filtration in the laboratory. For the dissolved load, a first aliquot of the bulk sample was filtered through pre-weighted 0.8 µm glass fiber filters (GFF) for the determination of suspended particulate matter SPM and particular organic carbon (POC) concentrations. During filtration, the first 50 ml of sample solution were discarded, thereby allowing saturation of the filter surface and collecting vessel prior to filtrate recovery. The resulting filtrate was acidified with 85% H₃PO₄ to pH ≤ 2 for dissolved organic carbon (DOC) concentration analyses and stored in amber glass vials. A second aliquot of the bulk sample was filtered through a 0.22 µm acetate-cellulose membrane. One sub sample of the corresponding filtrate was acidified with 15 N distilled nitric acid for further determination of

major and trace element concentrations. Another, non-acidified, sub sample of the filtrate was used for determination of anions concentration and alkalinity. After filtration, each collected water sample fraction (i.e. bulk, filtered) was stored in pre-cleaned, acid-washed polyethylene bottles at 4°C until analysis.

For the suspended load filtered in the laboratory with a 0.22 µm acetate-cellulose membrane (Millipore) using a Teflon cell and a peristaltic pump towards SPM accumulation. A part of SPM collected on filters was milled using agate mortar and pestle for the X-ray mineralogical composition analysis. Another part aliquot was digested by a tri acid attack (HF, HNO₃, HCl) (Shirai *et al.*, 2015) for the measurements of total major and trace elements concentrations.

2.2. Analytical techniques

2.2.1. Physico-chemical analysis

Water temperature, pH, and conductivity were measured in the field using a WTW 3410 Set 2 multi-parameter. Major anion concentrations (Cl⁻, F⁻, SO₄²⁻, NO₃⁻) were measured by ion chromatography (Thermo Scientific ICS 1100) with an accuracy of 5%. Alkalinity was measured using universal titrator Titrando 809, Metrohm. The dissolved organic carbon (DOC) concentration was determined using a Shimadzu TOC-VCSH analyzer (accuracy 1.5%, detection limit 200 µg/L). The particulate organic carbon (POC) was determined using NC Analyser (Flash 2000, Thermo Scientific) with an accuracy of 5%.

Total trace and major elements (Na, K, Mg, Ca, Sr, Ba, Fe, Al, Ni) concentrations, in solutions and suspended matter, were determined using a Thermo Fisher ICP 6200 Duo ICP-OES (accuracy of 5% and detection limit of 2 µg/L). Total trace elements (Mn, Co, Cu, Zn, Ag, Cd, Cs, Pb) with lower concentrations (< 2 µg/L) were measured by Thermo Scientific (Element II) high performance, double focusing ICP-MS (accuracy of 5% and detection limit of 1 ng/L). The SLRS 4 and 5 were used as certified reference materials

for those elements.

The mineralogical composition of SPM was determined using X-ray diffraction (XRD) analysis on a PANalytical X'pert Pro diffractometer equipped with a multichannel X'celerator detector and using the Co K α radiation ($\lambda=1.7889$ Å), in 2θ range of 20-100°.

2.2.2. Radionuclides analysis

The following non stable elements ^7Be , ^{60}Co , ^{137}Cs , ^{40}K , ^{228}Ac , ^{234}Th , ^{210}Pb were analyzed by gamma spectroscopy using Ultra low-level well-type HPGe detectors (Canberra) installed in the Modane underground laboratory (France) under 1 700 m of rock. The well-type HPGe detectors are calibrated by Monte Carlo type simulation performed by the codes GeSpeCor (Sima *et al.*, 2001) or Geant3. The simulated model has been validated with the measurements of a standard multi-gamma source in water equivalent resin, contained in 12 mL tubes filled up to different heights (1, 3, 6 and 12 mL). The effective germanium crystal volume is 450 cm³. The resolution of the detector is 1.9 keV at 59 keV; 2.2 keV at 662 keV and 2.4 keV at 1332 keV and its background rate is around 7.2 events/h. MeV in the energy range 30-2700 keV. Additional non stable elements were also measured but will not discussed here, the list is given in the supplementary information section.

The discharged water sample (COP-2), was analyzed by gamma spectrometry onto 3 L of the sampling solution by using an ultra-pure germanium gamma spectrometer (Canberra EGPC 42-190-R, P type, relative efficiency 41%) installed at Cadarache.

3. Geochemical modeling

In the following we will detail the general modeling strategy outlined in Fig. 3. Chemical calculations were made using the Visual Minteq computer code (Gustafsson, 2011, version 3.0 for Windows) which allows to calculate the chemical speciation of elements with

inorganic ligands, bindings onto organic compounds by using the NICA-Donnan approach (Benedetti *et al.*, 1995, 1996; Kinniburgh, 1999; Milne *et al.*, 2001, 2003) and trace elements sorption onto hydrous ferric oxide by using the model of Dzombak and Morel (1990). Adsorption onto clays was accessed by using a non-electrostatic ion exchange model with Gaines-Thomas exchange constants (Appelo and Postma, 2005). For the modeling of Cs adsorption onto clay borders sites including high affinity sites, the 'Fixed-charge site' model was used (Poinssot *et al.*, 1999). For the modeling of sorption onto calcite, a simplified non-electrostatic ion exchange model was used (Zachara *et al.*, 1991; Gaskova *et al.*, 2008, 2009). Input parameters for the simulation of K_d values were: pH, alkalinity, anions, cations, total trace elements (dissolved + SPM), DOC concentrations and the respective amounts of the mineral or organic phases in the SPM (such as POC, hydrous ferric oxide (HFO), clay and calcite) (Fig. 3).

In order to describe the interactions between dissolved organic matter and trace elements with the NICA-Donnan model, the knowledge of the nature of the organic matter and its amount is necessary. Humic acid (HA) and fulvic acids (FA) are the two main components used in the NICA-Donnan model as surrogate of the natural organic matter. In natural samples their concentration varies from one sample to another mainly depending on the origin of OM and its degree of degradation. Organic compounds are present in two forms in aquatic samples: the solid form (POC) in SPM, and the so-called dissolved one that may include colloidal components (DOC). According to Tipping (2002), the dissolved organic matter (DOM) is mostly fulvic and the particulate organic matter (POM), which mostly comes from the soils of the watershed, contains more HA. Different compositions with various HA/FA ratios were tested (results not shown) but no significant changes occurred on the log K_d values (i.e. they are within the uncertainties given for the average value of log R_d

in table S3 and S4). Consequently, let us assumed that DOM is 100% composed of FA and POM is 100% composed of HA.

The characterization of naturally occurring organic matter (NOM) is expected because the binding capacity of NOM for trace elements most generally depends on NOM quality (Chappaz and Curtis, 2013). Applying an adjustment factor, based on NOM UV-vis quality, Chappaz and Curtis (2013) adjusted the site density for representing the NOM quality but only improved by 30% the goodness of their fits. This gain is of course important for aqueous speciation of the trace elements but it would only lead to a very minor change in log K_d values. NOM's reactivity with trace elements can also be modified due to its own interaction with mineral surfaces. However, such mechanisms are difficult to assess for SPM samples. Therefore, we favored a conservative approach and a ratio of active DOM/DOC and POM/POC of 1.65 has been used as suggested by Sjöstedt et al., (2010).

In order to determine the constants related to Cs and Ag complexation with OM we used the approach of Milne (2003) that allows to predict the NICA-Donnan parameter values representative of FA and HA bounds from the first hydrolysis constant (K_{OH}) of the metal by using the correlations. The parameters used for modeling Cs and Ag complexation with OM are those from Milne (2003).

Three main types of (hydr)oxides in the SPM were considered: iron, aluminum and manganese (hydr)oxides. Since the concentration of manganese is very low ($<10 \mu\text{g/L}$), we assumed that trace element adsorption onto manganese oxides is negligible. Lofts and Tipping (2000) showed that the adsorption of metal ions onto aluminum oxides is similar to that generally observed onto iron oxides. Thus, we considered aluminum oxides as iron oxides and associated adsorption properties related to a single mineral grouping these two oxides. In order to describe complexation reactions associated to this generic metal oxide we used the diffuse layer model (DLM) for hydrous ferric oxide (HFO) from Dzombak and Morel (1990)

instead of the more robust CD-Music approach proposed by Ponthieu et al., (2006) since spectroscopic speciation data are lacking for the later approach.

Clay compounds are represented in the form of nontronite (smectite) with a surface area ranging from 650 to 800 m²/g and a cation exchange capacity (CEC) of 100 meq/100g (Dejou, 1987). For the adsorption modeling of Cs onto clay borders sites with a high selectivity (Poinssot *et al.*, 1999) we used a fixed charged model with a concentration of borders sites of 0.1 meq/100g. For the adsorption modeling of the others trace element onto clays we used a non-electrostatic ion exchange model with Gaines-Thomas exchange constants (Appelo and Postma, 2005).

The nature of adsorption and co-precipitation processes with calcite (CaCO₃) surface is complex (Lakshtanov and Stipp, 2007; Wolthers *et al.*, 2008, 2012; Lourino-Cabana *et al.*, 2010). Then for the adsorption modeling on calcite we used simplified non-electrostatic ion exchange model with an exchange position density of 3.6·10⁻⁶ mol/g and an average surface area of 12.5 m²/g (Zachara *et al.*, 1991; Gaskova *et al.*, 2008, 2009). The surface of calcite has a near-neutral charge in the range of natural pH values of the Seine River.

For a given metal (noted Me), the calculations of saturation index (SI) of the MeCO₃ show that there is no pure MeCO₃ mineral phase precipitation in the Seine River in our conditions. On the other side the SI of calcite (CaCO₃), aragonite (CaCO₃), dolomite ((Ca,Mg)CO₃), vaterite (CaCO₃) shows the oversaturation of the solution, so CaCO₃ could precipitate with associated metals.

The contribution in the K_d values of Sr, Co and Ba by co-precipitation with calcite was calculated using the equation (Lourino-Cabana *et al.*, 2010):

$$X_{Me(predicted)} = \frac{(Me^{2+}) * (X_{Ca}) * D_{Me}^{Calcite}}{(Ca^{2+})}$$

Where (Ca²⁺) and (Me²⁺) correspond to the ionic concentrations of Ca²⁺ and Me²⁺, respectively, X_{Ca} and X_{Me} are the Ca and Me molar fractions in the particulate calcite fraction

at the calcite surface, and $D_{Me}^{Calcite}$ corresponds to distribution coefficient between water and calcite. The $D_{Me}^{Calcite}$ values for Me = Ba, Sr, Ni and Co are 0.06, 0.46, 3.47 and 3.7, respectively (Lourino-Cabana *et al.*, 2010).

The adsorption of trace element and radionuclide on quartz (SiO_2) was not considered because of its low reactive surface and by the fact that binding constants to quartz are weak compared to those of OM and FeOOH (Schindler and Stumm, 1987; Benedetti *et al.*, 1996).

3 Results and discussion

3.1. Field data

DOC, POC, ion concentrations, trace and major elements concentrations, alkalinity, pH and conductivity measured in the river during field sampling operations are reported in Tables 2 to 4.

The studied waters are characteristic of the carbonated watersheds of the Seine River with pH ranging from 8.2 to 8.3 except at the discharge point that displays a pH value of 8.4. Cations concentrations (K^+ , Na^+ , Mg^{2+} , Ca^{2+}) along the lateral transect sampled are uniform (0.050 – 0.056, 0.24 – 0.26, 0.15 and 2.25 – 2.35 mmol/L, respectively) with systematically higher values for NPP's discharge (0.066, 0.345, 0.19 and 30 mmol/L, respectively). The distributions of major anions concentrations (Cl^- , NO_3^- , SO_4^{2-}) are 0.35-0.38, 0.25-0.26 and 0.15-0.21 mmol/L, respectively, with higher values for the NPP's discharge (0.49, 0.34 and 1.35 mmol/L, respectively). The alkalinity was of 3.79 ± 0.02 meq/L for the Seine river samples and 2.93 meq/L for the discharge. The DOC concentrations of the Seine river samples cluster around 1.6 ± 0.1 mg/L, a higher value of 2.2 mg/L was measured at the NPP discharge point. Concentrations in the water samples of the NPP's discharge are higher than in upstream and downstream samples (Tables 3 and 4) for: Be (4.2 times), Ba (5.7 times), Ca

(1.3), Cd (4.0), Cu (2.5), K (1.3), Mg (1.3), Na (1.4), Ni (1.8), Pb (2), Sr (1.2), Co (1.5), SO_4^{2-} (8.8), Cl^- (1.4), NO_3^- (1.4).

SPM concentrations range from 3.5 to 13.5 mg/L without any systematic variations as well as POC concentrations (4.7 – 9.9 %). X-ray analyses for mineral composition showed that SPM from each sample is composed of calcite (CaCO_3) at 75 %, quartz (SiO_2) at 20 % and nontronite ($\text{Fe}_2\text{H}_{10}\text{Na}_{0.3}\text{O}_{16}\text{Si}_4$) and clay (smectite type) at 5 %. XRD analyses did not detect the presence of crystalline iron (hydr)oxide minerals (i.e. < 1%), so iron hydroxide was considered as amorphous. XRD analyses did not detect manganese (hydr)oxide indicating a concentration below 1%.

Five percent of SPM is accounted by nontronite, the concentration of amorphous iron hydroxide can be calculated as the difference between the total iron concentration in SPM and the iron concentration in the clay. The amorphous FeOOH concentrations, expressed in mg of Fe per liter of Seine river water, are estimated to vary from 0.1 to 0.2 mg/L in the Seine River samples with the highest concentration observed for the NPP discharge (0.37 mg/L). The Mn concentration in SPM, expressed per liter of water, ranges from 2.6 to 11.4 $\mu\text{g/L}$

The concentrations of artificial radionuclides (^{137}Cs and ^{60}Co) issued from NPP and those of naturally occurring radionuclides (^7Be , ^{40}K , ^{228}Ac , ^{234}Th and ^{210}Pb) of the Seine River filtrate and SPM samples are reported in Table 3 and Table 4, respectively (see supplementary information for data on other trace elements and radionuclides in Table S1 and S2).

3.2. Measured field Rd

Measured field Rd values of stable trace elements and anthropogenic and natural radionuclides are presented in Table S3 and Table S4, respectively and in Figure 4.

A literature review, summarized in table S3, shows that average field Rd values of this study are within the range of previously reported values (Alison and Alison, 2005; Sheppard

et al., 2009 and Ji et al., 2016). It is, however important to realize that log values tend to minimize differences among samples and sites especially for some trace elements speciation. For instance, if we recompute them in term of percentage of adsorbed metal and dissolved metal similar log Rd will give different distributions. Here for sample COP-1, we give an example for Ba (5% sorbed, 95% dissolved), Cd (41% sorbed and 59% dissolved) and Pb (86% sorbed and 14% dissolved) using the data in tables 2, S2 and S3. Additional calculations, also show that going from COP-1 to COP-2 the Cd field Rd goes from 5.17 to 4.74, but concomitantly SPM concentration changes from 4.26 to 11.26 mg/L of SPM resulting in a much more significant difference in Cd distribution between the two samples (i.e. 20.5% Cd sorbed and 79.5% of Cd dissolved) while for Pb going from log Rd 6.11 to 5.88 we obtain 80% adsorbed and 20% dissolved a minor change compared to the distribution in COP-1. This clearly show that Rd to be interpreted needs to be used in combination with more advanced chemical or geochemical modelling concepts based on more detailed physico-chemical parameters, that we put forward in this manuscript. These measures and the geochemical modelling will provide information on the speciation both in the dissolved phase and in the solid phase which is a very important information regarding the bioavailability (and thus toxicity) of the trace metals and radionuclides and that is not available from a Rd parameter.

In most cases our results show no significant differences between Rds measured at the various sampling points. Indeed, for potassium Log Rd does not vary or very slightly either for its stable isotope (Table S3) or for its main naturally occurring radioactive isotope, namely ⁴⁰K (Table S4) without any significant trends between the samples' location. Log Rd values of stable Cs cluster around 6.2 while lower field Rd values were registered for ¹³⁷Cs (4.62 – 5.37). Log Rd for stable Sr and Ba cluster around 3 and 4.5, respectively (Table S3).

Log Rds for Ni, Co and Cu range from 4.35 to 4.91, from 5.10 to 5.81 and from 4.84 to 5.35, respectively, and the values increase with increasing distance from NPP's discharge (Table S3) reaching a maximum value in the point COP-5. Average Log Rd of Zn, Cd and Ag were similar and cluster around 5.

Log Rd of stable Pb was 5.9 for NPP's discharge and this value is centered at 6.1 for the Seine River samples without any significant trends between the samples' location. Log Rd of ^{210}Pb varies from 4.09, upstream, to 4.94, downstream (Table S4). There is a systematic difference between Rd values of stable Pb and ^{210}Pb continuously produced by the decay of atmospheric ^{222}Rn gas. For the upstream sample this difference is almost two orders of magnitude (Table S3, S4). Usually, this phenomenon can be explained by the different origins of stable and radioactive isotopes: the stable isotope is a constituent of mineral crystal lattices while the radioactive isotope is essentially sorbed onto the surface of particles (FeOOH, MO, clay, etc.) and, therefore, more mobile.

3.3. Comparison between modeled Kd and field Rd

Fig. 5 presents the modeled distribution of trace element and radionuclide on the different surfaces of SPM. Results show that sorption of Cu and Cd is controlled by complexation with particulate OM (99%). Zn, Ni, and Co are adsorbed predominantly on OM (60-75%) and at 25-40% on Fe hydroxide. Pb is adsorbed predominantly on Fe (hydr)oxide (80%) and 20% of particulate Pb is due to its complexation with particulate OM. Cs is absorbed on clay surface at 100 % (Fig 5).

Modeled values of Log Kd are also presented in **Figure 4 (Table S5)**. As observed for **field** Rd values, there are no systematic gaps between modeled Kd values for upstream, downstream and discharge samples.

It is to be noted that in the present work the parameters were not systematically adjusted to obtain the best fit possible between field R_d and K_d . This is simply because it is not the purpose of this paper. It would make no sense to try to have the perfect fit. Doing that, will jeopardize the demonstration that multicomponent models with generic parameters can be of help to simulate real world systems since they give good K_d predictions and that in addition you can get supplementary information on the major species phases controlling the fate of the elements under investigation for a given geochemical ecosystem. What can be useful is to have an idea on the uncertainties of the parameters used here to develop complementary or new approach based on probabilistic generation of parameters' values for given systems to see if the R_d is within the envelope of potential K_d values generated by the methods as shown by Ciffroy and Benedetti , (2018).

Differences induced by filtration will not strongly affect $\log R_d$ which are compared on $\log$ scale to $\log K_d$ since the concentration changes due to different filtration size will affect only by a few % of the bulk concentration the filtrate concentration. Especially for DOM and POM since NOM covers a continuum of sizes that cannot be delimited once for all. Differences observed over several orders of magnitudes like here for $\log K_d$ vs $\log R_d$ (i.e. 2 to 4) cannot be explained by filtration issues but by affinity constant values for the binding sites. Variations of the amount of matter for the simulated $\log K_d$ can modify the K_d value by less than a few tens of % but never by orders of magnitude (Ren et al,2015).

However, the difference between field R_d and modelled K_d values could be related to a kinetic effect rather than a defect from the theoretical assumption of equilibrium. Adsorption and desorption from the particle phase can take several hours and may not be equally fast in time (Ciffroy et al., 2003, Wang et al., 2000).

3.3.1 Elements for which modeled K_d and field R_d are similar (Be, Cd, Cu, Ni, Pb, Zn)

Field Rd values for stable Cd, Cu, Ni, Pb and Zn are in good agreement with modeled Kd values (Fig. 4). The minimum values assessed for ^{60}Co and Be^7 are also in good agreement with modeled Kd values, supporting the assumptions made for the modelling.

3.3.2 Elements for which modeled Kd is higher than measured Rd (^{234}Th and ^{210}Pb)

There is a difference between stable Pb and ^{210}Pb : modeled Kd are in good agreement with Rd of stable Pb and not with Rd of ^{210}Pb . Stable Pb is mostly complexed to SPM and does not take a part of the SPM crystal lattice (Priadi et al, 2011). The difference in Rd values of stable and ^{210}Pb could be explained by the fact that: (1) distribution of ^{210}Pb results from the sorption of this element but also on the sorption of previous elements of the decay chain of ^{210}Pb (e.g. U, Th, ...). These elements (U, Th...) could be more mobile (for example, $K_d \text{ Th} < K_d \text{ Pb}$), consequently more soluble ^{210}Pb could be observed compared to sorbed ^{210}Pb mobile, and so sorption sites could be different for radioactive and stable Pb (Ayrault et al., 2012). It is also possible that the flux of ^{210}Pb of atmospheric origin to fresh water increased the ^{210}Pb concentration in solution, decreasing the Rd if solid/liquid equilibrium is not reached (Ayrault et al., 2012).

3.3.3 Elements for which modeled Kd is smaller than measured Rd (Sr, Ba, Ag, Co, Cs and ^{137}Cs)

For Co and Cs measured Rd are systematically higher than modeled Kd. The explanations of these differences could be the following ones: (1) Cobalt is incorporated in surface precipitates that are not taken into account in the model (Muray, 1975; Thompson et al., 1999; Siebecker et al., 2014; Gou and Li, 2017); (2) constant of complexation OM-Cs and constant of sorption FeOOH-Cs are not well known (Du et al, 1998; Wang et al., 2000) or missing in the database of the speciation code leading to systematic underestimation of the modeled Kd .

373

374 Modeled K_d values of Th and Ag are systematically smaller than the measured R_d of
375 ^{234}Th and stable Ag. That could be explained by the lack of robustness of the constants of
376 complexation Th-MO used for the modeling. Like in the case of Pb-OM binding constants the
377 Th-OM and Ag-OM NICA-Donnan constants were estimated by Milne (2003) and not
378 experimentally obtained. In addition, Th and Ag correspond to the two extremes cases of this
379 method using a regression line relating K_{OH} and metal ion binding constant, with the first
380 constants of hydrolysis $\text{Log } K_{\text{OH}}$ of -3.197 and -11.997, respectively (Table S-5). Such
381 “extreme” binding constant values are derived from the linear regression obtained for small
382 range of K_{OH} and thus may explain the underestimation of modeled K_d values (Martin et al.,
383 2020).

384 Adsorption on calcite modeling in conjunction with modeling of complexation with OM
385 and FeOOH does not show any contribution of calcite in K_d values. So, in perspective for K_d
386 modeling, adsorption on calcite surface could not be considered (Zachara et al., 1991; Uygur
387 and Rimmer, 2000).

388 However, for elements, like Sr, that are known to be Ca analog further investigation is
389 are necessary by considering the element co-precipitation with calcite. Two simulations were
390 done considering the co-precipitation with a monolayer surface only or on the calcite
391 multilayer surface assuming the co-precipitation on the calcite is a long cycle process where
392 trace element co-precipitate and re-co-precipitate. By considering monolayer co-precipitation
393 no evolution of $\log K_d$ value is observed in comparison of $\log K_d$ calculated without
394 considering co precipitation (2.40 ± 0.17 and 2.35 ± 0.16 (L/kg), respectively). However, taking
395 into consideration the modeling of Sr multilayer co-precipitation increases $\log K_d$ values
396 (3.29 ± 0.16 (L/kg)) in line with the $\log R_d$ value measured (Table S3). Not taking into account
397 this phenomenon in $\log K_d$ calculation could explain the underestimation of modeled K_d for

Sr compare to measured Rd (Fig. 4). The same calculations are done for Ba and Co without generating modifications of Kd values suggesting that this phenomenon may not be a major process controlling the Kd values.

Similar observations are made when the adsorption onto clay is modeled. In the later, our results show that only Cs is a high selectivity element. Consequently, the modelling of adsorption onto clay is only taken into consideration in the case of Cs.

Knowing the trace element distribution between the different sites the current model can be simplified by considering only the major phases and species that control trace element association with solids.

3.5 Model fit by adjustment of constitutive fractions

Concentrations of stable Cs in SPM are in good agreement with concentrations of stable K, Fe and Al with R^2 of 0.85, 0.90 and 0.89, respectively (Fig. 6A). This could underline adsorption onto clay compounds (nontronite $\text{Fe}_2\text{H}_{10}\text{Na}_{0.3}\text{O}_{16}\text{Si}_4$) and ionic exchange with K. The concentrations of stable Sr correlate with stable Ca ($R^2=0.90$), that could indicate the repetitive long-term processes of multilayer co-precipitation with calcite. The concentrations of stable Ni and Co in SPM are in good agreement ($R^2=0.99$), so we may conclude that these two elements are governed by similar transfer mechanisms and display close adsorption site types. The concentrations of ^{137}Cs in SPM correlate with concentrations of ^{40}K , ^7Be , ^{210}Pb and ^{234}Th in SPM with R^2 of 0.99, 0.92, 0.93 and 0.98, respectively (Fig. 6B). We can consider that these radionuclides are concerned by close adsorption sites and behave in the same way in aquatic systems. However, we do not observe any correlations between radionuclides and stable elements. The R^2 of ^{137}Cs with stable K, Fe and Al is of 0.07, 0.11 and 0.007, respectively. We can assume therefore that (1) either the mechanism of the radionuclide (in particular ^{137}Cs) transport is not due to adsorption onto clay compounds (like in the case of

stable Cs), or (2) the water sampling, filtration and radionuclide concentrations measurements were performed before equilibrium could be reached. For example, the sorption equilibrium time of ^{137}Cs in the system "water - solid phase" is estimated of 1-3 days (Anikeev and Khristianova, 1973; Behrens et al., 1982; Nosov et al., 2010), whereas our sampling was performed 7-17 h (see Table 1) after the NPP discharge start.

Differences of environmental behavior between radiogenic and stable isotopes and consequently the gap between their K_d values are well-known. This was reported by Mundschenk (1996) where measured R_d values for ^{137}Cs in the Rhine river system (SPM/Water and Sediments/Water) were systematically one order of magnitude smaller than stable ^{133}Cs . Similar results are described in Sheppard *et al.* (2009) where R_d values for radiogenic Sr are lower than the R_d values for geogenic stable Sr. Nosov *et al.* (2010) reported that between two isotopes of one single element of significantly different half-lives, the short-lived one is generally mobile, because it does not associate with the crystalline grid of the mineral while weathering, and because, it does not instantaneously diffuse from the solution to the crystalline structure of the host rock. In the aquatic systems (vs rocks and soils) a ratio between 2 isotopes of one single element (ex. U, Th) may vary from the equilibrium one in ten - hundred times (Nosov *et al.*, 2010) depending on their origin. For example, the most common values of ratios $^{234}\text{U}/^{238}\text{U}$ and $^{228}\text{Th}/^{232}\text{Th}$ concentrations correspond of 1-1.5 and 0.9-2.5 for surface waters and 2- 15 and >5.0 for the crystal rocks waters, respectively (Bakhur, 1998).

4 Conclusions

The distribution coefficient, K_d , is an integrative representation of complex processes that characterize the partitioning of trace element between solid/liquid and depends on numerous site-specific environmental parameters. In the frame of health and environmental

449 risk assessments dealing with regulatory or accidental radioactive discharges, it is therefore
450 crucial to link K_d values to realistic environmental physico-chemical settings before they are
451 applied to trace element or radionuclides transport modeling in rivers.

452 Here we acquired in-situ solid/liquid ratios (R_d) values for the Seine river by sampling
453 during a NPP's liquid discharge from regulatory operations and compared the data with the
454 results from a geochemical speciation modeling dedicated to K_d calculation.

455 No significant variations of the solid/liquid ratios values were observed in the samples
456 collected in the Seine River during the discharge.

457 The comparison between measured in situ R_d and modelled K_d values for various trace
458 elements and radionuclides lead to identify the main adsorption phases and their dominant
459 transport mechanisms in aquatic systems.

460 The geochemical modeling of K_d for Cu, Zn, Cd, Ni, Co, Pb, Th, Ba, ^7Be (with POM
461 and HFO as adsorption phases) and the sequential implementation of additional phases (clay,
462 calcite) show that clay surfaces have to be considered only for Cs because of its high affinity
463 with clay borders and surface basal. For all other trace elements sorption onto clay is not
464 necessary because of its weak exchange constants when compared to complexation constants
465 with organic matter and iron(hydro)oxydes. Considering or not the calcite does not impact
466 significantly their sorption, and consequently their K_d , due to its low surface reactivity and its
467 electro neutrality in natural pH values, and weak constants of exchange TE-calcite by contrast
468 to constants of complexation TE-OM and TE-FeOOH. For further K_d modeling, we may not
469 take into consideration adsorption on calcite surface.

470 Contrariwise, Sr multilayer co-precipitation shows a significant contribution in final K_d .

471 The adsorption of trace element and radionuclide on quartz (SiO_2) was not considered
472 because of its low reactive surface and by the fact that quartz-binding constants are weak
473 compared to those of OM and FeOOH.

This work clearly demonstrate that classical field Rd can be interpreted and completed by advanced chemical or geochemical modelling concepts based on more detailed physico-chemical parameters. In order to test the method relevance further investigations on others nuclearized rivers (ex. Rhône or Loire) with different environmental settings (watershed bedrocks, SPM composition, clay proportion, water discharge, macro-composition, pH, etc.) are necessary.

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Figure Captions:

Figure 1. The sampling sites location along the Seine River. Samples were taken at depth between 0 and 0.5 meters.

Figure 2. Geochemical and radionuclide analysis conducted in the field and in the laboratory. The full data set is given in supplementary material. Water constituents taken into account to obtain model K_d values to be compared to field R_d retrieved from the geochemical analysis.

Figure 3. Modelling workflow used to compute trace elements and radionuclides speciation and derived model K_d . For each element the generic data bases of models' parameter were used. Please refer to given references for more detailed information.

Figure 4. Modelled $\log K_d$ versus field $\log R_d$ for trace elements and radionuclides. The * indicates minimum field $\log R_d$ values. Error bars are included in the symbols.

Figure 5. Modelled trace elements distribution among the different surfaces of the suspended particulate matter.

Figure 6. Panel A showing the correlations between the stable K, Fe and Al concentrations and stable Cs concentration. Panel B showing the correlations between concentrations of ^7Be , ^{40}K , ^{210}Pb , ^{234}Th and ^{137}Cs in the suspended particulate matter.

Geochemical Analysis:

Field Data: T°, pH, Conductivity, [O₂], Alkalinity.

Laboratory Measurements:

Dissolved Fraction: [Anions], [Cations], [DOC], [Trace Elements]
Suspended Matter : [SPM], [POC], [Trace Elements], Mineralogy

Input

Data

Radionuclide Analysis:

Dissolved Fraction: activity of RN,
Suspended Matter : activity of RN

Field **Rd**
(Stable Elements)

?
=

Field **Rd** (Natural RN)
Field **Rd** (Artificial RN)

Speciation Modelling

?
=

Modelled **Kd**
(Stable Elements)

Input Data:

T° , pH, $[O_2]$, Alkalinity.

Dissolved Fraction: [Anions],
[Cations], [DOC], [Trace Elements]

Suspended Matter : [SPM], [POC],
[Trace Elements], Mineralogy

Geochemical Speciation Modelling

Output Data:

Free ionic species : Me^{z+}

Inorganic Complexes : MeL_n

Bound to DOM : Me-DOM

Bound to POM : Me-POM

Sorbed to (Hydr)oxides : Me-HFO

Sorbed to Clays : Me-Clay

Sorbed to Calcite : Me- $CaCO_3$

Colloids :

POM: NICA-Donnan Model,
(Benedetti et al., 1996 - Kinniburgh et al., 1999)
With generic parameters from Milnes et al., (2001, 2003)

Clay: Ion exchange model Gaines Thomas (Appelo & Postma, 2005)
Clay: For Cs only, Fixed Charge site model (Poinssot et al., 1999)

(Hydr)oxides: Surface complexation model (Dzombak & Morel, 1990)

Carbonates: Ion exchange model
(Zachara et al., 1999 - Gaskova et al., 2009)

Particulate

DOM: NICA-Donnan Model,
(Benedetti et al., 1996 - Kinniburgh et al., 1999)
With generic parameters from
Milnes et al., (2001, 2003)

Inorganic Complexes
Visual Minteq data base.

Dissolved

Modelled K_d
(Stable Elements)

TABLES

Table 1. List of collected water samples

Sample point	Description	Time of sampling from start of NPP discharge, hours
COP-1	Upstream point, 250 m upstream the discharge	7
COP-2	Effluent Discharge pipe	8
COP-3	Middle course of the river, zone of full mix, 1 km downstream the Discharge	10.5
COP-3.1	Transect point 1, right waterside, 65 m downstream COP-3	10.5
COP-3.2	Transect point 2, middle flow, 65 m downstream COP-3	11.5
COP-3.3	Transect point 3, left waterside, 65 m downstream COP-3	13
COP-4	Downstream, 4.05 km downstream the Discharge	15
COP-5	Downstream, 14.15 km downstream the Discharge	17

Table 2. Geochemical characteristics of the sampling points (August 2013).

	COP-1	COP-2	COP-3.1	COP-3.2	COP-3.3	COP-4	COP-5
T, °C	20.2	25.2	21.1	21.1	21.4	21.7	21.7
pH	8.21	8.41	8.26	8.27	8.26	8.28	8.32
χ , $\mu\text{S}/\text{cm}$	484	565	493	500	503	500	493
O ₂ , %	94	100	98	99	100	100	100
TDS, mg/L	8.47	8.37	8.71	8.81	8.82	8.69	9.03
Alkalinity, $\mu\text{eq}/\text{L}$	3820	2934	3787	3787	3787	3770	3770
[DOC], mg/L	1.61	2.19	1.59	1.59	1.64	1.66	1.67
[F ⁻], $\mu\text{Mol}/\text{L}$	5.36	6.60	6.30	5.83	5.96	5.38	6.41
[Cl ⁻], $\mu\text{Mol}/\text{L}$	354	495	369	368	371	378	380
[NO ₃ ⁻], $\mu\text{Mol}/\text{L}$	251	341	255	253	253	260	259
[SO ₄ ²⁻], $\mu\text{Mol}/\text{L}$	154	1355	206	205	205	207	210
[K ⁺], $\mu\text{mol}/\text{L}$	50	66	51	50	51	52	56
[Na ⁺], $\mu\text{mol}/\text{L}$	241	345	249	250	256	256	261
[Mg ²⁺], $\mu\text{mol}/\text{L}$	154	191	153	154	156	154	155
[Ca ²⁺], $\mu\text{mol}/\text{L}$	2270	2970	2310	2313	2358	2333	2310
[SPM], mg/L	4.67	11.26	3.72	3.50	13.53	7.11	3.65
[POC], mg/L	0.36	1.11	0.37	0.33	0.64	0.47	0.27
[K] _{SPM} , g/kg	9.95	10.8	9.4	10.1	8.23	9.86	9.5
[Ca] _{SPM} , g/kg	205	174	184	190	174	194	206
[Mg] _{SPM} , g/kg	4.62	4.91	4.33	4.67	3.77	4.82	4.82
[Fe] _{SPM} , g/kg	26.8	30.5	25.1	28.2	22.3	29.9	27.7
[Al] _{SPM} , g/kg	46.5	50.6	42.9	49.0	38.4	51.2	45.9
[Mn] _{SPM} , g/kg	0.715	1.02	0.71	0.86	0.72	1.03	0.81
Calcite, % in SPM	75	75	75	75	75	75	75
Quartz, % in SPM	20	20	20	20	20	20	20
Clays, % in SPM	5	5	5	5	5	5	5

Table 3. Major and trace elements (µg/L) and radionuclides (Bq/L) concentrations in the dissolved load.

	COP-1	COP-2	COP-3	COP-3.1	COP-3.2	COP-3.3	COP-4	COP-5	
Cs	0.0047	0.00442	-	0.00412	0.00215	0.00201	0.00211	0.00217	
Sr	224	275	-	223	224	227	227	228	
Ba	16.31	91.13	-	17	16.51	16.68	16.55	16.93	
Co	0.047	0.0726	-	0.0463	0.047	0.0475	0.0476	0.046	
Ni	0.95	1.74	-	1.1	1.2	1.3	1.18	1.12	
Cu	0.676	1.79	-	0.594	0.461	0.4	0.462	0.405	
Zn	2.05	3.49	-	2.84	3.51	3.39	3.49	2.54	
Ag	<0.001	<0.001	-	0.002	<0.001	<0.001	0.002	<0.001	
Cd	0.0026	0.00832	-	0.00411	0.00164	0.00176	0.0031	0.00201	
Pb	0.018	0.0372	-	0.0236	0.0169	0.0167	0.0212	0.0183	
¹³⁷ Cs	<0.000021	<0.03	<0.000114	-	-	-	<0.000027	<0.000023	T _{1/2} 30.17 years
⁷ Be	0.0071	<0.5	0.0062	-	-	-	0.0081	0.0091	53.3 days
⁶⁰ Co	<0.000043	<0.03	<0.000071	-	-	-	<0.000059	<0.000058	5.27 years
²¹⁰ Pb	0.0048	<7.2	0.00078	-	-	-	0.00091	<0.0013	22.3 years
²³⁴ Th	0.0033	<7.6	0.0034	-	-	-	0.0042	0.0036	24.1 days

Table 4. Major and trace elements (mg/kg_{dry}) and radionuclides (Bq/kg_{dry}) concentrations in the suspended particulate matter.

	COP-1	COP-2	COP-3	COP-3.1	COP-3.2	COP-3.3	COP-4	COP-5
Cs	4.67	5.09	-	4.21	4.90	3.77	4.88	4.56
Sr	283	244	-	257	265	238	263	300
Ba	181	428	-	175	183	162	301	1200
Co	6.49	20.0	-	6.25	7.51	5.96	13.9	29.7
Ni	34	69	-	34	36	29	59	92
Cu	51	124	-	53	72	55	65	90
Zn	183	307	-	293	319	263	287	228
Ag	0.446	0.710	-	0.592	0.553	0.402	0.592	0.936
Cd	0.381	0.459	-	0.447	0.412	0.343	0.460	0.366
Pb	23	28	-	25	25	21	25	25
¹³⁷ Cs	4.78	2.9*	4.79	-	-	-	4.89	2.27
⁷ Be	159.9	49*	176.9	-	-	-	187.2	62.25
⁶⁰ Co	<0.46	<0.26*	0.74	-	-	-	1.32	0.39
²¹⁰ Pb	59.7	38*	67.3	-	-	-	73.4	34.6
²³⁴ Th	19.3	15*	19.35	-	-	-	18.8	12.45

* Suspended sediments from the **pump** (average sample of 1 month)

Declaration of interests

☐ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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Supplementary information

Solid/liquid ratios of trace elements and radionuclides during a Nuclear Power Plant liquid discharge in the Seine River: Field measurements vs geochemical modelling

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1- RN analysis

The following additional radionuclides were also measured ^{110m}Ag , ^{241}Am , ^{57}Co , ^{58}Co , ^{134}Cs , ^{154}Eu , ^{54}Mn , ^{22}Na , ^{106}Rh , ^{124}Sb , ^{125}Sb , were analyzed using Ultra low-level well-type HPGe detectors (Canberra) installed in the Modane underground laboratory (France) under 1 700 m of rock. The well-type HPGe detectors are calibrated by Monte Carlo type simulation performed by the codes GeSpeCor (Sima *et al.*, 2001) or Geant3. The simulated model has been validated with the measurements of a standard multi-gamma source in water equivalent resin, contained in 12 mL tubes filled up to different heights (1, 3, 6 and 12 mL). The effective germanium crystal volume is 450 cm³. The resolution of the detector is 1.9 keV at 59 keV; 2.2 keV at 662 keV and 2.4 keV at 1332 keV and its background rate is around 7.2 events/h. MeV in the energy range 30-2700 keV.

For ^{63}Ni analyses, samples were dissolved together with a known amount of stable nickel used as carrier and chemical yield. Solution were prepared in citrate medium at pH 8 and then passed on a chromatographic column containing dimethylglyoxime (DMG) to form a Ni-DMG complex. After washing the column, the nickel is eluted with 3 M HNO_3 . It is then precipitated with DMG again. After filtration and washing the precipitate, the Ni-DMG complex is oxidized to NiO by calcination oven at 500°C . The obtained oxide was dissolved in a mixture HNO_3/HCl . The solution is evaporated and the residue taken up in 6 ml of 0.1M HCl. An aliquot of the final solution is taken for the measurement of total nickel by ICP- AES for the determination of chemical yield and 4 ml were counted by liquid scintillation to determine the ^{63}Ni activity (from Holm *et al.*, 1992). Holm E., Rots P. and Skwarzec B. 1992. Radioanalytical Studies of Fallout ^{63}Ni . Appl. Radiat. Isot. 43(1/2), 371-376.

2- Results

Despite a protocol designed to decrease the quantification limits, the concentrations of $^{110\text{m}}\text{Ag}$, ^{58}Co and ^{63}Ni measured in the effluent discharge pipe and in the filtered water and SPM sampled in the Seine River display values below the quantification capabilities. In situ K_d values for these RN's from our field experiment are therefore unavailable. However, the concentrations of ^{137}Cs and ^{60}Co are below the quantification limits in the filtered waters but above the quantification limits in SPM so it is possible to estimate minimum K_d values for ^{137}Cs and ^{60}Co : $K_{d\text{min}} = [\text{RN}]\text{SPM} / [\text{RN}] \text{ w, detection limit}$.

All artificial RNs concentrations from the discharge were below the limit of quantification (Tables S-2 and S-3) even though suitable analytical tools were used for their detection.

3- Additional tables

Table S-1. Major and trace elements (µg/L) and radionuclides (Bq/L) concentrations in the dissolved fraction (august 2013).

	COP-1	COP-2	COP-3	COP-3.1	COP-3.2	COP-3.3	COP-4	COP-5	
Na	5506	7914	-	5702	5727	5871	5868	5968	
K	1941	2571	-	1986	1940	1993	2033	2192	
Cs	0.00470	0.00442	-	0.00412	0.00215	0.00201	0.00211	0.00217	
Mg	3743	4643	-	3720	3735	3789	3751	3774	
Ca	90787	118794	-	92449	92522	94331	93335	92361	
Sr	224	275	-	223	224	227	227	228	
Ba	16.31	91.13	-	17	16.51	16.68	16.55	16.93	
Al	1.54	1.49	-	0.652	2.02	<0.2	<0.2	<0.2	
Mn	1.20	0.925	-	1.62	1.70	1.93	1.87	1.82	
Fe	4.75	4.34	-	2.60	3.66	3.85	3.58	4.16	
Co	0.0470	0.0726	-	0.0463	0.0470	0.0475	0.0476	0.0460	
Ni	0.950	1.74	-	1.10	1.20	1.30	1.18	1.12	
Cu	0.676	1.79	-	0.594	0.461	0.400	0.462	0.405	
Zn	2.05	3.49	-	2.84	3.51	3.39	3.49	2.54	
Ag	<0.001	<0.001	-	0.002	<0.001	<0.001	0.002	<0.001	
Cd	0.00260	0.00832	-	0.00411	0.00164	0.00176	0.00310	0.00201	
Sb	0.0745	0.112	-	0.0728	0.0730	0.0736	0.0737	0.0783	
Pb	0.0180	0.0372	-	0.0236	0.0169	0.0167	0.0212	0.0183	
									T _{1/2}
⁴⁰ K	0.051	<0.4	0.055	-	-	-	0.056	0.068	1.3·10 ⁹ years
¹³⁷ Cs	<0.000021	<0.03	<0.000114	-	-	-	<0.000027	<0.000023	30.17 years
⁷ Be	0.0071	<0.5	0.0062	-	-	-	0.0081	0.0091	53.3 days
⁶⁰ Co	<0.000043	<0.03	<0.000071	-	-	-	<0.000059	<0.000058	5.27 years
²¹⁰ Pb	0.0048	<7.2	0.00078	-	-	-	0.00091	<0.0013	22.3 years
²²⁸ Ac	0.00069	<0.1	0.00059	-	-	-	0.00064	0.00076	6.15 hours
²³⁴ Th	0.0033	<7.6	0.0034	-	-	-	0.0042	0.0036	24.1 days

Table S-2. Major and trace elements (mg/kg_{dry}) and radionuclides (Bq/kg_{dry}) concentrations in suspended particulate matter (august 2013).

	COP-1	COP-2	COP-3	COP-3.1	COP-3.2	COP-3.3	COP-4	COP-5
Na	1495	877	-	850	670	661	730	1264
K	9955	10822	-	9395	10085	8229	9862	9496
Cs	4.67	5.09	-	4.21	4.90	3.77	4.88	4.56
Mg	4616	4906	-	4325	4669	3773	4819	4814
Ca	204489	173816	-	183974	189586	173620	193830	206170
Sr	283	244	-	257	265	238	263	300
Ba	181	428	-	175	183	162	301	1200
Al	46509	50584	-	42859	49011	38437	51174	45929
Mn	715	1016	-	709	861	724	1030	805
Fe	26812	30574	-	25141	28229	22324	29889	27709
Co	6.49	20.0	-	6.25	7.51	5.96	13.9	29.7
Ni	34	69	-	34	36	29	59	92
Cu	51	124	-	53	72	55	65	90
Zn	183	307	-	293	319	263	287	228
Ag	0.446	0.710	-	0.592	0.553	0.402	0.592	0.936
Cd	0.381	0.459	-	0.447	0.412	0.343	0.460	0.366
Sb	0.577	1.05	-	0.746	0.541	0.491	0.516	0.509
Pb	23	28	-	25	25	21	25	25
⁴⁰ K	275.7	181*	285.7	-	-	-	291.0	128.5
¹³⁷ Cs	4.78	2.9*	4.79	-	-	-	4.89	2.27
⁷ Be	159.9	49*	176.9	-	-	-	187.2	62.25
⁶⁰ Co	<0.46	<0.26*	0.74	-	-	-	1.32	0.39
²¹⁰ Pb	59.7	38*	67.3	-	-	-	73.4	34.6
²²⁸ Ac	18.4	17*	19.35	-	-	-	19.75	10.47
²³⁴ Th	19.3	15*	19.35	-	-	-	18.8	12.45

* Suspended sediments from the pump (average sample of 1 month)

Table S-3. Measured values of log Rd of the stable elements (L/kg). *literature search taken from J.D. Allison and T.L. Allison, 2005, SPM/Waterlog Kd, L/kg
**literature search taken from Sheppard *et al.*, 2009

COP-1	COP-2	COP-3.1	COP-3.2	COP-3.3	COP-3 average	COP-4	COP-5	Average this	Median
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									study	literature*
K	3.71	3.62	3.67	3.72	3.62	3.67	3.69	3.64	3.67±0.04	-
Cs	6.00	6.06	6.01	6.36	6.27	6.14	6.36	6.32	6.19±0.15	4.23**
Sr	3.10	2.95	3.06	3.07	3.02	3.04	3.06	3.12	3.05±0.05	2.68**
Ba	4.05	3.67	4.01	4.04	3.99	3.95	4.26	4.85	4.10±0.32	4.0 (2.9 - 4.5)
Co	5.14	5.44	5.13	5.20	5.10	5.20	5.46	5.81	5.31±0.23	4.7 (3.2 - 6.3)
Ni	4.56	4.60	4.49	4.48	4.35	4.50	4.70	4.91	4.57±0.16	4.6 (3.5 - 5.7)
Cu	4.88	4.84	4.95	5.19	5.14	5.00	5.15	5.35	5.06±0.16	4.7 (3.1 - 6.1)
Zn	4.95	4.94	5.01	4.96	4.89	4.95	4.92	4.95	4.95±0.03	5.1 (3.5 - 6.9)
Ag	-	-	5.50	-	-	5.50	5.50	-	5.50±0.00	4.9 (4.4 - 6.3)
Cd	5.17	4.74	5.04	5.40	5.29	5.13	5.17	5.26	5.15±0.19	4.7 (2.8 - 6.3)
Pb	6.11	5.88	6.03	6.17	6.11	6.06	6.07	6.14	6.07±0.08	5.6 (3.4 - 6.5)

Table S-4. Measured values of log Rd of the radionuclides (L/kg).

	COP-1	COP-3	COP-4	COP-5	Average this study
⁴⁰ K	3.73	3.72	3.72	3.28	3.61±0.22
¹³⁷ Cs	≥5.37	≥ 4.62	≥5.26	≥5.00	≥5.06±0.33
⁷ Be	4.35	4.46	4.36	3.84	4.25±0.28
⁶⁰ Co	≥4.02	≥4.02	≥4.35	≥3.82	≥4.05±0.22

²¹⁰ Pb	4.09	4.94	4.91	≥4.44	4.64±0.48
²³⁴ Th	3.76	3.75	3.65	3.54	3.68±0.10

Table S-5. Modelled values of log Kd (L/kg).

	COP-1	COP-2	COP-3	COP-4	COP-5
Cs	4.53	4.35	4.50	4.48	4.51
Be	4.68	-	4.56	4.63	4.54
Sr	2.63	2.30	2.30	2.21	2.30
Ba	2.33	2.24	2.41	2.22	2.33
Co	4.13	4.43	4.18	4.28	4.42
Ni	4.25	4.30	4.22	4.23	4.30
Cu	5.03	4.94	5.12	5.11	5.18
Zn	4.75	4.73	4.71	4.64	4.74
Ag	2.00	2.68	2.05	2.15	2.01
Cd	5.13	4.88	5.20	5.10	5.17
Pb	6.00	5.86	5.99	5.98	6.00
Th	4.99	-	5.14	4.91	4.97

Table S-6. Prediction of NICA-Donnan parameters for the metal binding by fulvic and humic acids from the first hydrolysis constant (K_{OH}) by Milne (2001, 2003).

$$n_1 = 0.13 - 0.056 \log K_{OH}$$

$$n_2 = 0.77n_1$$

$$n_1 \log K_1 (\text{fulvic}) = 0.36 \log K_{OH} + 2.47$$

$$n_2 \log K_2 (\text{fulvic}) = 0.91 \log K_{OH} + 9.02$$

$$n_1 \log K_1 (\text{humic}) = 0.26 \log K_{OH} + 2.55$$

$$n_2 \log K_2 (\text{humic}) = 0.40 \log K_{OH} + 4.93$$

	Ag	Cs	Th
$\log K_{OH}$	-11.997-15.6847	-3.197	
n_1	0.80	1.01	0.31
n_2	0.62	0.78	0.24
$\log K_1$ (fulvic)	-2.306	-3.150	1.65
$\log K_2$ (fulvic)	-3.073	-6.766	25.46
$\log K_1$ (humic)	-0.710	-1.515	5.44
$\log K_2$ (humic)	0.213	-1.731	15.21