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Highlights:

Reconstruction of historical SPM inputs of the Rhône River to the Mediterranean Sea

Influence of past anthropogenic inputs on source contribution modelling

Non-reactive fraction successfully estimated past SPM inputs

Geochemical (mixing) model results are consistent with documented past flood events

1. Introduction

An excess of suspended particulate matter (SPM) in rivers can cause environmental and economic damages (e.g., clogging spawning beds, degrading water quality or filling reservoirs; Navratil et al., 2012; Torres-Astorga et al., 2018). Since the 1970s, sediment fingerprinting approaches have been widely used to identify the SPM sources. Most fingerprinting studies in the literature use geochemical tracers, such as trace and major elements, to assess contemporary SPM inputs in rivers. However, few studies have focused on historical sediment inputs over a larger time-scale using the fingerprinting approach on sediment cores, which can provide retrospective information on past hydrological events (floods) or modifications of SPM fluxes, such as dam construction, bank stabilization or revegetation

(Collins et al., 1997; Navratil et al., 2012). Manjoro et al. (2017) studied several methodological factors related to the work on sediment cores, such as the spatial representativeness of a sediment core, the number of tracers selected and the optimal number of model iterations, on model estimations of source contributions. Other studies investigated the application of geochemical (Collins et al., 1997; Pulley et al., 2015), colorimetric (Pulley et al., 2018), magnetic (Pulley et al., 2015) and radiometric (Pulley et al., 2015) tracers for estimating source contributions of contemporary SPM in a sediment core; this was done for periods ranging from a few decades to 250 yr. The main objectives of fingerprinting studies applied on sediment cores are to investigate changes in SPM sources over time (Collins et al., 1997; Manjoro et al., 2017). The results were interpreted by comparing estimates of the historical source contributions against information related to land-use changes (Huang et al., 2019), reservoir construction (Gateuille et al., 2019), implementation of actions to reduce soil erosion (Wang et al., 2018), or available hydrological data (Navratil et al., 2012).

The reconstruction of historical SPM inputs into a river generally implies measurements of tracers in contemporary SPM used as source samples. However, Pulley et al. (2015) is one of the few studies that reported the risk of using non-conservative tracers (e.g., changes in organic matter content, particle size selectivity, geochemical and magnetic reactions along the sedimentary profile) to assess historical source contributions in sediment cores. Begorre et al. (2021) recently showed that the main issue with using fingerprinting approaches on sediment cores is the non-conservative behaviour of the geochemical tracers (i.e., total trace and major elements) because (i) tracers undergo diagenetic processes that modify their partitioning and concentrations in sediment layers, and (ii) tracers have been largely modified since the mid-1970s, notably because of changes in anthropogenic inputs (Audry et al., 2004; Dhivert et al., 2016). The proposed alternative was to use the non-reactive fraction to limit the effects of non-conservative behaviour of the selected tracers. One advantage of this novel approach is that it increases the number of conservative tracers available after passing the range test (Begorre et al., 2021).

Focusing on the Rhône River, historical sediment contamination by polychlorobiphenyls and metals (Mourier et al., 2014; Dendeviel et al., 2020) and contributions from contemporary sources of SPM across the river catchment (Zebracki et al., 2015; Dabrin et al., 2021) have previously been documented.

At the scale of the Bléone River, which is a sub-catchment of the Durance River (a tributary of the Rhône River), Navratil et al. (2012) reconstructed the geological sources of SPM over time via the analysis of a sediment core study using radionuclide and geochemical tracers. However, to date, no study has documented historical SPM contributions of the main Rhône River tributaries to the river outlet. Zebracki et al. (2015) quantified the contributions of three main SPM sources, which included tributaries grouped according to hydrological characteristics (Cévenol, Oceanic and Mediterranean rivers), and used radionuclide data to show that the Durance River is the main relative contributor of SPM at the outlet of the Rhône River. Interest in the study of the sources of sediments on the Rhône River is based on the major sedimentary contributions of the Rhône River to the Mediterranean Sea (Delile et al., 2020). Given that fine sediments affect water quality and aquatic biodiversity (Koiter et al., 2013), it is essential to identify sediment sources to reduce sediment inputs to the Mediterranean Sea. Dendeviel et al. (2020) have worked on historical metal contamination along the Rhône River continuum; but, to the best of our knowledge, no studies have been published on historical sediment sources to the Mediterranean Sea.

In this context, the main objective of the present study was to highlight the relevance of using tracers in the non-reactive fraction to retrace the historical SPM contributions of the main tributaries of the Rhône River basin to its global SPM discharge to the Mediterranean Sea over the last 40 yr. This study is based on the collection and analysis of a sediment core located close to the outlet of the Rhône River basin, which is only connected to the main channel during major flood events, and on SPM samples collected within the Rhône Sediment Observatory (OSR) monitoring network, which has been operational since 2012. To overcome the methodological biases resulting from changes in anthropogenic inputs and diagenetic processes potentially affecting concentrations of trace and major elements in sediment cores, we applied an original fingerprinting method based on the analysis of the non-reactive fraction of elements. This fingerprinting approach was previously used by Begorre et al. (2021) on a sediment core sampled on the Upper Rhône River, but the depth resolution of the sediment core was too limited to investigate sediment inputs at the flood-event scale, in contrast to the sediment core collected downstream of the Rhône River basin for the present study.

2. Material and Methods

2.1. Study area: the Rhône River basin

The Rhône River is one of Europe's major rivers and the largest supplier of sediments to the Mediterranean Sea, delivering an inter-annual mean of 5.5 Mt yr^{-1} over the 2008–2018 period (Delile et al., 2020). The basin covers an area of 95,600 km² spanning a broad diversity of geological and climatic conditions (Zebracki et al., 2015; Delile et al., 2020). Over the last 40 yr, eight major flooding events were reported at the Beaucaire station close to the outlet of the Rhône River basin: in 1982 (maximum water discharge, Q_{max} = 8025 m^3 s^{-1}), 1990 (Q_{max} = 5300 m^3 s^{-1}), 1993 (Q_{max} = 9800 m^3 s^{-1}), 1994 (Q_{max} = 11,006 m^3 s^{-1}), 1996 (Q_{max} = 8981 m^3 s^{-1}), 1997 (Q_{max} = 8020 m^3 s^{-1}), 2002 (Q_{max} = 9700 m^3 s^{-1}) and 2003 (Q_{max} = 11,500 m^3 s^{-1}) (DREAL, 2011). Concentrations and fluxes of SPM and associated contaminants are monitored in the Rhône River and its main tributaries under the Rhône Sediment Observatory ("OSR") program (Fig. 1). A monitoring network that has been set up and running since 2009 collects a large set of SPM samples and data via stations located across the entire basin (Thollet et al., 2021). The study area includes eleven tributaries located upstream of the sediment core location near the Rhone River outlet (Fig. 1), i.e., the Arve, Fier, Guiers, Ain, Bourbre, Saône, Gier, Isère, Ardèche, Durance and Gardon rivers.

2.2. Sampling strategy

2.2.1. Suspended particulate matter source sampling

The SPM samples were collected at five river stations representing the potential SPM sources to characterize geochemical signatures of sediment sources: the Middle Rhône River at the Andancette station (including inputs from seven tributaries, i.e., the Arve, Fier, Guiers, Ain, Bourbre, Saône and Gier rivers), the Isère, Ardèche, Durance and Gardon river stations (Fig. 1). The Andancette station is located on the Rhône River, upstream of its confluence with the Isère River. The other stations are located downstream of each tributary, at a few kilometres upstream from their confluence with the

Rhône River (Thollet et al., 2021). The SPM samples were collected using integrative particle traps deployed throughout the year and retrieved every month. In order to collect SPM samples during specific events, such as the Cévenol floods, event-based samplings were carried out using a continuous flow centrifuge (Westfalia KA 2-86-76) or by manually sampling large volumes of water. A more detailed description of the sampling methods can be found in Masson et al. (2018). Overall, 42 SPM samples were collected between 2011 and 2019 from five sources: the Middle Rhône River (n=11), the Isère River (n=14), the Ardèche River (n=6), the Gardon River (n=2) and the Durance River (n=9) (see Table 1).

2.2.2. Targeted sediment core sampling

To assess the historical SPM inputs from Rhône River tributaries, a 300-cm-long sediment master core was reconstructed by combining seven individual sediment cores collected from two holes (16 cm apart) at different depths at the Mas des Tours site, which is located 54 km upstream of the Mediterranean Sea (43.740000 N; 4.625194 E; Fig. 1), in May 2018 (Morereau et al., 2020). This sampling site was selected because it is only connected to the Rhône River during major floods events. Core drilling was carried out using a Cobra TT percussion driller equipped with a transparent 90-mm diameter PVC liner. Using a XRF core scanner (ITRAX, Cox Analytical Systems, Sweden), 43 layers ranging in thickness from 2–15 cm were identified. Each layer was subsampled using a ceramic knife to collect several grams of fresh sediment. A subsample was stored for particle size analysis. Other sediment subsamples were freeze-dried, ground, and stored in plastic bags until further analysis. All information about core dating are fully reported and discussed by Morereau et al. (2020).

2.3. Physicochemical analysis of SPM and sediment samples

The particle size distribution was determined on fresh SPM samples using a Cilas 1190 particle size analyzer under ultrasound and sample agitation, according to ISO standard 13320 (ISO, 2009). For the sediment core samples, the particle size distribution was determined on a Mastersizer 2000© instrument (Malvern Panalytical, Instruments Ltd., Malvern, UK) with a small-volume wet dispersion unit. Tests

carried out to compare results obtained by these two instruments showed that there are no significant differences between the results.

The analysis of geochemical properties involved the quantification of 20 trace and major elements (metals) in the total and reactive fractions (see supplementary material "Database_Rhône_River"). As highlighted by Dabrin et al. (2021), soft extraction using HCl has been used for many years to identify metals adsorbed on the reactive fraction of SPM, which is mainly present in anthropized systems. The total fraction was determined after triacid mineralization (12 M hydrochloric acid, 14 M nitric acid and 22 M hydrofluoric acid, respectively proportioned at 1.5 mL, 0.5 mL and 2 mL) on a heating plate. The reactive fraction was obtained by soft extraction using hydrochloric acid (1 M) at room temperature (Dabrin et al., 2014). The difference between the concentrations of the two fractions correspond to what we call a 'non-reactive fraction'. Further details can be found in Begorre et al. (2021). Major and trace elements were analyzed in both fractions by inductively-coupled plasma optical emission spectroscopy (ICP-OES, Agilent 720-ES) or triple-quadrupole inductively-coupled plasma mass spectrometry (TQ-ICP-MS, Thermo iCAP-TQ) according to their limit of quantification and concentration in the samples. Certified reference materials (IAEA-158, marine sediment for total extraction, and LGC-6187, river sediment) were analyzed in triplicates for each analytical series to control the accuracy of results. Precision was lower than 11% for each element analyzed. When considering sediment samples, precision of the analysis by ICP-OES was similar between the total and HCl fractions with values in the range of 0.3-9.7% depending on the metal. For analysis by ICP-MS, analytical precision on triplicates was lower than 7% for the total fraction against lower than 9% for the HCl fraction. In addition, blanks were systematically included in the mineralization and analytical series to confirm that the samples were not contaminated during the analytical process.

2.4. Sediment core dating

Sediment core dating was performed according to the procedure detailed in Morereau et al. (2020). Briefly, the sediment core could not be dated with the traditional markers such as ^{137}Cs and ^{210}Pbxs

142 (Appleby, 1998; Foucher et al., 2021). In fact, the Marcoule nuclear facility located along the Rhône
143 River also releases those radionuclides into the waters in proportion that diluted the contributions of the
144 watershed and masked the traditional markers (Provansal et al., 2010). For this reason, the dating of this
145 archive was carried out by modelling using the data on the releases from this facility (Morereau et al.,
146 2020). Dry samples of sediment were conditioned in 17-mL or 60-mL boxes depending on the quantity
147 of sediment available and were placed in vacuum-sealed packages and stored for at least one month
148 before analysis to ensure the secular equilibrium of the ^{210}Pb necessary to determine the concentration
149 of ^{210}Pbxs (Morereau et al., 2020). Measurements of gamma emitters were performed with a germanium
150 detector. Dating was confirmed using additional information input, such as the chronology of past
151 flooding events. Morereau et al. (2020) showed that, because of the location of the coring site, the
152 deposited sediments mainly correspond to flood deposits. Dating of the sediment core showed that the
153 43 layers included sediments deposited from 1981 to 2017. The mean apparent sedimentation rate was
154 estimated at 7.8 cm yr^{-1}.

155

156 ## 2.5. Statistical analysis and fingerprinting procedure

157 ### 2.5.1. Data treatment before implementation in the geochemical (mixing) model

158 Trace and major element concentrations in the total or residual (non-reactive) fraction were corrected
159 for differences in particle size between the SPM sources and the sediment core. The correction method
160 applied was the method described by Gellis and Noe (2013) and implied a particle size difference
161 between SPM from tributaries (source samples) and the sediment core (target samples). As illustrated
162 in Supplementary Information SI.1, the SPM of the Ardèche and Durance rivers had significantly
163 different D_{50} values (median value of the particle size distribution) than the sediment core samples. For
164 metals that correlate positively with D_{50} values, concentrations were corrected according to Eq. (1):

165 $$C_f = C_i - [D50_{(S)} - D50_{m(Sed)}] \times p \quad (1)$$

where C_f is corrected concentration of tracer i, C_i is initial concentration of tracer i in source s, $D50_{(S)}$ is median particle size value of source s, $D50_{m(Sed)}$ is average D_{50} value for all target sediment samples, and p is slope of the regression line.

Trace and major elements integrated in the geochemical model were selected by a three-step procedure: a range test to keep conservative metals (Eq. (2)), a Kruskal-Wallis test to remove redundant elements, and a discriminant factor analysis (DFA) to determine the signature that ensures optimal source discrimination. Results of this tracer selection process are reported in Table 2.

$$[\min(C_{is})]_{mean} - 0.10 \times [\min(C_{is})]_{mean} < C_i < [\max(C_{is})]_{mean} - 0.10 \times [\max(C_{is})]_{mean} \quad (2)$$

where C_{is} is concentration of tracer i in source s, and C_i is concentration of tracer i in sediment core layers. The concentration of tracer i in the sediment core must lie within the source range represented by the minimum and maximum concentrations of tracer i in sources for which a 10% error is accepted.

The distribution-mixing model coupled to Monte Carlo simulation resolved Eq. (3) to estimate the source contributions with their associated uncertainties from the selected tracers for each layer of the sediment core. Uncertainties associated with the source contributions were calculated based on 95% confidence interval and mean absolute error (MAE; Eq. 4).

$$C_i = \sum_{l=1}^{1000} \sum_{s=1}^{n} \left((P_s \times C_{is})/1000 \right) \quad (3)$$

where P_S is percentage contribution from SPM tributary s, C_{is} is concentration of tracer i in tributary s, n is number of tributaries, and C_i is tracer concentration in the target sediment samples (Hughes et al., 2009; Haddadchi et al., 2013). Note that this model is based on two conditions: the source contributions should be between 0 and 100%, and the sum of the contributions is equal to 100% (Hughes et al., 2009; Navratil et al., 2012; Collins et al., 2017).

$$MAE = 1 - \left(\sum_{i=1}^{m} \left| [C_i - (\sum_{s=1}^{n} P_s \times C_{si})]/C_i \right| /m \right) \quad (4)$$

where m is number of properties. If the MAE is greater than 0.85, then the model results are reliable.

2.5.2. Statistical tests to investigate metal reactivity in the sediment cores

To investigate metal reactivity in the sediment profile, a Student's *t*-test or Wilcoxon test was used to compare tracer concentrations between total and non-reactive fractions of SPM, concentrations between tributaries, and concentrations of metals between top (1991–2017 period) and bottom (1981–1990 period) layers of the sediment core. The level of significance used in statistical tests was set at a p-value < 0.05.

3. Results and Discussion

3.1. Reactivity of tracers in SPM and sediment core from the Rhône River basin

Total and non-reactive metal concentrations in SPM for each studied tributary are reported in Fig. 2. The two layers corresponding to sediment deposited in 2014 and 2017 were removed from further analysis because the non-reactive concentrations of 7 out of the 12 metals analyzed were below the limit of quantification, which could narrow the applicability of the fingerprinting method by decreasing the number of available tracers. The study reported here therefore considers the 1981–2013 period. To apply a robust fingerprinting method, it is necessary to select metals with low or moderate reactivity in SPM for all tributaries and in the sediment core. To investigate the spatial (contemporary SPM) and temporal (sediment core) variability in metal reactivity, we assessed metal reactivity according to percentage of reactive fraction to percentage of total fraction (see Table 2). Based on these percentages, we categorized the trace and major elements into three groups: low reactivity (< 20%), moderate reactivity (20%–50%) and high reactivity (>50%). The percentages listed in Table 2 were determined from the mean percentage values of all samples for each tributary. Only two samples were available for the Gardon River, and so we were unable to reach a definitive conclusion on metal reactivity for this tributary.

Begorre et al. (2021) found that all groups of metals in the Upper Rhône River presented the same reactivity in SPM across all the studied tributaries: Al, Cr, Ti and V displayed low reactivity, Co and Ni had moderate reactivity, and Cu, Mn and Sr showed strong reactivity. Here we found a globally similar pattern of results, although the SPM from the Ardèche and Durance rivers had the highest reactive fractions of most metals compared to other tributaries. In addition, the reactivity group of Ba,

Fe and Zn varied according to the source considered, whereas Al, Co, Cr, Cu, Mn, Ni, Sr, Ti and V were assigned to the same reactivity group whatever the tributary considered. For example, Ba showed low reactivity in SPM at the Andancette (Middle Rhône River) and Isère river stations (18% and 19%, respectively), whereas it was moderately reactive in the Ardèche and Durance rivers (32% and 40%, respectively). Iron also showed spatial variability in its reactivity, with low reactivity in SPM from the Isère River (19%), but moderate reactivity for SPM collected at the Andancette, Ardèche and Durance rivers (30%–31%). Finally, Zn showed moderate reactivity in SPM from the Isère and Durance rivers (33% and 43%, respectively), whereas it was highly reactive in SPM from the Andancette (56%) and Ardèche (65%) rivers. This higher reactivity of Zn at the Andancette and Ardèche river stations could be explained by Zn pollution caused by numerous anthropogenic activities, i.e., by vineyards and industries along the Middle Rhône River, and by farming and old mining tailings on the Ardèche River (Ollivier et al., 2011; Dendeviel et al., 2020).

Metal concentrations in the sediment core displayed different temporal patterns (Fig. 3). Based on linear regression (i.e., data not shown), total concentrations of Al, Ti, V, Mn, Ni, Co, Sr and Fe did not show a significant trend from the deepest layers through to the top of the sediment core. In contrast, Cr, Cu, Zn and Ba concentrations in the total sediment fraction decreased from 1981 to 2013 (statistically significant linear regression with $R^2_{Cr}=0.67$ and $p<0.05$, $R^2_{Cu}=0.65$ and $p<0.05$, $R^2_{Zn}=0.67$ and $p<0.05$, $R^2_{Ba}=0.78$ and $p<0.05$). In detail, total Cu, Zn, Cr and Ba concentrations before 1990 differed significantly from concentrations measured after 1990, and they all followed a decreasing trend in the total fraction from 1981 to 1990 (Fig. 3). For Cr and Ba, this temporal trend is also highlighted for non-reactive concentrations, which could mean that Cr and Ba were not influenced by past anthropogenic inputs. Conversely, non-reactive concentrations of Cu and Zn did not vary over time and were significantly different from their total concentrations, suggesting that only the reactive fraction of Cu and Zn decreased over time (from 1981 to 1990), which could be explained by historical anthropogenic inputs of reactive metals. This decrease in total Zn concentrations is consistent with Zn concentrations in the sediment core (Ferrand et al., 2012) and surface sediments from the National Basin Network of the French Water Agency, which highlighted a decreasing trend

from 1986 to 1990 (Ferrand et al., 2012). Furthermore, Dendeviel et al. (2020) highlighted (i) that Cu and Zn were delivered all along the Rhône River by multiple anthropogenic activities (i.e., vineyards, mining, cable production, a nuclear power plant, the Marcoule reprocessing spent fuel facility) in the 1980s, and (ii) that Cu and Zn concentrations decreased from 1960 to 1990. Moreover, Morereau et al. (2020) reported that the Marcoule facility (on the Rhône River, just north of the Durance tributary) released liquid effluents highly contaminated with Cu and Zn until 1990. Based on these observations, we supposed that some metals are more reactive in the deepest sediment core layers (1981–1990) compared to the more recent layers (1991–2013). We therefore scrutinized metal concentrations in the sediment core separately for these two periods, i.e., 1981–1990 and 1991–2013.

Concentrations of Al, Ti, V, Mn, Ni, Co, Sr, Fe, Cr and Ba measured in the non-reactive fraction co-evolved with the total fraction over time, whereas concentrations of Cu and Zn in the non-reactive fraction remained stable along the sediment core. This means that the total concentrations of these two elements may be influenced by variable anthropogenic inputs or variable reactivity, which makes them unreliable for tracing historical sediment sources. This is supported by our metal reactivity study based on proportions of the reactive fraction, which classified all metals except Zn into the same reactivity groups whatever the sediment core layer considered. Indeed, Zn showed moderate reactivity in the upper part of the core (50%) but was highly reactive in the deepest layers (1981–1990) of the sediment core (63%). Begorre et al. (2021) also showed that, in a sediment core sampled in the Upper Rhône River, the reactive fraction of Zn was higher before the 1990 layer (80%) compared to the more recent layers (66% for the 1991–2013 period).

Metal reactivity could also differ between SPM tributaries and the sediment core. Al, Co, Cr, Cu, Mn, Ni, Sr, Ti and V showed the same degree of reactivity in SPM tributaries and the sediment core, which is consistent with results obtained by Begorre et al. (2021) for the sediment core sampled in the Upper Rhône River. However, Sr showed significant differences between the highest reactive fraction in SPM from the Durance River (89%) and all other stations (~65%). The reactive fraction of Sr determined in the sediment core layers was similar between the top and bottom of the core at values of around 74–76%. These results showed that SPM from the Durance River were characterized by a

higher Sr reactivity than sediment core layers and SPM from the other tributaries. This could be explained by the high carbonate contents in SPM from the Durance River because of its sedimentary basin (Ollivier et al., 2011). Ollivier et al. (2011) showed that Sr is mainly associated with carbonates, which represent the most reactive fraction of particles, meaning that Sr can easily be removed from particles to the dissolved phase under varying physicochemical conditions. They also highlighted that the Rhône River drains mainly carbonate bedrocks, which are significant sources of SPM during major flood events, as in the case of the 2001 and 2002 floods (Ollivier et al., 2011). These events correspond to the increase in total concentrations of Sr found, in the present study, in the recent layers of the core (2001–2013) collected at the outlet of the Rhône River. Liu et al. (2013) studied changes in concentrations of metals associated with reducible and carbonate phases in two coastal sediment cores (Taiwan) and found that metal concentrations were correlated to the carbonate content and that Sr concentrations in the carbonate fraction were higher in the recent layers compared to the deepest layers (Liu et al., 2013). Given that Sr has a high affinity with the carbonate fraction in the Rhône River, it is consistent that total Sr concentrations were higher in the recent layers (2001–2013) of the sediment core studied here.

The reactive fraction of Ba, Fe and Zn also differed between the sediment core and SPM samples at some stations (Table 2). For example, in case of Ba, the reactive fraction measured in SPM from the Isère (19%) and Andancette (18%) stations was significantly different ($p<0.05$) than the reactive fraction in the sediment core (39% and 43% for the 1981–1990 and 1991–2013 periods, respectively). Conversely, the percentages of the reactive fraction of Ba in SPM from the Ardèche (32%) and Durance (40%) rivers were similar to those found in the sediment core. As reported by Kresse et al. (2007), the erosion of sedimentary rocks constituted by Ba-enriched carbonates could explain the higher reactivity of Ba in SPM from the Ardèche and Durance rivers, in comparison to other tributaries. Furthermore, comparison of our results against those obtained for the sediment core sampled on the Upper Rhône (Begorre et al. 2021) shows that Ba reactivity increased downstream of the watershed, i.e., from 20% for the Upper Rhône to 39%–43% at downstream sites. Ba-based minerals are generally found in the non-reactive fraction of the particles, but under anoxic conditions,

297 these minerals are dissolved and then precipitate again in the sedimentary deposits (Henkel et al.,
298 2012). This may explain, depending on the presence of such minerals, the increase in the total and
299 non-reactive concentrations of Ba with depth. The spatial variation in total and non-reactive Ba
300 concentrations from the Upper Rhône (mean of 253 mg kg^{-1} and 203 mg kg^{-1}, respectively) to the
301 Rhône River outlet (mean of 577 mg kg^{-1} and 336 mg kg^{-1}, respectively) may be explained by a
302 missing source of dissolved Ba that precipitates under oxic conditions. Values for the reactive fraction
303 of particulate Fe were similar between the Middle Rhône (Andancette station), Ardèche and Durance
304 rivers (30–31%) and also similar to those observed in the sediment core layers deposited between
305 1991 and 2013 (32%). The SPM from the Isère River was the only exception, with a lower percent
306 reactive fraction of Fe (19%). Liu et al. (2013) highlighted that Fe is mainly associated with the oxide
307 fraction of particles. However, to validate this assumption in the case of the Rhône River, it would be
308 necessary to have information about the oxide fraction in SPM samples from each tributary. For Zn, a
309 high reactivity was found in SPM from the Ardèche River (65%), which is almost two-fold higher
310 than the lowest value measured for SPM from the Isère River (33%). This Zn reactivity in SPM of the
311 Ardèche River (65%) was similar to the Zn reactivity in the deepest layers of the sediment core (63%
312 for the 1981–1990 period). We assume that because Zn is statistically selected and used in the
313 geochemical model, the high reactivity of Zn would introduce a bias in the contribution estimates for
314 the model based on the total fraction.

315 Note that the metal reactivity investigation can serve to identify the most appropriate tracers for
316 reliably estimating source contributions. Owens et al. (2016) highlighted that the range test, which is
317 commonly used to remove non-conservative elements, is not fully reliable. This was explained by the
318 fact that (1) even if total concentrations of a tracer remain within the range values of the sources, they
319 can still evolve because of tracer reactivity and move away from initial concentrations (e.g., metal
320 precipitation in the mixing zone may lead to higher tracer concentrations), and that (2) some elements
321 were removed from the procedure because of higher concentrations from an unidentified source
322 (Owens et al., 2016). In the present study, based on the range test results, metals included in the low
323 and moderate reactivity groups (i.e., Al, Ba, Co, Cr, Fe, Ni, Ti and V) could be used to reliably trace

sediment sources. However, total concentrations of metals in the third (high reactivity) group (i.e., Cu, Mn, Sr) are not recommended for estimating source contributions. Zn is a distinctive element as it is moderately reactive at the top of the sediment core (1990–2013 period) while it is highly reactive in the deeper layers (1981–1990; Table 2).

3.2. Historical reconstruction of relative contributions of SPM sources to the Rhône River

3.2.1. Selection of tracers in the geochemical model

The optimal composite signature integrated in the geochemical model was selected using the range test, as detailed in Section 2.5.1. The range test results (Table 3) show that four elements (i.e., Ba, Cr, Cu and Ti) were excluded from this procedure for the total fraction, and that Mn, Sr and Zn, which are highly reactive, were kept for further statistical tests (Kruskal-Wallis and DFA). For the non-reactive fraction, only two elements (i.e., Ba and Ti) were excluded from the fingerprinting procedure. Following the range test, the tracers selected by the combination of the Kruskal-Wallis test and DFA were Co, Fe, V and Zn for the total fraction, and Al, Cr, Fe, Mn and Zn for the non-reactive fraction. For the total fraction, the procedure statistically selected Zn to estimate the source contributions, which could influence the reliability of the results. For the non-reactive fraction, two reactive metals (i.e., Mn and Zn) were integrated into the geochemical model, but the estimation of source contributions based on their non-reactive concentrations made it possible to overcome problems associated with metal reactivity or past anthropogenic inputs. These results are in agreement with the work of Begorre et al. (2021), showing that tracer selection varied between both fractions leading to a larger number of available tracers for the non-reactive fraction.

3.2.2. Global trends in historical SPM inputs to the Mediterranean Sea

Fig. 4 shows the contributions of SPM sources, expressed as percentages, estimated from tracer concentrations in the total and non-reactive fractions. Overall, along the whole sediment core (1981–2013), the contributions modeled from the total fraction differed significantly ($p<0.05$) from the

contributions estimated using the non-reactive fraction for the Durance and Isère rivers. For example, the SPM contributions of the Durance River modeled using the total and non-reactive fractions were 22 ± 13% and 52 ± 18%, respectively. Given that the sediment core was collected in the Rhône River downstream of the confluence with the Durance, the sediment core is probably strongly influenced by SPM inputs from the Durance River (Vauclin et al., 2021).

Source contributions modeled using the total fraction showed that the Isère and Ardèche rivers were the main contributors to the SPM at the outlet of the Rhône watershed from 2013 to 1991 (27–175 cm depth) and from 1990 to 1981 (184–300 cm depth), respectively. Contributions estimated using non-reactive concentrations showed that the Durance River was the main source of deposited sediments over time, except in layers from 1989, 1996, 1998 and 2001 for which the main SPM inputs came from other tributaries (Fig. 4-b). Globally, the Middle Rhône River inputs were low and relatively stable (5.6 ± 3.1%) over time, except in the layers from 1989 (37%), 2001 (19%) and 2003 (16%). In the absence of historical SPM flux data, we compared our results against results from the literature (Zebracki et al., 2015; Poulier et al., 2019). Zebracki et al. (2015) used radionuclide analyses to investigate contemporary sources of SPM transported to the Rhône River outlet between 2001 and 2011, and identified three groups of tributaries: upstream (Ain, Fier, Isère, and Saône rivers); pre-alpine (Durance, Drôme rivers) and Cévenol (Ardèche, Gardon rivers). The Durance River was identified as the main contributor of SPM (53%), followed by the "Andancette + Isère" (35%) and Cévenol rivers (11%) (Zebracki et al., 2015). The results obtained here using the non-reactive fraction (52 ± 18%, 22 ± 13%, and 26 ± 16%, respectively) are therefore more consistent with the findings of Zebracki et al. (2015) than the results obtained using the total fraction. We also compared our estimates of source contributions against the relative SPM flux contributions calculated over the 2000–2016 period by Poulier et al. (2019) for the Middle Rhône (16%; Upper Rhône River + Saône), Isère (25%), and Durance (24%) rivers. The major SPM contributors to the Mediterranean Sea were the Isère and Durance rivers. According to these results, our estimates of SPM contributions based on the total fraction are likely more accurate than those based on the non-reactive fraction for the 2000–2016 period. However, these results should be interpreted with caution because Poulier et al. (2019)

376 did not include the Cévenol tributaries. The differences in conclusion between both comparisons
377 might be associated with the method applied to evaluate the contribution of SPM sources. Poulier et
378 al. (2019) used the SPM flux data calculated at each sub-watershed outlet without calculating relative
379 SPM proportions delivered to the Rhône River, whereas Zebracki et al. (2015) and the present study
380 compared geochemical signatures between SPM sources and sediment core layers. Zebracki et al.
381 (2015) noted the presence of a large number of dams along the Rhône River continuum, which may
382 explain the underestimated contributions from upstream tributaries. Estimates of source contributions
383 using geochemical models were therefore more representative of SPM inputs to the watershed outlet.
384 Regarding result reliability, the MAE calculated for each layer of the sediment core were higher for
385 the non-reactive fraction (average = 99.8%) than for the total fraction (average = 95.4%). Considering
386 each layer individually, it can be observed that all MAE were higher than 85%, which means that the
387 results are reliable except for the 2003 layer for the total fraction (MAE = 81%).

388 3.2.3. Temporal variations in historical SPM contributions

389 The contributions of the Andancette station estimated from total and non-reactive fractions were very
390 low and not significantly different in top (7 ± 3% and 8 ± 5% for the total and non-reactive fractions,
391 respectively; p=0.88) and bottom (4 ± 3% and 7 ± 8% for the total and non-reactive fractions,
392 respectively; p=0.07) layers of the sediment core. In contrast, the source contributions of the Isère,
393 Ardèche, Gardon and Durance rivers varied over time (Fig. 4).

394 Differences in source contributions between both fractions depended on the sediment core layers. For
395 the total concentrations, the contributions of SPM sources differed significantly between the top of
396 the core (from 1991 to 2013) and the deepest layers (from 1981 to 1990), whereas for the non-reactive
397 fraction, the contributions were not significantly different between both parts of the sediment core.
398 For example, in the top of the sediment core, the contributions of the Ardèche and Gardon rivers were
399 similar for those estimated based on the total fraction (13 ± 6% and 14 ± 13%, respectively) and the
400 non-reactive fraction (15 ± 5% and 13 ± 13% respectively), whereas in the deepest layers, the
401 estimated source contributions were significantly different between fractions (total fraction: 32 ± 16%
402 and 22 ± 14% for the Ardèche and Gardon rivers, respectively; non-reactive fraction: 12 ± 3% and

13 ± 9%, respectively). To explain these differences, a Pearson correlation test and a principal component analysis (PCA) were carried out based on the tracers selected by DFA for the total (Co, Fe, V, Zn) and non-reactive (Al, Cr, Fe, Mn, Zn) fractions, and results were interpreted according to the geochemical model results (Fig. 5). These statistical tests showed that the contributions of the Ardèche River were significantly correlated to Zn concentrations in the total fraction ($p<0.05$; Fig. 5-a). In addition, as previously demonstrated (see Section 3.1), Zn was characterized as highly reactive in the 1981–1990 layers, meaning that it was influenced by past anthropogenic inputs (Dendeviel et al., 2020). Consequently, the estimated increasing contributions from the Ardèche River from 1990 to 1981 did not reflect an increase in Ardèche River SPM inputs but instead revealed substantial historic anthropogenic inputs of Zn at the global Rhône River scale, as discussed above.

3.2.4. Cross-analysis of relative historical SPM contributions and past flood events

To discuss and confront the results of the two fingerprinting approaches, we compiled the main historical flood events (DREAL, 2011), and reported them in Fig. 4-c according to each identified layer of the sediment core. The discussion is presented in reverse chronological order.

In 2010 (42 cm depth), a flood of the Isère River with a ten-year return period, i.e., a flow exceeding 900 $m^3 s^{-1}$, was recorded, which implies higher SPM inputs from the Isère River compared to the other tributaries. For this layer, there was no marked peak in contributions for any particular tributary in either total or non-reactive fraction, as there was no sediment deposition from this flood event at the study site. For the total fraction, the Isère River SPM contribution was 39% against only 13% for the non-reactive fraction. Combining the contributions of the Middle Rhône with those of the Isère River for the present study, the SPM contributions modeled using the total and non-reactive fractions were 45% and 17% of total SPM inputs, respectively. For the Durance River, the SPM contributions modeled from the total and non-reactive fractions were 36 ± 19% and 59 ± 19%, respectively. Given that the Durance River is much closer to the sediment core site than the Isère River (see Fig. 1), it is possible that the flood peak of the Isère River was not observed at this time in the sediment core at the Rhône River outlet because of SPM storage in the dam reservoir located downstream of the confluence of the Isère River and the Rhône River (Zebracki et al., 2015).

In 2003 (96 cm depth), the deposited sediments were characterized by SPM transported during an extensive Mediterranean flood implying a flood on the Durance (1100 $m^3 s^{-1}$) and Ardèche (2510 $m^3 s^{-1}$) rivers. Total and non-reactive fractions showed a major contribution of the Durance River of 58% and 54%, respectively, which is consistent with the hydrological data illustrated in Fig. 4-c (DREAL, 2011) and with Zebracki et al. (2015), who estimated contributions of the Durance River at between 38% and 53% during the Mediterranean floods for the 2000–2012 period. Contributions of the Ardèche River were estimated at 21% and 25% for the total and non-reactive fractions, respectively. These contributions could be explained by the flood event that occurred on the Ardèche River and reached a water flow of 2510 $m^3 s^{-1}$, which is around three times higher than flood threshold ($Q = 845 m^3 s^{-1}$).

The generalized floods of 2001–2002 at the Andancette station (water flow of 4780 $m^3 s^{-1}$) and the Isère (928 $m^3 s^{-1}$) and Gardon (6700 $m^3 s^{-1}$) rivers was identified at 102 cm depth in the sediment core. The geochemical modeling results based on the total and non-reactive fractions were similar for the Ardèche (7% and 8%, respectively), Durance (11% and 8%) and Gardon (37% and 43%) rivers. Based on the occurrence of a generalized flood at Andancette station, the contribution obtained with the non-reactive concentrations (19%) was more relevant than the contribution estimated using the total fraction (5%). The SPM contribution from the Isère River was estimated at 23% based on the non-reactive fraction. Contributions modeled for the Gardon River could only be validated based on past flooding events because of the absence of hydro-sedimentary data for this period. The SPM contributions of the Gardon River for the total and non-reactive fractions (37% and 43%, respectively) are consistent with the reported water flow of 6700 $m^3 s^{-1}$, which is around six times higher than the flood threshold ($Q = 402 m^3 s^{-1}$). Consequently, based on the SPM source contributions modeled here for the Middle Rhône and Isère rivers, the non-reactive fraction appears to be more relevant than the total fraction for tracing the SPM contributions of this major event.

The sediments deposited in 1996 (131 cm depth) reflect the SPM inputs during a Cévenol flood. According to the 10-yr flood of the Ardèche River, which reached a maximum water flow of 1780 $m^3 s^{-1}$, the estimated SPM contribution for this tributary was very small (0.5%). Results obtained for the

sediment core showed that, based on the total fraction, the Isère and Gardon rivers were the main SPM contributors at 36% and 39%, respectively, while SPM inputs from the Durance, Ardèche and Middle Rhône rivers were much lower (19%, 0.5% and 6%, respectively). In contrast, the modeling performed with the non-reactive concentrations resulted in more relevant estimates than using the total concentrations, with contributions of 9% from the Ardèche River and 33% from the Gardon River. However, it is possible that the geochemical signatures (based on the tracers selected) of the Gardon and Ardèche rivers were not clearly distinct, which would suggest that part of the SPM inputs from the Ardèche River would be assimilated as inputs from the Gardon River. For this type of hydrological event, Zebracki et al. (2015) estimated that the contributions were similar between the upstream tributaries (31%; Andancette station, Isère), the pre-alpine tributaries (30%; Durance), and the Cévenol tributaries (39%; Ardèche, Gardon). According to these results, the estimated SPM contributions of the Durance River in the 1996 layer are more similar using the non-reactive fraction (23%) than the total fraction (19%). Moreover, by combining the estimated contributions for Andancette station and Isère River, the contribution for the non-reactive fraction (35%) was similar to the value estimated by Zebracki et al. (2015) (31%), in contrast to our geochemical modeling with the total concentrations (42%).

In 1993 and 1994 (i.e., at 142–151 cm depth), there were three extensive Mediterranean floods that led to moderate floods of the Isère River and the Middle Rhône at Andancette and high water flows for the southern tributaries (peaks of 2350 $m^3 s^{-1}$ and 4340 $m^3 s^{-1}$ for the Durance and Ardèche rivers, respectively). Therefore, the main expected SPM contributions are probably those of the Ardèche and the Durance rivers. As the only hydrological data available for the Gardon River was the occurrence of a 10-yr flood in 1993 (DREAL, 2011), it was not possible to validate the SPM contribution of this tributary. Geochemical modeling with the total fraction resulted in a major contribution from the Durance River (45%). In contrast to expected results, the Isère River had a larger relative SPM contribution (29%) than the Ardèche River (15%). Geochemical modeling with the non-reactive fraction confirmed the Durance River as the main source of SPM (75%), followed by the Ardèche River (13%). Moreover, SPM inputs from the Isère River were lower using the non-reactive fraction

484 (7%) than for the total fraction (29%), which once again suggests that the results obtained with the
485 non-reactive fraction are more reliable than results obtained with the total fraction.

486 Finally, in 1990 (184 cm depth), the Rhône was subjected to a very intense oceanic flood that
487 particularly affected the tributaries located upstream of the city of Lyon (Upper Rhône River) with
488 peak water flows of 4310 $m^3 s^{-1}$ and 1040 $m^3 s^{-1}$ for the Middle Rhône and Isère River, respectively.
489 Our estimates modeled using the total fraction showed that the Isère and Gardon rivers were the main
490 contributors to SPM inputs at the outlet of the Rhône River basin and that the other three tributaries
491 supplied less than 4% sediment each. In contrast, contribution estimates modeled using the non-
492 reactive fraction were equivalent between the Isère River (37%) and the Middle Rhône (37%), which
493 better reflects the SPM inputs of the major event studied. For this flooding event, the results modeled
494 from the non-reactive fraction are therefore more reliable than the results obtained with the total
495 fraction.

496

497 **4. Conclusion**

498 To overcome the non-conservative behavior of metals, we used the metal concentrations in the non-
499 reactive fraction of SPM/sediments on a sediment core collected at the outlet of the Rhône basin, a site
500 for which no information on the historical SPM contributions was available. This study focused on the
501 estimation of tributary contributions over the last 40 yr using a geochemical modeling approach. We
502 demonstrated that estimations of SPM contributions were significantly influenced by past
503 anthropogenic inputs responsible for an increase in total Zn concentrations in the deepest layers of the
504 sediment core. In fact, the range test selected Zn as a conservative tracer even though it is highly
505 reactive in the deepest layers of the sediment core, which may bias the results of contribution
506 modeling based on the total fraction. Based on a comparison with the results of Zebracki et al. (2015),
507 who used radionuclide data on SPM, it is clear that the results obtained with the non-reactive fraction
508 are closer to those obtained by Zebracki et al. (2015) compared to contributions estimated using the
509 total fraction. Indeed, using the non-reactive fraction, we showed that the main SPM contributor over

the 1981–2013 period was the Durance River. Moreover, the detailed study of major past flooding events showed that our estimates of tributary SPM contributions were more reliable and consistent when the non-reactive metal concentrations were used, especially to trace SPM sources in the deepest layers of the sediment core. Therefore, when concentrations of a geochemical element are influenced by anthropogenic inputs, as for investigations relative to historical SPM inputs, it is more relevant to use the non-reactive fraction rather than the total fraction. This study demonstrated that our original fingerprinting method based on the non-reactive fraction of metals in SPM/sediment is a robust tool for estimating source contributions in a sediment core, as it removed the influence of past anthropogenic inputs on tracer concentrations. Furthermore, this fingerprinting approach made it possible, for the first time in the Rhône River basin, to reconstruct the historical contributions of the main tributaries during major flooding events. It would now be instructive to apply this method to SPM/sediments in coastal environments or those affected by significant past anthropogenic inputs (e.g., rivers influenced by mining activities).

Thus, this fingerprinting method using the residual fraction at the Rhône River basin scale allows to:

- Increase the number of available tracers after the range test of SPM sources, as demonstrated by Begorre et al. (2021),
- Remove the influence of past anthropogenic inputs of metals such as Zn,
- Provide results that are more relevant when comparing with available hydrological and sedimentary data,
- Provide information on the major sources of sediments that are exported into the Mediterranean Sea that could impact its ecosystems.

In terms of recommendations for future studies, as presented by Begorre et al. (2021), the use of total metal concentrations, especially when they are highly reactive, is problematic. Indeed, source fingerprinting using total concentrations of metals must be applied only for metals with low reactivity to improve estimation of SPM source contributions. Therefore, before applying source fingerprinting in a river basin, it is necessary to investigate metal reactivity to avoid the use of high-reactive metals.

Finally, we highly recommend using tracers in the non-reactive fraction when sources and target samples were not sampled at the same period (e.g., with a difference of more than 5 or 10 yr).

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Fig. 1: Location of sampling sites for SPM sources (Middle Rhône River at Andancette station, Isère, Ardèche, Gardon, Durance river stations of the Rhône Sediment Observatory - OSR network) and sediment core (Mas des Tours at the outlet of the Rhône River).

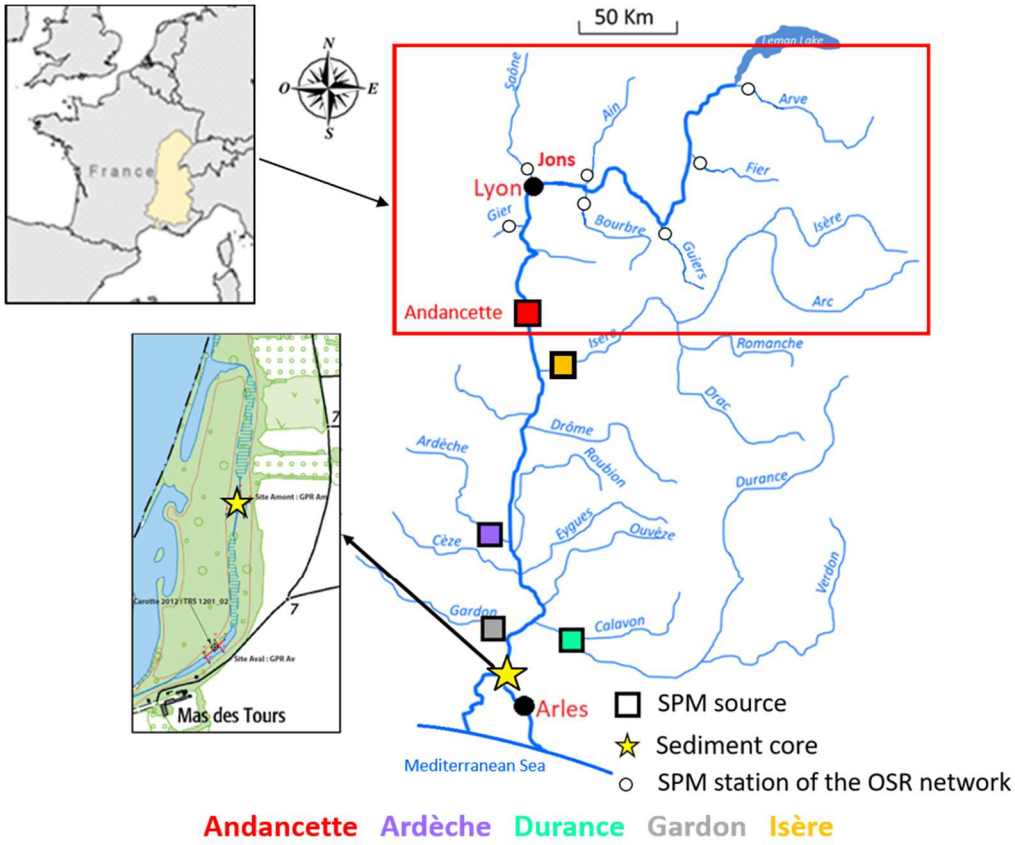
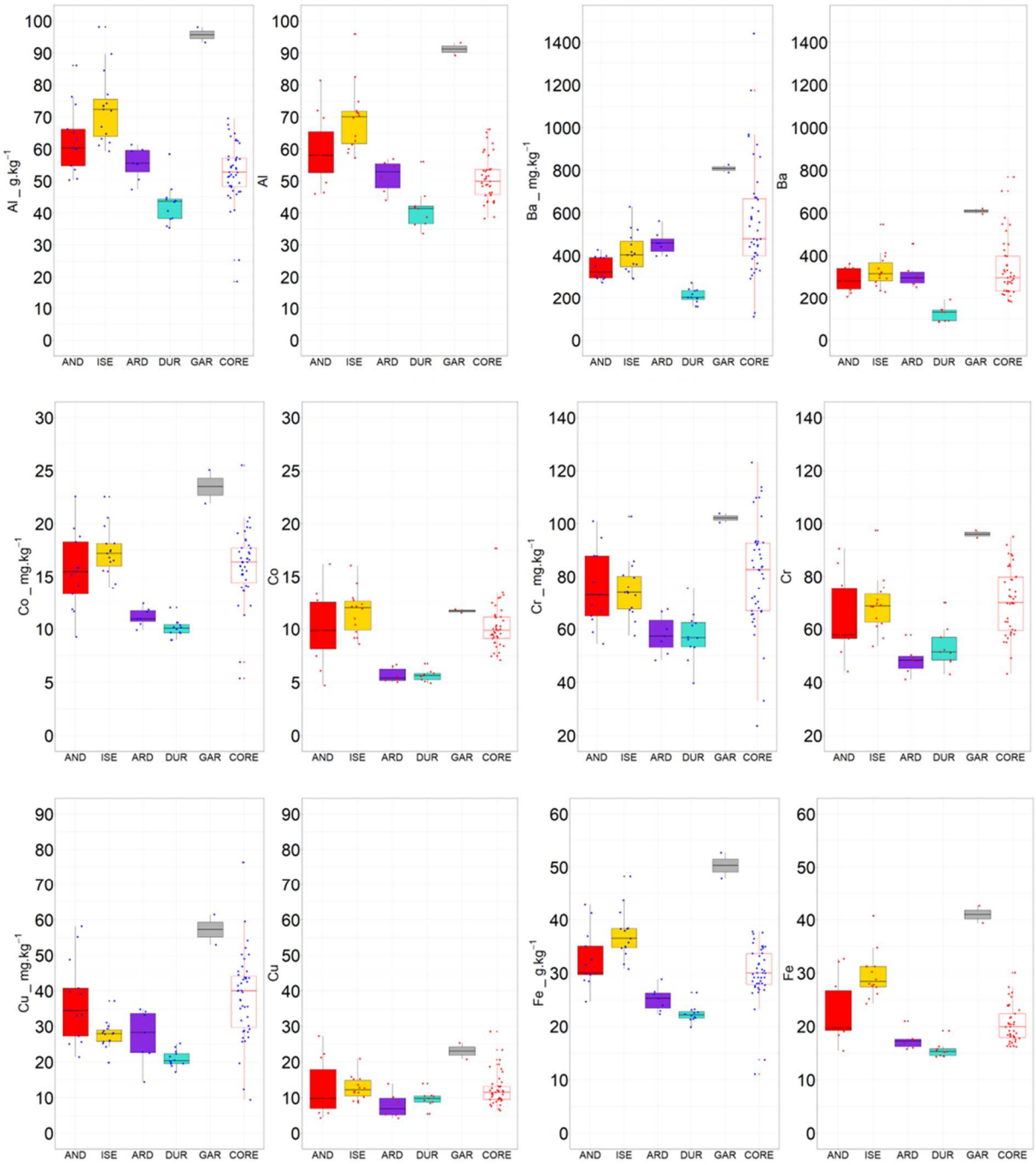


Fig. 2: Metal concentrations (non-corrected data by particle size) measured in the total (blue on the left) and non-reactive (red on the right) fractions of SPM in the Rhône River (Middle Rhône River station at Andancette - AND) and four tributaries (Isère –ISE, Ardèche – ARD, Durance- DUR, Gardon-GAR) and in the sediment core sampled in the Rhône at Mas des Tours site.



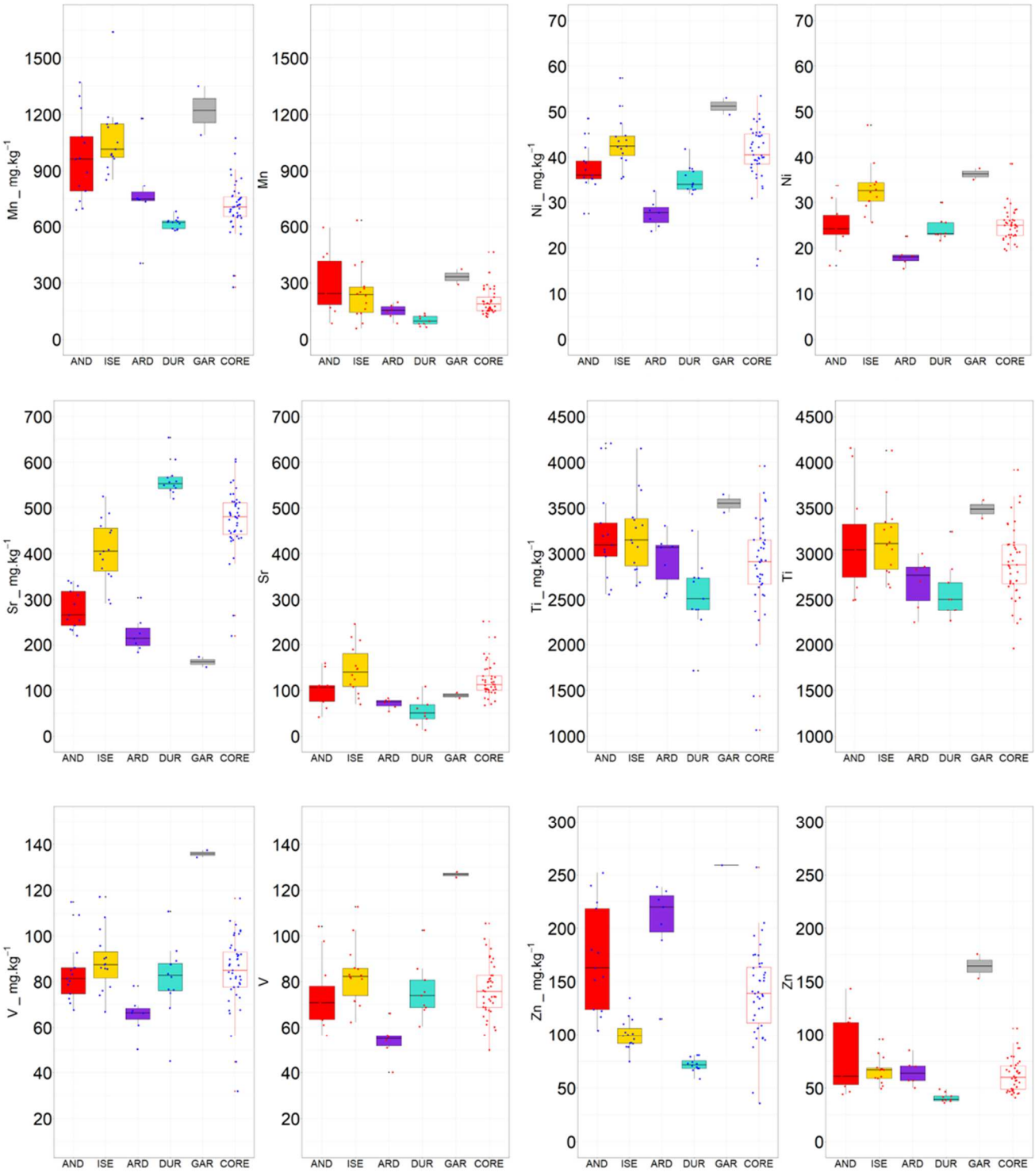
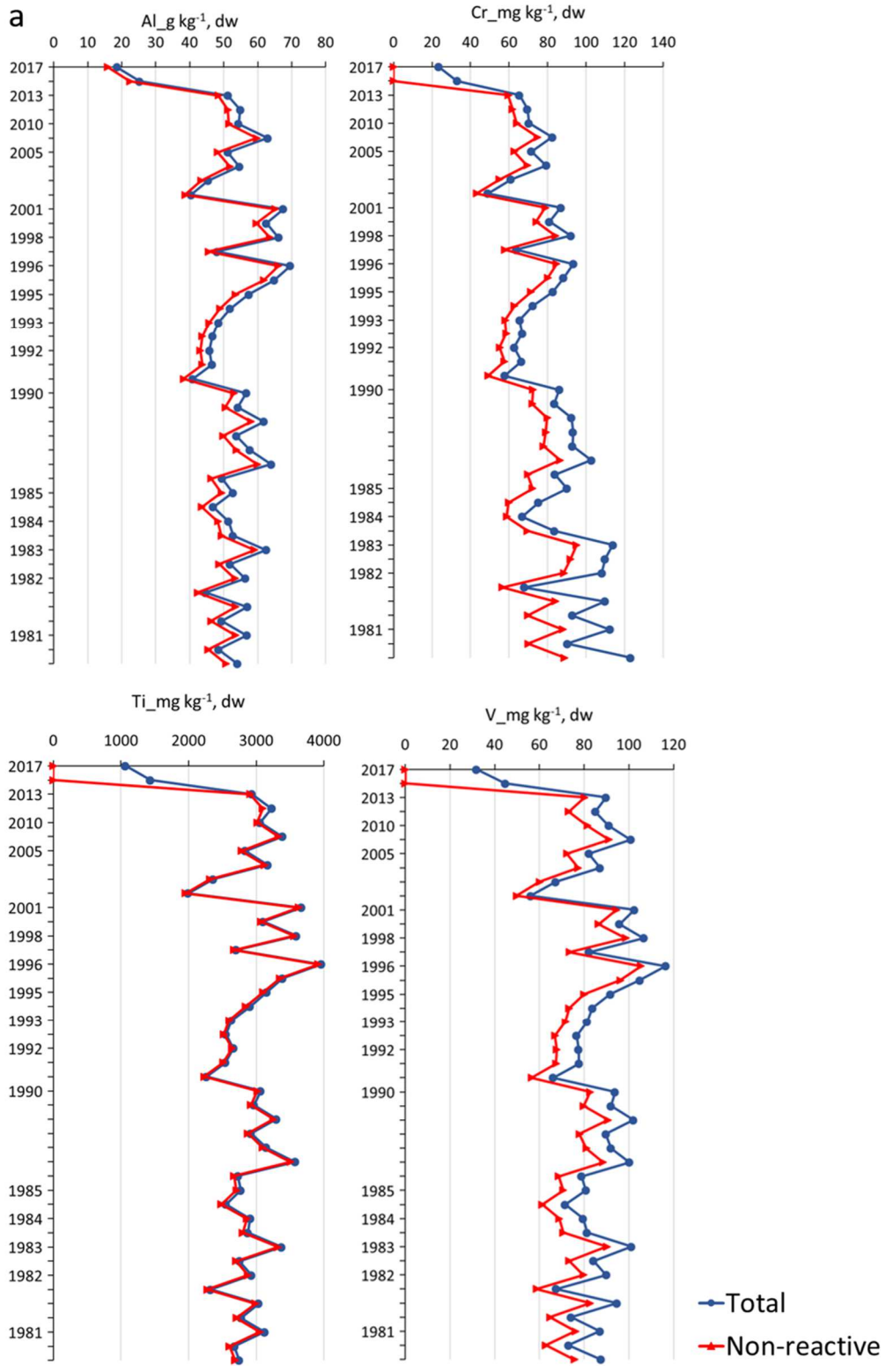
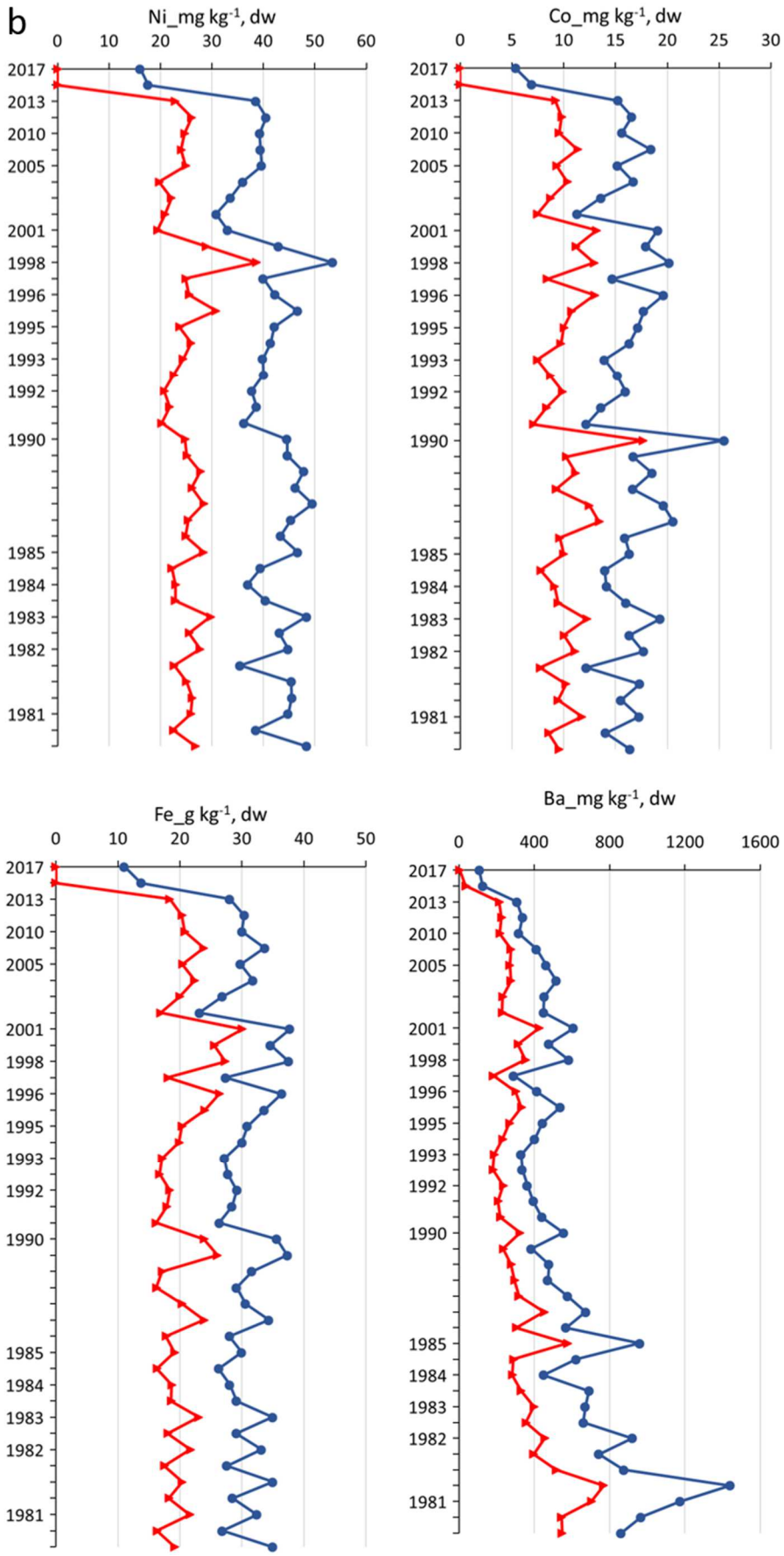

Mn_mg.kg-1
Mn
Ni_mg.kg-1
Ni
Sr_mg.kg-1
Sr
Ti_mg.kg-1
Ti
V_mg.kg-1
V
Zn_mg.kg-1
Zn
AND ISE ARD DUR GAR CORE

Fig. 3: Metal concentrations in the sediment core sampled in the Rhône at Mas des Tours site. The three identified groups represent metals that are not reactive (a), moderately reactive (b) and highly reactive (c). Example of three behaviours of metals along the sediment core by comparing concentrations in the total (blue line) and non-reactive (red line) fractions.




b
Ni_mg kg-1, dw
0 10 20 30 40 50 60
Co_mg kg-1, dw
0 5 10 15 20 25 30
Fe_g kg-1, dw
0 10 20 30 40 50
Ba_mg kg-1, dw
0 400 800 1200 1600
2017
2013
2010
2005
2001
1998
1996
1995
1993
1992
1990
1985
1984
1983
1982
1981

C

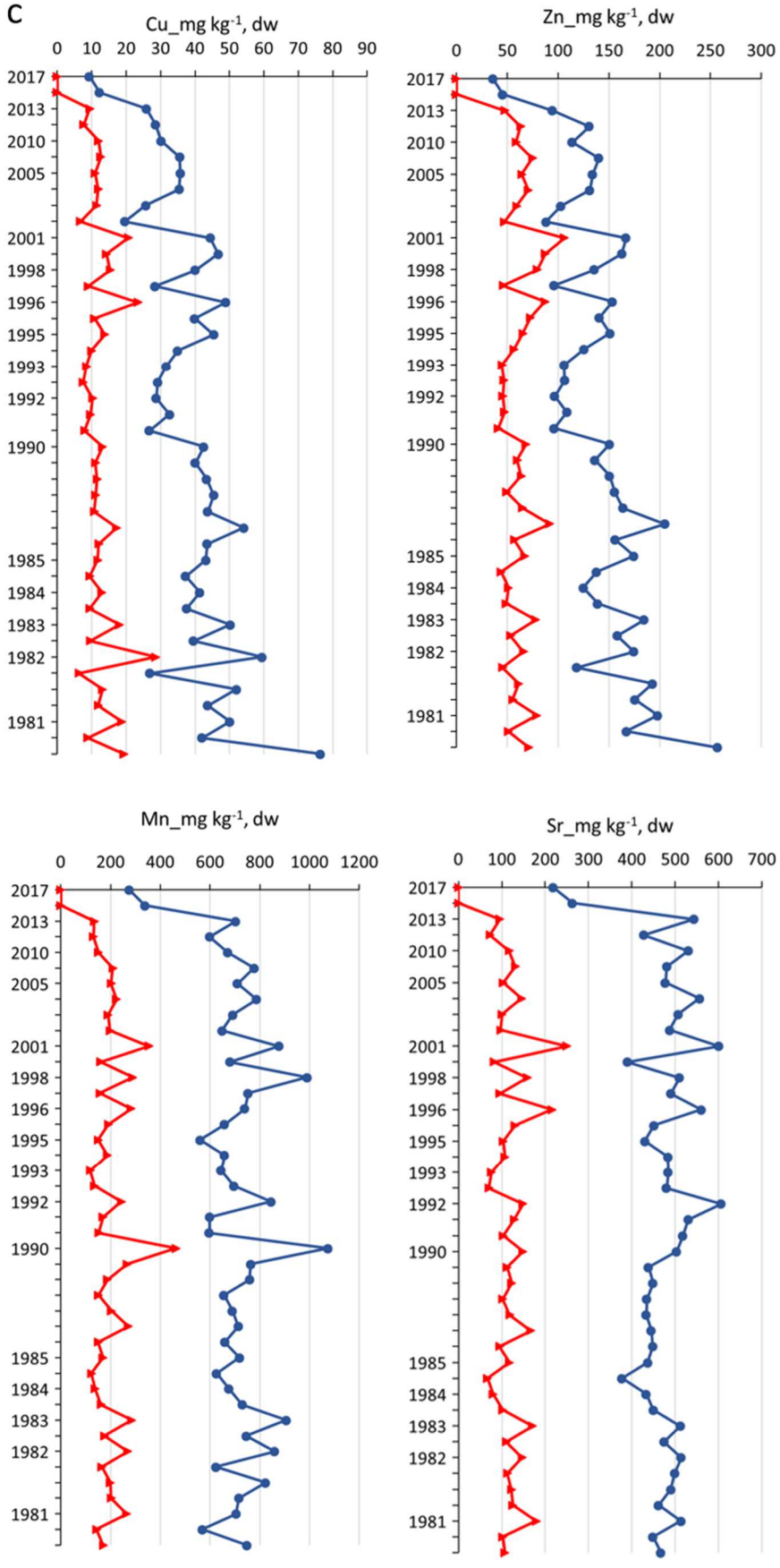

Cu_mg kg-1, dw
0 10 20 30 40 50 60 70 80 90
Zn_mg kg-1, dw
0 50 100 150 200 250 300
Mn_mg kg-1, dw
0 200 400 600 800 1000 1200
Sr_mg kg-1, dw
0 100 200 300 400 500 600 700
2017
2013
2010
2005
2001
1998
1996
1995
1993
1992
1990
1985
1984
1983
1982
1981

Fig. 4: Profile of source apportionment modelling by using tracers in the total (a) and non-reactive (b) fractions, in sediment core at Mas des Tours site, from 1981 to 2013. The black line represents the 1990 layer. Main historical flooding events (m^3 s^{-1}) are reported for the Upper Rhône River and each tributary over the 30-yr period (c)

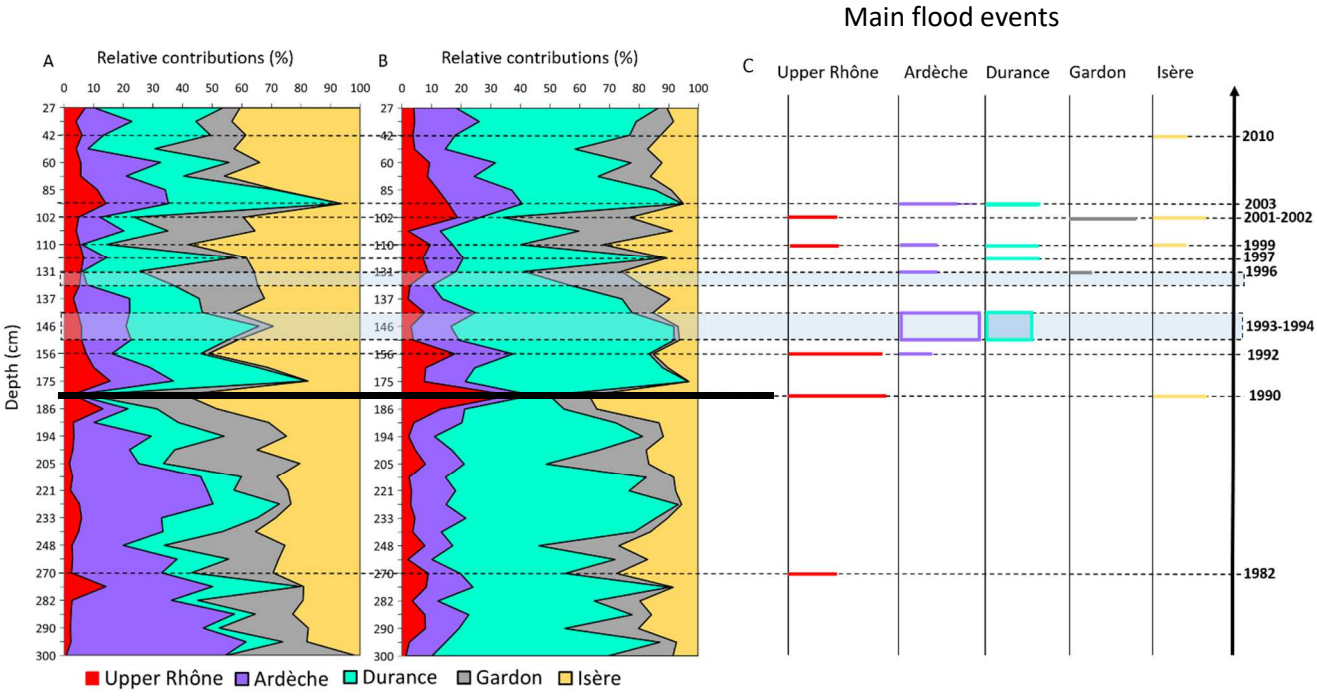


Fig. 5: Principal component analysis (PCA) performed using selected tracer concentrations in the total (a) and non-reactive (b) fractions of SPM at the Rhône River Middle station (Andancette) and tributaries. The concentrations of the tracers used are corrected for particle size. PCA shows correlations (or no correlation) between total (a) or non-reactive (b) concentrations and source contributions.

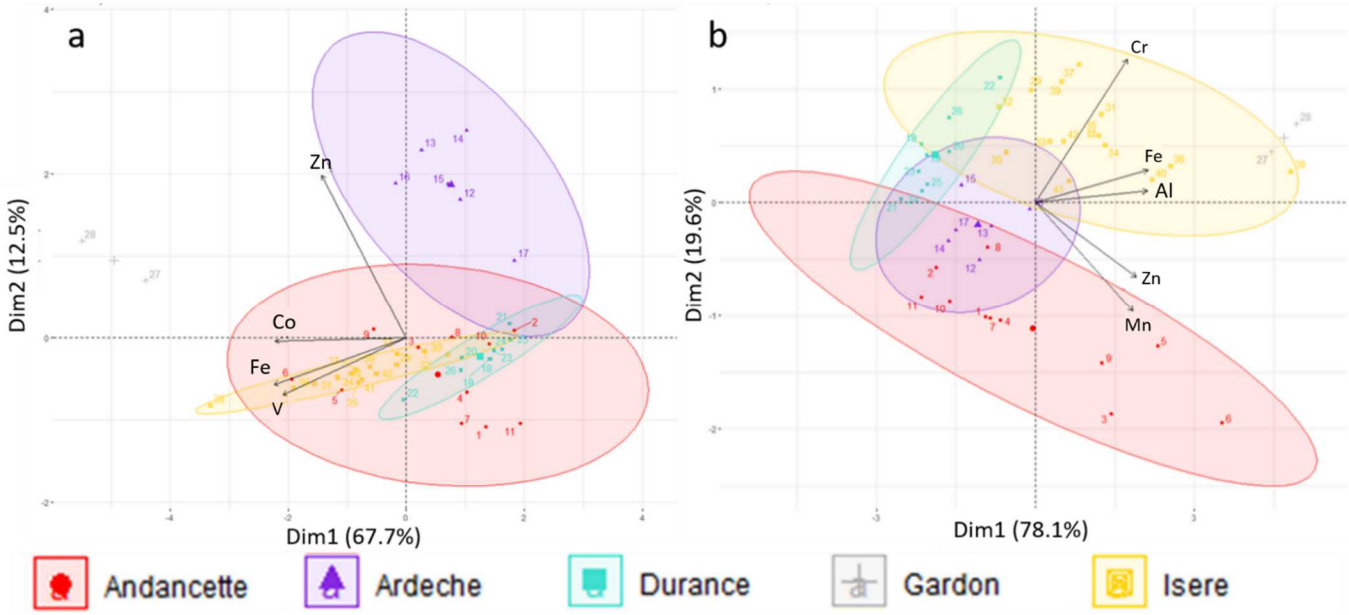


Table 1: Summary of sampling periods for each tributary and associated hydro-sedimentary conditions.

Tributary	N =42 samples	Water flow ($m^3 s^{-1}$)	SPM concentration ($mg L^{-1}$)
Middle Rhône River (Andancette station)	11 (flood: 3, base flow: 8)	263 - 1040 (2018-2019 period)	3.5 - 18.8 (2019)
Isère	14 (flood: 3, base flow: 11)	175 – 671 (2014-2018)	6.75 – 1488 (2014-2018)
Ardèche	6 (flood: 1, base flow: 5)	9 - 459 (2016)	1.7 - 13.8 (2016)
Gardon	2 (flood: 1, base flow: 1)	- (2017)	- (2017)
Durance	9 (flood: 2, base flow: 7)	38 – 1613 (2011-2016)	6.2 - 545 (2014-2016)

Table 2: Proportions (in %) of the reactive fraction compared to the total fraction for each trace and major elements. The results are presented for the SPM tributaries and for the sediment core samples divided in two main periods (1991-2013 and 1981-1990).

Elements	Proportions of the reactive fraction (%)						
	Middle Rhône	**Isère**	**Ardèche**	**Durance**	**Gardon**	**Sediment core (1991-2013)**	**Sediment core (1981-1990)**
Al	7±1	3.0±0.5	7.2±0.5	4.5±0.5	4.7±0.5	5.3±0.9	6.3±0.5
Ba	18±4	19±3	32±6	40±8	25±4	39±7	43±6
Co	38±7	32±5	48±6	43±5	50±6	39±4	38±4
Cr	14±3	7±1	16±4	9±1	5.9±0.3	11±2	18±4
Cu	68±9	54±7	68±10	55±8	60±1	66±7	72±6
Fe	31±6	19±2	30±2	30±3	19±1	32±5	37±5
Mn	72±10	76±11	78±7	82±7	72±9	73±6	72±7
Ni	35±5	23±3	33±3	31±2	29.0±0.2	39±5	42±3
Sr	66±9	64±9	66±7	89±7	45.2±0.1	76±7	74±5
Ti	3±1	0.7±0.1	8±2	0.4±0.1	1.8±0.2	1.5±0.7	2.0±0.4
V	13±2	5±1	17±2	10±1	6.7±0.2	11±2	13±1
Zn	56±7	33±6	65±7	43±5	42±1	50±6	63±5

Table 3: Statistical results for tracer selection procedure, which combines the range test, the Kruskal-Wallis test (KW, $p<0.05$) and the discriminant factor analysis (DFA), for total and non-reactive fractions of SPM sources. The "V" shows the geochemical tracers that are retained at each step and "X" shows those that fail. For the range test, the number of layers, for which metals failed the range test, are indicated in parenthesis. For DFA, the "X" shows the metals removed from the procedure while the metals retained are characterised by a value representing the discriminatory power of the selected tracers.

Elements	**Total fraction**			**Non-reactive fraction**		
	Range test	KW test	DFA	Range test	KW test	DFA
Al	V	V	X	V	V	1.00
Ba	X (5 layers)	X	X	X (2 layers)	X	X
Co	V	V	0.55	V	V	X
Cr	X (1 layer)	X	X	V	V	0.95
Cu	X (1layer)	X	X	V	V	X
Fe	V	V	0.95	V	V	0.62
Mn	V	V	X	V	V	0.98
Ni	V	V	X	V	V	X
Sr	V	V	X	V	V	X
Ti	X (1 layer)	X	X	X (1 layer)	X	X
V	V	V	1.00	V	V	X
Zn	V	V	0.88	V	V	0.81

Supplementary material

Fig. SI.1: Box-and-whisker plot of median grain size (D50, values in µm) in SPM tributaries (Upper Rhône River station at Andancette – AND, Isère –ISE, Ardèche – ARD, Durance- DUR, Gardon- GAR) and in the sediment core sampled in the Rhône at Mas des Tours site.

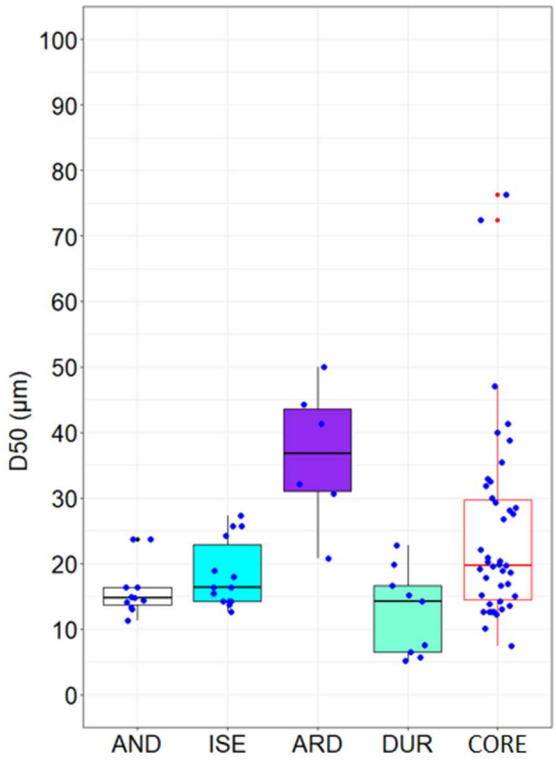


Fig. SI.2: Profile of median particle size (D50; µm) in the sediment core.