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Data Article

Dataset of natural metal background levels inferred from pre-industrial palaeochannel sediment cores along the Rhône River (France)

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ABSTRACT

Natural metal background levels in sediments are critical to assess spatial and temporal trends of contamination in hydrosystems and to manage polluted sediments. This is even more sensitive that multi-factors such as geogenic basement, depositional context, and past or long-term pollution can affect the level of metals in sediments. This article provides natural metal background levels and ancillary data (location, chronology, grain-size, total organic carbon – TOC) in pre-industrial sediments along the Rhône River (France). Two distinct areas were selected to take into account the geological variability of the watershed: the Dauphiné Lowlands (Upper Rhône River) and the Tricastin Floodplain (Middle Rhône River). On each area, the sediment cores were retrieved from palaeochannel sequences and the sampled sections were dated by radiocarbon from the Roman to the Modern Times (AD 3–1878). Regulatory metals (Al, Fe, Cd, Cr, Cu, Ni, Pb, and Zn) and other trace elements (Ba, Co, Li, Mg, Mn, Na, P, Sr, Ti, V) were analysed following both *Aqua Regia* (AR) and Total Extraction (TE) procedures. Classically, TE

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provides metal concentrations greater than AR because TE includes crystalline lattice, while AR is close to the potentially bio-accessible part of metals (used for ecotoxicological purposes). Due to the small number of samples and to the non-normal distribution of the results, a median-based approach was chosen to establish the geochemical background values and ranges (MGB) for each sample and area. These MGBs are valuable to identify pollution sources, to characterise a contamination (spread and timing), and to estimate the state of rivers regarding pollution legacy. Along the Rhône River, these two continental MGBs were used to reconstruct the metal geo-accumulation trajectories in river sediments from 1965 to 2018 [1].

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Specifications Table

Subject	Environmental Chemistry
Specific subject area	Geochemical background for metal elements in river sediments
Type of data	Map, Tables, Boxplots
How data were acquired	Sampling on the field with a percussion corer (Cobra TT type); mineralisation by *Aqua Regia* (AR) and Total Extraction (TE); analysis of metal elements by ICP-OES (Al, Cr, Cu, Ni and Zn) and ICP-MS (Cd and Pb); ancillary data: grain-size (Mastersizer 2000, Malvern) and Total Organic Carbon (TOC, pyrolysis)
Data format	Raw and analysed
Parameters for data collection	The sediment cores were extracted from eight palaeochannels located in the Rhône floodplain and disconnected of the main stream (since at least 350 years).
Description of data collection	Nineteen samples were taken from the palaeochannel cores. Four were rejected due to a coarse grain-size (i.e. clay + silt $<$ 60%). The geochemical background was calculated by using median values and ranges for each river section: in the Upper Rhône (Dauphiné Lowlands) and in the Middle Rhône River (Tricastin Floodplain).
Data source location	Cores coordinates (decimal degrees, WGS84): CHCO-S2: 45.679 N, 5.597E; LMS1: 45.675 N, 5.604E; EM-5: 45.699 N, 5.593E; PDC-S8: 45.651 N, 5.520E; DZ-1: 44.424 N, 4.704E; DZR-C3: 44.428 N, 4.659E; MGN-C1: 44.202 N, 4.709E; LPP-C1: 44.324 N, 4.669E
Data accessibility	With the article
Related research article	A.-M. Dendievel, B. Mourier, A. Dabrin, H. Delile, A. Coynel, A. Gosset, Y. Liber, J.-F. Berger, J.-P. Bedell, Metal pollution trajectories and mixture risk assessed by combining dated cores and subsurface sediments along a major European river (Rhône River, France), *Environment International* 2020, 144, 106032. doi:https://doi.org/10.1016/j.envint.2020.106032

Value of the Data

- This article proposes detailed information to define geochemical backgrounds from the coring of pre-industrial palaeochannels in several areas located along a large and heterogeneous river such as the Rhône River (France).
- The dataset provides metal concentrations (ranges and medians) for major and regulatory metals (Al, Fe, Cd, Co, Cr, Cu, Hg, Ni, Pb, Zn) and also other elements (Ba, Li, Mg, Mn, Na, P,

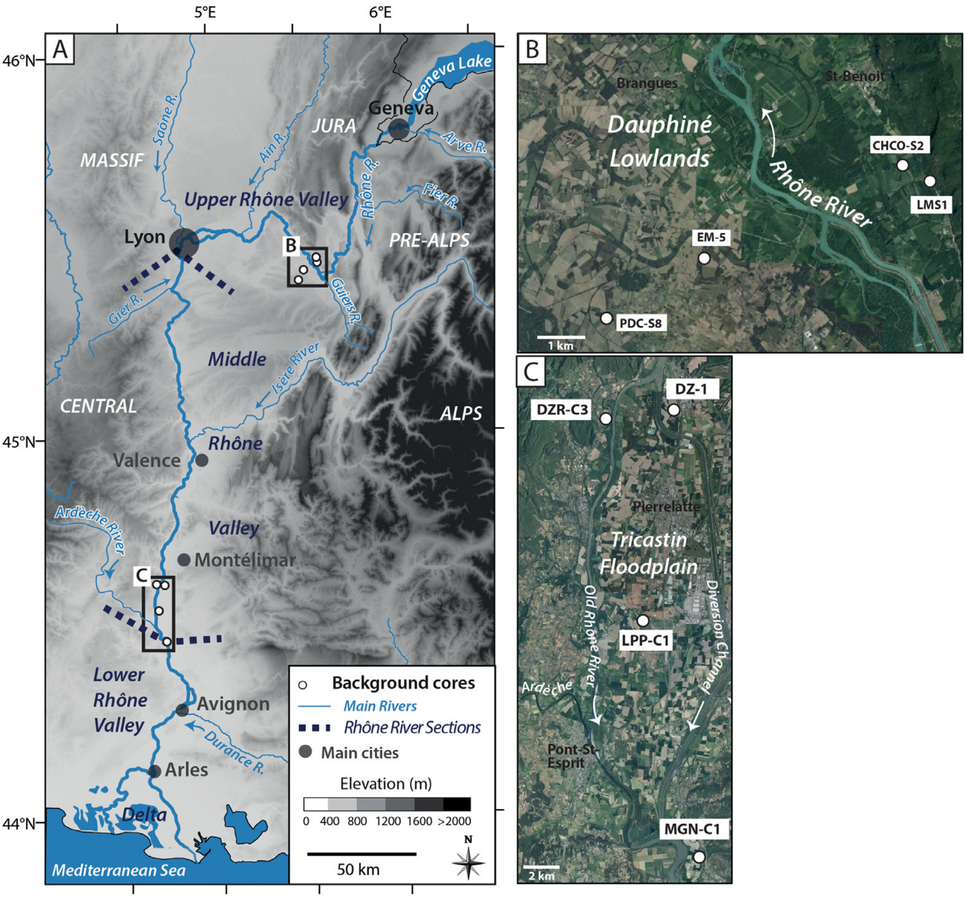

Fig. 1. Location of the sampling sites. A) Overview of the French course of the Rhône River. B) Focus on zone B: Dauphiné Lowland Area (Upper Rhône River). C) Focus on zone C: Tricastin Floodplain (Middle Rhône River) on IGN images (2015–2017).

Sr, Ti, V), total organic carbon and grain-size data suitable for researchers and stakeholders to estimate the natural level of metal contamination.

- A description of depositional environments, extraction methods (*Aqua Regia* and Total Extraction), sedimentological settings and a large set of radiocarbon ages are provided in order to specify the environmental and analytical context of the data.

1. Data Description

Two sets of geochemical background samples (GBS) were obtained from two areas located along the Rhône River (Fig. 1): Dauphiné Lowlands (Upper Rhône River) and Tricastin Floodplain (Middle Rhône River). After radiocarbon dating, lithological description, organic carbon and particle size measurements, fifteen sediment samples were used for metal analysis and the calculation of the Median-based Geochemical Background (MGB).

In the Upper Rhône River, the MGB is based on seven samples from three of the four sediment cores sampled on this area (validated samples from: EM5, CHCO-S2, and PDC-S8; re-

Table 1
Location of the background cores and number of samples analysed along the Rhône River (France). Latitude (Lat.) and Longitude (Long.) are expressed in decimal degrees (WGS84). The distance is expressed in kilometers upstream of estuarine areas (UEA). The samples with a fine fraction (i.e. clay + silt) $>$ 60% were accepted, and rejected on the opposite case.

	Core name	Lat. (N)	Long. (E)	Distance UEA (km)	Number of samples	Status
Upper Rhône River	CHCO-S2	45.679	5.597	420	2	All accepted
	LMS1	45.675	5.604	420	2	All rejected
	EM-5	45.699	5.593	418	2	All accepted
	PDC-S8	45.651	5.520	418	3	All accepted
Middle Rhône River	DZ-1	44.424	4.704	157	2	All accepted
	DZR-C3	44.428	4.659	157	2	1 Accepted; 1 Rejected
	MGN-C1	44.202	4.709	130	3	2 Accepted; 1 Rejected
	LPP-C1	44.324	4.669	146	3	All accepted

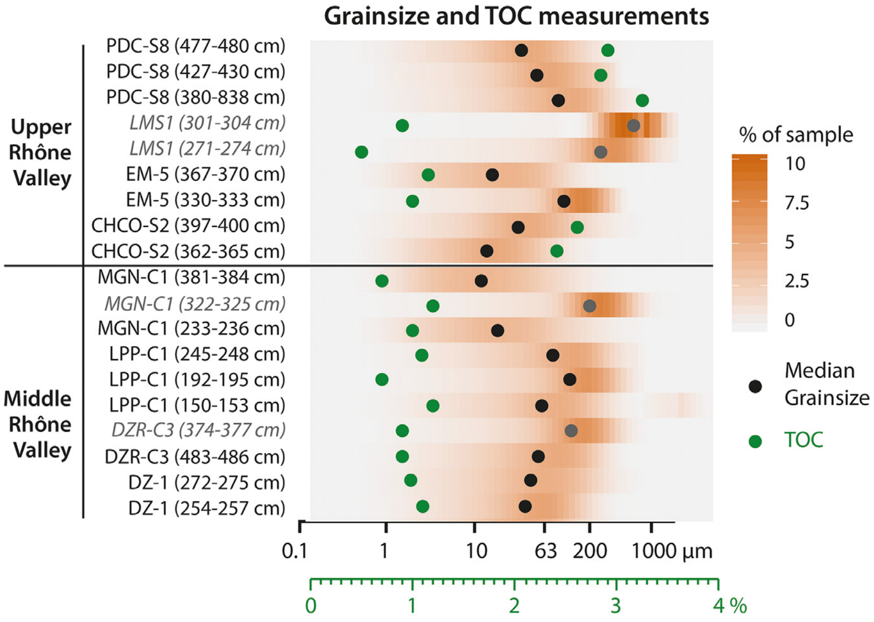

Fig. 2. Grain-size and Total Organic Carbon (TOC) distribution.

jected coarse samples from LMS1; Fig. 1b and Table 1). All these samples were deposited in a palaeochannel environment between AD 3 and 1670 (Table 2). The basal part of these palaeochannel fillings is highly laminated with silts (due to the Rhône River flood inputs), while they show alternating peaty or gleyed-silty facies in the upper and subsurface layers. It suggests a progressive loss of connectivity with the main stream (less regular flooding, more authigenous organic matter, and pedogenic process). The median level of organic carbon is about 2.6% (26 g kg^{-1}) while the median proportion of fine particles (FF $<$ 63 µm) is about 90% (Fig. 2 and Table 3). As showed in Fig. 3 and Table 3, metal concentrations according to *Aqua Regia* (AR) and Total Extraction (TE) treatments are within a similar range for Cd, Cu, Ni, Pb, and Zn (less than 18% of difference for these metals). However, the distribution of the data is quite different between the results obtained for Al, and Cr (70% and 46% of divergence, respectively). The MGB

Table 2

Radiocarbon dating of the background sediment cores. Measured ^{14}C ages are in expressed BP, i.e. Before Present (1950), whereas "pMC" refers to the proportion of Modern Carbon for recent ages. Bold lines represent the nearest dates to the geochemical background samples (GBS) as explained in the rightmost column.

	Core	Dated material	Depth (cm)	Lab code	Measured ^{14}C age (BP; 1 σ)	Calibrated age (cal. AD; 2 σ)	Relationships with GBS
Upper Rhône River	EM-2	charcoal	110–114	Poz-46822	60 ± 110	AD 1650–1950	
	EM-2	wood	261–264	SacA 21423	615 ± 30	AD 1294–1401	
	EM-2	**charcoal**	**329–333**	**Poz-46825**	**350 ± 80**	**AD 1418–1670***	Close to EM-5 330–333
	EM-5	**charcoal**	**453.5–455**	**Poz-96872**	**655 ± 30**	**AD 1278–1394**	Prior to EM-5 367–370
	EM-5	charcoal	603–605	Poz-96870	780 ± 35	AD 1190–1283	
	CHCO-S2	plant remains	119–122	Poz-116812	102.28 ± 0.34 pMC	Modern	
	CHCO-S2	plant remains	192–196	Poz-116813	395 ± 30	AD 1439–1628	
	CHCO-S4	**charcoal**	**363.5–367.5**	**Poz-116814**	**330 ± 30**	**AD 1477–1643**	Close to CHCO-S2 362–333
	CHCO-S4	**leaves**	**521–524**	**Poz-116809**	**395 ± 30**	**AD 1439–1628**	Prior to CHCO-S2 397–370
	CHCO-S4	leaves	571–574	Poz-116807	400 ± 80	AD 1400–1660	
	LM S8	wood	216	Poz-109138	280 ± 30	AD 1498–1795	
	PDC	charcoal	110	SacA-7488	1740 ± 30	AD 236–386	
	PDC-S8	**charcoal**	**351**	**Poz-115452**	**1875 ± 35**	**AD 65–231**	After PDC-S8 380–383
	PDC-S8	**charcoal**	**404**	**Poz-115453**	**1920 ± 30**	**AD 3–204**	After PDC-S8 427–430
	PDC-S8	**charcoal**	**495**	**Poz-115454**	**1905 ± 30**	**AD 25–211**	Just prior to PDC-S8 477–480
Middle Rhône River	**DZ-1**	**seeds**	**236.5–238**	**Poz-92592**	**195 ± 30**	**AD 1648–1810***	After DZ-1 254–257
	DZ-1	**charcoal**	**278–280**	**Poz-96866**	**175 ± 30**	**AD 1656–1878***	Related to DZ-1 277–280
	DZR-C3	charcoal	45–48	Poz-99626	152.69 ± 0.46 pMC	Modern	
	DZR-C3	charcoal	206–209	Poz-99627	80 ± 40	AD 1682–1937	
	DZR-C3	leaves	314	Poz-115451	80 ± 40	AD 1682–1937	
	DZR-C3	**leaves**	**416**	**Poz-115448**	**150 ± 110**	**AD 1517–1888***	Posterior to DZR-C3 483–486
	MGM-C1	**charcoal**	**156–159.5**	**Poz-116832**	**520 ± 100**	**AD 1277–1633**	Posterior to MGM-C1 233–236
	MGM-C1	**charcoal**	**272**	**Poz-109204**	**1180 ± 30**	**AD 730–951**	Prior to MGM-C1 233–236
	MGM-C1	*leaves*	*337–339*	*Poz-116833*	*135 ± 30*	*AD 1671–1943*	*Rejected*
	MGM-C1	*leaves*	*386–388.5*	*Poz-116834*	*155 ± 35*	*AD 1665–1891**	*Rejected*
	MGM-C1	**leaf remains + charcoal**	**421–424**	**Poz-116835**	**920 ± 40**	**AD 1026–1206**	Prior to MGM-C1 381–384
	MGM-C1	*seeds*	*466–468*	*Poz-116836*	*100 ± 35*	*AD 1681–1938*	*Rejected*
	LPP-C1	*plant remains*	*150*	*Poz-109205*	*103.46 ± 0.33 pMC*	*Modern*	*Rejected*
	LPP-C2	plant remains	58–61	Poz-109206	108.7 ± 0.35 pMC	Modern	
	LPP-C2	**plant remains**	**154**	**Poz-109101**	**1100 ± 30**	**AD 887–1013**	Related to LPP-C1 150–153; after LPP-C1 192–195 and LPP-C1 245–248

* potential interval extension up to 1949.

Table 3

Geochemical background samples (GBS), median values (MGB) and ranges for the Upper and Middle Rhône River. FF = fine fraction (clay + silt < 60%). TOC = Total Organic Carbon. Extraction methods (Ext.): AR = *Aqua Regia* and TE = Total Extraction.

	Core	Depth (cm)	Clays (%)	FF (%)	TOC (%)	Ext.	Al (g kg^{-1})	Fe (g kg^{-1})	Cd (mg kg^{-1})	Cr (mg kg^{-1})	Cu (mg kg^{-1})	Ni (mg kg^{-1})	Pb (mg kg^{-1})	Zn (mg kg^{-1})	Ba (mg kg^{-1})	Co (mg kg^{-1})	Li (mg kg^{-1})	Mg (mg kg^{-1})	Mn (mg kg^{-1})	Na (mg kg^{-1})	P (mg kg^{-1}	Sr (mg kg^{-1})	Ti (mg kg^{-1})	V (mg kg^{-1})
Upper Rhône	EM5	330–333	3.3	58.1	1.00	AR	11.196	16.823	0.11	37	10.2	35.2	10.4	44	36.8	7.3	22.6	7.6	486.1	<LOQ	0.53	207.8	475.8	24.4
	EM5					TE	50.984	22.629	0.12	72.7	12.5	41	13.4	53.6	253.1	11.3	40	10.1	589.1	11.45	<LOQ	302.3	2478.5	58.5
	EM5	367–370	12.98	97.01	1.15	AR	25.700	27.656	0.19	71.3	23.2	76.1	16.6	78.8	94.2	14.8	40.8	11.1	647.5	0.21	0.54	217.6	309.1	50.7
	EM5					TE	70.895	35.447	0.21	119.6	26	84.9	19.9	91.4	295.1	20.4	67	14.6	730.6	5.66	<LOQ	285.7	3501.5	107.6
	CHCO-S2	362–365	13.05	98.73	2.40	AR	18.383	26.796	0.17	43.4	18.3	46.7	17.2	71.3	62.8	11.5	36.2	8.8	572.3	0.2	0.58	222.4	350.3	36.3
	CHCO-S2					TE	67.591	36.190	0.22	90.2	22.2	55.4	20.5	88.6	281.8	17.2	70.8	12.5	684	6.47	<LOQ	317.5	3249.5	100.6
	CHCO-S2	397–400	7.08	89.63	2.60	AR	12.320	16.326	0.17	32.7	13.2	33.9	11.3	53.2	43.1	7	24.8	6.5	373.1	<LOQ	0.53	194.5	195.8	26.9
	CHCO-S2					TE	43.051	20.013	0.18	63.2	14.2	36.5	12.5	59.1	182.8	10.5	44.9	8.2	400.5	4.64	<LOQ	248.1	2202.4	65
	PDC-S8	380–383	4.52	71.73	3.25	AR	10.078	11.951	0.14	26.2	7.3	18.2	11.4	37.3	27.8	5.4	16.1	5.6	310.7	<LOQ	0.52	311.4	229.5	24.2
	PDC-S8					TE	36.217	16.830	0.14	49.9	10.1	22.4	12.6	47.2	160.3	8.6	32.5	7.8	391.7	5.38	<LOQ	409.6	1910.7	51.7
	PDC-S8	427–430	5.02	81.02	2.83	AR	11.397	14.284	0.12	26.9	7.2	18.8	10.9	39.2	33	5.2	17.7	6	425.6	0.16	0.61	329.4	221.4	25.9
	PDC-S8					TE	36.417	19.052	0.15	47.5	8.6	22.9	13.2	48.6	155.2	8.2	34.4	8	509.5	4.87	<LOQ	418.3	1858.5	52.4
	PDC-S8	477–480	7.48	91.71	2.90	AR	16.791	18.099	0.18	36.1	10.1	27.5	14.7	54.3	50.7	7.8	25.6	7.4	504.9	0.19	0.63	282.4	311.2	34.8
	PDC-S8					TE	49.155	23.649	0.2	63.8	12.1	33.2	17	66.1	213.6	11.8	45.9	9.8	582.8	5.09	<LOQ	358.7	2335.6	71.4
	MGB (AR)		**5.02**	**89.63**	**2.6**	**AR**	12.320	16.823	0.17	36.1	10.2	33.9	11.4	53.2	43.1	7.3	24.8	7.4	486.1	0.2	0.54	222.4	309.1	26.9
	MGB (AR) Range					AR	2–27	5–33	0.06–0.24	14–56	0–26	0–68	4–22	10–95	2–90	1–15	4–47	3–11	191–748	0–0	0.43–0.69	86–423	68–489	10–51
	MGB (TE)					**TE**	49.155	22.629	0.18	63.8	12.5	36.5	13.4	59.1	213.6	11.3	44.9	9.8	582.8	5.4	<LOQ	317.5	2335.6	65
	MGB (TE) Range					TE	10–89	5–45	0.05–0.3	19–119	1–29	0–78	4.5–27	12–117	28–411	2–22	8–85	3–16	183–909	3–8	<LOQ	159–519	845–4075	10–132
Middle Rhône	DZ1	254–257	5.76	90.55	1.1	AR	17.203	22.439	0.14	32.3	22.1	38.6	20.9	77.8	61.1	12.1	42.1	9.2	456.7	0.2	0.64	267.1	294.5	33.7
	DZ1					TE	69.465	27.391	0.17	74.8	22.1	40.7	24.6	84.8	323	18.1	70.5	11.8	489.7	7.75	<LOQ	354.1	3538.2	99
	DZ1	272–275	5.99	83.59	1.00	AR	11.621	17.206	0.14	26.5	17.1	31	18	63	45.1	10	30.9	7.2	412.1	<LOQ	0.52	287.2	241.6	26.9
	DZ1					TE	61.025	24.121	0.16	67.5	19.3	36.7	21.7	78.6	295.4	16.9	63.2	10.5	496.4	8.21	<LOQ	398.9	3333.7	87.1
	DZRC3	483–486	5.1	81.42	0.87	AR	13.324	24.959	0.21	28.1	23.3	36.9	77.6	90.8	53.1	11.8	36.2	14.1	853.2	50.48	0.73	352.7	297.8	27.5
	DZRC3					TE	69.039	34.433	0.23	73.4	25.9	46.6	89.8	101.7	365.7	15.3	78.7	14.1	990.7	9.54	<LOQ	487.3	3643.5	95.3
	MGNC1	233–236	11.68	91.8	1.0	AR	24.144	23.181	0.16	40.7	20.7	37.2	26.4	84	101.5	12	38.1	11.5	422	43.69	0.59	298.5	387.4	48.7
	MGNC1					TE	92.254	35.555	0.17	100.2	26.6	51.4	30.1	114.8	434.8	22.1	90	12.2	569.5	6.04	<LOQ	442.8	4696.5	135.6
	MGNC1	381–384	16.24	96.46	0.71	AR	21.307	21.044	0.14	37.7	19.4	29.4	12.9	65.4	105.9	7.9	22.8	9.7	484.7	44.57	0.41	348.3	81.3	49.7
	MGNC1					TE	74.829	32.884	0.19	89.2	24.9	42.2	17.3	89.4	326.6	15.3	67.9	9.4	625.2	<LOQ	<LOQ	461.1	3365.9	125.7
	LPPC1	150–153	5.05	72.8	1.2	AR	15.131	31.101	0.14	30.4	15.7	30.1	17.5	63.7	74.6	11.4	31.8	10.9	1086.8	41.5	0.6	277	539.7	34.6
	LPPC1					TE	67.784	42.820	0.18	69.8	19.3	39.6	23	82.6	355	18.9	66.3	10.5	1338.3	10.61	<LOQ	392.4	3814.3	90.4
	LPPC1	192–195	2.63	53.59	0.74	AR	9.209	16.251	0.11	22.1	13.4	27.4	13.5	51.7	33.4	7.8	25.9	11.5	403	46.52	0.59	263.8	295.1	20.8
	LPPC1					TE	69.364	26.282	0.15	65.9	17.4	37.7	20.7	74	370.8	16.1	60.3	11.7	576.7	14.13	<LOQ	410.3	3414.5	83.5
	LPPC1	245–248	4.06	69.25	1.1	AR	11.761	19.376	0.15	27.4	17.5	34.3	16	61.8	49.7	10.8	29.6	11.3	520.3	38.65	0.61	278.2	343.1	26.3
	LPPC1					TE	60.985	25.331	0.18	65	18.5	38.6	21.3	72.2	317.7	16.4	55.8	10.3	606.1	10.88	<LOQ	360.8	3129.3	79.1
	MGB (AR)		**5.08**	**81.42**	**0.99**	**AR**	14.228	21.742	0.14	29.3	18.4	32.7	17.7	64.6	57.1	11.1	31.3	11.1	470.7	43.69	0.59	282.7	296.5	30.6
	MGB (AR) Range					AR	2–28	12–31	0.12–0.17	17–43	10–27	19–48	5–33	38–104	0–130	6–15	17–49	7–14	144–880	32–54	0.5–0.59	220–366	172–464	10–55
	MGB (TE)					**TE**	69.202	30.137	0.17	71.6	20.7	40.1	22.3	83.7	340.8	16.6	67.1	11.1	591.4	9.5	<LOQ	404.6	3476.4	92.8
	MGB (TE) Range					TE	59–78	13–48	0.15–0.2	50–95	10–34	31–51	14–33	55–115	254–435	12–22	47–88	8–14	303–965	4–15	<LOQ	290–542	2865–4179	57–135
Limits of Quantification (LOQ)						AR	0.170	0.170	0.02	0.67	0.67	0.67	0.02	0.67	0.67	0.67	0.67	0.17	0.67	0.17	0.17	0.67	0.67	0.67
						TE	2.500	2.500	0.03	5	5	2.5	0.03	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5

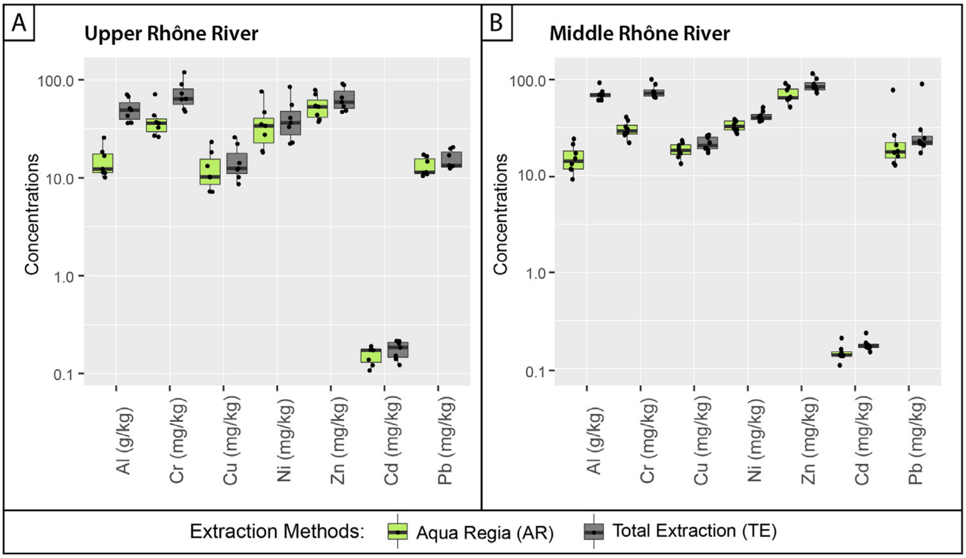

Fig. 3. Distributions of *Aqua Regia* (AR) and Totally Extracted (TE) metal concentrations for the geochemical background samples (GBS) on the Upper Rhône River (A) and Middle Rhône River (B).

and associated ranges are as follows for the regulatory metals (the other trace metal median and ranges are available in Table 3):

- Al is within the range of 2 and 27 g kg^{-1} (lower and upper whiskers of a Tukey's boxplot; i.e. confidence interval = 95.6%) with a median of 12 g kg^{-1} for the AR procedure, and within 10 and 89 g kg^{-1} with a median of 49 g kg^{-1} for the TE procedure. The Fe values are rather close with a median rounded to 17 g kg^{-1} (interval = 5-33) according to the AR procedure, and a median rounded to 23 g kg^{-1} (interval = 5-45) for the TE procedure.
- Cd is within 0.06 and 0.024 mg kg^{-1} with a median of 0.17 mg kg^{-1} (AR), and within 0.05 and 0.3 mg kg^{-1} with a median of 0.18 mg kg^{-1} (TE).
- Cr is within 14 and 56 mg kg^{-1} with a median of 36 mg kg^{-1} (AR), and within 19 and 119 mg kg^{-1} with a median of 64 mg kg^{-1} (TE).
- Cu is within 0.1 and 26 mg kg^{-1} with a median of 10 mg kg^{-1} (AR), and within 0.1 and 29 mg kg^{-1} with a median of 12.5 mg kg^{-1} (TE).
- Ni is within 0.1 and 68 mg kg^{-1} with a median rounded up to 34 mg kg^{-1} (AR), and within 0.1 and 78.5 mg kg^{-1} with a median of 36.5 mg kg^{-1} (TE).
- Pb is within 4 and 23 mg kg^{-1} with a median of ca. 11 mg kg^{-1} (AR), and within 4.5 and 27 mg kg^{-1} with a median of 13 mg kg^{-1} (TE).
- Zn is approx. within 10 and 95 mg kg^{-1} with a median of 53 mg kg^{-1} (AR), and within 12 and 117 mg kg^{-1} with a median rounded at 59 mg kg^{-1} (TE).

In the Middle Rhône River, the MGB is based on eight samples from four palaeochannel cores (DZ-1, DZR-C3, MGN-C1, LPP-C1; Fig. 1c and Table 1) dated from AD 887 to AD 1878 (Table 2). Depositional conditions are equivalent to those described for the Upper Rhône, with higher oxidation of the sedimentary column in general. The median concentration of organic carbon is about 0.9% (9 g kg^{-1}) while the median proportion of fine particles is 81% (Fig. 2 and Table 3). A major difference existed between AR and TE-derived concentrations for Al, and Cr (78% and 59% of divergence, respectively), while the difference is less pronounced for Cu, Cd, Ni, Pb, and Zn (from 14 to 21%; see also Fig. 3 and Table 3).

Further than defining two regional geochemical backgrounds, these analyses also demonstrated that the difference of Cd, Cu, Ni, Pb and Zn concentrations after AR and TE procedures were relatively constant and almost entirely extracted after the AR mineralisation (up to 86% compared to TE). By contrast, only 46% of Cr, and 23% of Al total concentrations were extracted by AR, especially because these 2 elements could be considered as relatively immobile during weathering. In the Middle Rhône River, the MGB and associated ranges are as follows for the regulatory metals (the median and ranges for the other elements are also available in Table 3):

- Al is within 2 and 28 g kg^{-1} (lower and upper whiskers of a Tukey's boxplot) with a median of 14 g kg^{-1} for the AR procedure, and within 59 and 78 g kg^{-1} with a median of 69 g kg^{-1} for the TE procedure. Regarding Fe, the median is about 22 g kg^{-1} (rounded) according to the AR procedure and about 30 g kg^{-1} for the TE procedure, with ranges of 12-31 g kg^{-1} and 13-48 g kg^{-1}, respectively.
- Cd is within 0.12 and 0.17 mg kg^{-1} with a median of 0.14 mg kg^{-1} (AR), and within 0.15–0.2 mg kg^{-1} with a median of 0.17 mg kg^{-1} (TE).
- Cr is within 17 and 43 mg kg^{-1} with a median of 29 mg kg^{-1} (AR), and within 50 and 95 mg kg^{-1} with a median of 72 mg kg^{-1} (TE).
- Cu is within 10 and 27 mg kg^{-1} with a median of 18 mg kg^{-1} (AR), and within 10 and 34 mg kg^{-1} with a median of 21 mg kg^{-1} (TE).
- Ni is within 19 and 48 mg kg^{-1} with a median rounded up to 33 mg kg^{-1} (AR), and within 31 and 51 mg kg^{-1} with a median of 40 mg kg^{-1} (TE).
- Pb is within 5 and 33 mg kg^{-1} with a median rounded up to 18 mg kg^{-1} (AR), and within 14 and 33 mg kg^{-1} with a median of 22 mg kg^{-1} (TE).
- Zn is approx. within 37 and 104 mg kg^{-1} with a median of 65 mg kg^{-1} (AR), and within 55 and 115 mg kg^{-1} with a median rounded at 84 mg kg^{-1} (TE).

2. Experimental Design, Materials, and Methods

The cores were retrieved into pre-industrial meanders – i.e. palaeochannels active before the Modern period – in two regions typical in terms of geology, tributary inputs and water discharge along the Rhône River (Fig. 1; Table 1). The sediments used to establish the regional geochemical backgrounds were sampled from deep core sections, i.e. between 2 and 5 m in depth (please refer to the Fig. SI-1 available in: [1]). A chronological control was based on multiple radiocarbon dating measured by accelerator mass spectrometry (^{14}C AMS) at Poznan (Poland), and Saclay (France, within the ARTEMIS project). The radiocarbon dates were performed on charcoals, and on uncharred plant remains such as well-preserved wood, seeds and leaves to prevent old wood effects when possible (Table 2). The measured ages (originally expressed as BP – i.e. before AD 1950, a date considered as the present), were calibrated by using the “Intcal13” curve [2] and the OxCal software (v.4.3) [3]. After calibration, the dates were expressed in calendar years Anno Domini (AD) in Table 2. However, in such alluvial context, these measures do not prevent the potential influence of reworked material in the dated sediment, which could present an age older than expected.

In the Upper Rhône River, four cores were sampled in the Dauphiné Lowlands (Fig. 1b). This area is a floodplain offering numerous meanders filled during the Holocene, after the Rhône River avulsion eastwards to the Brégnier-Cordon Valley [4]. In this area, the Rhône River is mainly supplied by fine sediment loads transported by Alpine, and Pre-Alpine rivers (Arve, Fier, and Guiers rivers). These tributaries delivered circa 500 Kt/yr of suspended particulate matter – SPM (mainly rock flour); while limestones, molasse, moraines and fluvio-glacial deposits composed the local *substratum* [4,5].

Four other cores were sampled in the Middle Rhône area, especially in palaeomeanders located in the Tricastin floodplain (Fig. 1c). This region received inputs of sediments from rivers of the Massif Central mountains (granitic and basaltic rocks), such as the Cance, the Eyrieux, and the Ardèche rivers (right bank tributaries), while significant inputs also come from subalpine tributaries draining limestone and marls, such as the Isère and Drôme rivers, and locally the Roubion, the Lauzon, and the Lez rivers (left bank tributaries).

Two to three samples were selected along each core (for lithological details, see SI-1 in: [1]) and subsampled for the analysis. A subsample (0.5 g) was crushed and burned at 900 °C to estimate Total Organic Carbon content (% TOC) by using a TOC analyser under an oxygen flow, followed by a gas chromatography with a thermal conductivity detector (Thermo Scientific Flash 2000 Elemental Analyzer available at the INRAE laboratory). Another subsample (about 1 g) was used to measure grain-size distribution. The particle size analysis was achieved with a Mastersizer 2000© (Malvern Panalytical) mounted with a hydro SMsmall dispersion unit (ENTPE laboratory). The grain-size classes ranged between 0.012 μm and 1000 μm. These initial analyses led to the exclusion of the two samples from the core LMS1 (Upper Rhône River), one sample from the core DZR-C3 and another from the core MGN-C1 (both in the Middle Rhône River), due to a poor content in fine sediments (i.e. clay + silt < 60%).

After a preliminary sieving at 63 µm, the remaining samples (0.1–0.3 g each) were powdered and homogenised before metal extraction. The extraction was achieved by using both *Aqua Regia* – AR (HNO_3, HCl), and Total Extraction – TE – micro-wave assisted (HF, HNO3, HCl) – procedures. Then, the AR mineralisation was based on a mixture of 0.5 ml HNO_3 (14 M, Suprapur) and 0.5 ml HCl (12 M, Suprapur). For TE, sub-samples were digested in closed, previously acid-cleaned PP reactors (DigiTUBEs; SCP Sciences) by using 1.5 ml HCl, 0.5 ml HNO_3, and 2 ml HF (22 M, Suprapur). The reactors were kept at 110 °C in an automatic heating block for 2 h. Dry residues were dissolved with 250 ml HNO_3 and 5 ml of Ultrapure water (Elga), before a heating for 30 min at 100 °C. Exactly 3.5 mL of the solution was brought to 10 mL using 6.5 mL of ultrapure water. Accuracy of extraction and analytical methods was steadily controlled by using certified reference material for AR (LGC 6187) and TE (IAEA 158) and was < 10% of the certified values.

Most of the metals (see Table 3 for the full list) were analysed by inductively coupled plasma with optical emission spectrometry (ICP-OES; Agilent 700). Cadmium (Cd) and lead (Pb) were analysed by inductively coupled plasma mass spectrometry due to lower concentrations (ICP-MS; Thermo Scientific iCAPTM TQs). The limits of quantification (LOQs) were 0.2 g kg^{-1} and 2.5 g kg^{-1} for Al (AR and TE respectively), 0.7 mg kg^{-1} and 2.5 mg kg^{-1} for Cr, Cu, Ni and Zn (AR and TE), 0.02 mg kg^{-1} and 0.03 mg kg^{-1} for both Cd and Pb (AR and TE).

Finally, a range between the lower and upper whiskers of Tukey's boxplot (95.6%) and a median value were calculated to define the local geochemical background (MGB) for each studied section of the Rhône River (Table 3).

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships which have, or could be perceived to have, influenced the work reported in this article.

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