

A Compilation of Silicon, Rare Earth Element and Twenty-One other Trace Element Concentrations in the Natural River Water Reference Material SLRS-5 (NRC-CNRC)

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The natural river water certified reference material SLRS-5 (NRC-CNRC) was routinely analysed in this study for major and trace elements by ten French laboratories. Most of the measurements were made using ICP-MS. Because no certified values are assigned by NRC-CNRC for silicon and 35 trace element concentrations (rare earth elements, Ag, B, Bi, Cs, Ga, Ge, Li, Nb, P, Rb, Rh, Re, S, Sc, Sn, Th, Ti, Tl, W, Y and Zr), or for isotopic ratios, we provide a compilation of the concentrations and related uncertainties obtained by the participating laboratories. Strontium isotopic ratios are also given.

Keywords: river water reference material, ICP-MS, rare earth elements, trace elements.

Le matériau de référence certifié d'eau de rivière naturelle SLRS-5 (NRC-CNRC) est analysé régulièrement comme contrôle qualité par dix laboratoires français étudiant les éléments majeurs et en trace dans les solutions naturelles. La plupart des mesures sont réalisées par ICP-MS. Le silicium et 35 éléments en trace (terres rares, Ag, B, Bi, Cs, Ga, Ge, Li, Nb, P, Rb, Rh, Re, S, Sc, Sn, Th, Ti, Tl, W, Y et Zr) ne sont pas certifiés par NRC-CNRC. Aucun rapport isotopique n'est disponible. Nous proposons, pour ces éléments, des valeurs moyennes et leurs incertitudes associées obtenues par les différents laboratoires participants. Le rapport isotopique de Sr est aussi mesuré.

Mots-clés : matériau de référence d'eau de rivière, ICP-MS, terres rares, éléments en trace.

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Natural river water reference materials are widely used in order to verify routine water analyses by geochemists and hydrogeologists (Tosiani *et al.* 2004, Lawrence *et al.* 2006, Bayon *et al.* 2010, Birke *et al.* 2010). Among these reference materials, the Ottawa River water SLRS, prepared by the Canadian National Research Council (NRC-CNRC Canada), has been used by ten French geoscience laboratories. This study is a follow-up to the SLRS-4 compilation performed by French laboratories within the framework of the CNRS 'Isotrace' network (Yeghicheyan *et al.* 2001): because the batch of SLRS-4 is now exhausted, a new batch referred to as SLRS-5 was made available and is currently used for trace element determinations, which are useful for tracing sources and studying geochemical processes. The ten participating French laboratories (the Service d'Analyse des Roches et des Minéraux of Nancy, the Laboratoire d'Environnements et Paléoenvironnements Océaniques et Continentaux of Bordeaux, the Geosciences Laboratory of Rennes, the HydroSciences Laboratory of Montpellier, the Geosciences Laboratory of Montpellier, the Laboratoire d'Etudes en Géophysique et Océanographie Spatiales of Toulouse, the Laboratoire Inter-universitaire des Systèmes Atmosphériques of Paris, the Laboratoire de Géochimie des Eaux of Paris, the Geoscience Environnement of Toulouse (research team) and the Observatoire Midi-Pyrénées (OMP ICP-MS Facility group) routinely analysed the SLRS-5 CRM by ICP-MS and to a lesser extent by ICP-AES. In addition to certified elements and depending on the aims of each laboratory, uncertified elements were also measured in the SLRS reference water. This present compilation includes 2 years of individual routine results and also proposes a compilation mean for uncertified elements. Statistical treatments were performed by each laboratory, which were responsible for eliminating their own outliers and for providing average values and standard deviations. Additional statistical treatments based on ISO Guides (ISO 5725-2, 13528 and 21748) were carried out: (a) calculation of the compilation mean and its related uncertainty from all acquired data and (b) evaluation of the performance of the compilation calculation by comparing compilation results with certified values when these are available. We stress the fact that our approach is experimental and compilation data do not contribute to determining reference values. We simply indicate additional, very useful, information for laboratories with random and systematic biases included in our calculations from all our results. Isotopic Sr values ($^{87}\text{Sr}/^{86}\text{Sr}$) were also proposed by the Service d'Analyse des Roches et des Minéraux (Nancy). Compilation results were then compared with the SLRS-4 batch and to results obtained by a standardisation procedure with SLRS-4 performed by Heimburger *et al.* (2013).

Instrumentation and statistical treatment

Instruments

Equipment used by each laboratory is reported in Table 1. All the laboratories used quadrupole or high-resolution ICP-MS. Instrumental operating parameters were similar for all ICP-MS instruments, but sample introduction systems, subtracted blanks, acid molarity of analysed solutions and calibration methods were specific to each laboratory. Oxides and doubly charged ions were lower than 3%, and the different laboratories applied oxide and hydroxide interference corrections (Aries *et al.* 2000) both monitored with mono-elemental solutions, except for the LISA/LGE-IPGP, which worked under high-resolution conditions in order to avoid these interferences (Heimburger *et al.* 2013). All of these corrections are reported in Table 1. Furthermore, CCT (Collision Cell Technology) with He gas was used to limit or eliminate interference corrections (*cf.* Table 2). Since it is routine in performance, the choice to use CCT was left to each participant. Most laboratories used CCT for the same element, mainly the transition metals (e.g., Zn). This choice was made based on the manufacturers' recommendations and on the individual experiments and internal tuning (Tanner *et al.* 2002). In addition, the SARM and LISA laboratories also used ICP-AES (iCap3500 ThermoFisher Scientific and Arcos Spectro, respectively) for Si and S measurements using wavelengths without spectral interferences. Even though the LEGOS laboratory used more than one sample introduction system, they felt that their results were coherent enough to group their measurements together.

Instrument calibrations were carried out using synthetic multi-element solutions. Instrumental drift was monitored and corrected where necessary by using one of two techniques: (a) addition of an internal standard to samples such as In (Geosciences, Rennes), In and Re (OMP, Toulouse), In, Ge and Bi (HydroSciences, Montpellier) or (b) measurement of a standard solution every 4–5 samples (LISA, EPOC, Geosciences Rennes, SARM Nancy). Two groups (GET and LEGOS, Toulouse) added spikes for REE isotope dilution measurements. Subtracted blanks and acids are listed in Table 1. Blanks were acidified with 2% v/v HNO_3 by all laboratories (Carignan *et al.* 2001). Geosciences Rennes, EPOC, the Toulouse teams, HydroSciences and Geosciences Montpellier added 2% v/v HNO_3 to samples to reach pH 1 (instead of pH 1.6 reported by NRC-CNRC for SLRS-5) because a more stable signal was observed for all the elements under this condition. Table 2 summarises the isotopes taken into account, as well as spikes and internal standards

Table 1.
Instrumentation and procedures of the participating laboratories

Laboratory	Instrument	Methods and introduction systems	Blank	Acid medium	Calibration	Interferences corrections
EPOC (Bordeaux)	ICP-MS (Thermo Scientific X series II)	Direct with concentric nebuliser conical 1 ml min ⁻¹ and spray chamber impact bead	De-ionised water purified with a Milli-Q (Millipore) system	HNO ₃ 2% v/v (Ulrex II Baker)	Multi-elemental	⁵⁷ Fe ⁺ , ⁴⁰ Ca ¹⁷ O ⁺ , ⁴⁰ Ca ¹⁶ O ⁺ H ⁺ , ¹⁴² Sm ⁺ , ¹³⁰ BaOH ⁺ ;
Geosciences Rennes	ICP-MS (Agilent 4500)	Direct with cross-flow nebuliser and Scott spray chamber	De-ionised water purified with a Milli-Q (Millipore) system	HNO ₃ 2% v/v	Multi-elemental with internal standard In	¹⁵² Eu ⁺ , ¹³⁷ BaO ⁺ , ¹³⁶ BaOH ⁺ ; ¹⁵⁸ Gd ⁺ , ¹⁴² CeO ⁺ , ¹⁴² NdO ⁺ ; ¹⁴¹ PrOH ⁺ ; ¹⁵⁹ Tb ⁺ ; ¹⁴³ NdO ⁺
GET (Toulouse)	HR-ICP-MS (Thermo Scientific Element XR)	Offline AG-50 × 8 Cationic separation for matrix and Ba removal. Aridus 2 desolvator	De-ionised water purified with a Milli-Q (Millipore) system	Bidistilled HNO ₃ 2% v/v	Three standards according to the concentration range of the element (In 100 ng ml ⁻¹) Mass bias corrected isotopic dilution (La, Ce, Nd, Sm, Eu, Gd, Dy, Er, Yb Lu). External analysis for monoisotopes (Pr, Tb, Ho, Tm) with certified multi-element solution (100 pg ml ⁻¹) yield, sensitivity and dilution factor correction with spiked elements	Oxides: Monitoring of BaO/Ba, LaO/La, CeO/Ce, PrO/Pr, NdO/Nd, SmO/Sm, EuO/Eu, GdO/Gd, DyO/Dy and TbO/Tb. Corrections on ¹⁵¹ Eu, ¹⁵³ Eu, ¹⁵⁵ Gd, ¹⁵⁷ Gd, ¹⁶³ Dy, ¹⁶⁵ Dy, ¹⁶⁷ Er, ¹⁶⁹ Er, ¹⁷¹ Yb, ¹⁷² Yb ¹⁷⁵ Lu, ¹⁷⁶ Lu and ¹⁷⁷ Hf Isobaric: ¹³⁶ Ba and ¹³⁵ Xe on ¹³⁶ Ce, ¹³⁸ Ba and ¹³⁸ Ce on ¹³⁸ La, ¹⁷⁶ Yb and ¹⁷⁶ Hf on ¹⁷⁶ Lu ¹⁵¹ Eu; ¹³⁵ BaO, ¹⁵⁷ Gd, ¹⁴¹ PrO + ¹⁴⁰ CeOH; ¹⁵⁹ Tb; ¹⁴³ NdO; ¹⁶³ Dy, ¹⁶⁷ Er, ¹⁶⁹ Er, ¹⁷¹ Yb, ¹⁷² Yb, ¹⁷⁵ Lu, ¹⁷⁶ Lu, ¹⁷⁷ Hf ¹⁶⁵ Ho; ¹⁴⁵ SmO, ¹⁶⁷ Er; ¹⁵¹ EuO, ¹⁶⁹ Er; ¹⁷⁵ Lu; ¹⁵⁷ GdOH; ¹⁷⁵ Lu; ¹⁵⁹ TbO
HydroSciences (Montpellier)	ICP-MS (Thermo Scientific X series II)	Direct (all elements except REE) Off-line preconcentration (REE) Micro-concentric glass nebuliser and impact bead spray chamber	De-ionised water purified with a Milli-Q (Millipore) system	HNO ₃ ultrapur 2,5% v/v	Multi-elemental with internal standards In, Bi 1, 5, 10 µg l ⁻¹ (Ce = In = Bi = 10 µg l ⁻¹)	
Geosciences Montpellier	ICP-MS (Agilent 7700x)	Direct with Meinhard nebulizer and Scott spray chamber	De-ionised water purified with a Milli-Q (Millipore) system	HNO ₃ 2% v/v	4 Mono-element solutions for Na, Mg, Si, Ca, K and Fe, multi-elemental for all others. Internal standards used were In and Bi	Medium or High Resolution
Laboratoire Géochimie des Eaux (LGE-IGP) Laboratoire Interuniversitaires des Systèmes Atmosphériques (LISA, Université Paris Diderot) LEGOS (Toulouse)	HR-ICP-MS (Thermo Scientific Element 2)	Direct with APEX HF with PFA ST Nebuliser (100 ml min ⁻¹)	De-ionised water purified with a Milli-Q (Millipore) system	Distilled HNO ₃ (DST-1000) 1% v/v	Multi-elemental 1 µg ml ⁻¹ to 10 ng ml ⁻¹	
	ICP-MS (Agilent 7500, Thermo Scientific Element XR)	Micromist nebuliser 0.1 ml min ⁻¹ Pellet-cooled spray chamber Aridus II desolvator SIS spray chamber (cyclonic + Scott) Aridus II desolvator	De-ionised water purified with a Milli-Q (Millipore) system	Bi-distilled HNO ₃ 0.32 ml l ⁻¹	Multi-elemental with In and Re as internal standard. For Nd and Yb isotope dilution (¹⁵⁰ Nd and ¹⁷² Yb spikes) in some cases.	Aries <i>et al.</i> (2000) for REE: MoO for ¹¹¹ Cd; SF ₆ for ⁴³ Ca and ⁴⁴ Ca
OMP service ICP-MS (Toulouse)	ICP-MS (Agilent 7500 ce)	Direct with concentric nebulizer and Scott spray chamber	De-ionised water purified with a Milli-Q (Millipore)	HNO ₃ 2% v/v	Multi-elemental with internal standards In, Re	Collision cell + fileview
SARM (Nancy)	ICP-MS (Agilent 7700x)	Direct with concentric nebulizer and Scott spray chamber	De-ionised water purified with an Elga system	Ultrapur HNO ₃ 2% v/v	Multi-elemental	Aries <i>et al.</i> (2000) for REE
	TIMS (Thermo Scientific Triton Plus)	30 ml Evaporated and eluted on SFSpec resin (Eichrom)	De-ionised water purified with an Elga system	Ultrapur HNO ₃ 2% v/v	NBS 987	Internal normalisation with exponential law and ⁶⁶ Sr/ ⁸⁶ Sr = 0.1194

Table 2.
Isotopes used for ICP-MS and wavelengths used for ICP-AES by the participating laboratories

	EPOC (Bordeaux)	Géosciences Rennes	GET (Toulouse)	HydroSciences Montpellier	Geosciences Montpellier	LGE-LISA (Paris)		LEGOS (Toulouse)			OMP (Toulouse)	SARM (Nancy)
								Agilent 7500ce	Element XR			
Ag	-	-	-	-	-	107	LR	-	-	MR	-	-
Al	-	27	-	27	27	27	HR	27	27	HR	27	27
As	75	-	75	75	75	75	HR	75	CCT	HR	75	CCT
B	-	11	-	11	11	11	LR	11	-	LR	-	-
Ba	135-136-137	137	136-137	138	138	137	LR	137-138	137-138	LR	137	137
Be	-	-	-	-	-	-	-	-	-	-	9	9
Bi	-	-	209	-	-	209	LR	209	-	LR	209	209
Ca	-	44	-	43	43	-	LR	43-44	CCT	MR	44	CCT
Cd	111-112-113	111	-	110	110	-	-	111	-	LR	114	114
Ce	-	140	136-140	140	140	140	HR	140	-	LR	140	140
Co	59	59	-	59	59	59	MR	59	CCT	MR	59	CCT
Cr	52	53	-	52	52	52	MR	52	CCT	MR	52	CCT
Cu	63-65	65	-	63-65	65	63	MR	63	CCT	MR	63	CCT
Cs	-	-	-	133	-	-	-	133	-	LR	133	133
Dy	162-163	163	161-163	163	-	163	HR	162-163	-	LR	161	161
Er	166-167	166	166-167	167	-	166	HR	166-167	-	LR	166	166
Eu	153	153	151-153	151	-	153	HR	151-153	-	LR	151	151
Fe	-	57	-	56	57	56	MR	54-56-57	CCT	MR	56	CCT
Ga	71	-	-	-	-	-	-	-	-	-	71	CCT
Gd	-	158	155-157	157	-	157	HR	156-157-158	-	LR	157	157
Ge	-	-	-	-	-	-	-	72	CCT	HR	72	CCT
Ho	165	165	165	165	-	165	HR	165	-	LR	165	165
In	-	115	-	115	115	-	-	115	With and without CCT	LR, MR, HR	-	-
K	-	39	-	-	39	-	-	39	CCT	HR	39	39
La	-	139	138-139	139	139	139	HR	139	-	LR	139	139
Li	-	7	-	7	7	7	LR	-	-	-	7	7
Lu	175	175	175-176	175	-	175	HR	175	-	LR	175	175
Mg	25-26	25	-	25	25	-	-	24	-	MR	24	CCT
Mn	55	55	-	55	55	55	MR	55	CCT	MR	55	CCT
Mo	95-98	-	-	95	-	95	LR	95	-	LR	95	95
Na	-	23	-	-	23	-	-	23	-	MR	23	23
Nb	-	-	-	-	-	-	-	93	-	LR	-	-
Nd	143-146	146	145-146	146	-	146	HR	143-146-150	-	LR	146	146
Ni	60-62	62	60-62	62	62	60	MR	60	CCT	MR	60	CCT
P	-	-	-	-	-	-	-	31	-	MR	-	-

Table 2 (continued).
Isotopes used for ICP-MS and wavelengths used for ICP-AES by the participating laboratories

	EPOC (Bordeaux)	Géosciences Rennes	GET (Toulouse)	HydroSciences Montpellier	Geosciences Montpellier	LGE-LISA (Paris)		LEGOS (Toulouse)			OMP (Toulouse)	SARM (Nancy)
								Agilent 7500ce	Element XR			
Pb	206-208	208	-	206-208	208	208	LR	208		LR	208	All isotopes
Pr	141	141	141	141	141	141	HR	141		LR	141	141
Rb	85	85	85	85	85	85	LR	85		LR	85	85
Re	-	-	-	-	-	185			With and without CCT	LR, MR, HR	-	185
Rh	-	-	-	-	-	-					-	103
S	-	-	-	-	-	180.7 nm					-	180.7 nm
Sb	121-123	-	-	123	121	121	LR	121		LR	121	121-123
Sc	-	-	-	-	45	45	MR	-			-	-
Si	-	29	-	29	29	28		28		MR	-	288.4 nm
Sm	147-149	147	155	147	147	147-152	HR	147-152		LR	-	147
Sn	-	-	-	-	-	-	LR	-			-	-
Sr	-	88	-	86	86	88	LR	88		LR	88	86
Tb	159	159	159	159	159	159	HR	159		LR	-	159
Th	232	232	-	-	232	232		232		LR	-	232
Ti	-	-	-	47	-	47	MR	47	CCT	MR	47	47
Tl	203-205	-	-	203-205	-	205		205		LR	-	205
Tm	169	169	169	169	-	169	HR	169		LR	-	169
U	238	238	-	238	238	238	LR	238		LR	238	238
V	51	51	-	51	51	51	MR	51	CCT	MR	51	51
W	-	-	-	89	89	89		89		LR	-	182
Y	-	-	-	89	89	89		89		LR	89	89
Yb	172-174	174	171-173	173	-	172-173-174	LR	172		LR	-	172
Zn	-	66	-	66	68	66	MR	66		MR	66	66
Zr	-	-	-	-	90	90	LR	90		LR	90	90

Internal standard isotopes or spikes are in bold type.
LR, low resolution; MR, medium resolution; HR, high resolution; CCT, collision cell technology.

measured by the different teams. When several isotopes were measured, we chose that with the smallest standard deviation after verifying the absence of interferences.

For Sr isotope determination, 30 ml of SLRS-5 was evaporated in triplicate. Strontium isolation from the rest of the matrix was then carried out following an analytical protocol similar to that of Pin *et al.* (1994). Briefly, the samples were diluted with 2 ml of HNO₃ (2 mol l⁻¹) and loaded onto Sr Spec resin (Eichrom), which had been previously washed and conditioned. Strontium was then isolated from Rb, Ba and REE using nitric acid solutions at various values of molarity. The Sr fraction was then dried and ready for measurement by TIMS.

Measurements of Sr isotopes were made at the CRPG using TIMS (Triton Plus from Thermo Electron) in multi-collection mode using Re as the filament. Five Faraday cups were used to monitor Rb also. To correct for instrumental mass bias, internal normalisation with a ⁸⁶Sr/⁸⁸Sr ratio of 0.1194 and an exponential law were used. International Sr reference material NBS 987 was used to control the method accuracy. The blank processed and measured along with the samples gave a value of less than 100 pg, which is negligible compared with the amount of Sr from the sample (about 1.5 µg).

Statistical methods

All laboratories proposed their own average working values after outlier rejection by their own methods. The Dixon and Grubbs tests at the 95% confidence level (Miller and Miller 1993, Prichard *et al.* 1995, Feinberg 1996) were applied by LEGOS and SARM (Nancy). Detailed statistical methods were not available for the others. The statistical tests classically used to interpret the results of a round-robin study assume a population meeting the criteria of a normal distribution defined by the mean and the variance. Differences in data size (n = 2–284) did not allow the certification of element concentrations in SLRS-5 because it did not follow any statistical law. Therefore, the aim of this paper is only to propose compilation values for uncertified elements. Instead of using robust statistical methods for which no hypothesis concerning the distribution is necessary, we chose the general approach based on the ISO 5725-2 procedural standard, in order to define the criteria of repeatability, reproducibility and the knowledge of compilation value, to reveal the possible existence of a bias

between laboratories. Thus, compiled data were interpreted using a homogeneous statistical model for both certified and uncertified elements.

The mean values for each laboratory were calculated using the following equation:

$$\bar{y}_i = \frac{1}{n_i} \sum_{j=1}^{n_i} y_{ij} \quad (1)$$

where \bar{y}_i is the mean of j repeats for the laboratory i and n_i is the number of repeats for the laboratory i .

The compilation mean is the mean of all \bar{y}_i of p laboratories and is defined in Equation 2:

$$\bar{y} = \frac{\sum_{i=1}^p n_i \bar{y}_i}{\sum_{i=1}^p n_i} \quad (2)$$

The compilation means \bar{y} are thus weighted by taking into account the numbers of results per laboratory (n_i).

The ISO 5725 procedural standard was also used for determining the standard deviation of repeatability (σ_r , intralaboratory reproducibility), which measures the dispersion of the results obtained for tests by each laboratory and of reproducibility (σ_R , interlaboratory reproducibility), which measures the dispersion of the mean results obtained by all the participating laboratories.

The standard deviation of repeatability σ_r is defined as follows:

$$\sigma_r = \sqrt{\frac{\sum_{i=1}^p (n_i - 1) \sigma_i^2}{\sum_{i=1}^p (n_i - 1)}} \quad (3)$$

where σ_i is the standard deviation of each laboratory (denoted as 's' in tables).

The standard deviation of reproducibility σ_R is defined as follows:

$$\sigma_R = \sigma_r + \sigma_1, \text{ where } \sigma_1 = \sqrt{\frac{\sigma_d^2 - \sigma_r^2}{\bar{n}}} \quad (4)$$

with

$$\sigma_d^2 = \frac{1}{p-1} \sum_{i=1}^p n_i (\bar{y}_i - \bar{y})^2 \text{ and } \bar{n} = \frac{1}{p-1} \left[\sum_{i=1}^p n_i \cdot \frac{\sum_{i=1}^p n_i^2}{\sum_{i=1}^p n_i} \right] \quad (5)$$

In our case, we took σ_R as an estimation of the uncertainty for the compiled data as proposed in the ISO 21748 recommended procedure. All results are expressed with an expanded uncertainty U (in agreement with ISO 5725-2) defined as follows:

$$U = k \cdot \sigma_R \quad (6)$$

where k is a coverage factor chosen at a prescribed level of confidence (under the assumption of a Gaussian law). In our case, we chose to use the 95% level of confidence with $k = 2$ instead of 1.96, which is commonly applied in interlaboratory comparisons.

To check the reliability of our compilation, we chose to calculate the E_n number (typically used in measurement comparison schemes and described in ISO 13528), which is a performance statistic calculated as follows:

$$E_n = \frac{\bar{y} - \mu}{k \sqrt{\sigma_{\text{lab}}^2 + \sigma_{\text{ref}}^2}} \quad (7)$$

where μ is the reference target value, k is the coverage factor ($k = 2$, here), σ_{lab} is the uncertainty of a participant's result (σ_R in our case), and σ_{ref} is the uncertainty obtained by the reference provider's assigned value.

We used a critical value of 1 with E_n numbers because E_n numbers are calculated using expanded uncertainties in the denominator. If $E_n < 1$, we consider results compatible, and if $E_n > 1$, then incompatible, considering the given uncertainties.

Results and discussion

Compiled and individual results are reported in Tables 3–5, while statistical and published data are reported in Appendices A–C. Although ten participants are cited, the GET (Toulouse) measured only REEs and, therefore, only appears in Table 4. On the other hand, LGE-IPGP and LISA (Paris) performed analyses on the same instrument but not at the same time and with different calibration procedures: except for REEs, both reported their own results separately. We assumed that blanks and standard solution purities were checked by participants and that instrument calibration cannot be involved if scattered results were observed.

Certified values

Compiled data for elements having certified concentrations in SLRS-5 are detailed in Table 3. Mean, repeatability, reproducibility and E_n score are shown with certified values of SLRS-5 and SLRS-4 in Appendix A.

The individual standard deviations varied from 1% (Mg from EPOC) to 26% (Cd from HydroSciences, Montpellier). This difference is mainly due to the eight orders of magnitude difference in concentration between Mg ($2540 \mu\text{g l}^{-1}$) and Cd (7 ng l^{-1}) and to a lesser extent to the individual methodology.

Most elements fall within the certified limits if we take into account the individual and the compiled uncertainties. Even for very low-level concentrations, there was good agreement with the certified values (Cd from five laboratories).

Figure 1 shows compiled data normalised to the certified values. For Be, Co and Sb, certified ranges are not available, but compiled values were close to the information values given by NCR-CNRC (differences of less than 10%). In all other cases, the compilation value fell into the certified range except for Mo and Zn, where the compiled weighted average was about 20% lower and 20% higher than the certified value.

Standard deviations of repeatability and reproducibility are rather similar in Appendix A, which may suggest no interlaboratory bias. The E_n numbers calculated indicate that compilation values were consistent with target values. Note that the certified value for Mo, which was recently added to the certificate by the provider ($0.27 \pm 0.04 \mu\text{g l}^{-1}$), is slightly higher than that of the compilation ($0.22 \pm 0.05 \mu\text{g l}^{-1}$) and of the proposed value by Heimbürger *et al.* (2013) ($0.21 \pm 0.04 \mu\text{g l}^{-1}$).

As reported, for example, by Date and Gray (1989) and May and Wiedmeyer (1998), uncorrected/corrected polyatomic interferences on K (ArH⁺), Zn (ArMg, sulfur species) and Ni (CaO) might explain most of the outliers and high standard deviations observed for these elements (Table 3). Furthermore, possible contamination on blanks or calibration methodologies for elements such as Cd, Co, Ni, Pb and Zn would introduce noise in measurements (Figure 1).

Therefore, individual laboratories obtained consistent values for certified elements within the NRC-CNRC limits, and all compiled data fell within these limits, except for Zn. This indicates the proficiency of the participating laboratories and thus suggests that they also produce trustworthy results. It

Table 3. Average concentration values ($\mu\text{g l}^{-1}$), standard deviation (s), relative standard deviation (RSD) from each laboratory, compilation mean with expanded uncertainty (U) and relative expanded uncertainty (rU) for certified elements in the river water certified reference material SLRS-5

	Certified values			EPOC (Bordeaux)			Geosciences Rennes			HydroSciences Montpellier			Geosciences Montpellier			LGE-IPGP (Paris)							
	$\mu\text{g l}^{-1}$	U	rU (%)	n	Average	s	% RSD	n	Average	s	% RSD	n	Average	s	% RSD	n	Average	s	% RSD				
Al	49.5	5	10.1	—	—	—	—	55	49.1	1.3	3	60	48.6	2.2	5	6	43.9	3.8	9	28	41.8	3.7	9
As	0.413	0.039	9.4	48	0.407	0.028	7	—	—	—	—	60	0.361	0.062	17	6	0.357	0.042	12	43	0.404	0.024	6
Ba	14	0.5	3.6	48	13.9	0.3	2	55	14.2	0.3	2	60	14.3	0.3	2	6	13.7	0.5	4	55	13.7	1.4	10
Be	0.005	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Ca	10500	400	3.8	—	—	—	—	55	10241	266	3	60	10166	523	5	6	9925	331	3	—	—	—	—
Cd	0.006	0.001	23.3	48	0.0068	0.0010	15	55	0.0047	0.0006	14	60	0.0074	0.0019	26	—	—	—	—	—	—	—	—
Co	0.05	—	—	48	0.054	0.006	10	55	0.060	0.004	6	60	0.055	0.005	9	6	0.045	0.003	7	43	0.058	0.005	8
Cr	0.208	0.023	11.1	48	0.207	0.022	11	55	0.223	0.014	7	60	0.221	0.021	10	6	0.198	0.011	6	52	0.204	0.021	10
Cu	17.4	1.3	7.5	48	15.6	0.7	4	55	17.9	0.5	3	60	17.5	0.5	3	6	16.0	0.9	5	70	17.4	1.8	10
Fe	91.2	5.8	6.4	—	—	—	—	55	86.6	3.8	5	60	92.0	5.6	6	6	87.7	8.1	9	45	89.9	7.6	8
K	839	36	4.3	—	—	—	—	55	839	26	3	—	—	—	—	—	—	—	—	—	—	—	—
Mg	2540	160	6.3	15	2480	27	1	55	2542	67	3	60	2528	76	3	6	2508	69	3	—	—	—	—
Mn	4.33	0.18	4.2	26	3.98	0.21	5	55	4.21	0.12	3	60	4.22	0.12	3	6	3.88	0.30	8	73	4.13	0.43	10
Mo	0.27	0.04	14.8	48	0.21	0.01	5	—	—	—	—	60	0.23	0.03	12	—	—	—	—	54	0.20	0.01	5
Na	5380	100	1.9	—	—	—	—	55	5470	127	2	—	—	—	—	—	—	—	—	6	5305	133	3
Ni	0.476	0.064	13.4	48	0.480	0.042	9	55	0.485	0.035	7	60	0.485	0.092	19	6	0.432	0.063	15	12	0.334	0.009	3
Pb	0.081	0.006	7.4	48	0.080	0.007	8	55	0.077	0.004	5	60	0.084	0.013	16	6	0.073	0.005	7	30	0.087	0.010	12
Sb	0.3	—	—	48	0.34	0.02	7	—	—	—	—	60	0.30	0.01	4	6	0.35	0.06	17	70	0.32	0.06	18
Sr	53.6	1.3	2.4	—	—	—	—	55	53.0	1.5	3	60	53.7	1.5	3	6	50.9	2.5	5	35	51.1	3.7	7
U	0.093	0.006	6.5	48	0.088	0.004	4	55	0.090	0.006	7	60	0.093	0.003	3	6	0.094	0.006	7	30	0.109	0.008	7
V	0.317	0.033	10.4	48	0.333	0.025	8	55	0.340	0.010	3	60	0.347	0.017	5	6	0.321	0.020	6	55	0.319	0.009	3
Zn	0.845	0.1	11.2	—	—	—	—	55	0.935	0.033	4	60	0.888	0.211	24	6	0.802	0.111	14	45	1.093	0.057	5

Table 3 (Continued). Average concentration values ($\mu\text{g l}^{-1}$), standard deviation (s), relative standard deviation (RSD) from each laboratory, compilation mean with expanded uncertainty (U) and relative expanded uncertainty (rU) for certified elements in the river water certified reference material SLRS-5

	Certified values			LISA (Paris)			LEGOS (Toulouse)			OMP (Toulouse)			SARM (Nancy)			Compilation							
	$\mu\text{g l}^{-1}$	U	rU (%)	n	Average	s	% RSD	n	Average	s	% RSD	n	Average	s	% RSD	n	Average	U	rU (%)				
Al	49.5	5	10.1	5	46.5	0.8	2	12	48.7	3.3	7	103	50.1	3.9	8	35	50.7	2.5	5	304	48.7	7.9	16
As	0.413	0.039	9.4	10	0.408	0.017	4	3	0.402	0.014	3	-	-	-	-	35	0.390	0.031	8	205	0.388	0.090	23
Ba	14	0.5	3.6	15	14.2	0.4	3	12	14.2	0.6	4	44	14.2	0.4	3	35	14.8	0.4	3	330	14.2	1.4	10
Be	0.005	-	-	-	-	-	-	-	-	-	-	-	-	-	-	35	0.0046	0.0008	17	35	0.0046	0.0016	34
Ca	10500	400	3.8	-	-	-	-	11	10445	475	5	64	10450	901	9	35	10500	476	5	231	10320	1185	11
Cd	0.006	0.001	23.3	-	-	-	-	1	0.007	-	-	-	-	-	-	35	0.0078	0.0010	13	199	0.007	0.004	55
Co	0.05	0.023	11.1	10	0.228	0.008	4	11	0.221	0.027	12	64	0.217	0.015	7	35	0.054	0.003	5	265	0.056	0.011	19
Cu	17.4	1.3	7.5	15	18.1	0.5	3	12	17.2	0.6	3	64	17.8	0.3	2	35	18.8	1.5	4	365	17.5	2.6	15
Fe	91.2	5.8	6.4	5	92.7	0.8	1	11	90.7	1.9	2	62	94.5	6.8	7	35	95.1	5.7	6	279	91.4	12.7	14
K	839	36	4.3	-	-	-	-	6	777	24	3	112	873	91	10	35	858	28	3	214	859	142	17
Mg	2540	160	6.3	-	-	-	-	11	2473	203	8	61	2476	258	10	35	2568	75	3	243	2518	297	12
Mn	4.33	0.18	4.2	15	4.34	0.13	3	12	4.19	0.17	4	59	4.13	0.15	4	35	4.49	0.13	3	341	4.2	0.5	13
Mo	0.27	0.04	14.8	15	0.23	0.01	5	10	0.21	0.02	9	61	0.24	0.03	11	35	0.22	0.01	7	283	0.22	0.05	22
Na	5380	100	1.9	-	-	-	-	7	5463	520	10	25	5596	1108	20	35	5375	162	3	128	5461	1016	19
Ni	0.476	0.064	13.4	10	0.504	0.016	3	3	0.482	0.024	5	-	-	-	-	35	0.498	0.032	6	229	0.477	0.135	28
Pb	0.081	0.006	7.4	5	0.067	0.001	1	12	0.084	0.006	8	26	0.102	0.018	18	35	0.080	0.008	10	277	0.083	0.025	30
Sb	0.3	1.3	2.4	5	54.7	0.5	1	5	0.28	0.02	8	102	0.32	0.02	7	35	0.31	0.01	3	326	0.32	0.07	22
Sr	53.6	1.3	2.4	5	54.7	0.5	1	8	54.0	2.1	4	58	56.3	2.9	5	35	54.2	2.5	5	262	53.8	5.7	11
U	0.093	0.006	6.5	15	0.090	0.003	4	10	0.091	0.004	5	24	0.090	0.003	3	35	0.093	0.004	4	283	0.093	0.015	16
V	0.317	0.033	10.4	10	0.294	0.009	3	12	0.315	0.021	7	63	0.353	0.021	6	35	0.350	0.012	3	344	0.338	0.045	13
Zn	0.845	0.1	11.2	10	0.875	0.058	7	3	0.955	0.024	2	74	1.083	0.196	18	35	1.013	0.084	8	288	0.993	0.347	35

- no measurement available; n number of results.

Table 4. Average concentration values (ng l⁻¹), standard deviation (s), relative standard deviation (RSD) from each laboratory, compilation mean with expanded uncertainty (U) and relative expanded uncertainty (rU) of REEs in the river water certified reference material SLRS-5

	EPOC (Bordeaux)			Géosciences Rennes			GET (Toulouse)			HydroSciences Montpellier			Géosciences Montpellier							
	n	Aver- age	s	% RSD	n	Aver- age	s	% RSD	n	Aver- age	s	% RSD	n	Aver- age	s	% RSD				
La	—	—	—	—	55	205.4	5.6	3	11	213.6	4.6	2	15	207.7	6.1	3	6	206.7	7.2	3
Ce	—	—	—	—	55	252.8	6.0	2	11	254.8	3.1	1	15	253.1	6.7	3	6	249.8	8.2	3
Pr	26	44.2	1.2	3	55	49.2	1.5	3	11	50.3	0.6	1	15	51.5	1.7	3	6	46.4	2.3	5
Nd	26	178.0	3.6	2	55	193.8	5.7	3	11	197.1	2.4	1	15	199.6	5.3	3	—	—	—	—
Sm	26	30.5	1.3	4	55	33.3	1.6	5	11	33.1	0.1	0.3	15	35.3	1.6	5	6	31.2	0.5	2
Eu	—	—	—	—	55	5.81	0.34	7	11	5.88	0.04	1	15	6.33	0.54	9	—	—	—	—
Gd	—	—	—	—	55	25.0	1.0	4	11	26.1	0.3	1	15	27.5	0.8	3	—	—	—	—
Tb	26	3.80	0.20	6	55	3.31	0.20	6	11	3.42	0.05	2	15	3.68	0.46	12	—	—	—	—
Dy	26	18.6	0.6	3	55	18.5	0.9	5	11	18.9	0.1	1	15	19.6	0.8	4	—	—	—	—
Ho	26	3.70	0.30	7	55	3.67	0.20	6	11	3.65	0.03	1	15	3.73	0.19	5	—	—	—	—
Er	26	10.4	0.3	3	55	10.6	0.4	4	11	10.6	0.0	0	15	11.0	0.9	8	—	—	—	—
Tm	26	1.50	0.50	31	55	1.47	0.15	10	11	1.49	0.01	1	15	1.68	0.34	20	—	—	—	—
Yb	26	9.30	0.30	3	55	9.68	0.58	6	11	10.13	0.08	1	15	11.20	0.74	7	—	—	—	—
Lu	26	1.90	0.20	13	55	1.56	0.15	10	11	1.64	0.01	1	15	1.78	0.23	13	—	—	—	—

	LGE – LISA (Paris)			LEGOS (Toulouse)			OMP (Toulouse)			SARM (Nancy)			Compilation				
	n	Aver- age	s	% RSD	n	Aver- age	s	% RSD	n	Aver- age	s	% RSD	n	Aver- age	U	rU (%)	
La	20	198.1	8.4	4	25	209.9	5.2	2	107	207.0	6.2	3	64	209.6	12.8	12.8	6
Ce	20	245.2	13.2	5	25	256.5	5.0	2	110	244.4	47.0	19	64	265.7	8.4	59.7	24
Pr	15	47.7	4.2	9	25	50.5	1.1	2	28	46.8	6.4	14	63	51.2	1.6	7.2	15
Nd	20	186.5	9.2	5	25	199.4	3.9	2	107	189.3	38.4	20	64	197.2	15.7	46.4	24
Sm	15	32.5	2.4	7	21	34.6	1.3	4	—	—	—	—	64	35.4	1.7	4.4	13
Eu	5	5.89	0.75	13	22	6.75	0.98	15	—	—	—	—	64	6.11	0.43	1.1	18
Gd	5	25.7	3.2	13	20	30.6	1.7	5	—	—	—	—	64	26.9	1.3	4.4	16
Tb	5	3.19	0.38	12	20	3.52	0.34	10	—	—	—	—	64	3.29	0.27	0.6	18
Dy	15	17.8	1.3	8	20	19.7	0.8	4	—	—	—	—	64	19.7	0.8	2.0	10
Ho	15	3.51	0.29	8	20	3.91	0.30	8	—	—	—	—	64	3.77	0.33	0.4	12
Er	15	10.9	1.0	9	21	11.4	0.7	6	—	—	—	—	64	11.2	0.7	1.2	11
Tm	14	1.41	0.11	8	20	1.66	0.24	14	—	—	—	—	64	1.58	0.24	0.5	31
Yb	15	9.70	0.80	8	21	10.68	0.67	6	—	—	—	—	64	10.57	0.64	1.6	16
Lu	11	1.53	0.14	9	19	1.71	0.20	12	—	—	—	—	55	1.75	0.28	0.4	23

—, no measurement available; n, number of results.

Table 5. Proposed mean concentration values ($\mu\text{g l}^{-1}$), standard deviation (s), relative standard deviation (RSD) from each laboratory, compilation mean with expanded uncertainty U and relative expanded uncertainty (rU) of uncertified elements in the river water certified reference material SLRS-5

	EPOC (Bordeaux)				Géosciences Rennes				HydroSciences Montpellier				Géosciences Montpellier				LGE-IPGP (Paris)			
	n	Average	s	% RSD	n	Average	s	% RSD	n	Average	s	% RSD	n	Average	s	% RSD	n	Average	s	% RSD
Ag	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	10	0.0098	0.0002	1.7
B	-	-	-	-	55	6.41	0.25	4	60	6.66	0.60	9	-	-	-	-	10	6.72	0.21	3.2
Bi	-	-	-	-	-	-	-	-	35	0.0054	0.0010	19	-	-	-	-	-	-	-	-
Cs	-	-	-	9	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Ga	26	0.015	0.001	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Ge	-	-	-	-	55	0.46	0.03	6	60	0.46	0.03	7	6	0.41	0.02	6	7	0.33	0.04	12.1
Li	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Nb	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
P	-	-	-	-	-	-	-	-	60	1.30	0.06	4.6	6	1.04	0.07	6.6	48	1.05	0.10	9.2
Rb	26	1.13	0.04	4	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Rh	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Re	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
S	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Sc	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	6	0.037	0.002	6
Si	-	-	-	-	55	1951	49	3	35	1934	82	4.3	6	1732	51	3	-	-	-	-
Sn	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Th	48	0.014	0.002	16	55	0.013	0.001	10	-	-	-	-	6	0.014	0.004	29	-	-	-	10.0
Ti	-	-	-	-	-	-	-	-	35	2.00	0.18	9	-	-	-	-	37	1.75	0.16	-
Tl	26	0.0037	0.0002	5	35	0.0040	0.0020	50	-	-	-	-	-	-	-	-	-	-	-	-
W	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Y	-	-	-	-	15	0.112	0.002	1.8	-	-	-	-	6	0.108	0.005	4.6	-	-	-	-
Zr	-	-	-	-	-	-	-	-	-	-	-	-	6	0.032	0.002	7.3	-	-	-	-
⁸⁷ Sr/ ⁸⁶ Sr	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

Table 5 (Continued).
Proposed mean concentration values ($\mu\text{g l}^{-1}$), standard deviation (s), relative standard deviation (RSD) from each laboratory, compilation mean with expanded uncertainty U and relative expanded uncertainty (rU) of uncertified elements in the river water certified reference material SLRS-5

	LISA (Paris)			LEGOS (Toulouse)			OMP (Toulouse)			SARM (Nancy)			Compilation				
	n	Average	s	% RSD	n	Average	s	% RSD	n	Average	s	% RSD	p	n	Average	U	rU (%)
Ag	—	—	—	—	—	—	—	—	—	—	—	—	1	10	0.0098	0.0008	8
B	10	6.56	0.20	3	3	6.69	0.41	6	—	—	—	—	5	138	6.56	0.91	14
Bi	10	0.0008	0.0001	7	2	0.00135	0.00003	2	—	—	—	—	3	48	0.0009	0.0003	38
Cs	—	—	—	—	5	0.0041	0.0001	3	—	—	—	—	3	76	0.0049	0.0019	39
Ga	—	—	—	—	—	—	—	—	33	0.0025	0.0004	18	2	59	0.014	0.014	67
Ge	—	—	—	—	3	0.006	0.001	15	—	—	—	—	2	34	0.015	0.014	93
Li	—	—	—	—	—	—	—	—	5	0.46	0.06	14	5	133	0.45	0.09	20
Nb	—	—	—	—	5	0.0036	0.0004	11	—	—	—	—	1	5	0.0036	0.0016	44
P	—	—	—	—	8	8.19	0.87	11	—	—	—	—	1	8	8.19	3.40	42
Rb	—	—	—	—	5	1.27	0.05	4	108	1.32	0.21	16	7	284	1.24	0.37	30
Rh	—	—	—	—	3	0.0019	0.0008	41	—	—	—	—	2	37	0.0009	0.0015	161
Re	—	—	—	—	—	—	—	—	35	0.066	0.003	4	1	35	0.066	0.012	18
S	29	2347	126	5	—	—	—	—	10	2428	39	2	2	39	2368	244	10
Sc	13	0.008	0.001	8	—	—	—	—	—	—	—	—	2	19	0.017	0.041	241
Si	—	—	—	—	5	1839	121	7	—	—	—	—	5	129	1922	165	9
Sn	10	0.0050	0.0004	8	—	—	—	—	28	1904	65	3	1	10	0.0050	0.0004	8
Th	—	—	—	—	3	0.014	0.001	10	—	—	—	—	5	148	0.0136	0.0033	24
Ti	—	—	—	—	11	1.78	0.23	13	64	1.84	0.12	7	5	181	1.86	0.34	18
Tl	—	—	—	—	3	0.0034	0.0003	9	—	—	—	—	4	99	0.0039	0.0024	62
W	—	—	—	—	3	0.025	0.017	70	—	—	—	—	2	35	0.014	0.018	125
Y	—	—	—	—	3	0.113	0.002	2	83	0.111	0.005	5	5	142	0.112	0.009	8
Zr	5	0.066	0.002	3	5	0.034	0.021	62	106	0.019	0.004	13	5	158	0.02	0.03	113
⁸⁷ Sr/ ⁸⁶ Sr	—	—	—	—	—	—	—	—	3	0.711011	0.000059	—	1	3	0.711011	0.000059	—

Element determined by at least three laboratories are shown in bold, by two laboratories in normal typeface, and by one laboratory in italic typeface.
n, number of results; —, no measurement available; p, number of laboratories.

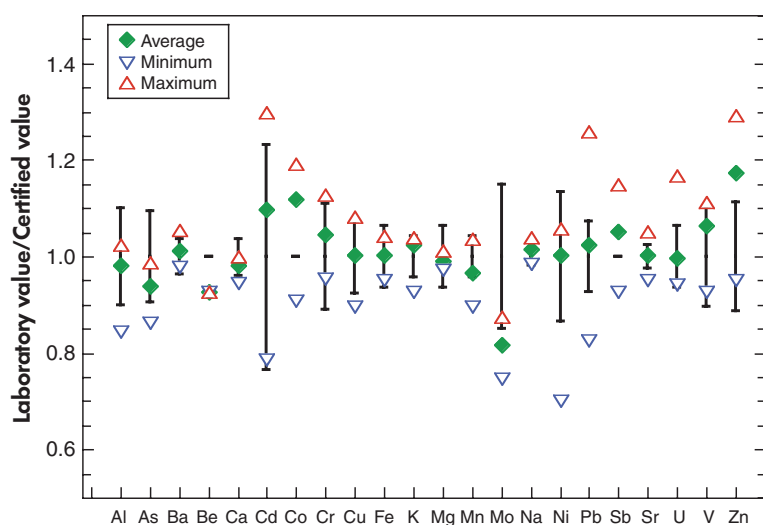


Figure 1. Comparison of compiled data versus certified values for the river water reference material SLRS-5. Diamonds represent compiled data. Triangles are the minimum and the maximum values from the results of individual laboratories. Bars represent certified values with uncertainty ranges. For Be, Co and Sb (not certified by NCR-CNRC), the information values given by the NRC-CNRC were used.

also allows us to have confidence in our mode of calculation for uncertified elements (mean values and expanded uncertainty).

Uncertified values: Tables 4 and 5 show compilation means with expanded uncertainty U obtained from participating laboratories, while published data are reported in Appendices B and C.

Rare earth elements: Compiled and individual results for REEs are shown in Figure 2 and reported in Table 4. Their concentrations varied from 252 ng l^{-1} (Ce) to 1.5 ng l^{-1} (Tm) and relative expanded uncertainty (rU) varied from 6% (La) to 31% (Tm), suggesting homogeneous results between laboratories and techniques. Uncertainty values correlate somewhat with concentration.

Larger interlaboratory variation for middle REEs may be partly explained by the noise introduced by isobaric interference corrections for oxides of low atomic number REEs (LREEs) and Ba. Higher values for Eu and Gd reported by the LEGOS are difficult to explain by insufficient interference correction: this laboratory used both a desolvating and a classic sample introduction technique and did not observe any bias between the results obtained, despite the fact that desolvation is known to generate very small amounts of oxides. The high value for Lu given by EPOC is most likely explained by a calibration bias, because none of the participants applied oxide corrections to the mass 175. The GET laboratory applied an isotope dilution method using

ten enriched REE spikes and achieved uncertainties better than 2% RSD on all REEs. This high precision method yielded REE concentrations that overlapped narrowly with the REE compilation concentrations based on all participating laboratories (Table 4).

REE patterns normalised to upper crust concentrations (Taylor and McLennan 1985) are reported in Figure 2a. The patterns display LREE enrichment relative to high atomic number REEs (HREEs) as well as a large negative Ce anomaly. The SLRS-5 compilation pattern is reported in Figure 2b. The SLRS-5 pattern from Heimburger *et al.* (2013) and the SLRS-4 pattern are shown for comparison. Systematically lower concentrations (3–19%) are reported by Heimburger *et al.* (2013) compared with this study (Appendix B). The authors deduced data from SLRS-5/SLRS-4 ratios that correspond to an indirect standardisation. This relative determination may lead to errors compared with individual absolute determinations. Thus, a bias in the compiled data calculated by Yeghicheyan *et al.* (2001) and used for calibration by Heimburger *et al.* (2013) induced a proportional bias in their REE concentrations. The largest discrepancies are observed for the two lowest concentrations: Tm ($1.3 \pm 0.3 \text{ ng l}^{-1}$ compared with $1.5 \pm 0.5 \text{ ng l}^{-1}$ for compiled data in this study) and Lu ($1.5 \pm 0.2 \text{ ng l}^{-1}$ vs. $1.7 \pm 0.4 \text{ ng l}^{-1}$). However, in both cases, the results overlap within uncertainties and fall within the same concentration range.

Other elements: Twenty-two other elements, including silicon, without certified values were also analysed.

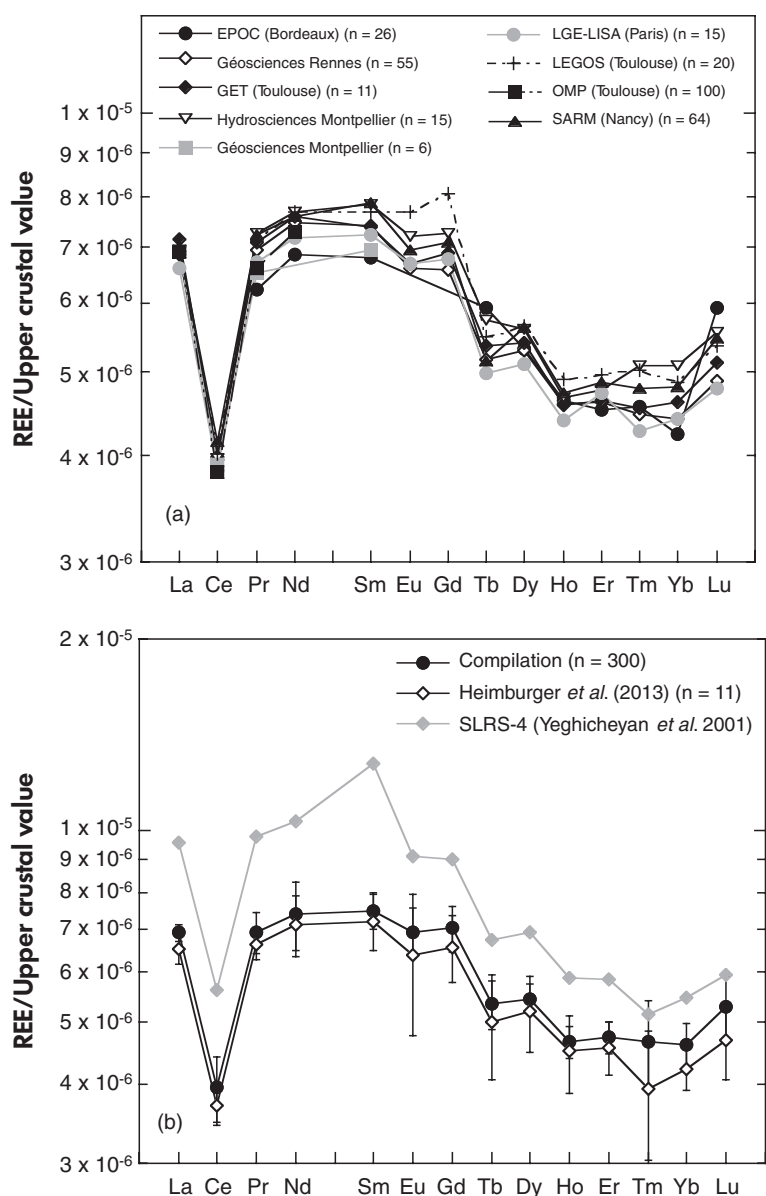


Figure 2. Upper crust-normalised REE patterns of the river water reference material SLRS-5 obtained by the different laboratories. n = number of results. Upper crust data from Taylor and McLennan (1985).

Compiled results are reported in Table 5 and compared with published data in Appendix C.

Eleven elements (B, Bi, Cs, Li, Rb, Si, Th, Ti, Tl, Y and Zr), out of the twenty-two were determined by at least three different laboratories or methods (Figure 3 and in bold in Table 5). All the available data were used for compiled values, including complementary data by ICP-AES for Si.

Reported individual results and compiled values are in good agreement even for low-level concentrations such as that of Tl ($3.9 \pm 2.4 \text{ ng l}^{-1}$ compiled value). Figure 3 shows

examples of results from the different laboratories (for B, Bi, Li, Si, Th and Zr). All elements measured fell within the range of compiled values considering uncertainties, except for Bi (LEGOS) (Figure 3b) and Zr (LISA) (Figure 3f). In both cases, the discrepancy can be mostly explained by the very low uncertainties obtained by LEGOS and LISA for Bi and Zr, respectively, which do not allow overlap with the compiled values. Silicon concentration was measured by two techniques: ICP-MS and ICP-AES (Table 5). ICP-MS individual values ranged from 1732 to $1951 \text{ } \mu\text{g l}^{-1}$, whereas the average value obtained by ICP-AES from the SARM (Nancy) was intermediate ($1904 \pm 65 \text{ } \mu\text{g l}^{-1}$). The underestimated

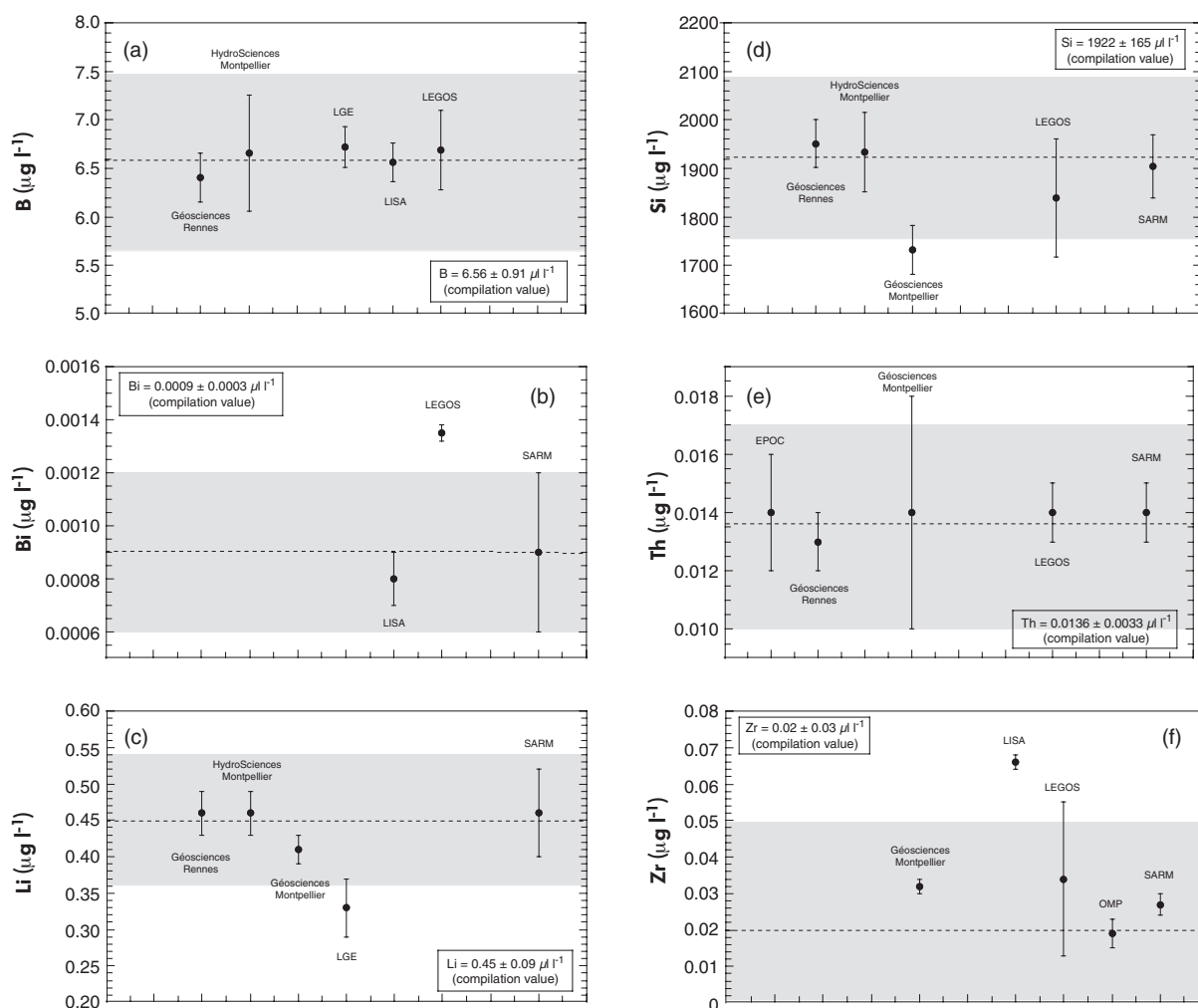


Figure 3. Average concentrations of (a) B, (b) Bi, (c) Li, (d) Si, (e) Th and (f) Zr in the river water reference material SLRS-5 determined by each participating laboratory. The compilation value for each is displayed in the respective legends. The shaded area represents the expanded uncertainty of the compiled value.

value for Si given by Geosciences Montpellier is most probably explained by a calibration bias (Figure 3d).

Eleven other trace elements were determined only by one (Ag, Nb, P, Re, Sn) or two (Ga, Ge, Rh, S, Sc, W) laboratories (in italics and normal type in Table 5, respectively). Except for S, W and Rh, results for these elements were not identical between laboratories even considering uncertainties. More dispersed values with high uncertainties were observed for Ga, Ge and Sc. The slightly dispersed results observed for Ga and Ge could have been resulted from uncorrected isobaric interferences from sulfide, argide and chloride species (May and Wiedmeyer 1998). In the case of Sc, LISA and Geosciences Montpellier found values of 0.008 and $0.037 \mu\text{g l}^{-1}$, respectively. Silicon species are usually involved in Sc concentration overestimation. It therefore

seems likely that results from medium-resolution analysis performed by the LISA are more accurate than the others.

Mercury is often studied in environmental cycles and is increasingly easy to determine with new analytical methods. Even if the provider does not note any sampling/storage precaution for Hg, the SARM attempted to determine Hg using a Hg analyser (DMA-80 from Milestone) from four different provider bottles; Hg is unstable in low molarity HNO_3 and Hg concentrations varied from 1 to $0 \mu\text{g l}^{-1}$ as a function of the date of bottle opening. The longer the bottle was opened, the smaller the amount of mercury was present. Hg^0 degassing and adsorption onto bottle walls from water might induce decreasing concentrations (Leopold *et al.* 2010). Therefore, Hg is unstable and cannot be determined under the present conditions of storage for SLRS-5.

Sr isotopic ratio: Strontium isotope measurements provided an average value of 0.711011 (Table 5) ranging between 0.710960 and 0.711075, each individual measurement having an uncertainty less than 10 ppm. Such a value is consistent with the mixture of various lithologies represented in the river basin. Note that to the authors' knowledge, no Sr isotopic measurements on SLRS-4 are available, limiting the potential for comparison. However, the SLRS-5 Sr content is two times higher than that reported for SLRS-4, indicating slight variations in the contribution of various lithologies. Thus, the $^{87}\text{Sr}/^{86}\text{Sr}$ value reported here could be different from that of SLRS-4.

SLRS-5 versus SLRS-4: SLRS-4 certified concentrations are also reported in Appendix A, as well as data from Yeghicheyan *et al.* (2001) in Appendices B and C for comparison purposes. As far as certified values are concerned, the two batches were found to be different: Al, As, Be, Cd, Cr, Fe, Ni, Pb, V and Zn were lower in SLRS-5 than in the SLRS-4 batch. While V differed only by 1%, Cd was a factor of two lower in SLRS-5. On the other hand, Ba, Ca, Co, Cu, K, Mg, Mn, Mo, Na, Sb, Sr and U were found to have higher concentrations in SLRS-5. For Cu, the difference reached 861%, suggesting contamination during sampling rather than solid charge variations in the reference water. REE concentrations were depleted by about 30% for LREEs and 12% for HREEs in SLRS-5 relative to SLRS-4 (Appendix B). Moreover, the REE concentration comparison of both Heimburger *et al.* (2013) and this study with the SLRS-4 compilation data (Yeghicheyan *et al.* 2001) showed the same trend (Figure 2b). However, Sm concentrations showed the largest variation (33.2 ng l⁻¹ instead of 57.4 ng l⁻¹), whereas HREEs were rather similar. Such a difference may be explained by the inclusion of some uncorrected values in the compilation of the SLRS-4 paper (Yeghicheyan *et al.* 2001).

For other elements (Appendix C), variations between batches were more obvious: Ag, Cs, Li, P, Rb, Th, Tl, Y and Zr were lower, while B, Ga, Ge, Si, Ti and W were higher than in SLRS-4. These variable proportions directly depend on sampling and lithological contributions.

Conclusions

We report a compilation of concentrations for certified and uncertified elements in the natural river water certified reference material SLRS-5 (NRC-CNRC) from 2 years of routine analysis in ten different French laboratories. The reported results show coherent values for REE concentrations,

with relative expanded uncertainties ranging from 6% to 31%. Strontium isotopic ratios were also determined.

Seventeen elements (B, Bi, Cs, Ga, Ge, Li, Rb, Rh, S, Sc, Si, Th, Ti, Tl, W, Y and Zr) determined by at least two laboratories yielded compiled values having relative expanded uncertainties ranging from 8% to 241%. Five more trace element (Ag, Nb, P, Re and Sn) concentrations were reported, but with a more restricted number of results.

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Appendix A.
Compilation means ($\mu\text{g l}^{-1}$), repeatability σ_r , reproducibility σ_R , expanded uncertainty ($U = 2 \cdot \sigma_R$), relative expanded uncertainty (rU) and E_n score calculated for certified elements in the river water certified reference material SLRS-5, as well as certified values and expanded uncertainty in the SLRS-5 and SLRS-4 batches

Element	Certified values			Compilation							E _n score			Certified values SLRS-4			
	$\mu\text{g l}^{-1}$	U	rU (%)	p	n	Average	Repeatability (σ_r)	r σ_r (%)	Reproducibility (σ_R)	r σ_R (%)	U	rU (%)	E _n	Compatibility	$\mu\text{g l}^{-1}$	U	rU (%)
Al	49.5	5	10.1	8	304	48.7	2.9	6	4.0	8	7.9	16	0.07	Yes	54	4	7.4
As	0.413	0.039	9.4	7	205	0.388	0.040	10	0.045	12	0.090	23	0.21	Yes	0.68	0.06	8.8
Ba	14	0.5	3.6	9	330	14.2	0.6	4	0.7	5	1.4	10	0.09	Yes	12.2	0.6	4.9
Be	0.005	—	—	1	35	0.0046	0.0008	17	—	—	—	—	—	—	0.007	0.002	28.6
Ca	10500	400	3.8	6	231	10320	57.6	6	593	6	1185	11	0.13	Yes	6200	200	3.2
Cd	0.006	0.001	23.3	5	199	0.007	0.001	18	0.002	28	0.004	55	0.13	Yes	0.012	0.002	16.7
Co	0.05	—	—	8	265	0.056	0.004	8	0.005	9	0.011	19	0.56	—	0.033	0.006	18.2
Cr	0.208	0.023	11.1	9	341	0.217	0.018	8	0.020	9	0.041	19	0.15	Yes	0.33	0.02	6.1
Cu	17.4	1.3	7.5	9	365	17.5	0.9	5	1.3	7	2.6	15	0.02	Yes	1.81	0.08	4.4
Fe	91.2	5.8	6.4	9	279	91.4	5.5	6	6.4	7	12.7	14	0.01	Yes	103	5	4.9
K	839	36	4.3	5	214	859	67	8	71	8	142	17	0.12	Yes	680	20	2.9
Mg	2540	160	6.3	7	243	2518	146	6	148	6	297	12	0.05	Yes	1600	100	6.3
Mn	4.33	0.18	4.2	9	341	4.2	0.2	6	0.3	6	0.5	13	0.22	Yes	3.37	0.18	5.3
Mo	0.27	0.04	14.8	7	283	0.22	0.02	9	0.02	11	0.05	22	0.53	Yes	0.21	0.02	9.5
Na	5380	100	1.9	5	128	5461	510	9	508	11	1016	19	0.08	Yes	2400	200	8.3
Ni	0.476	0.064	13.4	8	229	0.477	0.056	12	0.068	9	0.135	28	0.01	Yes	0.67	0.08	11.9
Pb	0.081	0.006	7.4	9	277	0.083	0.010	12	0.012	14	0.025	30	0.07	Yes	0.086	0.007	8.1
Sb	0.3	—	—	8	326	0.32	0.03	10	0.03	15	0.07	22	0.23	Yes	0.23	0.04	17.4
Sr	53.6	1.3	2.4	8	262	53.8	2.2	4	2.8	11	5.7	11	0.04	Yes	26.3	3.2	12.2
U	0.093	0.006	6.5	9	283	0.093	0.004	5	0.008	5	0.015	16	0.01	Yes	0.050	0.003	6.0
V	0.317	0.033	10.4	9	344	0.338	0.016	5	0.023	8	0.045	13	0.26	Yes	0.32	0.03	9.4
Zn	0.845	0.1	11.2	8	288	0.993	0.145	15	0.173	7	0.347	35	0.37	Yes	0.93	0.10	10.8

p, number of laboratories; n, number of results; —, no measurement available.

Appendix B.

Published data, average concentration values (ng l⁻¹), standard deviation (s), relative standard deviation (RSD) from each laboratory, compilation mean with expanded uncertainty (U) and relative expanded uncertainty (rU) of REEs in the river water certified reference materials SLRS-5 and SLRS-4

	Compilation					Heimburger <i>et al.</i> (2012)		SLRS-4 Yeghicheyan <i>et al.</i> (2001)	
	p	n	Average	U	rU (%)	Average	2s	Average	s
La	8	303	207.2	12.8	6	196.0	11.0	287.0	8.0
Ce	8	306	252.3	59.7	24	236.0	16.0	360.0	12.0
Pr	9	244	49.1	7.2	15	46.9	2.5	69.3	1.8
Nd	9	323	192.1	46.4	24	185.0	20.0	269.0	14.0
Sm	8	213	33.7	4.4	13	32.4	3.3	57.4	2.8
Eu	6	172	6.1	1.1	18	5.6	1.4	8.0	0.6
Gd	6	170	26.7	4.4	16	24.9	3.0	34.2	2.0
Tb	7	196	3.4	0.6	18	3.2	0.6	4.3	0.4
Dy	7	206	19.1	2.0	10	18.2	2.5	24.2	1.6
Ho	7	206	3.7	0.4	12	3.6	0.5	4.7	0.3
Er	7	207	10.9	1.2	11	10.5	1.0	13.4	0.6
Tm	7	205	1.5	0.5	31	1.3	0.3	1.7	0.2
Yb	7	207	10.1	1.6	16	9.3	0.7	12.0	0.4
Lu	7	192	1.7	0.4	23	1.5	0.2	1.9	0.1

p, number of laboratories; n, number of results; –, no measurement available.

Appendix C.

Published data, proposed mean concentration values (µg l⁻¹), number of measurements, number of participants, standard deviation (s), relative standard deviation (RSD) from each laboratory, compilation mean with expanded uncertainty U and relative expanded uncertainty rU of uncertified elements in the river water certified reference materials SLRS-5 and SLRS-4

	Compilation					Heimburger <i>et al.</i> (2012)		SLRS-4 Yeghicheyan <i>et al.</i> (2001)	
	p	n	Average	U	rU (%)	Average	2s	Average	s
Ag	1	10	<i>0.0098</i>	<i>0.0008</i>	8			0.035	0.005
B	5	138	6.56	0.91	14	7.46	0.58	5.95	0.22
Bi	3	48	0.0009	0.0003	38	0.00086	0.00016		
Cs	3	76	0.0049	0.0019	39	0.0057	0.0013	0.0090	0.0010
Ga	2	59	0.02	0.01	67	0.015	0.001	0.0119	0.0004
Ge	2	34	0.015	0.014	93	0.0063	0.0038	0.010	0.003
Li	5	133	0.45	0.09	20	0.50	0.13	0.54	0.07
Nb	1	5	<i>0.0036</i>	<i>0.0016</i>	44	0.0038	0.0006		
P	1	8	<i>8.19</i>	<i>3.40</i>	42	13.1	2.2	9.13	0.78
Rb	7	284	1.24	0.37	30	1.23	0.08	1.53	0.05
Rh	2	37	0.0009	0.0015	161				
Re	1	35	<i>0.066</i>	<i>0.012</i>	18				
S	2	39	2368	244	10				
Sc	2	19	0.017	0.041	241	0.0087	0.0015		
Si	5	129	1922	165	9	1881	99	1864	48
Sn	1	10	<i>0.0050</i>	<i>0.0004</i>	8	0.0057	0.0005		
Th	5	148	0.0136	0.0033	24	0.011	0.004	0.018	0.003
Ti	5	181	1.86	0.34	18	2.28	0.05	1.46	0.08
Tl	4	99	0.0039	0.0024	62	0.0042	0.0007	0.0076	0.0006
W	2	35	0.014	0.018	125			0.013	0.001
Y	5	142	0.112	0.009	8	0.120	0.010	0.146	0.008
Zr	5	158	0.02	0.03	113			0.120	0.015
⁸⁷ Sr/ ⁸⁶ Sr	1	3	<i>0.711011</i>	<i>0.000059</i>	–	–	–	–	–

Elements determined by at least three laboratories are shown in bold, by two laboratories in normal typeface and by one laboratory in italic typeface. n, number of results; p, number of laboratories.