



## From geochemistry to ecotoxicology of rare earth elements in aquatic environments: Diversity and uses of normalization reference materials and anomaly calculation methods

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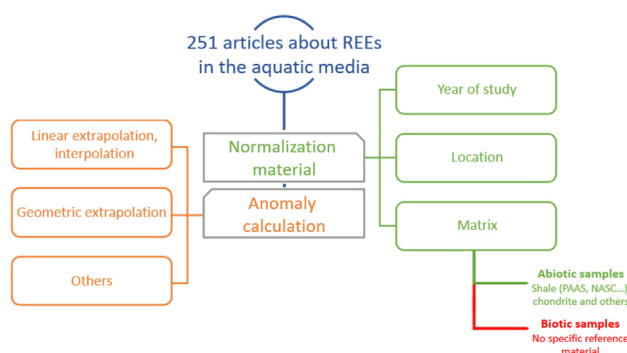
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### HIGHLIGHTS

- Reference materials for REEs and anomaly calculation methods need to be harmonized.
- Among all reference materials, PAAS is the most used for the study of abiotic samples.
- No specific reference material exists nowadays for biotic samples normalization.
- New references for biota are needed to consider interspecific differences.
- PAAS should be systematically used to allow better comparison between REE studies.

### GRAPHICAL ABSTRACT



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### ABSTRACT

The geochemistry of rare earth elements (REEs) has been studied for a long time and has allowed us to highlight enrichments or depletions of REEs in aquatic ecosystems and to estimate anthropogenic inputs through normalization of data to different reference materials. This review of current literature on REE normalization highlighted the large number of different reference materials (a total of 12), as well as different anomaly calculation methods. This statement showed a real need for method harmonization to simplify the comparison between studies, which is currently very difficult. Normalization to Post-Archean Australian Shale (PAAS) emerged as being the most used (33 % of reported studies) regardless of the location and the nature of the studied samples and seem to be of higher quality. The interest of other reference materials was nevertheless underlined, as they could better represent the geographical situation or the nature of samples. Two main anomaly calculation methods have been highlighted: the linear interpolation/extrapolation and the geometric extrapolation using logarithmic modeling. However, due to variations in the estimation of neighbors' values, these two methods produce many different equations for the anomaly calculation of a single element. Current normalization practices based on shales and chondrites are suitable for abiotic samples but are questionable for biota. Indeed, normalization is increasingly used in studies addressing ecotoxicological issues which focus on biota and often aim to estimate the anthropogenic origin of bioaccumulated REEs. Due to the interspecific variability, as well as the complexity of mechanisms occurring in organisms when exposed to contaminants, new reference materials need to be established to consider the bioaccumulation/metabolization processes and the anthropogenic inputs of REEs based on the results of biotic samples.

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## 1. Introduction

The use of rare earth elements (REEs) in industries and particularly for future technologies are of growing importance and make REEs critical and strategically important raw materials in the functioning of the global economy. They enter in the composition of many products like batteries, LED lighting, permanent magnets, fertilizers, or contrast agent for medical imaging. They are also increasingly used in high-tech devices, e.g., liquid crystal displays or communication devices. Moreover, they contribute to the substitution of oil and nuclear energies as they are extremely used in the renewable energy sector: in wind turbines, electric cars, catalytic converters or solar panels, etc. (Castor and Hedrick, 2006; Bru et al., 2015). This way, due to their worldwide popularity, the global extraction and the use of REEs in anthropogenic activities continue to rise, leading to an increase of environmental concentrations which can disrupt natural biogeochemical cycles and lead to their gradual enrichment in aquatic environment (De Baar et al., 1985a, 1985b; Bau and Dulski, 1996; Alibo and Nozaki, 1999; Kulaksiz and Bau, 2013; Merschel and Bau, 2015). The increase of REEs in the environment is a threat for the living organisms since they can lead to negative impacts at different biological and ecological organization levels as reported in studies focusing on laboratory exposures (Cui et al., 2012; Hanana et al., 2017; Cardon et al., 2019; Freitas et al., 2020).

REEs represent the group of the fifteen lanthanoids (from lanthanum ( $Z = 57$ ) to lutetium ( $Z = 71$ )) to which yttrium ( $Z = 39$ ) and scandium ( $Z = 21$ ) are often added because of similar chemical properties (column III of the periodic classification). Two main classifications exist. One separates REEs depending on their electronic configuration into two groups: the light rare earth elements (LREEs) composed of lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), promethium (Pm), samarium (Sm) and europium (Eu) and the heavy rare earth elements (HREEs) comprising gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), ytterbium (Yb) and lutetium (Lu) (Castor and Hedrick, 2006). The other separates them depending on their atomic weight into three groups: the LREEs (Ce to Pm), the medium rare earth elements (MREEs) (Sm to Gd) and the HREEs (Tb to Lu) (Mehmood, 2018). Yttrium (Y) is always classified in the heavy rare earth element group due to its chemical similarities even if it has a lower atomic weight.

On the contrary, scandium (Sc) is often excluded due to its different chemical properties. Apart from scandium, REEs have coherent chemical properties derived from the similar electronic configuration across the series (partially filling 4f electron shell), providing remarkable electromagnetic properties sought in many fields as mentioned above.

More and more studies about REEs are currently carried out and focus on aquatic environment. Enrichments in La, Gd and Sm have already been reported in watercourses (Elbaz-Poulichet et al., 2002; Kulaksiz and Bau, 2013; Merschel and Bau, 2015) but despite these observations, current knowledge on their risk to environment is piecemeal and define REEs as emerging contaminants. To remedy this lack, some studies aimed to investigate the environmental levels and impacts of anthropogenic uses of REEs (Möller et al., 2002; Klaver et al., 2014; Hissler et al., 2015; Song et al., 2017). However, as these contaminants are naturally present in the earth's crust at concentrations from 0.5 to 70 ppm (Buissette and Le Mercier, 2019), distinguishing anthropogenic and background contributions can be difficult. In this context, normalization methods have been used and consist in calculating the ratio of concentrations measured in matrix of interest to concentrations measured in reference materials. Normalization permits to flatten REE spectra allowing to overcome the Oddo-Harkins Rule effect (elements with even atomic number show higher abundances in the crust than the ones with odd atomic number) and to better visualize and calculate anomalies that characterize REE enrichments or depletions. This procedure was elaborated in the aim of characterizing and understanding geochemical behavior of REEs in natural environments (Sholkovitz et al., 1989; Elderfield et al., 1990; De Baar et al., 1991; Sholkovitz et al., 1994; Sholkovitz, 1995). Most REEs are found in nature at the trivalent oxidation level, which is the most stable. However, some can be oxidized to the tetravalent form, like Ce, or reduced to the bivalent form, like Eu, in particular temperature or redox conditions (De Baar et al., 1985a). This approach allows to investigate particular speciation processes of REEs occurring in the environment and to assess anthropogenic inputs. It was first used by geochemists to characterize water and sediment (Elderfield and Greaves, 1982; Sholkovitz, 1988), but it has now been extended to biota and is increasingly used in order to further investigate the risks REEs pose to the environment. Although this procedure could be very useful in the ecotoxicological and the biogeochemical fields as it can be performed on different

materials (such as water, sediment or biota) (Rabiet et al., 2009; Li et al., 2013; Yang et al., 2016), the considerable number of normalization reference materials and methods for anomaly estimation can make REE studies difficult to apprehend for non-geochemists. Added to this, it makes the comparison between studies difficult and sometimes even impossible.

This review, summarizing literature about REEs in the aquatic media, aims to facilitate the apprehension of environmental studies on REEs for non-geochemists through the analysis of the diversity and the evolution of uses of the different normalization reference materials that exist nowadays as well as the major methods for the calculation of REE anomalies. The most used reference materials are defined and compared then reported according to the location, the year of study and the matrices. Finally, the limits of their applications for ecotoxicological issues as well as associated research needs and prospects are discussed.

## 2. Literature search strategy and data analyses

The bibliographic research was carried out using different combinations of keywords in ScienceDirect and Google Scholar databases: *rare earth elements, lanthanoids, lanthanide(s), normalization, fractionation, partitioning, speciation, bioaccumulation, biomonitoring, monitoring, anomaly/ies, seawater, freshwater, groundwater, pore water, water, sediment, biota, species/organisms, aquatic, marine* and the names of individual REEs. This research only focused on scientific published articles and allowed to identify an exhaustive list of 251 ones from the beginning of the use of normalization and anomaly calculation; the last update being in November 2021. The articles were sorted and selected manually by reading the entire papers and the following exclusion criteria were applied: studies not being research articles, studies about REEs but not performing normalization or anomaly calculation, studies not treating about aquatic environments, or dealing with wastewater treatment plant (WWTP) effluents or tap water only. Thus, only studies dealing with natural aquatic environments were included: marine and freshwater environments, surface water and groundwater. No geographical or temporal restrictions were applied in order to describe the diversity of the REE normalization practices, their evolution and to understand the current uses.

Normalization material as well as anomaly calculation methods were identified in each publication. In order to investigate the influence of the year of publication, the location and the studied matrix on the practices, the articles were classified by three methods into (i) four subgroups for the year of publication: 1962–1990, 1991–2000, 2001–2010, 2011–2022, each containing 26, 38, 44 and 143 publications respectively; (ii) four subgroups regarding the location: America/Atlantic Ocean, Europe/Africa, Asia/Australia/Pacific Ocean and Worldwide (not corresponding to any other subgroup) each regrouping 53, 76, 103 and 18 articles respectively and (iii) three subgroups according to the studied matrix: water, sediment and aquatic biota, each comprising 97, 88 and 24 publications respectively.

Then, to analyze differences in the use of normalization reference materials depending on the considered factor of influence (year of study, location, and matrix), the percentages of use of each normalization material for each subgroup of the three classifications mentioned above were calculated. To be more representative of current habits, the percentages according to location and matrix have also been calculated considering only articles published in the last decade. For the matrix influence, 42 articles dealt with both two or the three matrices. Consequently, normalization materials used have been identified for each matrix and have been added to the percentage calculation of their corresponding subgroup (water, sediment, aquatic biota).

Finally, articles calculating anomalies were classified into three groups depending on the calculation method used: (i) linear extrapolation or interpolation using close or distant neighboring elements, (ii) geometric extrapolation using logarithmic modeling, (iii) completely different calculation method; each containing 130, 12 and 9 publications respectively. Moreover, for each REE, anomaly calculation equations have been listed and a total of 5 recurrent equations have been highlighted for Ce, Eu and Gd which correspond to the three main REEs considered in terms of anomalies

in the scientific literature. Then, the percentages of use of these equations have been calculated.

## 3. Literature overview

### 3.1. Main existing normalization reference materials

Several normalization reference materials exist and are used when investigating on REE environmental concentrations and fate. They can be gathered into two main types: shales, representative of average composition of the upper continental crust, and chondrites (either ordinary or carbonaceous) corresponding to bulk earth. A wide number of datasets exist and are currently used for both materials.

For shale normalization, up to five different datasets are commonly used (Table 1), i.e. PAAS, NASC, WSA, EUS and AS. Firstly, the “Post-Archean Australian Shale” (PAAS) is widely used and has been initially established from twenty-three samples of Australian shale by Nance and Taylor (1976) and later mathematically updated by McLennan (1989). A new set of data based on nine other samples from Australian shales and analytically improved by Pourmand et al. (2012) is also often used. The analytical determination is supposed to give more accurate REE concentrations compared to theoretical estimation performed for Tm and Lu concentrations initially. Secondly, the “North American Shale Composite” (NASC) is another dataset measured by Haskin and Haskin (1966) and other co-workers (Haskin et al., 1966a) in a composite powder constituted by a pool of a wide number of samples (forty in total) from the United States (20), Zimbabwe (3), Antarctic (2) and unknown locations (15). The concentrations, not complete for all the REEs at the beginning (Gromet et al., 1984; Goldstein and Jacobsen, 1988), were analytically updated by McLennan (1989) to constitute a set commonly used for normalization. Another frequently used one is the “World Average Shale” (WSA) that was calculated by Piper (1974) after Haskin and Haskin (1966) based on REE concentrations measured in shales from North America, Europe, and Russia. The “European Shale” (EUS) dataset originally analyzed by Minami (1935) on a European shale composite sample and later improved by Haskin and Haskin (1966) is also sometimes used for REE normalization. Recently, Bau et al. (2018) proposed a new set of data for EUS, based on the same composite sample analyzed with improved analytical methods. Finally, the “Archean Shale” (AS) is another dataset established by McLennan and Taylor (1984) on Archean shale samples and is more representative of Archean upper continental crust than the others previously described.

As for shales, many datasets are also available for chondrite normalization (Table 1). The first one is a set regrouping REE concentrations measured in ordinary chondrites (L6, H-group) from the Leedey meteorite shower (Oklahoma, November 1943) by Masuda et al. (1973). Many other sets were established on carbonaceous chondrites (CI). One of them was determined by Evensen et al. (1978) on fifteen chondrite samples, later mathematically revised by Taylor and McLennan (1985). Anders and Grevesse (1989) and Sun and McDonough (1989) also determined two others. Sometimes data from various chondrite types (carbonaceous (types I, II and III), ordinary (H and L groups), soko-banjitic and enstatitic chondrites) were used to establish reference REE mean concentrations (Schmitt et al., 1963; Haskin et al., 1966b).

Other materials than shales and chondrites can also be used to normalize REE concentrations (Table 1), i.e. MUQ, UCC, MORB, DMM WRAS and WRAC. The “Mud from Queensland” (MUQ) is a recent dataset proposed by Kamber et al. (2005) for normalization. It is based on measures of thirty-three alluvial fine-grained sediment samples from Australia. Moreover, analyses of the composition of insoluble elements in fine-grained clastic sedimentary rocks or glacial deposits allowed to estimate the composition of “Upper Continental Crust” (UCC) providing three different datasets used for REE normalization as well. The first one was established by Taylor and McLennan (1985) and was revised by the same authors in 1995. The second one also considering the composition of rocks exposed at the surface was reported by Wedepohl (1995). Then, more recently, Rudnick and Gao (2003) proposed a new updated set that is now commonly

**Table 1**  
REE concentrations in different reference materials used for rare earth elements normalization.

Reference material	Study	REEs (ppm)															
		Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	
PAAS	1	28	38	80	8.9	32	5.6	1.1	4.2	0.77	4.4	1	2.9	0.5	2.8	0.5	
	2–3	27	38.2	79.6	8.83	33.9	5.55	1.08	4.66	0.774	4.68	0.991	2.85	0.405	2.82	0.433	
	4	27	44.56	88.25	10.15	37.32	6.884	1.215	6.043	0.8914	5.325	1.053	3.075	0.451	3.012	0.4386	
NASC	5–6	27	32	70	7.9	31	5.7	1.24	5.21	0.85	5	1.04	3.4	0.5	3.1	0.48	
	7	–	31.1	66.7	–	27.4	5.59	1.18	–	0.85	–	–	–	–	3.06	0.456	
	2–3	27	32	73	7.9	33	5.7	1.24	5.2	0.85	5.8	1.04	3.4	0.5	3.1	0.48	
	8	–	34	66.7	–	30.1	5.8	1.16	5.12	–	4.67	–	2.73	–	2.67	0.41	
WSA	9	–	41	83	10.1	38	7.5	1.61	6.35	1.23	5.5	1.34	3.75	0.63	3.53	0.61	
EUS	10	30	16	33	4.9	28	7.6	1.2	8.5	1	6.2	1.9	3.3	0.26	3.9	1.1	
	6	31.8	41.1	81.3	10.4	40.1	7.3	1.52	6.03	1.05	–	1.2	3.55	0.56	3.29	0.58	
	11	31.9	44.3	88.5	10.6	39.5	7.3	1.48	6.34	0.944	5.86	1.17	3.43	0.492	3.26	0.485	
AS	12	–	20	42	4.9	20	4	1.2	3.4	0.57	3.4	0.74	2.1	0.3	2	0.31	
Chondrite	13	–	0.378	0.976	–	0.716	0.23	0.0866	0.311	–	0.39	–	0.255	–	0.249	0.0387	
	5–14–15"	1.9	0.32	0.9	0.13	0.57	0.21	0.074	0.31	0.051	0.3	0.074	0.21	0.032	0.18	0.032	
	16	–	0.2446	0.6379	0.09637	0.4738	0.1540	0.05802	0.2043	0.03745	0.2541	0.0567	0.166	0.02561	0.1651	0.02539	
	2	2.1	0.367	0.957	0.137	0.711	0.231	0.087	0.306	0.058	0.381	0.0851	0.249	0.0356	0.248	0.0381	
	17	1.56	0.2347	0.6032	0.0891	0.4524	0.1471	0.056	0.1966	0.0363	0.2427	0.0556	0.1589	0.0242	0.1625	0.0243	
	18	1.57	0.237	0.612	0.095	0.467	0.153	0.058	0.2055	0.0374	0.254	0.0566	0.1655	0.0255	0.17	0.0254	
MUQ	19	31.85	32.51	71.09	8.46	32.91	6.88	1.57	6.36	0.99	5.89	1.22	3.37	0.51	3.25	0.49	
UCC	2–20	22	30	64	7.1	26	4.5	0.88	3.8	0.64	3.5	0.8	2.3	0.33	2.2	0.32	
	21	20.7	32.3	65.7	6.3	25.9	4.7	0.95	2.8	0.5	2.9	0.62	–	–	1.5	0.27	
	22	21	31	63	7.1	27	4.7	1	4	0.7	3.9	0.83	2.3	0.3	2	0.31	
MORB	18*	28	2.5	7.5	1.32	7.3	2.63	1.02	3.68	0.67	4.55	1.01	2.97	0.456	3.05	0.455	
	18*	22	6.3	15	2.05	9	2.6	0.91	2.97	0.53	3.55	0.79	2.31	0.356	2.37	0.354	
	23	32	3.7	11.5	1.8	10	3.3	1.3	4.6	0.87	5.7	1.3	3.7	0.54	3.7	0.56	
DMM	24	3.328	0.192	0.550	0.107	0.581	0.239	0.096	0.358	0.070	0.505	0.115	0.348	–	0.365	0.058	
WRAS	25	29.40	37.80	77.7	8.77	32.69	6.15	1.188	5.19	0.819	4.95	1.019	2.97	–	3.01	0.456	
WRAC	25	29.84	44.61	89.2	9.69	35.6	6.70	1.383	5.37	0.831	4.87	0.980	2.78	–	2.72	0.406	

1: Nance and Taylor, 1976, 2: Taylor and McLennan, 1985, 3: McLennan, 1989, 4: Pourmand et al., 2012, 5: Haskin et al., 1966a, 6: Haskin and Haskin, 1966, 7: Gromet et al., 1984, 8: Goldstein and Jacobsen, 1988, 9: Piper, 1974, 10: Minami, 1935, 11: Bau et al., 2018, 12: McLennan and Taylor, 1984, 13: Masuda et al., 1973; Masuda, 1975, 14: Schmitt et al., 1963, 15: Haskin et al., 1966b, 16: Evensen et al., 1978, 17: Anders and Grevesse, 1989, 18: Sun and McDonough, 1989 (\*N-Type, \*E-type), 19: Kamber et al., 2005, 20: Taylor and McLennan, 1995, 21: Wedepohl, 1995, 22: Rudnick and Gao, 2003, 23: Taylor and McLennan, 2002, 24: Workman and Hart, 2005, 25: Bayon et al., 2015. \*: note that Haskin et al., 1966a, 1966b have different concentration values than Schmitt et al., 1963 for Ce and Tb that are respectively: 0.84 and 0.058 ppm. PAAS: Post-Archean Australian Shale, NASC: North American Shale Composite, WSA: World Shale Average, EUS: European Shale, AS: Archean Shale, MUQ: Mud from Queensland, UCC: Upper Continental Crust, MORB: Mid-Ocean Ridge Basalt, DMM: Depleted Mid-ocean ridge basalt Mantle, WRAS: World River Average Silts and WRAC: World River Average Clays.

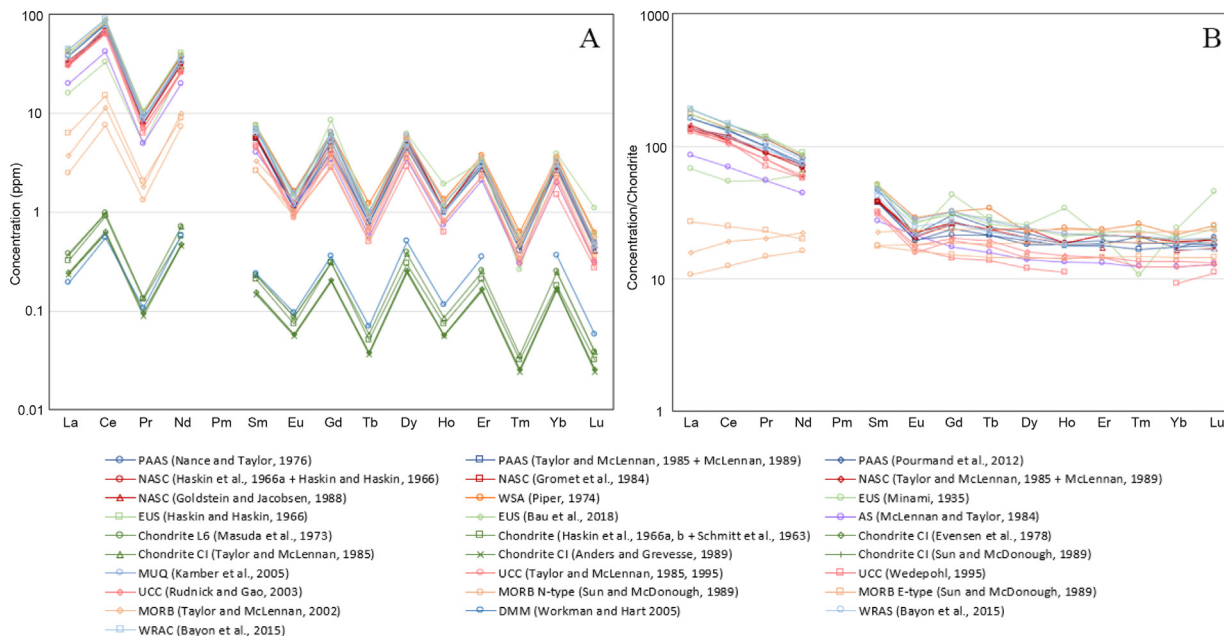
used. The “Mid-Ocean Ridge Basalt” (MORB) is based on the analysis of oceanic basalts and is sometimes used for normalization as it is more representative of the oceanic crust composition. Sun and McDonough (1989) provided two MORB datasets: the first one defined as normal-type (N-type) and the second one as enriched-type (E-type). Another set defined as MORB average has also been reported by Taylor and McLennan (2002). Workman and Hart (2005) proposed a new calculated set of data supposed to be representative of “Depleted mid-ocean ridge basalt mantle” (DMM) and is, as MORB, sometimes used in studies for REE normalization. Recently, Bayon et al. (2015) established two new datasets: the “World River Average Silt” (WRAS) and the “World River Average Clay” (WRAC) meant to be representative of the average composition of the weathered and eroded upper continental crust. These sets are based on the REE measures of twenty-two samples from rivers from all around the world and might get used in the next years for normalization. Finally, many studies performed what is called “local” normalization. It consists in normalizing REE concentrations in the matrix of interest to concentrations measured in another matrix coming from the same study site.

### 3.2. Comparison of normalization reference materials

All the concentration values of the different datasets of normalization previously presented are reported in the Table 1. Globally, the datasets determined from a same reference material are quite similar. Nevertheless,

some sets stand out more from the others with different concentrations (particularly for light REEs). For PAAS, Pourmand et al. (2012) dataset presents higher LREE concentrations than previous studies (Nance and Taylor, 1976; Taylor and McLennan, 1985; McLennan, 1989). This is explained by improved instrumentation leading to a better accuracy of REE measures. The same observation is possible for EUS: Minami (1935) dataset shows much lower concentrations of LREEs than the two other datasets (Haskin and Haskin, 1966; Bau et al., 2018) for the same reasons. Moreover, it appears that all shale normalizations (PAAS, NASC, WSA and EUS) have similar concentration values (Table 1). Only two shale datasets differ from the others with lower REE concentrations (especially for LREEs): Minami’s EUS with distant points for La, Ce, Pr, Gd, Ho and Lu and McLennan and Taylor’s AS with distant points for La, Ce, Pr and Nd (Fig. 1.A). MUQ, UCC, WRAS and WRAC also have relatively close patterns whereas MORB is differentiating from the other normalizations with much lower REE values, especially for LREEs (La to Sm) (Sun and McDonough, 1989; Taylor and McLennan, 2002). These differences can be explained by its representativity to the oceanic crust contrarily to the representativity to the continental crust of the other ones (Table 1, Fig. 1.A). Finally, the values obtained for chondrites and DMM are the most standing out from the other normalization patterns with much lower concentrations for all REEs, probably due to the specific meteoric origin of chondrite (Table 1).

As for the shales, variations among chondrite datasets can also be observed. The three CI chondrites have similar values (Evensen et al., 1978;



**Fig. 1.** A. REE concentrations in different published datasets used for normalization of REEs. B. Chondrite-normalized REE patterns for different published datasets used for REE normalization. PAAS: Post-Archean Australian Shale, NASC: North American Shale Composite, WSA: World Shale Average, EUS: European Shale, AS: Archean Shale, MUQ: Mud from Queensland, UCC: Upper Continental Crust, MORB: Mid-Ocean Ridge Basalt, DMM: Depleted Mid-ocean ridge basalt Mantle, WRAS: World River Average Silts and WRAC: World River Average Clays. Chondrite normalization was performed using [Anders and Grevesse \(1989\)](#) dataset.

[Anders and Grevesse, 1989; Sun and McDonough, 1989](#)) whereas the fourth one ([Taylor and McLennan, 1985](#)) is standing out and is closer to the ordinary chondrites ([Masuda et al., 1973; Haskin et al., 1966a, 1966b; Schmitt et al., 1963](#)) (Fig. 1.A). This difference is probably because it is a mathematic revision of [Evensen et al. \(1978\)](#) data made by Taylor and McLennan (values multiplied by 1.5) in 1985, while the other pattern determinations were analytical. Chondrite-normalized REE patterns can help to qualitatively differentiate reference datasets based on the flatness of the pattern. For this purpose, REE levels in reference materials were normalized to chondrite ([Anders and Grevesse, 1989](#)) and their REE pattern is presented in Fig. 1.B. Most of the reference datasets have a similar pattern with LREE enrichment, as supposed in the earth's crust and a europium anomaly. AS, MORB and Minami's EUS are diverging with a lower LREE enrichment than the other datasets (especially MORB). Various element anomalies (Gd, Tb, Ho, Tm Yb and Lu) are depicted in several patterns (Minami's EUS, Piper's WSA, Wedepohl et al. UCC) certainly due to earlier analytical methods introducing bias.

### 3.3. Normalization practices

#### 3.3.1. Global normalization practices

An overview of the bibliographic research that has been carried out in order to list the different existing REE normalization reference materials is shown in the Table S1. A wide number of studies have been carried out over the past sixty years. A total of 251 publications ranging from 1962 to 2022 and studying various matrices (water, sediment, aquatic biota) of natural aquatic environments have been reported. Samples from many different locations were analyzed (France, Italy, Japan, China, Pacific and Atlantic Oceans, USA, etc.). Most of the studies focused on natural water samples (either sea or freshwater) and sediment rather than aquatic biota. Indeed, for biota, only a few numbers of studies performing a normalization of REE concentrations have been reported. A wide number of normalization materials have been used in the different studies. Sometimes, different materials have also been used in the same study (e.g. [Alibo and Nozaki, 1999; Elias et al., 2019](#)). More than ten normalization reference materials are thus listed (PAAS, NASC, WSA, chondrite, MUQ, UCC, EUS, MORB, DMM, AS, WRAS/WRAC and local) implying even many more datasets.

A summary of the Table S1 can be seen in the Fig. 2. PAAS is the most common normalization material used in the past sixty years, reaching 33 % of the published studies. The second is chondrite with 17.3 %, closely followed by NASC, WSA and local normalization with 14.8, 12.3 and 11.6 % respectively. The seven other normalization materials (DMM, MUQ, UCC, EUS, MORB, AS and WRAS) are less employed with percentages of use ranging from 0.3 to 5 %.

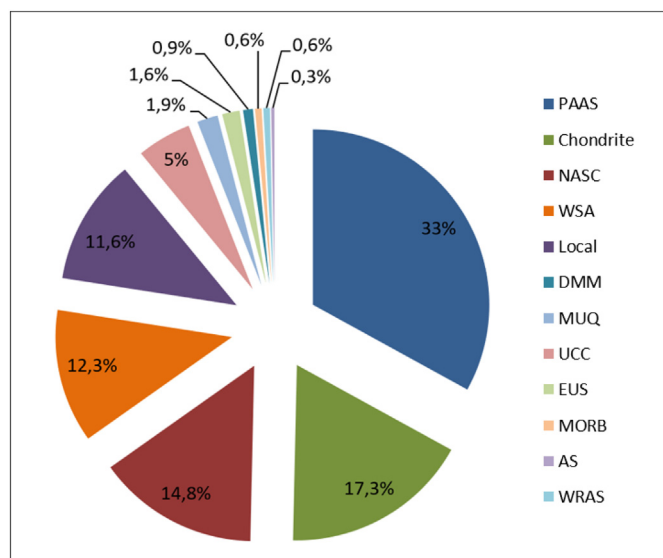
#### 3.3.2. Evolution over time

The Fig. 3 summarizes the use of different normalization reference materials over time. The articles were divided into four groups, the period before 1990 then each decade until 2022. For each one, the percentages of use of each normalization material have been calculated.

In the early years (1962 to 1990), only five normalization reference materials were used (Fig. 3.A). The most widely used was the WSA reaching 54.3 % of the studies, compared to the four others: chondrite, local, NASC and PAAS with percentages ranging from 2.9 to 17.1 %. Later, between 1991 and 2000, NASC and PAAS became more widely used, representing 19.2 and 17.3 % of the reference materials (Fig. 3.B) explaining the decrease of WSA normalization (54.3 to 30.8 %). Local and chondrite normalizations carried on being used almost similarly to the last decade with 19.2 and 11.5 % respectively. At the beginning of the 21st century (2001 to 2010), the use of NASC increased with a percentage reaching 36 %, close to PAAS percentage of 32 % (Fig. 3.C). Local normalization was less used during this decade (4 %) and chondrite stayed used in 12 % of the studies. This last decade (2011 to 2022) is marked by the increase of the number of normalization materials used, reaching eleven (Fig. 3.D). NASC normalization that was predominant in the previous decade became less employed (8.8 %) and the frequency of PAAS kept an important percentage up to 43.6 %, just as well as chondrite with 20.4 %. Local and UCC normalizations were used in 10.5 and 8.3 % of the studies.

#### 3.3.3. Evolution according to the location

The different normalization practices are based on datasets established on measures of various materials from several continents. The location of the studied samples might have influenced the researchers in choosing the normalization reference material they should employ. Aiming to



**Fig. 2.** Percentage of different normalization reference materials used when studying REEs over the past 60 years. Pie chart established on the basis of bibliographic research presented in Table S1 containing 251 publications in total. PAAS: Post-Archean Australian Shale, NASC: North American Shale Composite, WSA: World Shale Average, DMM: Depleted Mid-ocean ridge basalt Mantle, MUQ: Mud from Queensland, UCC: Upper Continental Crust, EUS: European Shale, MORB: Mid-Ocean Ridge Basalt, AS: Archean Shale and WRAS: World River Average Silts, Local: Normalization using local concentrations either from local references or from concentrations reported among same study or previous ones.

highlight different uses depending on the location of the studied samples, the 251 articles were divided into four groups, each representing a part of the world except for the one considering worldwide studies (Fig. 4).

A restricted number of normalization reference materials is used in studies carried out on samples from America to Atlantic Ocean. PAAS normalization is indeed the most used material with a percentage reaching 32.9% (Fig. 4.A). Local and WSA follow with an equal percentage of 21.4% and surprisingly NASC percentage is lower (12.9%). For works focusing on samples from Europe to Africa, PAAS normalization appears mostly used again in 43.8% of the articles, followed by NASC and chondrite with 21.3 and 14.6% respectively (Fig. 4.B) whereas EUS is used in only 5.6% of the studies. Compared to the two other world parts, studies carried out on samples from Asia, Australia and Pacific Ocean show a large variety of normalization materials (Fig. 4.C). PAAS is mostly used with a percentage of 27.1%, followed by chondrite, WSA and NASC normalizations with percentages of 24.1, 14.3 and 10.5% respectively. In addition to these four normalizations, seven others are also employed: local, UCC, MUQ, DMM, MORB, WRAS and AS. Lastly, regarding the Worldwide group (Fig. 4.D), PAAS and WSA are mostly used (29.2 and 20.8% respectively) and NASC, local, chondrite, UCC and WRAS are less used with percentages ranging from 4.2 to 16.7%.

As shown in the Fig. 3, the choice of the normalization reference material highly depends on the year of the publication. Therefore, to be representative of the current practices, the percentages in each part of the world have been calculated considering studies carried out during the last decade only (Fig. 4.E, F, G, H). With these new considerations, only four different normalization reference materials are employed in the studies carried out on samples from America to Atlantic Ocean: mostly PAAS (66.7%), then local normalization (18.5%), NASC and chondrite (both 7.4%) (Fig. 4.E). For Europe to Africa, PAAS normalization is again mainly used, reaching a percentage of 49.2% (Fig. 4.F) and EUS increased (5.6 to 7.7%). Publications on samples from Asia, Australia and Pacific Ocean, still show a wide number of normalization materials in the past decade (Fig. 4.G). PAAS and chondrite are preponderant (30.4 and 29.1% each) and are

followed by many other normalization reference materials like UCC, NASC, local, etc. Finally, there is an increase of the use of PAAS during the last decade (29.2 to 50%) in the Worldwide group (Fig. 4.H). UCC is also more employed with 20% and is followed by chondrite, local and WRAS with an equal percentage of 10%.

### 3.3.4. Evolution according to the studied matrix

Normalization practices also depend on the studied matrix as shown in the Fig. 5. Studies were split into three groups, representing main investigated natural matrices, i.e., water, sediment and aquatic biota.

Globally, a wide range of normalization materials were used for characterizing the three matrices, but some preferences can be highlighted. For works focusing on water samples, PAAS is mostly used, with 40.1%, followed by NASC normalization reaching 16.6% (Fig. 5.A). Local and WSA normalizations are also employed with respective percentages of 14.6 and 14%. For sediment samples, PAAS and chondrite normalizations come first, appearing in 26.6 and 23.4% of the studies, followed by four other normalizations (NASC, WSA, local and UCC) representing 9.1 to 15.6% (Fig. 5.B). About aquatic biota, less normalization reference materials are mentioned in studies (Fig. 5.C). As for both other matrices, PAAS is mainly used, reaching 37%. Chondrite and local normalizations are also often used with 26.1 and 15.2%, respectively; whereas, NASC and WSA are less employed (8.7%).

Here again to be representative of the current practices, percentages were also calculated considering only the last decade (Fig. 5.D, E, F). For water samples, PAAS is predominant reaching 65.1% of the articles (Fig. 5.D). Local normalization is also employed at 14.3%. Many normalization reference materials have been used in studies about sediment samples and have similar percentages (Fig. 5.E) to those obtained considering all the studies. PAAS and chondrite come first with percentages of 35 and 23.3% and they are followed by UCC and NASC with 13.6 and 11.7%, respectively. Studies investigating on aquatic biota samples mainly used PAAS (42.1%), chondrite (28.9%) and local normalization during the last decade (Fig. 5.F).

### 3.3.5. Overview

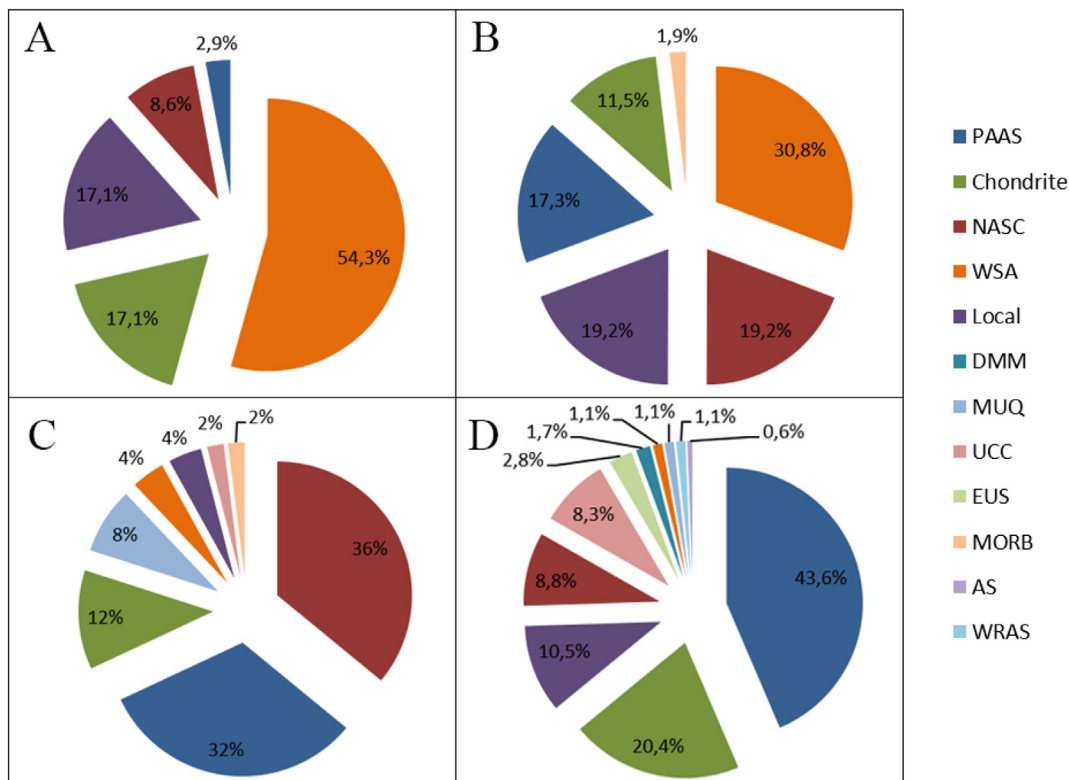
To summarize, PAAS appears to be the most used material followed by chondrite, NASC, and local normalization. The investigation of the trend according to the year of publication showed that over time more and more normalization reference materials were used, with WSA predominant in the early years, and PAAS and chondrite nowadays. Depending on the location of the studies, preferences are observable. Independently of time, PAAS remains the mostly used material in America/Atlantic Ocean and Europe/Africa regions, as well as in the Worldwide group; whereas, chondrite is particularly used in the Asia/Australia/Pacific Ocean region. Considering the matrix influence, PAAS is also preferentially used for water, coming close with chondrite for aquatic biota samples. No real preferential material has been highlighted for sediment samples, independently of the year of the publication, even if PAAS and chondrite are the first ones.

## 3.4. Anomaly calculation methods

### 3.4.1. Diversity of the methods

Measuring and normalizing REE concentrations in different matrices of interest generally lead to anomaly calculation for specific REEs. This procedure allows REE environmental enrichment or depletion to be highlighted, and therefore could inform on particular fractionation processes and/or anthropogenic inputs.

Out of the 251 studies reported in the Table S1, 151 proceeded to anomaly calculations representing 60.2% of the studies. Anomalies are most of the time quantified by linear extrapolation or interpolation using neighboring elements. (Elbaz-Poulichet et al., 2002; Klaver et al., 2014; Ponnurangam et al., 2015; Briant et al., 2021 etc.). Values >1 indicate positive anomalies and values <1 indicate negative anomalies. This method assumes that the difference in concentrations between neighboring pairs is constant. However, as it is not always the case, anomalies are sometimes



**Fig. 3.** Percentage of the different normalization reference materials used depending on the year of the study. A. Percentage calculated for the 26 articles published between 1962 and 1990, B. Percentage calculated for the 38 articles published from 1991 to 2000, C. Percentage calculated for the 44 articles published between 2001 and 2010 and D. Percentage calculated for the 143 articles published from 2011 to 2022. For every chart, articles published in the bordering years are included. PAAS: Post-Archean Australian Shale, NASC: North American Shale Composite, WSA: World Shale Average, DMM: Depleted Mid-ocean ridge basalt Mantle, MUQ: Mud from Queensland, UCC: Upper Continental Crust, EUS: European Shale, MORB: Mid-Ocean Ridge Basalt, AS: Archean Shale and WRAS: World River Average Silts, Local: Normalization using local concentrations either from local references or from concentrations reported among same study or previous ones.

calculated by geometric extrapolation using logarithmic modeling (Kulaksiz and Bau, 2011, 2013; Merschel et al., 2015). A reference equation following linear extrapolation method has been elaborated by Alibo and Nozaki (1999) for anomaly calculation:

$$REE_n/REE^*_n = 2[REE]_n / ([REE]_{n-1} + [REE]_{n+1})$$

with n corresponding to the atomic number of the studied REE, and \* corresponding to the geogenic background concentrations. Despite this general equation, the Table S1 highlights up to 82 different equations used for the anomaly calculation of REEs. These equations have been established either following the two main methods mentioned above or other. Therefore, equations and their corresponding articles can be gathered into three groups. Most of the studies calculated anomaly on the basis of linear extrapolation/interpolation (86.1 %) using either close (76.8 %) or distant (9.3 %) neighboring elements rather than based on geometric extrapolation (7.9 %). Some other studies used another method of calculation, completely diverging from the reference equation (6 %).

The Table S1 also clearly shows that many different equations are used to calculate the anomaly for a single element. A total of 5 recurrent equations have been listed: 3 for Ce, 1 for Eu and 1 for Gd. These three REEs are indeed the most studied ones in terms of anomalies. After identifying these 5 recurrent equations, their percentages of use in articles have been calculated and are presented in the Fig. 6.

### 3.4.2. Ce anomaly

Cerium is the main element for which anomalies are calculated, since cerium negative anomaly is a characteristic of seawater (Piper and Bau, 2013) and many listed publications are focusing on seawater samples (Table S1).

Indeed, under oxic conditions, trivalent Ce can be easily oxidized to the tetravalent state on the surface of Mn oxides (German and Elderfield, 1990). The solubility of Ce is thus decreased, leading to a Ce depletion in solution relatively to the other trivalent REEs. Out of the 151 publications performing anomaly calculations, 116 focused on Ce and a total of 20 different equations have been reported for the calculation. Among these equations, 3 have been highlighted as the most often used, as shown in the Fig. 6. The first equation (eq. (1)), mentioned in 33.9 % of the studies, corresponds to the reference one, proposed by Alibo and Nozaki (1999):

$$Ce/Ce^* = 2Ce_N / (La_N + Pr_N) = Ce_N / (0.5La_N + 0.5Pr_N) = Ce_N / [(La_N + Pr_N) / 2] \tag{1}$$

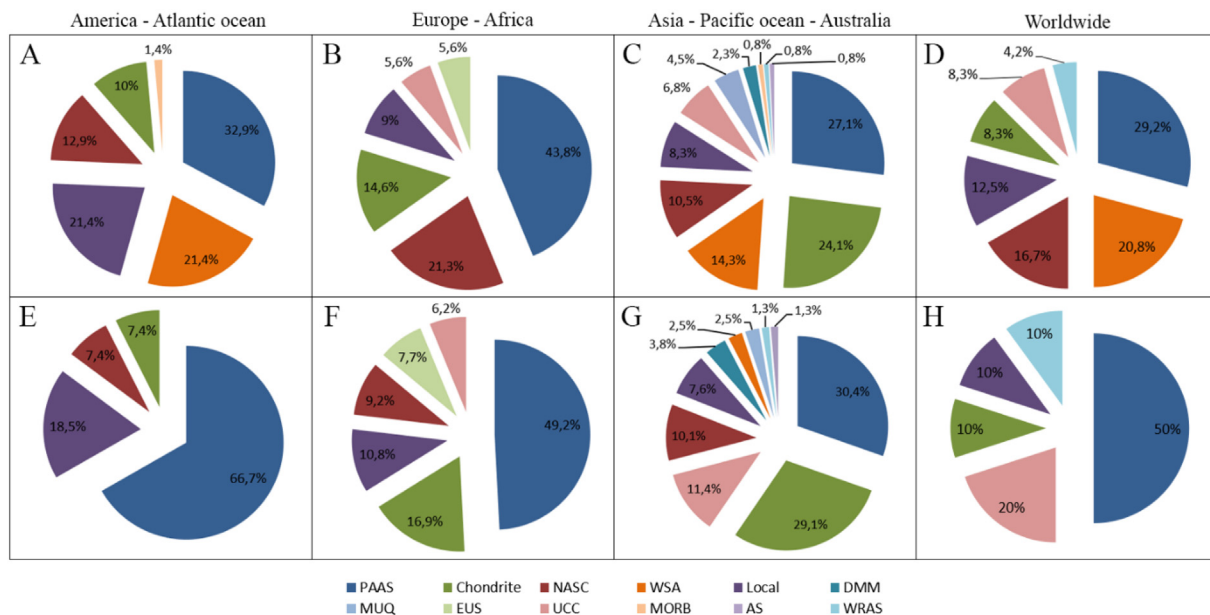
with N corresponding to normalized concentrations. The two others employed equations (eq. (2) and (3)) reach 22.3 and 18.2 % of the studies, respectively:

$$Ce/Ce^* = Ce_N / [(La_N \cdot Pr_N)^{0.5}] = Ce_N / \sqrt{La_N \cdot Pr_N} \tag{2}$$

$$Ce/Ce^* = 3Ce_N / (2La_N + Nd_N) = Ce_N / [(2La_N + Nd_N) / 3] \tag{3}$$

These 3 equations are based on linear extrapolation and use more or less close neighbors' concentrations for calculation (either La and Pr or La and Nd). Finally, 25.6 % of the studies employ other equations than eq. (1), (2) and (3) for cerium anomaly calculation like eq. (4) which is also often used and is based on geometric extrapolation:

$$Ce/Ce^* = \log[Ce_N / (2/3La_N + 1/3Nd_N)] \tag{4}$$



**Fig. 4.** Percentage of the different normalization reference materials used depending on the location of studied samples (A, B, C, D: including all studies from the last 60 years and E, F, G, H: including only studies published in the last 10 years (2010 to 2022 included)). A. Percentage calculated for the “America/Atlantic Ocean” group corresponding to 53 articles, B. Percentage calculated for “Europe/Africa” group containing 76 articles, C. Percentage calculated for the “Asia/Australia/Pacific Ocean” group containing 103 articles and D. Percentage calculated for the “Worldwide” group corresponding to 18 articles. E. Percentage calculated for the “America/Atlantic Ocean” group corresponding to 22 articles, F. Percentage calculated for “Europe/Africa” group containing 54 articles, G. Percentage calculated for the “Asia/Australia/Pacific Ocean” group containing 60 articles and H. Percentage calculated for the “Worldwide” group corresponding to 7 articles. PAAS: Post-Archean Australian Shale, NASC: North American Shale Composite, WSA: World Shale Average, DMM: Depleted Mid-ocean ridge basalt Mantle, MUQ: Mud from Queensland, UCC: Upper Continental Crust, EUS: European Shale, MORB: Mid-Ocean Ridge Basalt, AS: Archean Shale and WRAS: World River Average Silts, Local: Normalization using local concentrations either from local references or from concentrations reported among same study or previous ones.

Moreover, some authors calculate Ce anomaly based on Pr and Nd concentrations rather than La and Nd concentrations with the following eq. (5) and (6) to avoid bias involved by the possible overabundance of La in natural systems (Lawrence et al., 2006):

$$Ce/Ce^* = Ce_N / [Pr_N \cdot (Pr_N / Nd_N)] \quad (5)$$

$$Ce/Ce^* = Ce_N / (2Pr_N - Nd_N) \quad (6)$$

### 3.4.3. Eu anomaly

Europium is the second main element for which anomalies are calculated. Out of the 151 articles performing an anomaly calculation, 72 calculated europium anomaly and up to 18 different equations have been reported in these publications. A specific equation, using linear close neighbors' concentrations interpolation (Sm and Gd), is used in most of the studies (eq. (7)) reaching 49.3 % of the articles versus 50.7 % using other equations (Fig. 6):

$$Eu/Eu^* = Eu_N / [(Sm_N \cdot Gd_N)^{0.5}] = Eu_N / \sqrt{Sm_N \cdot Gd_N} \quad (7)$$

with N corresponding to normalized concentrations. The second mainly used equation is one corresponding to Alibo and Nozaki's reference equation (eq. (8)) representing 15.5 % of the 50.7 % others:

$$Eu/Eu^* = 2Eu_N / (Sm_N \cdot Gd_N) \quad (8)$$

Also, as Gd is often demonstrating anomalous chemical behavior, authors sometimes use the Tb neighboring element instead to calculate Eu anomaly, as in the eq. (9):

$$Eu/Eu^* = Eu_N / (0.67Sm_N + 0.33Tb_N) \quad (9)$$

### 3.4.4. Gd anomaly

The third main element for which anomalies are calculated is gadolinium. Indeed, research leads a great interest to this element because it is widely used in medicine (as contrast agent in MRI (magnetic resonance imaging)) which causes considerable anthropogenic input in the environment (Elbaz-Poulichet et al., 2002; Bau et al., 2006; Hatje et al., 2016). Out of the 151 publications proceeding to anomaly calculation, 43 calculated Gd anomaly and a total of 15 different equations have been reported. Although many equations are used, only one is mostly mentioned (eq. (10)), corresponding to a linear extrapolation using normalized close neighbors' concentrations (Sm and Tb) and reaching 39.6 % of the studies (Fig. 6):

$$Gd/Gd^* = Gd_N / (0.33Sm_N + 0.67Tb_N) \quad (10)$$

with N corresponding to normalized concentrations. Nevertheless, 60.4 % of the other studies use many other equations for Gd anomaly calculation. As for europium, the second mainly used equation for Gd is one corresponding to Alibo and Nozaki's reference equation (eq. (11)) representing 8.3 % of the 60.4 % others:

$$Gd/Gd^* = 2Gd_N / (Eu_N + Tb_N) \quad (11)$$

Two others can also be cited as they are often used (eq. (12) and (13)):

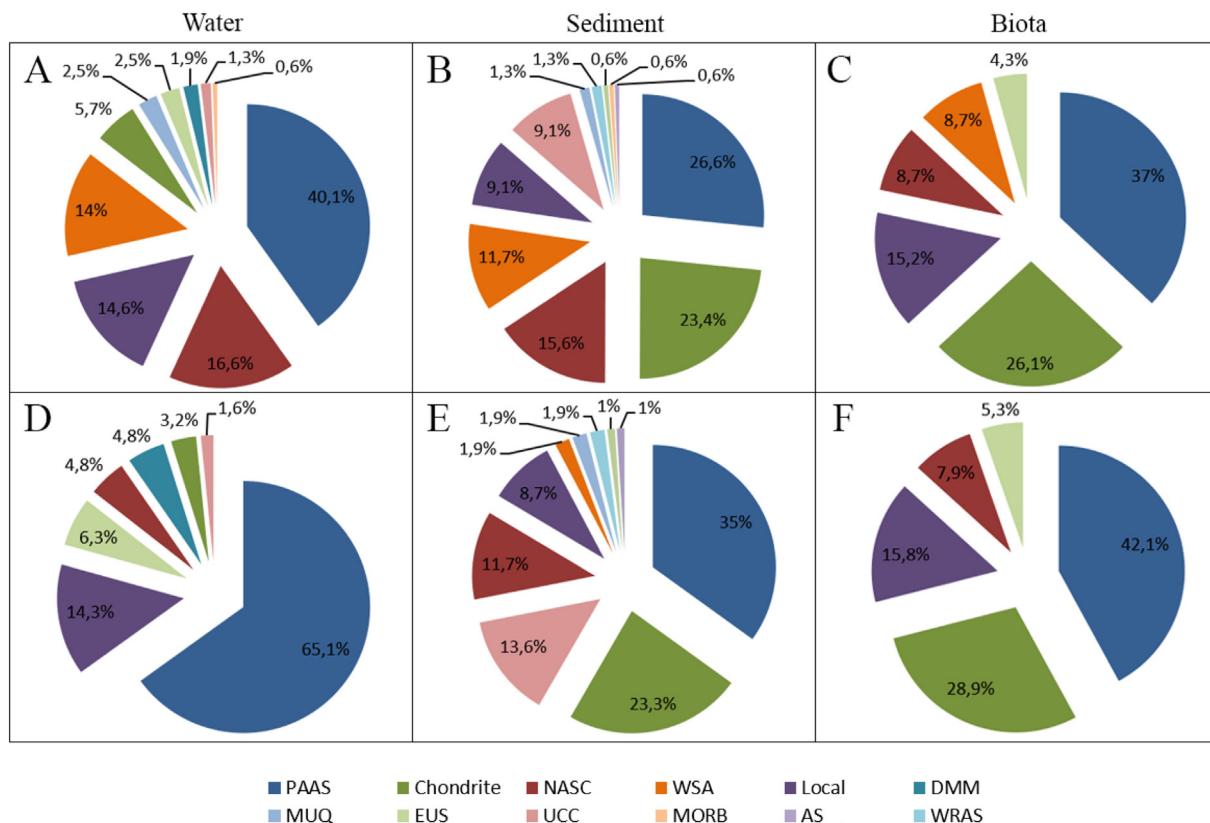
$$Gd/Gd^* = Gd_N / [(Tb_N^2 \cdot Sm_N)^{1/3}] \quad (12)$$

$$Gd/Gd^* = Gd_N / (0.4Nd_N + 0.6Dy_N) \quad (13)$$

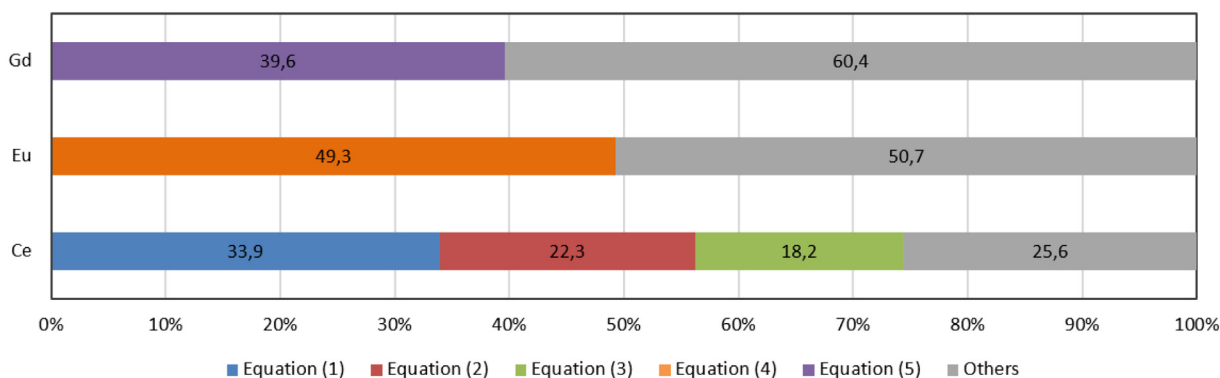
### 3.4.5. Other anomalies

Anomalies are calculated for many other REEs (La, Pr, Lu, Sm, Yb, Nd, Tm, Y, Tb, Dy and Ho) as reported in the Table S1. However, for all these





**Fig. 5.** Percentage of the different normalization reference materials used depending on the material studied (A, B, C: including all studies from the last 60 years and D, E, F: including only studies published in the last 10 years (2010 to 2022 included)). A. Percentage calculated for water samples corresponding to 97 articles, B. Percentage calculated for sediment samples comprising 88 articles and C. Percentage calculated for biota samples corresponding to 24 articles. D. Percentage calculated for water samples corresponding to 39 articles, E. Percentage calculated for sediment samples comprising 62 articles and F. Percentage calculated for biota samples corresponding to 21 articles. Some publications were studying several materials (42 articles for A, B and C and 21 publications for D, E and F), normalization materials used in these studies have been identified for each material and has been added to the calculation of percentage of their corresponding group (water, sediment, biota). PAAS: Post-Archean Australian Shale, NASC: North American Shale Composite, WSA: World Shale Average, DMM: Depleted Mid-ocean ridge basalt Mantle, MUQ: Mud from Queensland, UCC: Upper Continental Crust, EUS: European Shale, MORB: Mid-Ocean Ridge Basalt, AS: Archean Shale and WRAS: World River Average Silts, Local: Normalization using local concentrations either from local references or from concentrations reported among same study or previous ones.



**Fig. 6.** Percentage of articles using the five main anomaly calculation equation. For cerium based on 116 articles, for europium based on 72 articles and for gadolinium based on 43 articles.

(1)  $Ce/Ce^* = 2Ce_N / (La_N + Pr_N) = Ce_N / (0.5La_N + 0.5Pr_N) = Ce_N / [(La_N + Pr_N) / 2]$

(2)  $Ce/Ce^* = Ce_N / [(La_N \cdot Pr_N)^{0.5}] = Ce_N / \sqrt{La_N \cdot Pr_N}$

(3)  $Ce/Ce^* = 3Ce_N / (2La_N + Nd_N) = Ce_N / [(2La_N + Nd_N) / 3]$

(4)  $Eu/Eu^* = Eu_N / [(Sm_N \cdot Gd_N)^{0.5}] = Eu_N / \sqrt{Sm_N \cdot Gd_N}$

(5)  $Gd/Gd^* = Gd_N / (0.33Sm_N + 0.67Tb_N)$

Others: For cerium, equation used for anomaly calculation different from eq. (1), (2) and (3); for europium, equation used for anomaly calculation different from eq. (4); for gadolinium, equation used for anomaly calculation different from eq. (5), with N corresponding to normalized concentrations and \* corresponding to geogenic background concentrations.

REEs, no equation was standing out from others. For this reason, no percentages of use were calculated.

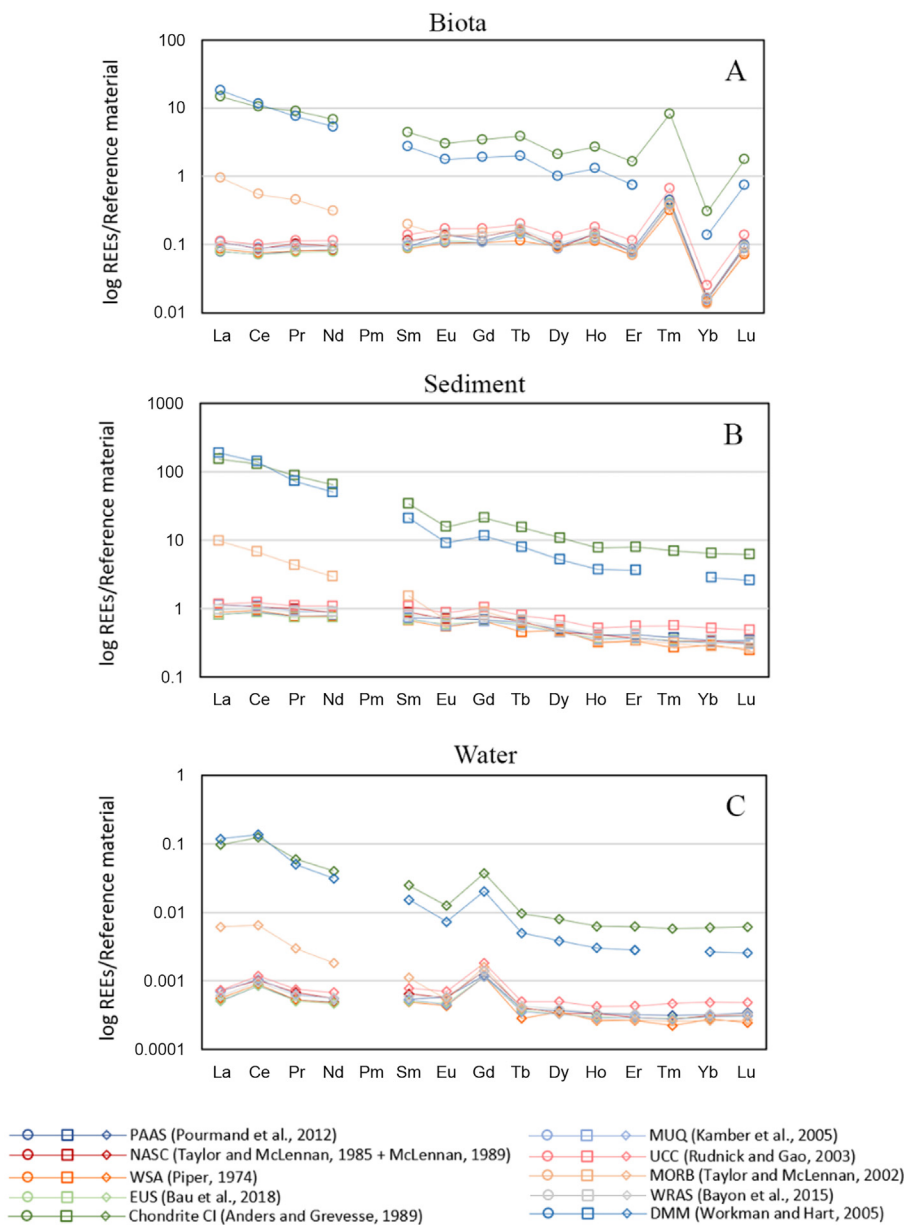
#### 4. Preferred reference material, limits, and improvements

As depicted in the Table S1, many normalization reference materials exist and are commonly used in studies about REEs in aquatic ecosystems, based on the use of a various number of datasets. These different methods lead to a heterogeneity of REE normalization and complicate the comparison of results between studies employing different methods (Table 1) even if the conclusion could be the same using different reference materials and/or anomaly equations. The five main normalization reference materials involve PAAS, chondrite, NASC, WSA, local normalization, with PAAS being the most common (Fig. 2). The consideration of the articles depending on the publication year allows to observe that the normalization of concentrations started in 1962 with only five normalization materials. WSA was globally the predominantly used method, allowing easy comparisons between studies (Fig. 3.A). However, all datasets used at this time were based on values determined with anterior analytical methods that were later questioned for the accuracy of their representativity to the continental crust. New datasets based on improved analytical methods or new normalization materials were established over time multiplying widely the number of reference material available nowadays for REE normalization. Even if these new sets are supposed to allow more accurate characterizations of REE concentrations in the environment, due to the higher performances of the analytical instrumentation, in fact, they make the comparison of study results complicated (Fig. 3.B, C, D). Nevertheless, depending on the location of the studied samples, it is understandable to use the reference material corresponding to the same geographic region. It is not the case for two out of the three established world regions. Indeed, NASC is not the most used normalization reference material in the American region (Fig. 4.A, E); and although EUS is only used in the European region, it is not used as much as PAAS (Fig. 4.B, F). For Australia/Asia region, PAAS is the main reference material but it is closely followed by chondrite although it does not specifically correspond to this geographical area (Fig. 4.C, G). Finally, for the Worldwide group, PAAS is again mostly used (Fig. 4.D, H). These differences in use of reference materials between regions, not following the geographical location of the study site, are not that surprising. Indeed, many of these reference materials are established either on composite samples (EUS and NASC) or by estimation / calculation based on several samples from various world regions (WSA, WRAC, WRAS and UCC). They are therefore not intended to be representative of a specific geographic location but of a global average of the continental crust REE composition (Gromet et al., 1984; Bau et al., 2018). Thus, the choice of reference material highly depends on author and peers' preferences/habits or other parameters like the nature of studied samples. Preferences have also been highlighted depending on the studied matrix. Considering natural water samples, PAAS is mostly used (Fig. 5.A, D). For sediment, no normalization material is standing out among the wide number of different reference materials that are used (Fig. 5.B, E). For aquatic biota samples, PAAS, chondrite and local normalization are commonly used (Fig. 5.C, F). This can be explained by the nature of the samples and depends on the study objective. Chondrites are meant to represent the initial condition of the earth's crust at the time of formation (Nance and Taylor, 1976). Therefore, chondrite-normalization highlights post-earth formation processes. However, as chondrites are pretty different to most studied samples, by their nature and REE composition, they do not really allow to estimate inter-sample variations and are mainly used in igneous geochemistry and cosmochemistry (McLennan, 1989; Bau et al., 2018). Regarding shales, they are meant to be parallel to the average upper continental crust composition (Taylor and McLennan, 1985) and they have a closer nature/REE composition to the studied samples allowing to better detect differences between samples. Shale-normalization can help to understand the exact nature of sources and inter-sample variations and is therefore more used in sedimentary, aqueous and environmental geochemistry (Bau et al., 2018). Thus, for sediment samples various material can be used to characterize

REE fractionation but for water samples, PAAS is preferred. Indeed, when studying marine phases, chondrite-normalization emphasizes the differences of samples to chondrites (due to their extremely contrasting REE concentrations) rather than highlighting the lesser but significant differences between individual marine phases (Piper, 1974), which isn't a problem encountered with PAAS. This explains differences of reference material uses for water and sediment samples but not for aquatic biota. Indeed, neither chondrite nor shale come close to the biota matrix nature, therefore both are often used. The local normalization is also often employed as it could be more representative of the local biota exposure (both geogenic and anthropogenic). Finally, normalization to a matrix of the same nature might be more appropriate for biota.

Many studies used different normalization materials to characterize their impact on the concentrations and patterns of REEs. Two studies performed both PAAS and NASC normalizations (Alibo and Nozaki, 1999; Elias et al., 2019), and allowed to highlight that even if there are slight differences of HREE reference values between them (Alibo and Nozaki, 1999), REE patterns are globally similar. Three studies comparing chondrite and PAAS normalization, by performing both of them on the same data (Rezaee et al., 2009, 2010; Li et al., 2013), concluded to great differences of produced REE patterns especially for LREEs and also often for HREEs. Moreover, in many cases, PAAS and local normalizations are used in a same study (Nozaki et al., 1999; Strady et al., 2015; Hatje et al., 2016). Differences on LREEs and HREEs have been observed but are less obvious than those between chondrite and PAAS. To confirm these observations and in order to analyze variations in REE patterns after performing different normalizations, values from several studies about various matrices (aquatic biota, sediment and natural water) have been obtained. Then, all normalization materials that are available and used nowadays were applied to the data and the REE spectra are presented in the Fig. 7. Only one dataset for each reference material was used to perform data normalization. The most recent dataset was selected for all materials (PAAS, WSA, EUS, chondrite, MUQ, UCC, MORB, WRAS, DMM) as it is supposed to be more accurate due to updated analytical methods and if it was not complete, the latest complete for all REEs dataset was chosen (NASC). AS and WRAC normalizations were not performed as they are less used. For the three studied matrices (aquatic biota, sediment and natural water), REE patterns produced from shale (PAAS, NASC, WSA and EUS), MUQ and WRAS normalizations are very similar (Fig. 7. A-C). REE patterns for UCC normalization slightly differ from the ones obtained with the six previous normalizations (Fig. 7. A-C). This result is particularly noticeable for sediment and water on HREEs (Fig. 7. B, C), even if the pattern remains very close to the others. MORB is again contrasting with all other normalizations with higher LREE enrichments showed in all three patterns of studied samples. Finally, as mentioned before, REE patterns obtained with chondrite and DMM normalizations are diverging, especially for LREEs which have higher levels than the others (Fig. 7. A-C). Considering other scientific articles performing several normalizations and dealing with few differences between REE patterns, these results highlight a great similarity of patterns obtained after shale-normalizations regardless of their origin. Consequently, it would be possible to compare data from studies already published which used different shale normalizations (PAAS, NASC, WSA and EUS).

No harmonization about the reference material used for normalization exists for REE patterns, but this review highlights PAAS as the most used normalization reference material. Added to its popularity, PAAS was recently updated by Pourmand et al. (2012) allowing better accuracy of REE measurements due to improved analytical methods (MC-ICP-MS (Multiple Collector - Inductively Coupled Plasma - Mass Spectrometry)) leading to a better estimation of continental crust composition compared to other references, like NASC or WSA, that were elaborated based on anterior analytical methods that can induce bias (NAA (Neutron Activation Analysis) or ID-MS (Isotope Dilution - Mass Spectrometry)). Moreover, PAAS not being a shale composite avoids potential inclusion of aberrant material as it can be the case with a composite sample like for NASC or EUS (McLennan, 1989). Finally, as described earlier, PAAS allows to better highlight differences between samples due to its similarity in REE composition; whereas, it is



**Fig. 7.** Normalization patterns (PAAS, NASC, WSA, EUS, chondrite, MUQ, UCC, MORB, WRAS and DMM) of REEs measured in different environmental matrices. A. For biota samples, B. for sediment samples and C. for natural water samples. REE concentrations used for biota normalizations come from a study by Squadroni et al. (2017) on Mediterranean seaweeds (data for *Codium bursa* were used), those of sediments are taken from Hannigan et al. (2010) study on Chesapeake Bay’s surface sediments and water concentrations come from a study by Merschel et al. (2015) on Lake Paranoa. PAAS: Post-Archean Australian Shale, NASC: North American Shale Composite, WSA: World Shale Average, EUS: European Shale, Chondrite CI: Carbonaceous chondrite, MUQ: Mud from Queensland, UCC: Upper Continental Crust, MORB: Mid- Ocean Ridge Basalt, WRAS: World River Average Silts and DMM: Depleted Mid-ocean ridge basalt Mantle.

not always possible when using chondrite-normalization. Therefore, and for all of these reasons, it could be advised to favor PAAS-normalization when investigating on REEs. This way, comparisons between studies from all around the world would be possible. However, depending on the location, the studied matrix or the study objective, other normalizations might give more precise information and have a great interest. These other ways of normalization, representing geographical situation and/or being more representative of the sample matrix (e.g., MORB, EUS, local normalization, etc.) should be used in these studies in addition to PAAS.

Regarding anomaly calculation, even if a reference equation has been proposed by Alibo and Nozaki (1999), this review highlights that many different equations are used to calculate REE anomalies. In most of the studies, anomalies are quantified by linear extrapolation or interpolation using either close or distant corrected neighbors' concentrations. Indeed,

depending on the environmental characteristics of the studied samples, direct neighbor's concentration cannot be used to calculate an element anomaly as it presents itself an anomaly. To minimize bias involved by neighbor's anomalies, either various distant neighbors or geometric extrapolation methods are used multiplying the number of equations seen in the literature (Lawrence et al., 2006). This phenomenon might therefore be the explanation for the wide number of different equations reported in this review for the calculation of the anomaly of a single element (Fig. 6). In some cases, anomaly calculation equations are really diverging from the reference one and no real explanations about the choice or the establishment of the equation are given in the articles. These reasons should be really mentioned as it would help to better understand the results and to compare anomalies from diverse studies. Several studies devoted an important interest in comparing anomaly values obtained by using different

equations for their calculation. Lawrence et al. (2006) investigated differences of anomaly obtained for La, Ce, Gd and Eu after using either linear or geometric methods. It highlighted up to 30 % differences in La anomaly values between the two applied methods, but <2 % of variation for Ce, Gd and Eu anomalies. In the same way, Louis et al. (2020) tested four different equations for the calculation of Gd anomalies and demonstrated that using an equation based on Nd and Dy tend to maximize the anomaly whereas using one involving Sm and Nd tend to minimize it. Thus, the choice of the method or equation to calculate an anomaly highly conditions the produced results which can lead to misinterpretations if they are inaccurate. Moreover, in some publications, authors employ the modeling of the shape of the normalized REE pattern using a third-order polynomial fit to calculate an element anomaly (Möller et al., 2002, 2003; Hatje et al., 2016; Pereto et al., 2020; da Costa et al., 2021). This method could be more accurate avoiding bias as it allows to exclude from the model, elements that might have an anomalous chemical behavior as it is often the case for Eu and Ce. Its systematic use could help to homogenate anomaly calculation to reduce the number of equations used for the same element and to simplify the understanding and the comparison of the studies. However, as it is more challenging to implement than using an already established equation, this method is not really popularized.

## 5. Further developments for ecotoxicological issues

REE normalization to reference material is for a long time used in geochemistry to investigate on rare earth elements' behavior in natural ecosystems. It is nowadays used increasingly for ecotoxicological issues dealing with many types of matrices, but mainly focusing on aquatic biota. For water and sediment samples, it makes sense to normalize REE concentrations with values from shales and chondrites, but not really for biota as many biological mechanisms (e.g., uptake, biological membrane transfer, accumulation, metabolism, excretion) can occur within organisms. As it was demonstrated for non-essential metals or for essential metals in excess in cells, some of these processes control the intracellular homeostasis of each metal to limit their adverse effects on cell functioning (Luk et al., 2003; Martinez-Finley et al., 2012; Blindauer, 2012). These species- and tissue-dependent mechanisms directly impact the metal internalization. Even if the studies dealing with REE internalization are scarce, it can be assumed that some of these processes are elicited to control intracellular REE homeostasis.

Little is known about REE uptake and excretion but their similarities with  $\text{Ca}^{2+}$  could be a possible explanation for their internalization within cells. Indeed, trivalent REEs have varying ionic radii (from 9.6 to 11.5 nm) similar to calcium ions radius that is 9.9 nm. Because of this and due to their higher valency (+3), REEs might be able to bind in place of calcium (Cui et al., 2012). Moreover, as REEs are metals, it is possible that they are excreted due to different detoxification mechanism actors like metallothionein (MT) for example (Andrés et al., 2003; Kawagoe et al., 2005; Dubé et al., 2019; Hanana et al., 2021). As it has already been proved with non-essential metals, demonstrating various fates depending on the species due to different detoxifications capacities and inducing therefore diverse adverse toxic effect (Le Croizier et al., 2019), it might also be the case for REEs (Técher et al., 2020). Their bioaccumulation is, however, well documented. Many studies demonstrated REE bioaccumulation after laboratory exposures in various aquatic organisms like *Dreissena polymorpha*, *Mytilus galloprovincialis*, *Cyprinus carpio*, *Daphnia magna*, *Chironomus riparius* and *Oncorhynchus mykiss* (Qiang et al., 1994; Hanana et al., 2017; Cardon et al., 2019; Freitas et al., 2020). Some of them also highlighted different accumulations depending on the studied organ or on the exposure dose. Cardon et al. (2020) highlighted higher Y concentrations in the intestine of *O. mykiss* compared to the muscles, the liver and the gills. Moreover, Freitas et al. (2020) demonstrated higher Nd concentrations in *M. galloprovincialis* when exposed to high (40  $\mu\text{g/L}$ ) compared to low concentrations (2.5  $\mu\text{g/L}$ ). REE partitioning within cells was also investigated with subcellular fractionation studies and allows to characterize precisely REE accumulation and fate in cells and can inform

on potential detoxification processes. A study performed by Cardon et al. (2019) highlighted different REE accumulations in subcellular fractions depending on the species. REEs were mainly quantified in the metal detoxified fraction (MT and metal rich granules) for *D. magna* whereas they were mostly accumulated in the metal sensitive fraction (corresponding to cytosolic fraction containing mitochondria and heat denaturated proteins) in *O. mykiss*. Thus, these results demonstrate that accumulation and detoxification mechanisms are depending on the species. Although REEs can induce negative effects at high concentrations, they can also have positive effects at low concentrations (hormesis phenomenon, Cook and Calabrese, 2007). Indeed, some REEs can have a beneficial effect on organisms as they can have a role in functional and structural molecules in the biological system. Various favorable REE-associated effects have already been characterized on different species like enhancing growth (for example on *Dryopteris Erythrosora*, Ozaki et al., 2000) or increasing immunity responses for fish (Abdelnour et al., 2019). These results demonstrate that the presence of REEs in cells is not always involving an adverse effect.

Therefore, the complexity of living organisms cannot be considered with current normalization practices. The normalization of aquatic biota REE concentrations to current shale or chondrite reference materials can help to identify the biological mechanisms involved in REE bioaccumulation from the abiotic compartments. Nevertheless, due to biological processes mentioned above, it may not allow a reliable assessment of exposure to anthropogenic releases. For this purpose, the establishment of new datasets intended specific to aquatic biota is needed. Different ways could be explored. Organisms from sampling archives could be used as references since they can be considered as unexposed to anthropogenic REEs. Indeed, organisms subjected to time series sampling for monitoring programs could be used as reference and allow the estimation of background geogenic concentrations of the elements (e.g., ROCCH (Réseau d'Observation de la Contamination Chimique) program conducted by Ifremer (Institut français de recherche pour l'exploration de la mer) in the aim of French coast chemical monitoring with oyster and mussel sampling since 1974) (Briant et al., 2021). However, these archived organisms are not available for all the species and even if it would be required for each one, having species-dependent reference materials wouldn't help homogeneity of normalization within aquatic biota. Nevertheless, normalization could be performed using REE patterns measured from organisms, representative of an order, as some studies highlighted similar biological processes among different species belonging to the same order. For example, Perrat et al. (2017) demonstrated similar Gd accumulations of two mollusk species (*Dreissena rostriformis bugensis* and *Corbicula fluminea*), that were higher in the digestive gland compared to the gills. Wang et al. (2019) also highlighted similar REE accumulation for three species of fish (*Pagrosomus major*, *Tilapia nilotica* and *Harengula zunasi*). However, this study also showed different accumulation in mollusk and crustacean although they belong to the same phylum. Another way would be to consider the REE concentrations measured in individuals sampled in pristine or most preserved sites as reference pattern, as it is sometimes done in abiotic compartment studies (Costa et al., 2021). This proposition assumes that the sites would present similar physical-chemical characteristics, except anthropogenic discharges, which is rarely the case and is therefore little used. Nevertheless, it has been successfully carried out by Pereto et al. (2020) in one of their studies; *Corbicula fluminea* was used as a sentinel species in the field for the determination of anthropogenic REE origin and Gd bioaccumulation in bivalves. Waiting for new references for aquatic biota, a double normalization seems the most appropriate. The first one using PAAS, as it combines many quality criteria and is the most commonly used, allowing to simplify the comparisons between different studies, and the second one using local normalization to help the interpretation of specific biological mechanisms.

## 6. Conclusion

This review highlights the wide number of datasets and normalization reference materials that exist nowadays to characterize REE environmental concentrations in aquatic systems. Many different equations for anomaly

calculation are also reported from the literature. Homogenization of the use of these methods is necessary to simplify REE investigation and allow the comparison of results from different studies. PAAS normalization is the most commonly used and should be systematically employed because, in addition to its popularity, it meets many quality requirements: a recent update with accurate analytical methods, the detection of inter-samples variations, not based on a composite sample; which is not always the case for others. However, it could be completed with normalization to other reference materials, newly established, that can be more appropriate depending on both the studied location and matrix. Moreover, for articles already published, a comparison of studies that use either PAAS, NASC, WSA or EUS normalizations might be possible, as different studies, including this review, showed only few differences exist between the REE patterns they produce. For natural water and sediment samples, the use of current normalization materials (shale and chondrite) is suitable. Although a wide number of datasets and reference materials is available for abiotic compartment studies, this literature study highlights the lack of reference material that could serve ecotoxicological issues for the biotic compartment. New reference values need to be established in order to better consider the interspecific variability and to assess the anthropogenic origin of bioaccumulated REEs in exposed organisms from natural aquatic ecosystems.

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## CRediT authorship contribution statement

**Julie Rétif:** Conceptualization, Methodology, Formal analysis, Investigation, Resources, Visualization, Writing – original draft. **Aurore Zalouk-Vergnoux:** Conceptualization, Supervision, Project administration, Validation, Resources, Writing – review & editing. **Nicolas Briant:** Conceptualization, Supervision, Validation, Resources, Writing – review & editing. **Laurence Poirier:** Conceptualization, Funding acquisition, Supervision, Project administration, Validation, Resources, Writing – review & editing.

## Data availability

No data was used for the research described in the article.

## Declaration of competing interest

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

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