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Review

Aquatic ecotoxicity of lanthanum – A review and an attempt to derive water and sediment quality criteria

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ABSTRACT

Rare earth elements (REE) used to be taken as tracers of geological origin for fluvial transport. Nowadays their increased applications in innovative environmental-friendly technology (e.g. in catalysts, superconductors, lasers, batteries) and medical applications (e.g. MRI contrast agent) lead to man-made, elevated levels in the environment.

So far, no regulatory thresholds for REE concentrations and emissions to the environment have been set because information on risks from REE is scarce. However, evidence gathers that REE have to be acknowledged as new, emerging contaminants with manifold ways of entry into the environment, e.g. through waste water from hospitals or through industrial effluents. This paper reviews existing information on bioaccumulation and ecotoxicity of lanthanum in the aquatic environment. Lanthanum is of specific interest as one of the major lanthanides in industrial effluents. This review focuses on the freshwater and the marine environment, and tackles the water column and sediments. From these data, methods to derive quality criteria for sediment and water are discussed and preliminary suggestions are made.

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1. Introduction

Lanthanum (La) is the first element of the lanthanides (or lanthanoides), a series of 15 metals from lanthanum to lutetium with atomic numbers from 57 to 71 (Holden and Coplen, 2004). Together with the elements yttrium and scandium, the lanthanides are also called rare earth elements (REE). The term REE refers to the fact that these metals are often less concentrated than other metals, although they are relatively frequent in the earth crust (US-EPA, 2012). Rare Earth Elements play an essential role in the development of innovative environmental technologies, and with increasing application in most modern electronic technology and in industrial and medical products, emission to freshwater systems is expected to increase in the form of waste water emissions, industrial emissions, e-waste and recycling emissions, surface run-off and atmospheric deposition. Few studies, however, are available on the distribution of REE in freshwater systems, but those, that are, clearly show anthropogenic signals from e.g. industrial emissions (e.g. 1.5 t of Lanthanum in the Rhine (Kulaksız and Bau, 2011)) and from waste water treatment plants (an increase in gadolinium concentration by more than 2 orders of magnitude in the area of Berlin, Germany (Bau and Dulski, 1996)). In order to determine, whether elevated REE-concentrations present an environmental risk, the hazard potential needs to be assessed. Studies on the ecotoxicity of REE have been summarized in reports by Sneller et al., (2000) and Ng et al. (2011). With the increasing number of publications and data gathered for aquatic toxicity (more than 70 reports and publications since 2011), we get an increasingly better picture on the effects of REE on organisms. With this article, we critically review the current knowledge on ecotoxicological effects of lanthanum as one of the major industrially emitted lanthanides on freshwater and marine organisms, in water and in sediment.

As with other metals, the availability of lanthanum is strongly influenced by pH and by the presence of other cations in the environment. It can be accumulated by organisms, it can interfere with cellular functions and it adsorbs to particles. Experimental results, however, are often not conclusive, but for performing a risk assessment, quantitative and reliable data need to be available. Based on critically selected information, an attempt is made to derive quality criteria for freshwater and sediments.

2. Lanthanides (Ln) in the aquatic systems with special emphasis on lanthanum (La)

The lanthanides form a geochemical coherent group and possess similar physicochemical properties, since they all build trivalent cations. The ionic radius decreases steadily from lanthanum through lutetium, which is referred to as lanthanide contraction. While lanthanum predominantly exists in the stable oxidation state $+3$, some other lanthanides could occur in different oxidation states and thus exhibit deviating chemical behavior; for example cerium and terbium as $+4$, samarium and europium as $+2$ (Cotton, 2007). Lanthanides possess a low solubility and easily precipitate or bind to complexing ions, like hydroxide, carbonate, fluoride, phosphates, or organic ligands (Wood, 1990; Sneller et al., 2000; Ng et al. 2011). The solubility products (K_{sp}) of most complexes are very low; the K_{sp} for lanthanum phosphate is about 10^{-25} mol^2 L^{-2} (Liu and Byrne 1997).

The distribution and bioavailability of lanthanides in the aquatic environment (water and sediment) depends on the lanthanide speciation, which is influenced by physicochemical parameters, i.a. pH-value, alkalinity, and ionic strength, and the presence of different organic and inorganic complexing agents (Moermond et al., 2001; Elderfield et al., 1990).

The natural lanthanide pattern of suspended load in small rivers depend mainly on the geological catchment area and could show huge differences, while that of major rivers is relatively uniform (Goldstein and Jacobsen, 1988). Lanthanides in river waters are fractionated between colloidal and suspended particles, and solution phases. Because of the high affinity of lanthanides to colloids and particles these are mainly responsible for lanthanide transport and distribution (Sholkovitz, 1992). In organic-rich rivers, the lanthanide transportation via colloids can cover up to 100% (Tang and Johannesson, 2003; Pourret et al., 2007). Generally, the lanthanide load in rivers decreases from riverine to brackish to seawater, since mixing processes from fresh and saltwater in estuary zones result in coagulation of colloidal and particulate-bound lanthanides and subsequent sedimentation. This estuarine removal can reduce the lanthanide load by 30% to 90% (Elderfield et al., 1990; Sholkovitz, 1992).

Lanthanides also show different speciation patterns between river-, surface and pore water on one hand and seawater on the other. A speciation modeling for lanthanum conducted by Moermond et al. (2001) described a speciation gradient from riverine to sea water. The model that also addressed complexation with dissolved organic matter showed that lanthanum formed predominantly complexes with humic substances in riverine waters, followed by carbonates and bicarbonates, whereas in seawater the order for lanthanum species was La-carbonates, bicarbonates, and then free ions. An increase of the pH-value (from 6 to 9) was followed by a decrease of the free ions and of lanthanum bound to humic ligands, and an increase of lanthanum carbonate- and bicarbonate-complexes.

Lanthanides have a high affinity to sediments and are enriched in fine grain size fractions. For lanthanum the log K_d (partition coefficient) for sediment/pore water in the Rhine estuary was reported as 5.6–6.2 L kg^{-1} for the fraction <63 μm and 5.5–5.7 L kg^{-1} for the fraction <2 mm (Weltje et al., 2002b). Due to the lower affinity to sandy sediments from the North Sea the log K_d for sediment/pore water was considerably lower with 4.8–

5.1 L kg^{-1} (Tijink and Yland, 1998). The dominant lanthanum species in sediment are the residual forms. Among the forms of bound lanthanides, organic matter is the most relevant complexing agent. Chakraborty et al. (2011) investigated lanthanum speciation in estuarine and coastal sediments and identified TOC as most important factor for speciation and bioavailability. While 50–60% of lanthanum was bound to inert complexes and not bioaccessible, about 20–30% is associated with TOC. Other identified lanthanum fractions in the sediment were bound to iron and manganese compounds (8.5–16%) and (bi)carbonates (3–6%) or were water soluble (1–11%). A similar order for lanthanum fractionation with higher amounts of residuals and lower ones for exchangeable forms were found by Zhang et al. (1998) in sediments from the Yangtze river.

Although dissolved lanthanum species represent a very small proportion of lanthanum compounds in water and sediment, the trivalent ion La^{3+} is bioavailable and possesses the greatest risk of biological effects (Das et al., 1988). In an extensive review, Das et al. (1988) described the cytotoxic effects of the lanthanum-ion which has chemical properties similar to alkaline earth elements. Mechanistic action of La^{3+} on a cellular system is often mediated through the competition for binding sites with calcium-ions (Ca^{2+}), since both ions have comparable ionic radii. Among numerous effects, La^{3+} could inhibit Ca-channels in cell membranes, interact with membrane-associated enzymes, and affect different tissue components.

3. Bioaccumulation of lanthanum compounds

The amount of metal, which can be accumulated by aquatic organisms, is determined by two main dynamic processes both changing with environmental conditions: the bioaccessibility (environmental availability) and the bioavailability. In this paper, we follow the definitions that have been proposed by Semple et al. (2004): Bioaccessible compounds are *potentially* available but may be currently out of reach for the individual organisms. That fraction of bioaccessible compounds, which is actually able to cross an organism's membrane, is termed "bioavailable". Inaccessible would be e.g. residues that are firmly bound to a matrix (Harmsen, 2007; McGeer et al., 2004).

Bioaccumulation of a chemical is affected by rates of uptake, metabolism, and elimination as well as the storage capacity of an organism. Accumulation can occur through the body surface from ambient media (bioconcentration) or by uptake with food (biomagnification) (McGeer et al., 2004). Several abiotic and biotic factors affect the bioavailability of metal compounds, e.g. metal speciation, physicochemical parameters of the environment, and biological–physiological properties of the exposed organism. Metal compounds can be taken up as freely dissolved ions, metal complexes or particle-bound metals byingestion. In the latter case, the ingestion can lead to metal desorption by gastrointestinal fluids with a subsequent increasing potential of accumulation or, alternatively, to direct elimination via fecal pellets (McGeer et al., 2004).

The main factors describing the bioaccumulation are as follows: The ratio of the concentration of a chemical in biota (C_{biota}) to that in ambient water (C_w) is called bioconcentration factor (BCF) and is usually derived from and applied in laboratory studies. If different sources of exposure contribute to the biota concentration, for example under field conditions, this ratio is called bioaccumulation factor (BAF) (1). The uptake from sediment could be expressed as biota-sediment accumulation factor (BSAF), which is the ratio of the C_{biota} to the concentration in sediment C_{sed} (Gobas and Morrison, 2000).

$$BCF(BAF) = C_{biota} * C_w^{-1} \quad (1)$$

$$BSAF = C_{biota} * C_{sed}^{-1} \quad (2)$$

Due to large differences in sediment properties, the BCF calculated with pore water concentration is more reliable for bioaccumulation in benthic organisms than the BSAF (McGeer et al., 2004).

Bioaccumulation studies with different metals (essential, non-essential) and with a variety of organisms from different trophic levels sometimes show negative correlations between metal concentration in water and BCF, because the biota concentrations increase more slowly with increasing dissolved concentrations, thus leading to declining BCF and BAF with C_w (McGeer et al., 2003). Zhang et. al (2010) and Xu et al. (2012) observed the same trend with La.

Similar relationships were observed by DeForest et al. (2007) for the relation between metal concentration from all possible uptake routes, including the trophic transfer of metals, and the corresponding bioaccumulation factor. This negative correlation is mainly caused by the homeostatic system with its different regulation mechanisms for metal uptake, the saturated uptake kinetics at increased concentrations and the influence of pre-existing background concentration (DeForest et al., 2007; McGeer et al., 2003). In addition, the BCFs for inorganic metals demonstrate a large variability due to environmental properties and the characteristics and conditions of exposed organisms. Therefore, the BCFs for metals do not represent good proxies for hazard identification, in contrast to those of neutral lipophilic organic compounds. Nevertheless, metal accumulation studies are valuable tools to investigate metal fate and toxicity in aquatic environments (McGeer et al., 2003).

Lanthanides (Ln) as non-essential elements can be detected in nearly all biota and the accumulation pattern in biota as in other environment samples follows generally the Oddo–Harkins rule (Weltje et al., 2002b) with lanthanum (La) usually being the second most common lanthanide after cerium (Ce) (Weltje et al., 2002b; e.g. Moermond et al., 2001). There is a large variability in lanthanum bioaccumulation among the presented studies, since lanthanum-uptake is altered by several abiotic and biotic factors. In addition, bioavailability is influenced by La speciation, which is determined by environmental conditions (e.g. Moermond et al., 2001; Bustamante and Miramand, 2005; Sun et al., 1997). Unfortunately, information on exposure concentration, environmental parameters and La speciation are often not recorded in publications. In order to increase the extent of information, some results from non-peer reviewed papers were collected and used in this chapter. Also, information on trophic transfer of La and secondary poisoning is very scarce, especially for marine organisms, and no studies with vertebrates could be found.

The bioaccumulation studies are subdivided with regard to freshwater and saltwater species (Table 1 and 2). Organisms living predominantly in brackish water are mostly considered in the marine chapter.

3.1. Lanthanum bioaccumulation in freshwater organisms (Table 1)

3.1.1. Microorganisms

In a laboratory study about the effects of lanthanum chloride on the bacterium *Escherichia coli* Zhang et al. (2010) also observed an inverse relationship between BCF and exposure concentration. The highest BCF of 1,840,000 L kg^{-1} was reported at the lowest exposure concentration of 0.03 μg La g^{-1} and when *E. coli* was exposed to the highest concentration of 242 μg La g^{-1} the lowest BCF of 44,760 resulted (Table 1). Next to the higher surface to

Table 1
Lanthanum concentration in biota, bioconcentration factors (BCF) and selected exposure conditions for freshwater species. Small lines (-) indicate missing or incomplete information, gaps ( ) refer to information from the same study in the previous row.

Species [a]	Compound[b]	Exposure scenario[c]	Exposure time[d]	Alkalinity [mEq L^{-1}]	pH-value [-]	Temp. [°C]	Biota, target tissue	Biota conc.[e] [µg La g^{-1} dw]	Exposure conc.[f] [µg La L^{-1}]	BCF, BAF[g] [L kg^{-1}]	Reference
Bacteria											
Escherichia coli	$LaCl_3$	L	24 h	–	–	–	Whole bacteria	55.2	0.03	1,840,000[h]	Zhang et al. (2010)
								544	0.33	1,648,485[h]	
								3027	3.65	829,315[h]	
								5783	18.9	305,979[h]	
								10,832	242	44,760[h]	
Microalgae											
Chlorella vulgaris	$La(NO_3)_3$	L	48 h	–	6.0	25 ± 1	Whole algae	–	1000[i]	4800[j]	Sun et al. (1997)
		L (+ CIT)								3480[j]	
		L (+ NTA)								2600[j]	
		L (+ EDTA)								260[j]	
Macrophytes											
Lemna minor	$LaCl_3$	L	216 h	–	5.0–5.6	25 ± 2	Whole plant	0.972[k]	1.39[i]	1145[ww,l]	Weltje et al. (2002a)
										17,175[l]	
		L	167 h					0.417[k]		1917[ww,l]	
										28,755[l]	
		L	48 h					1.597[k]		2198[ww,l]	
										32,970[l]	
Lemna minor	La	F (sw)	–	–	7.3–8.6	19–20	Whole plant	0.139–0.347[k]	0.008–0.042[k]	120,00–20,000[k]	Weltje et al. (2002b)
Potamogeton pectinatus		F (sw)			7.3–8.7	18–21		0.111–11.1[k]	0.008–0.042[k]	7000–300,000[k]	
		F (pw)			6.9–7.6				0.021–0.070[k]	2000–300,000[k]	
Spirodela polyrhiza	$La(NO_3)_3$	L (Mi)	16 d	–	6.5–6.8	22 ± 1	Whole plant	10–110[ww,k]	1000[i]	138.1[ww]	Yang et al. (1999)
Hydrocharis dubia	$La(NO_3)_3$	L	7 d	–	–	–	Leaves	1050[ww]	5556[i]	189[ww,h]	Xu et al. (2012)
								1521[ww]	11,112[i]	137[ww,h]	
								1540[ww]	16,669[i]	92[ww,h]	
								2641[ww]	22,225[i]	119[ww,h]	
Ceratophyllum demersum	La	F	–	–	–	–	Whole plant	5.3	< 0.22	> 24,091	Wolterbeek and van der Meer (1996)
Azolla filiculoides								0.385	< 0.22	> 750	
Ceratophyllum demersum	La	F	–	–	–	–	Whole plant	18.8–51.6	–	–	Cowgill (1973)
Potamogeton praelongus								19.8			
Potamogeton crispus								42.8			
Pontederia cordata							Flowers, leaves, stems	18.7–43.9			
Nuphar advena								23.0–52.3			
Nymphaea odorata								27.4–63.2			
Decodon verticillatus								36.2–64.2			
Gastropods											
Bellamya aeruginosa	$La(NO_3)_3$	L (Mi)	16 d	–	6.5–6.8	22 ± 1	–	0.1–0.8[ww,k]	1000[i]	2.11[ww]	Yang et al. (1999)
Five snail species	La	F (sw)	–	–	7.3–8.7	19–21	Soft tissue	0.125–4.17[k]	0.008–0.042[k]	9000–250,000[k]	Weltje et al. (2002b)
								–	–	0.55–5.50[k,m]	
							Shell	0.003–0.417[k]	0.008–0.042[k]		
Bivalves											
Corbicula fluminae	La	F (sw)	–	–	8.2	18	Soft tissue	0.417[k]	0.035[k]	12,000[h]	Weltje et al. (2002b)
							Shell	0.139[k]			
Dreissena polymorpha							Soft tissue	1.111[k]	0.035[k]	32,000[h]	
							Shell	0.278[k]			

Corbicula fluminae	La	F (pw)	–	8.2–24.4	7.6–7.7	–	Soft tissue	1.03–6.23	0.0419–0.1251	25,000–50,000[k]	Tijink and Yland (1998)
							Shell	0.08–0.53		1500–6300[k]	
		F (sed)					Soft tissue	1.03–6.23	26.6–93.8[n]	0.04–0.07[k,o]	
							Shell	0.08–0.53		0.003– 0.015[k,o]	
Crustaceans											
Paranephrops planifrons	La	F (c)	0, 14, 60 d	–	–	–	Muscle tissue	0.03, 0.02, 0.01	–	–	Landman and Ling (2006)
							Hepatopancreas	0.11, 0.24, 0.08			
	La (P)	F					Muscle tissue	0.06, 0.07, 0.09			
							Hepatopancreas	0.17, 0.54, 0.93			
Paranephrops planifrons	La	F (c)	0, 14, 60 d	–	–	–	Hepatopancreas	< LOD	–	–	Landman et al. (2007)
(m)	La (P)	F						0.20, 0.60, 0.80			
(f)								0.10, 0.65, 1.05			
Fishes											
Cyprinus carpio	$La(NO_3)_3$	L (c)	45 d	2.3–4.3[p]	6.0	11–14	Muscle	0.04[ww]	–	–	Tu et al. (1994)
							Skeleton	0.14[ww]			
							Gill	0.26[ww]			
							Internal organs	0.12[ww]			
		L	5–45 d				Muscle	0.30–1.59[ww]	500[i]	0.60–3.18[ww,h]	
							Skeleton	0.86–2.91[ww]		1.72–5.82[ww,h]	
							Gill	2.62–8.92[ww]		5.24–17.8[ww,h]	
							Internal organs	10.0–45.6[ww]		20.0–91.2[ww,h]	
Hiodon alosoides (f, j)	La	F (1)	–	–	–	–	Muscle	0.00203 ± 0.00168[ww]	–	–	Donald and Sardella (2010)
(f, a)								0.00073 ± 0.00084[ww]			
(f, a)		F (2)						0.00036 ± 0.00044[ww]			
(f, a)							Ovaries	0.00097 ± 0.00056[ww]			
able 1 – Continued											
Cyprinus carpio	$La(NO_3)_3$	L (c)	3–43 d	2.3–4.3[p]	6.0	11–14	Muscle	0.01[ww]	–	–	Sun et al. (1996)
							Skeleton	0.02[ww]			
							Gill	0.05[ww]			
							Internal organs	1.04[ww]			
		L					Muscle	0.08–0.36[ww,q]	300[i]	0.27–1.20[ww]	
							Skeleton	0.12–1.10[ww,q]		0.40–3.66[ww]	
							Gill	1.16–4.14[ww,q]		3.86–13.8[ww]	
							Internal organs	13.6–248.4[ww,q]		45.2–828[ww]	
Oncorhynchus mykiss (m, f)	La	F (c)	14 d	–	–	–	Flesh	< LOD	–	–	Landman and Ling (2006)
(m)		F (c)	0, 14, 60 d				Liver	0.25 , 0.30 , 0.35			
(f)								0.05 , 0.20 , 0.01			
(m, f)	La (P)	F	14 d	–	–	–	Flesh	0.0029–0.0095			
(m)		F	0, 14, 60 d				Liver	0.40 , 0.50 , 0.85			
(f)								0.15, 0.50, 0.35			
Oncorhynchus mykiss (m, f)	La	F (c)	0, 14, 60 d	–	–	–	Flesh	< LOD	–	–	Landman et al. (2007)
(m)							Liver	0.35, 0.25, 0.30			
(f)								0.10, 0.05, 0.10			
(m, f)	La (P)	F					Flesh	< LOD			
(m)							Liver	0.55, 1.15, 1.20			
(f)								0.25, 0.30, 0.75			
Reptiles											
Emys trinacris	La	F (1)	–	–	–	–	Blood	0.00005[ww,r]	0.00322	13.9[ww,h]	Censi et al. (2013)
							Scute	0.03926[ww,r]		12,200[ww,h]	
		F (2)					Blood	0.00031[ww,r]	0.00651	48.1[ww,h]	
							Scute	0.02859[ww,r]		4400[ww,h]	

[a] f – female, m – male, j – juvenile, a – adult.
[b] La(P) – application of Phoslock®, a lanthanum-modified clay used as water treatment technology for remediation of eutrophied waterbodies. La concentration in leachates was measured/calculated.
[c] F – field, L – laboratory, Mi – microcosm, c – control, sw – surface water, pw – pore water, sed – sediment. CIT, NTA, EDTA – applied organic ligands (for details, see text). Figures indicate different samples/sampling sites.
[d] h – hours, d – days.
[e] Biota concentration in μg La per g dry weight (dw), unless stated as [ww] (wet weight); units converted, if necessary.
[f] Exposure concentration for water (sw, pw), unless otherwise stated.
[g] BCF – bioconcentration factor (laboratory), BAF – bioaccumulation factor (field), unless otherwise stated (for details, see text). [ww] – BCF/BAF based on wet weight.
[h] BCF calculated as $C_{biota}*10^3*(C_{water})^{-1}$.
[i] nominal concentration.
[j] Converted from $L\,g^{-1}$.
[k] Estimated from graph and units converted, if necessary.
[l] BCF dynamic, converted from ww to dw by a factor of 15 as suggested from the authors.
[m] Biomagnification factor calculated from La concentration in kg dry plant material $*kg^{-1}$ snail dry tissue.
[n] Concentration for sediment in $mg\,kg^{-1}$.
[o] BSAF – biota sediment accumulation factor [–].
[p] Recalculated from $mmol\,L^{-1}$.
[q] Calculated as $C_{biota(ww)}=BCF*C_{water}*10^{-3}$.
[r] Mean values calculated from supplementary data.

volume ratio of smaller organisms, it was assumed that a rapid adhesion of La^{3+} to the negatively charged cell envelope occurred within 24 h. In this study *E. coli* also served as a food source for the nematode *Caenorhabditis elegans* and it was concluded that the main uptake route of La into *C. elegans* was via trophic transfer and not directly from the ambient medium.

Sun et al. (1997) investigated the bioconcentration of three REE compounds including lanthanum nitrate within green algae *Chlorella vulgaris* under the influence of organic ligands. The applied ligands EDTA (ethylenediaminetetraacetic acid), NTA (nitrilotriacetic acid), and CIT (citrate) have been suggested as analogues for natural complexing compounds by Sun et al. (1997). In addition, species calculation were applied with the geochemical program MINTEQA. The three REE (lanthanum, gadolinium, yttrium) showed similar uptake characteristics with the free ion controlling bioavailability. The kinetic and the thermodynamic study both showed similar bioconcentration potentials for different species of the investigated REE: Organic ligands considerably decreased bioavailability and subsequently bioconcentration of REE by forming REE-organic complexes. The BCFs for La species ranked in descending order were as follows: La^{3+} > La-CIT > La-NTA > La-EDTA (4800–260 $L\,kg^{-1}$). The bioconcentration of REE was described as a first order uptake kinetic. A rapid uptake occurred within the first 10 h, which was most likely induced by a fast REE adsorption to binding sites of the surface membrane, e.g. functional groups of proteins. This was followed by a slower uptake of REE via slow diffusion into algae cells or by metabolic processes until equilibrium was reached within 24 h. The bioconcentration was directly related to the free ion concentration and was proportional to REE bound to membranes. Therefore, the presence of REE-organic complexes reduced the bioconcentration by means of direct competition with free ions for membrane binding sites.

3.1.2. Freshwater plants

In a 7-d laboratory study with *Hydrocharis dubia* biota concentrations up to 2641 μg La g^{-1} were reported (Xu et al., 2012). These are the highest observed among the macrophytes, however, very high exposure levels were applied and the corresponding BCFs were low (92–189 $L\,kg^{-1}$). An inverse relationship of BCF and exposure concentration was observed for lower concentrations while at higher concentrations the resulting BCFs for *H. dubia* seemed to be approximately constant. La was absorbed from surrounding water via roots and leaves and suggested to enter the plants by active transport. It was shown to cause several ultrastructural and physiological alterations (see chapter toxicity).

A similar BCF (138 $L\,kg^{-1}$) at approximately one order of magnitude lower exposure concentration was derived for the duckweed species *Spirodela polyrhiza* in a 16 day static microcosm study with different lanthanides (La, Ce, Sm, Gd, Y) (Yang et al., 1999) and different test organisms (next to the duckweed: Daphnia, gastropod, goldfish). The highest La accumulation was measured after one day for *S. polyrhiza* followed by a nearly continuous decline during the experiment.

In a third laboratory study Weltje et al. (2002a) investigated accumulation and elimination of La in the common duckweed *Lemna minor* in combination with speciation modeling of lanthanum. The La exposure level was comparable with that of polluted Rhine river water (1.39 μg La g^{-1}). No adverse effects could be observed and the duckweed showed exponential growth. The fastest uptake of La was within the first 24 h followed by slower accumulation up to approximately 96 h. Afterwards the La content in biota declined, most effectively by maintaining a high growth rate. La reduction in the medium was caused by the uptake in *L. minor* and adsorption to glass vessels (up to 25%). A comparative approach demonstrated that refreshing the medium did not result

Table 2
Lanthanum concentrations in biota, bioconcentration factors (BCF) and selected exposure conditions for marine species. Small lines (–) indicate missing or incomplete information, gaps ( ) refer to information from the same study in the previous row.

Species[a]	Compound[b]	Exposure scenario[c]	Alkalinity [mEq L^{-1}]	Salinity (‰)	pH-value [dimensionless]	Temp. [°C]	Biota, target tissue	Biota conc.[d] [μg La g^{-1} dw]	Exposure conc.[e] [μg La L^{-1}]	BCF, BAF[f] [$L\ kg^{-1}$]	Reference
Algae											
Ice algae	La	F	–	–	–	–	Whole algae	0.009 ± 0.002^{ww}	–	–	Campbell et al. (2005)
Macrophytes											
Desmarestia menziesii	La	F (up)	–	–	–	–	Whole thallus	< 0.123	–	–	Runcie and Riddle (2004)
		F(p)						0.303 ± 0.131			
Himantothallus grandifolius		F (up)						< 0.123			
		F(p)						0.229 ± 0.102			
Iridaea mawsonii		F (up)						< 0.123			
		F(p)						0.241 ± 0.077			
Ecklonia cava	La	F	–	–	–	–	Blade	0.0179	0.00216	8287[g]	Fu et al. (2000)
Ecklonia cava							Stipe	0.0083		3843[g]	
Delisea fimbriata							Whole algae	0.0340		15,741[g]	
Ptilonia okadai								0.0334		15463[g]	
Ulva fasciata								0.1110		51,389[g]	
Codium fragile								0.0329		15,231[g]	
Different brown algae	La	F	–	–	–	–	Whole algae	0.928 ± 0.798	–	300,000[h]	Hou and Yan (1998)
Different red algae								6.73 ± 8.78		2,000,000[h]	
Different green algae								10.14 ± 7.56		2,000,000[h]	
Cephalopods											
Nautilus macromphalus	La	F (1)	–	–	–	–	Digestive gland	0.30 ± 0.07	–	–	Pernice et al. (2009)
							Pericardial app.[i]	0.11 ± 0.02			
							Renal appendages	< LOD			
Nautilus pompilius	La	F (2)					Digestive gland	1.00 ± 0.04			
							Pericardial app.[i]	0.24 ± 0.03			
							Renal appendages	< LOD			
Sthenoteuthis oualaniensis (j)	La	F	–	–	–	–	Liver	$0.0044–0.1600^{ww}$	–	–	Ichihaschi et al. (2001)
(a)								$0.0019–0.0069^{ww}$			
(a, f)							21 tissues	$0.0001–0.0019^{ww}$			
Bivalves											
Mytilus edulis	La	F (1)	–	–	–	–	Kidney	0.26	–	–	Lobel et al. (1991)
							Digestive gland	0.32			
							Gills	0.19			
							Mantle	0.18			
							Foot	0.11			
		F (2)					Kidney	0.58 ± 0.033			
							Foot	0.15 ± 0.008			
Mytilus edulis	La	F	–	–	–	–	Soft tissue	1.50–5.52	–	–	Riget et al. (1996)
Pectinidae	La	F	–	–	–	–	Shell	0.013–0.018	–	–	Ohde (1998)
Glycymeridae								0.011–0.025			
Tellinidae								0.024–0.066			
Chlamys varia	La	F (up)	–	–	–	–	Digestive gland	0.08–0.28	–	–	Bustamente and Miramand (2005)

							Kidney	0.11–0.22			
							Gills	0.23–0.46			
							Gonads	0.53–0.79			
							Muscle	0.02–0.03			
							Whole soft parts	0.12–0.32			
		F (p)					Digestive gland	7.53–8.12			
							Kidney	1.28–2.11			
							Gills	2.79–5.06			
							Gonads	4.35–5.73			
							Muscle	0.21–0.32			
							Whole soft parts	2.74–2.96			
Polychaetes											
Nereis diversicolor	La	F (pw)	7.7–8.2	1.7–2.6	7.7–7.9	–	–	6.94–9.14	0.0419–0.0834	80,000–160,000[h]	Tijink and Yland (1998)
		F (sed)							26.6–37.9[j]	0.2–0.3[h,k]	
Nephtys cirrosa, Scoloplos armiger, i.a.		F (pw)	3.0	34	7.5	–	–	0.45	0.0603	7500[g]	
		F (sed)							6.3[j]	0.07[h,k]	
Crustaceans											
Paramoera walkeri	La	F	–	–	–	–	Whole body	0.10	–	–	Palmer et al. (2006)
		F (Me, up)						0.15–0.17			
		F (Me, p)						0.15–0.16			
Calanus hyperboreus		F	–	–	–	–	–	0.005 ± 0.002^{ww}	–	–	Campbell et al. (2005)
Mixed zooplankton								0.011 ± 0.016^{ww}			
Themisto libellula								0.019 ± 0.007^{ww}			
Mysis oculata								0.015 ± 0.004^{ww}			
Corophium multisetosum, Gammarus tigrinus	La	F (pw)	7.7–12.4	0.3–2.6	7.7–7.9	–	Whole body	1.25–3.74	0.0419–0.0834	20,000–63,000[h]	Tijink and Yland (1998)
		F (sed)							26.6–37.9[j]	0.05–0.15[k]	
Urothoe poseidonis, Bathyporeia guilliamsoniana, Thia scutellata, i.a.	La	F (pw)	3.0	34	7.5			0.71	0.0603	11,700[g]	
		F (sed)							6.3[j]	0.1[k]	
Corophium volutator	La	L (sw)[l]	1.2–4.5	10–30	7.3–8.4	15	Whole body	0.847–1.917	0.023–0.337		Moermond et al. (2001)
		L (pw)[l]	5.6–13.8		7.3–7.8				0.156–2.263		
		L (sed)		30	7.1					0.38[k,h]	
					7.7					0.42[k,h]	
					8.1					0.40[k,h]	
					8.5					0.48[k,h]	
		L (sed)		10	8.1					0.34[k,h]	
				20						0.30[k,h]	
				30						0.40[k,h]	
		L (sed) 0 d		30	8.1					0.02[k,h]	
		0.5 d								0.29[k,h]	
		1 d								0.31[k,h]	
		2 d								0.31[k,h]	
		10 d								0.40[k,h]	
		20 d								0.29[k,h]	
		L (sed, P+)		30	8.1					0.55[k,h]	
		L (sed, F+)								0.50[k,h]	
		L (sed, r+)								0.82[k,h]	
		F (sw)	2.2–2.4	–	7.6–8.2	14–20		0.071–0.375	0.016–0.204		
		F (pw)	3.0–30.9		7.4–8.0				0.042–0.125		
		F (sed)							6.39–130.0[j]	0.043–0.138[k]	
Corophium volutator	La	L (pw)	–	10–30	7.0–8.5	15.5	Whole body	9.0–19.0[h]	0.2–2.2[h]		Stronkhorst and Yland (1998)

L (pw)	–	28.7	7.0			9.0[h]	0.4[h]	25,000[h]	
			7.7			10.0[h]	0.5[h]	22,000[h]	
			8.5			11.0[h]	2.2[h]	5000[h]	
L (pw)		10	8.2			13.0[h]	0.3[h]	48,000[h]	
		20				12.0[h]	0.2[h]	54,000[h]	
		30				11.0[h]	2.2[h]	5000[h]	
L (pw, r+)		30	8.2			19.0[h]	0.3[h]	75,000[h]	
L (pw)	–	–	–	–	–	–	–	22,387	
F (pw)	–	–	–	–	–	–	–	28,840	

[a] j – juvenile, a – adult, f – female.
[b] No specific La compound was mentioned in the laboratory studies.
[c] F – field, L – laboratory, Me – mesocosm, up – unpolluted, p – polluted, sw – surface water, pw – pore water, sed – sediment. d – days. P+ – PO_4 added. F+ – Fluoride added. r+ – Test with sediment resuspension. Numbers in brackets indicate different samples/sampling sites.
[d] Biota concentration in μg La per g dry weight (dw), unless stated as [ww] (wet weight); units converted, if necessary. LOD – limit of detection.
[e] Exposure concentration for water (sw, pw), unless otherwise stated.
[f] BCF – bioconcentration factor (laboratory), BAF – bioaccumulation factor (field), for details, see text.
[g] BAF calculated as $C_{biota} * 10^{3*}(C_{water})^{-1}$
[h] Estimated from graph.
[i] pericardial appendages.
[j] Concentration given for sediment in mg/kg.
[k] BSAF – biota sediment accumulation factor [–].
[l] Tested under different exposure conditions.

in higher La concentration in biota. Speciation calculation revealed that La was in solution up to pH 5.6 and was mainly associated with EDTA (99.9%). Higher pH-values and lower EDTA concentration would have led to precipitation of La with phosphate. It was assumed that La could be taken up in macrophytes as La-EDTA complex and as La^{3+}. Since no equilibrium was reached, a dynamic BCF was calculated. With increasing exposure time, the corresponding BCF of *L. minor* declined. The BCF based on wet weight (1145–2198 L kg^{-1}) was about one order of magnitude higher at a much lower nominal exposure concentration than those in previous mentioned experiments. However, a comparison of the La accumulation potential of these different macrophytes is questionable due to large concentration varieties among the studies.

The results for the duckweed were supported by measurements from a field survey in the Netherlands (Weltje et al., 2002b). At five locations in the catchment of Rhine and Meuse estuary the distribution of 14 lanthanides between sediment, water, and biota were examined.

Organisms with different exposure routes were collected and the Ln concentrations of the related compartments were determined. The BAFs (12,000–20,000 L kg^{-1}) for *L. minor* from this field survey (Table 1) were roughly in same order of magnitude as the ones for *L. minor* from the laboratory study with BAFs of 17,000–33,000 L kg^{-1} (Weltje et al., 2002a). The La content in the sago pondweed *Potamogeton pectinatus* from the field survey and the resulting BAF had a larger range (2000–300,000 L kg^{-1}) and were mostly higher than those of the duckweed. Variation in accumulation between both plants with biota concentrations of 0.139–0.347 μg La g^{-1} and 0.111–11.1 μg La g^{-1}, respectively, could probably be explained by different numbers of sampling sites and varying exposure routes. *L. minor* accumulated via surface water, whereas for *P. pectinatus* pore water was the main uptake route and, to a lesser extent, surface water.

Moreover, the authors suggested that the large differences among the sago pondweed samples might also be related to biological variations and divergent bioavailability of contaminants at the sampling sites.

Wolterbeek and van der Meer (1996) found similar BAFs and biota concentrations for the macrophytes *Azolla filiculoides* and *Ceratophyllum demersum* compared to *L. minor*. They assumed that the submerged species *C. demersum* probably accumulated a larger amount due to the larger surface for absorption than the floating plant *A. filiculoides*. In comparison to these findings Cowgill (1973) measured higher La concentrations in seven aquatic macrophytes from a pond with only a minor variation among the species. Greater accumulation was observed in emerged plants in comparison with submerged plants and the suggested main uptake route was via the roots from sediment. In most plants, there were no specific distribution patterns between the different parts. An exception was provided by the La enriched flowers and flower stalks of *Nymphaea odorata*.

3.1.3. Mollusks

In the previously mentioned field study from Weltje et al. (2002b) different mollusks possessed a similar range of biota concentrations and BAFs as the macrophytes. Five snail species from various locations had BAFs from 9000–250,000 L kg^{-1} and the BAFs for the bivalves *Corbicula fluminae* and *Dreissena polymorpha* collected from the same location were 12,000 and 32,000 L kg^{-1}, respectively, indicating a higher bioaccumulation in *D. polymorpha* (Table 1). Significant variations in bioaccumulation between the mollusks from different locations could possibly be explained by different feeding pathways (snails as grazers, bivalves as filter feeders), exposure routes (surface water or pore water, e.g. for sediment-burrowing species), and site-specific La availability.

For snails, food is a dominant source for lanthanides. But in this study only little biomagnification occurred with biomagnification factors of 0.55–5.50 kg kg^{-1}. For all species, the soft tissue concentration exceeded the concentration in the shell with a shell to tissue ratio of 0.01–0.3 kg kg^{-1}. In comparison to this study Tijink and Yland (1998) reported considerably higher La content in the soft tissue of *C. fluminae* (factor 2–15). However, the BAFs were only two to four-fold increased, because accumulation was based on pore water concentration. Porewater usually has a higher La concentration than surface water, which had been used for calculating BAFs in the former study.

An increase of La uptake in soft tissue was also observed with increasing sediment concentration but BSAF values were small (0.04–0.07) and indicated low La accumulation ability from the sediment by these bivalves. La amounts in the shells of gastropods and bivalves from both surveys were in the same order of magnitude.

3.1.4. Vertebrates

Two laboratory studies with juvenile carp *Cyprinus carpio* examined the accumulation of lanthanum nitrate and other REE from water into different fish tissues at various exposure times (Sun et al., 1996; Tu et al., 1994). Both experiments revealed similar accumulation patterns with by far the highest bioconcentration into internal organs (up to 45.6 μg La g^{-1}and 248.4 μg La g^{-1}, respectively), followed by gills, skeleton and muscle (Table 1). While the BCFs for internal organs were higher in the study with lower La exposure (828 L kg^{-1} vs. 91 L kg^{-1}), it was the opposite with regard to the other tissues. Tu et al. (1994) showed that accumulation increased with time in all organs for single and mixture REE application and reached equilibrium approximately at the end of the 45-d experiment. Further, no synergistic or antagonistic response was observed while the REE-mixture was applied. Also, a similar accumulation pattern for the different REE occurred, whereby La and Gd accumulated to a greater extent than Y. The accumulation study of Sun et al. (1996) with five light lanthanides included an elimination experiment. For Ln, the elimination process from muscles, gills, and skeleton could be described as a two-compartment model, where a rapid loss of unbound lanthanides during the first days was succeeded by a slower elimination of bound forms until the equilibrium was reached. A different elimination process was described for the internal organs. At first, accumulation increased for two days because lanthanides were distributed from other tissues to the internal organs. In a second phase the elimination starts in form of a one-compartment model, in which lanthanides were detoxified and stored. Although the Ln concentrations in internal organs were high, the BCFs in carp were comparatively low, especially those of the muscles. This probably indicates a minor risk of biomagnification.

Donald and Sardella (2010) collected juvenile and adult female goldeyes *Hiodon alosoides* from two relatively pristine lakes and measured several trace metals in muscles and ovaries. Due to the long life span, slow growth and similar food sources throughout the life of *H. alosoides,* a long-term equilibrium of internal metal concentrations was assumed. The La concentrations in muscles of juvenile females were significantly higher than those of adult females. Moreover, ovaries contained significantly greater amounts of La than muscles of adult goldeyes (factor 2.7). This enrichment was comparable to those of essential elements like zinc and manganese and indicated a loss of metal content via eggs during spawning. Both results showed that La concentration in tissues, similar to other metals, depends on the life stage of the goldeye.

Phoslock®, a lanthanum modified clay, is used for remediation purposes in eutrophic lakes, where the active component lanthanum generates insoluble phosphate complexes. During a large-scale treatment in Lake Okareka a three-year fish health monitoring program was implemented to get information on bioaccumulation and on chronic effects of released La (Landman and Ling, 2006). From the second year of application, another lake served as an untreated reference site. Lanthanum accumulation in rainbow trout *Oncorhynchus mykiss* and the freshwater crayfish *Paranephrops planifrons* was measured each year before the lake treatment as well as 14 d and 60 d afterwards. In the flesh of rainbow trout from both lakes only a few samples exhibited La concentrations above the limit of detection (LOD). In contrary, a significant raise of La accumulation occurred in the liver of male trout from Lake Okareka up to the third sampling (0.85 μg La g^{-1}) when compared with fishes from the reference lake. The content in female trout increased significantly until the second sampling. In the third year the accumulation pattern was similar, as La concentrations in the liver of both, male and female, significantly increased during the whole sampling period (Landman et al., 2007). Moreover, uptake in male livers was faster and to a greater extent (1.25 μg La g^{-1}) than that in female livers (0.75 μg La g^{-1}), indicating sex-specific variations in uptake. In addition, the pre-application measurement yielded in slightly higher biota concentrations and the maximum values were elevated compared with the previous monitoring. This could probably be a consequence of the long-term exposure without full recovery between the treatments. However, it was supposed that seasonal and physiological impacts could have altered the La bioavailability. In comparison, only minor La accumulation was observed in muscle tissue of the crustacean *P. planifrons*, but La was taken up significantly into the hepatopancreas of the crayfish from the treated lake with a maximum concentration of 0.93 μg La g^{-1} (Landman and Ling, 2006). Similar results were reported by Landman et al. (2007) for the third monitoring, indicating a biological depuration mechanism for La.

The accumulation of environmental lanthanide concentrations in aquatic turtles *Emys trinacris* collected from two wetland areas with different anthropogenic impact were examined by Censi et al. (2013). Very low Ln content was measured in blood samples, whereas especially with La, increasing exposure was accompanied by a raise of concentration in the blood. Bioaccumulation, however, occurred largely in the exoskeleton of *E. trinacris* with BAFs of about 4400 and 12,200 L kg^{-1}. In this case an inverse relationship between exposure concentrations and BAFs could be observed. The BAFs of the turtles are in a range similar to those of the bivalve *C. fluminae*. The authors assumed that lanthanide accumulation as phosphates into the exoskeleton serves as a physiological measure reducing the Ln content in blood.

3.2. Lanthanum bioaccumulation in marine organisms (Table 2)

3.2.1. Macroalgae

The highest La concentration in marine organisms was reported by Hou and Yan (1998) for macroalgae. During a field survey 35 different algae species were collected at the Chinese coast from 'relative clean sampling sites' and were analyzed for different elements. La absorption capacity in green and red algae (10.14 μg La g^{-1} and 6.73 μg La g^{-1}, respectively) exceeded that in brown algae by approximately one order of magnitude. The BAFs of La (2,000,000 L kg^{-1}) were among the highest for metals and indicated elevated bioaccumulation (Table 2). In comparison with marine algae, terrestrial plants (kale and spinach) accumulated REE to a 10–20 fold lower extent and BAFs were much smaller ($<$ 1000 L kg^{-1}), while concentration in seawater was much lower than that in soil solution. Additionally, seasonal variation in metal uptake was investigated with the brown algae *Sargassum kjellmanianum*. La showed a less pronounced increase of accumulation during the middle growth period in February in comparison with some other elements.

Fu et al. (2000) conducted a study with five seaweed species collected from a Japanese coastal area. The biota concentration of La and BAFs were about one to two orders of magnitude lower than in the previous study, but exhibited a similar pattern with higher BAFs for green and read algae (15,200–51,400 L kg^{-1}) than for brown algae (3800–8300 L kg^{-1}). Different REE patterns among the seaweed species were related to different ambient distributions of lanthanides: The brown algae *Ecklonia cava* showed Ln composition similar to that of seawater, whereas the patterns for green algae (*Ulva fasciata*, *Codium fragile*) and red algae (*Delisea fimbriata*, *Ptilonia okadai*) were comparable to those of REE-containing suspended silicate particles. Therefore, different uptake routes were suggested with a lower efficiency for Ln accumulation from seawater than from silicate particles.

Lanthanum concentration in marine macroalgae from East Antarctica showed intermediate values among the macrophytes. Runcie and Riddle (2004) measured metal concentrations in three different species at three locations, one site with contaminated melt water run-off from an abandoned waste area as well as two reference sites. The La content from all reference samples were below LOD, while the biota concentrations in macrophytes from the contaminated site were all significantly enhanced with low inter-specific variation among two brown and one red algae (0.229–0.303 μg La g^{-1}).

3.2.2. Invertebrates

Two relevant investigations with cephalopods were conducted. Pernice et al. (2009) analyzed trace elements in digestive and excretory tissues of two nautilus species with similar physiology but from different geographic areas. The results supported the importance of digestive glands for accumulation, metabolism and storage. Lanthanum uptake in digestive glands of *Nautilus macromphalus* and *Nautilus pompilius* were three and four times higher compared with pericardial appendages, whereas concentrations in renal appendages were below LOD (Table 2). In the tissues of *N. pompilius* lanthanide concentrations (but no other elemental concentrations) were significantly increased in comparison with those of *N. macromphalus*, with concentrations in the digestive gland of 1.0 and 0.3 μg La g^{-1}, respectively. This phenomenon was probably related to specific environmental conditions like volcanic activity and upwelling at the habitat of *N. pompilius*.

Purpleback flying squid *Sthenoteuthis oualaniensis* collected in the Indo-Pacific Ocean demonstrated age dependent differences in accumulation of trace elements (Ichihashi et al., 2001). Among 21 tissues of mature female squids a variation in La concentrations was observed whereas the liver contained the highest amounts. The liver of adult squids possessed significantly lower La concentrations (0.0019–0.0069 μg La g^{-1}) with a smaller range than that of juveniles (0.0044–0.16 μg La g^{-1}). The same pattern occurred for other lanthanides and some essential elements. Squids represent a high trophic level in the marine food web thus, besides seawater, diet may contribute to accumulation. Therefore it was assumed, that changing food sources during the life span of *S. oualaniensis* were responsible for the variations between stages. However, analyzing the adult stomach content yielded relatively high amounts of lanthanides and other elements, which seemed to contradict this hypothesis, as stated by the authors.

Several investigations of the fate of La after uptake by molluscs indicate that they undergo detoxification processes through adsorption to insoluble fractions within the cells of the digestive gland. Chassard-Bouchard and Hallegot (1984), for example, deduced from the observation, that La was usually accompanied by high phosphorous amounts in the lysosomes of *M. edulis*, that La was accumulated as insoluble lanthanum-phosphate in organelles, after uptake of soluble La-species via the gills or the digestive gland. The storage of large amounts of insoluble compounds, not involved in intracellular regulation mechanisms, could also well be responsible for the high residual variability in tissue concentration of elements like lanthanides (Lobel et al., 1991).

Bustamante and Miramand (2005) argued in the same direction when they compared the tissue concentration and partitioning of the lanthanides La, Nd, and Ce among other trace elements in the variegated scallop *Chlamys varia*. The animals were collected from an unpolluted and a polluted location in the Atlantic Ocean near the French coast. The contamination resulted from different anthropogenic sources, such as discharges from a lanthanide extracting plant. All bivalve tissues from the polluted site showed higher concentrations of most trace metals, also of La and the other lanthanides. Digestive glands followed by gonads and gills showed the highest uptake of REE (e.g. up to 8.12, 5.73, and 5.06 μg La g^{-1}, respectively). Lowest La-concentrations were measured in muscle (up to 0.32 μg La g^{-1}). While the elevated lanthanide concentration in gills was explained by direct seawater exposure it was assumed, that the high assimilation in gonads was caused by transport from the intestine after uptake via food particles. On a subcellular level, the three lanthanides, as well as Ag and Al, were mainly found associated with organelles, membranes or granules in the digestive gland but not dissolved in the cytoplasm (La: 81%; Ce: 83%; Nd: 82%). As bioaccumulation in these insoluble fractions is a known detoxification process of scallops, transfer along the food chain was suggested to be limited.

This assumption is supported by the results of Campbell et al. (2005) investigating the trophodynamics of trace elements in the Artic marine food web. La among other non-essential elements showed higher amounts in algae and zooplankton (0.005–0.019 μg/g ^{ww}) in comparison with the tissue concentrations in fish, seals and birds. The authors concluded that these elements could be easily bioconcentrated by pelagic plankton, while the trophic transfer via food uptake to higher biotic levels was supposed to be limited.

The relationship between elemental concentration and length of blue mussels *Mytilus edulis* from four unpolluted sites in the West Greenland fjord system was investigated over three years by Riget et al. (1996). For lanthanides and some other metals, shell length and elemental concentration were significantly positively correlated, indicating that elements were accumulated faster than mussels grew. The lanthanum level exhibited the strongest positive relation with mussel size with an increase of about 100% while shell length was doubled. Accumulation in *M. edulis* (1.50–5.52 μg La g^{-1}) from artic seawater was the highest among bivalves from uncontaminated sites. The observed variability of the relationship between length and elemental uptake could not be related to different locations and years.

Recent shells from several molluskan species collected in the Pacific Ocean (Ohde, 1998) showed similar La amounts as those of freshwater bivalves (Tijink and Yland, 1998). In comparison with soft tissue concentration from the previous studies, the La content in recent marine shells was about one order of magnitude lower.

In an extensive field monitoring program in the Rhine-Meuse estuary and North Sea, Tijink and Yland (1998) examined bioaccumulation in different species from brackish and seawater locations with different anthropogenic impact. The biota concentrations (6.94–9.14 μg La g^{-1}) of the polychaete ragworm *Nereis diversicolor* collected from brackish water were among the highest values for marine and freshwater fauna. The same holds true for the BAFs (80,000–160,000 L/kg) related to La concentration in pore water and the BSAFs in the range of 0.2–0.3. Considerably lower accumulation, about one order of magnitude, was assessed for a group of marine polychaetes (e.g. *Nephtys cirrosa*) from a seawater site with a similar exposure concentration. It was assumed that elevated ion content probably caused lower La availability due to formation of La-hydroxide-complexes. A similar distinction was

observed between crustaceans from brackish and marine locations, with higher accumulation in *Corophium multisetosum* and *Gammarus tigrinus* with a range of 1.25–3.74 μg La g^{-1} and elevated BAFs of 20,000–63,000 L/kg and BSAFs of 0.05–0.15 μg La g^{-1} in comparison to those of some crustaceans from a marine habitat, i.a. *Urothoe poseidonis* (Tijink and Yland, 1998). In addition, a comparable range of BAFs was observed during the same monitoring for the bivalve *C. fluminae* (see freshwater section), as well as for the amphipod *Corophium volutator* (BAF 28840 L/kg) in a field study by Stronkhorst and Yland (1998). On the other hand, biota concentration of La in *C. volutator* from field sampling and corresponding BSAFs examined by Moermond et al. (2001) were about one order of magnitude below those of *C. multisetosum* and *G. tigrinus*.

Stronkhorst and Yland (1998) and Moermond et al. (2001) conducted a comprehensive laboratory experiment where *Corophium volutator* was exposed to all non-radioactive light and heavy rare earth elements. Since the design and the results of the studies are nearly identical, they presumably relate to the same experiment. To avoid redundancy in Table 2 the BSAFs were taken from Moermond et al. (2001) only, supplemented by the BCFs from Stronkhorst and Yland (1998). Since *C. volutator* lives in mud flats, pore water and sediment were expected to be the main routes of exposure. The bioassays were carried out with natural sediments under different experimental conditions regarding pH-value, salinity, duration, sediment resuspension, and separate addition of phosphate and fluoride to simulate gypsum disposal. A test series with durations between 0.5 to 20 days showed a rapid La uptake during the first day and a subsequent lower rise with the highest accumulation after 10 days, which was used as the exposure time for the following experiments. No clear relationship between a change in pH-value or salinity and the BSAF could be observed. On the other hand the BCF decreased considerably at the highest pH-value (8.5) and maximum salinity (30‰) by a factor of five and ten, respectively, to 5000 L/kg. Daily resuspension of sediment during the experiment led to a decrease in pore water concentration and a strong enhancement in bioavailability, as well as bioaccumulation from water and sediment. The BSAF was also increased by separate addition of phosphate and fluoride. Lanthanides' BSAFs decreased with atomic number, from lanthanum to lutetium with a factor of two, and had the same order of magnitude as the BSAF for heavy metals, since both potentially were affected by the same conditions. The BSAFs for *C. volutator* determined from field samples were significantly lower than those of the laboratory experiments, probably indicating an adaptation of the amphipod to environmental conditions. Among the few marine studies all derived field BSAFs were in a similar range.

In addition, Moermond et al. (2001) investigated the influence of lanthanide distribution, speciation and accumulation in *C. volutator* during laboratory experiments and field monitoring. Lanthanide speciation was determined with equilibrium model MINEQL+ and showed clear differences between the various elements. In fresh as well as marine waters, complexation to Ln $(CO_3)_2$ increased, and relative abundances of the free ion (Ln^{3+}) and of $LnCO_3$ decreased, for all Ln from La to Lu. Accordingly, lanthanum was calculated to occur predominantly as carbonate (not bicarbonate) and humate complexes in fresh- and pore-waters, with the abundance of humate complexes decreasing towards the sea, with increasing ionic strength. Moreover, pH had a major influence on lanthanum speciation. At low pH 6 the humate complexes were most abundant, followed by free ions, lanthanum sulfates and small amounts of carbonates. With increasing pH (up to 7.5–8) free ions and sulfates vanished, while the abundance of carbonates rose simultaneously. At higher pH (up to 9) carbonates were the main complexes. Moermond et al. demonstrated that no single Ln species was specifically relevant for uptake into organisms and several correlations between lanthanide species and accumulation factors existed. A multiple-regression model identified especially alkalinity, pH, ionic strength, and organic carbon concentration as most significant environmental variables describing bioaccumulation. The negative correlation between biotic uptake and alkalinity indicated that increasing carbonate complexation reduces the abundance of bioavailable species like free ions and hydroxides. pH and ionic strength influenced uptake from the water phase, while they had no strong effect on the BSAF.

The gammaridean amphipod *Paramoera walker* was deployed as a biomonitor for metal accumulation in a mesocosm study during a remediation process of a disposal waste site in East Antarctica (Palmer et al., 2006). The biota concentrations in amphipods were slightly enlarged during experiments (0.15–0.17 μg La g^{-1}) compared with a previously deployed sample, probably due to differences in nutrition. However, no variations in La bioaccumulation of *P. walker* could be found between the reference sites and those potentially impacted by contaminated melt water. These findings are in contrast to the results of Runcie and Riddle (2004), which demonstrated site-specific differences in the La uptake of macroalgae from the same catchment.

4. Aquatic ecotoxicity of lanthanum compounds

Bioaccumulation itself is not an indicator for a toxic response, since only a certain proportion of the total internally accumulated metal concentration, the body burden, might be metabolically available. This fraction then causes adverse effects at the target site by metal binding to specific receptors essential for cellular function. Other portions of metals can become detoxified within the cells by binding to metallothionein or other proteins regulating the cellular metal content, or by precipitating with sulfides or phosphates (McGeer et al., 2004). By quantifying these physiologically inactive metals on a sub-cellular level, e.g. by fractionation of organelles, an indicator for site-specific adverse effects could be found (Vijver et al., 2004).

In terms of a mechanistic concept, toxicity occurs when the metal uptake rate into an organism from all exposure routes exceeds the loss rate by detoxification and excretion (Luoma and Rainbow, 2005). The relationship between bioaccumulation and toxicity is influenced by several factors, such as metal speciation (free-ion, complex, particle-bound), uptake routes (waterborne, sediment-borne, diet-borne) and subsequent sequestration, species-specific physiological activities, and environmental conditions (Ahlf et al., 2009; Luoma and Rainbow, 2005). Therefore, it is challenging to identify and measure the responsible fractions for toxic pressure. In risk assessment, effect concentrations are usually derived from external exposure concentrations (water, sediment) investigated in experimental studies. The statistical endpoints for acute toxicity are reported mostly as the half-maximum effective or lethal concentrations (EC50 and LC50, respectively) and for chronic toxicity as no observed effect concentration (NOEC) or the concentration that causes an effect in 10% of the organisms (EC10).

The toxicity of lanthanum has been described by a wide range of effect thresholds. Apart from interspecies differences, the main reasons for this are numerous variations in test designs and conditions, which could alter its speciation and bioavailability. In particular, the strong association of lanthanum with various ligands and the potential precipitation during experiments is an ambitious challenge for conducting ecotoxicological tests.

Experiments used different La compounds, mostly La salts like lanthanum chloride ($LaCl_3$) and lanthanum nitrate ($La(NO_3)_3$), but also lanthanum oxide (La_2O_3) and lanthanum carbonate ($La_2(CO_3)_3$). Furthermore, numerous studies were carried out with Phoslock® (Douglas, 2002; Robb et al., 2003; Haghseresht et al.,

2009) which has been introduced differently in test systems (Afsar and Groves, 2009). In general, Phoslock® studies were only considered in this review if La concentrations in Phoslock® leachates were used to derive an effect level. To prepare leachates a suspension of modified clay in water is usually filtered through a 0.45 μm membrane, as described in detail, for example, in the standard Toxicity Characteristic Leaching Procedure used by Stauber (2000).

Concentration and availability of lanthanum is greatly influenced by the exposure method, with static or renewed test media, and by the medium composition with various physicochemical parameters, e.g. pH, temperature, complexing ions, chelating agents, and water hardness. Especially the latter could have a huge impact on the ecotoxicity of lanthanum (Evans, 1983; Barry and Meehan, 2000). Moreover, the assessment of toxicity parameters largely depends on the way the La concentrations were captured. In most studies, rapid La precipitation took place after the start followed by a further decline of the La amount. As a consequence, nominal and measured concentrations could differ considerably as well as initially measured concentrations compared with averaged ones from the whole test period (e.g. Stauber and Binet, 2000; Lürling and Tolman, 2010; Bogers 1995c). Dissolved concentrations of La are mainly responsible for adverse effects (Weltje 2002). When EC50s are calculated from total concentrations, the toxicity is underestimated. Additionally, material of filter membranes could affect the La ion concentration by adsorption processes (Weltje et al., 2003). In order to achieve a better comparability across the studies, the ecotoxicity data in Tables 3 to 5 are supplemented by further relevant information of the test design.

Since only a small number of peer-reviewed papers for La toxicity exist, the databases for the tables were enlarged with other available and scientifically sound sources, such as GLP-studies and reports to gain further insight into impacts of lanthanum in aquatic systems and identify research gaps. By far the most studies were performed with freshwater species (Table 3), whereas only a few studies exist with marine organism (Table 5). The few experiments addressing sediments were conducted with freshwater species only (Table 4).

4.1. Toxicity of lanthanum in freshwater (Table 3)

4.1.1. Algae, ciliates and bacteria

When testing the toxicity of La to microorganisms, care must be taken not to confuse indirect and direct toxic effects. La has a high affinity to phosphate and forms insoluble lanthanum phosphate complexes which precipitate in the medium (Petersen et al., 1974; Stauber and Binet, 2000). An observed adverse effect on algae growth could thus be due to phosphate-limitation rather than to direct interactions of the organisms with La. In a study with the green algae *Raphidocelis subcapitata* (formerly: *Pseudokirchneriella subcapitata* and, *Selenastrum capricornutu*m), Petersen et al. (1974) measured residual phosphate–phosphorus (PO_4–P) and concluded that lanthanum chloride ($LaCl_3$) had removed 100% of phosphate from artificial medium and pond water at a cation: PO_4–P molar ratio of 0.9–1.0 and a pH range of 6–9 and 6–10, respectively. While the algae cell count was reduced with increasing La concentration (no EC was given) in a batch experiment, this effect was not observed when the phosphorus concentration was reconstituted to approximately that of the control medium. The authors concluded the residual La had no significant toxic effect up to a nominal concentration of 2.0 mg $LaCl_3$ L^{-1}. Reversible inhibitions were caused by $LaCl_3$ (225–250 μM) on several cellular systems of the green algae *Micrasterias torreyi* like differentiation of dividing cells, the division of interphase cells as well as growth (Lehtonen, 1984). Further, La reversibly inhibited the phototaxis of green algae *Chlamydomonas reinhardtii* and the photophobic response in blue–green algae *Phormidium uncinatum* by blocking the Ca^{2+}-pump and reducing conductivity (Nultsch, 1979; Häder, 1982).

Information from four chronic algal studies is available which were all performed with green algae and lanthanum salts, $LaCl_3$ or $La(NO_3)_3$ (Table 3). The water hardness was reported in only one study, so its impact on algal toxicity remains unclear. Furthermore, due to the use of nominal and total concentrations in most studies the toxicity could also be underestimated.

Effect levels for the growth inhibition differ markedly with an EC50 of 0.45 mg La L^{-1} (NOEC 0.13 mg La L^{-1}) for *Raphidocelis subcapitata* (Stauber and Binet, 2000) and an EC50 of 13.0 mg La L^{-1} (EC10 of 1.30 mg La L^{-1}) for *Scenedesmus subspicatus* (Bogers, 1995c). The La concentrations given in both studies were derived from initial measurements, since some lower concentrations had been beneath the LOD at the end of the studies. Stauber and Binet (2000) assumed that the high sensitivity was due to an indirect toxicity caused by nutrient depletion as stated above. Additionally, Bogers (1995c) investigated the impact from algae on La concentration, comparing saturated La solutions with and without algae in the medium. After 72 h the La concentration in the algae free medium was nearly stable, while it decreased in the presence of algae. Accordingly, adsorption of La^{3+} to the surface of algae cells was suggested as the depletion mechanism.

In a long-term study Jin et al. (2009) analyzed the effects from $La(NO_3)_3$ in the presence of different EDTA-levels on growth and competition of microalgae (*Scenedesmus quadricauda*) and cyanobacteria (*Microcystis aeruginosa*). Low amounts of EDTA and low La concentrations (7.2 μmol L^{-1}) stimulated the growth of both organisms, while La concentrations of 72 μmol L^{-1} significantly inhibited the growth of *M. aeruginosa* and *S. quadricauda*. The latter has been supported by findings from Oosterhout and Lürling (2013). However, intermediate amounts of complexing agents (2.69–13.4 μmol L^{-1} EDTA) reduced inhibitory lanthanum effects on *M. aeruginosa* but not that on algal growth, so community structure could be disturbed with the possibility of cyanobacteria blooms (Jin et al., 2009).

Tetrahymena shanghaiensis, a ciliate grazing on planktonic bacteria, showed very low sensitivity in short and long-term exposure on cell proliferation (Wang et al., 2000). Growth inhibition occurred only at high La concentrations, while at low concentrations growth was stimulated.

4.1.2. Macrophytes

Two available studies displayed huge species-specific differences in the toxicity of $La(NO_3)_3$ to macrophytes. was exposed to, already Numerous significant physiological and cellular effects occurred in the leaves of *Hydrocharis dubia* from the frog's-bit family at a low La concentration of 5.56 mg La L^{-1} (Xu et al., 2012). This were, for example, a decrease of Ca^{2+} and Mg^{2+}, a decline of the pigments chlorophyll (Chl.a, Chl.b) and carotenoids, an increase of the activities of some antioxidant enzymes and malondialdehyde (MDA) content as indicator for lipid peroxidation. Furthermore, alteration of the cellular ultrastructure of chloroplasts, mitochondria and nucleus were observed at a concentration of 11.1 mg La L^{-1}, probably caused by oxidative damages triggered by a lanthanum induced rise of ROS (reactive oxygen species) production. The deficiency of Mg^{2+} and Zn^{2+} caused by La was probably responsible for the disturbance of chlorophyll biosynthesis and ultrastructural damages in chloroplasts (Wang et al., 2007; Xu et al., 2012). Since no phosphorus deficiency had occurred during La application in *H. dubia* leaves, all effects were attributed to the toxicity of lanthanum. The reported EC50, however, is beneath the lowest tested concentration and therefore hardly meaningful. In contrast to these results, significant toxic

Table 3
Effect concentrations and selected exposure conditions for freshwater species. Small lines (-) indicate missing or incomplete information, gaps ( ) refer to information from the same study in the previous row. Table structure is according to Ng et al. (2011) with modifications.

Species[a]	Compound[b]	Exposure method[c]	Exposure time[d]	Exposure data[e]		Hardness [mg $CaCO_3$ L^{-1}]	pH-value [-]	Temperature [°C]	Endpoint, biological	Endpoint, statistical[f]	Effect conc.[g] [mg La L^{-1}]	Reference
Bacteria												
Microcystis aeruginosa	$La(NO_3)_3$	S	20 d	N	T	–	8.0	28	Growth	NOEC	1.00[h]	Jin et al. (2009)
Microcystis aeruginosa	$La(NO_3)_3$	S	7 d	N	T	–	–	21	Growth rate	NOEC	2.50	Oosterhout and Lürling (2013)
Microalgae												
Scenedesmus subspicatus	$LaCl_3$	S	72 h	MI	D	24	6.7–8.4	21–22	Cell growth	EC50	13.0[i]	Bogers (1995c)
										EC10	1.40[i]	
									Growth rate	EC50	16.0[i]	
										EC10	1.30[i]	
Raphidocelis subcapitata	$LaCl_3$	S	72 h	MI	T	–	5–10	24 ± 2	Growth	EC50	0.450[i]	Stauber and Binet (2000)
										NOEC	0.13[h]	
Scenedesmus quadricauda	$La(NO_3)_3$	S	20 d	N	T	–	8.0	28	Growth	NOEC	1.00[h]	Jin et al. (2009)
Scenedesmus obliquus	$La(NO_3)_3$	S	72 h	N	T	–	–	21	Growth rate	NOEC	2.50	Oosterhout and Lürling (2013)
Ciliates												
Tetrahymena shanghaiensis	$La(NO_3)_3$	S	24 h	N	T	–	7.0	27	Cell count	IC50	277.8	Wang et al. (2000)
			96 h						Pop. growth	NOEC	55.6[h]	
Macrophytes												
Hydrocharis dubia	$La(NO_3)_3$	SR	7 d	M	T	–	–	–	Chlorophyll	EC50	2.778	Xu et al. (2012)
										NOEC	< 5.560[h]	
Lemna minor	$La(NO_3)_3$	S	5 d	N	–	–	–	24	Chlorophyll	NOEC	695.0[h]	Ippolito et al. (2010)
Crustaceans												
Daphnia magna	$LaCl_3$	SR	21 d	MA	D	250	7.0–8.4	20–21	Reproduction	EC50	> 0.620	Bogers (1995a)
									Mortality	LC50	0.552	
										NOEC	0.100	
Daphnia magna	$La(NO_3)_3$	SR	14 d	N	T	88	7.6	20	Mortality	NOEC	1.000	Lürling and Tolman (2010)
									Reproduction	NOEC	0.330	
		SR	14 d	M	D	88	7.6	20	Mortality	NOEC	1.001	
									Reproduction	NOEC	0.099	
Daphnia magna	$LaCl_3$	S	72 h	N	T	29–30	7.0 ± 0.2	18 ± 2	Mortality	TL_m	1.590	Peterson et al. (1974)
			96 h							TL_m	0.910	
Daphnia magna	$La_2(CO_3)_3$	S	48 h	N(M)A	T (D)	250	7.8	20	Immobility	NOELR	> 100 (> 0.097)[j]	Seyfried (2007a)
Daphnia magna	La_2O_3	S	48 h	N(M)	T (D)	250	7.8–7.9	20	Immobility	NOELR	> 100 (> LOD)[j]	Seyfried (2007b)
Daphnia magna	La_2O_3	SR	21 d	N(M)	T (D)	250	7.2–8.7	19–21	Reproduction	NOELR	> 100 (> 0.048)	Höger (2009)
Daphnia magna	–	S	48 h	M	T	210	6.5–8.2	–	Immobilization	EC50	24.0	Den Ouden (1995)[k]
Daphnia magna	La (P)	S	48 h	M	D	128	6.8–8.3	20 ± 2	Mortality	LC50	> 63.3[i]	Watson-Leung (2009)
Daphnia carinata	$LaCl_3$	SR	48 h	MA	D	160	7.5	20 ± 2	Mortality	EC50	1.180	Barry and Meehan (2000)
						98	7.8			EC50	0.049	
						22	7.8			EC50	0.043	
Daphnia carinata	$LaCl_3$	SR	21 d	MA	D	160	7.5	20 ± 2	Mortality	NOEC	0.040[h]	Barry and Meehan (2000)
									Age of maturity	NOEC	0.030[h]	
Ceriodaphnia dubia	$LaCl_3$	SR	48 h	MI	T	40–48	7.0	25 ± 1	Mortality	LC50	5.000[i]	Stauber and Binet (2000)

										NOEC	2.600	
Ceriodaphnia dubia	$LaCl_3$	SR	7 d	MI	T	40–48	7.9	25 ± 1	Mortality	LC50	0.510	Stauber and Binet (2000)
									Reproduction	EC50	0.430	
										NOEC	0.050	
Ceriodaphnia dubia	La (P)	S	48 h	MI	D	40–48	7.9	25 ± 1	Mortality	LC50	0.080[m]	Stauber (2000)
					D (uf)					LC50	0.056[m]	
					D	–	7.0			LC50	0.040[m]	
Ceriodaphnia dubia	La (P)	SR	7 d	M	D	40–48	7.9	25 ± 1	Mortality	LC50	0.824[m]	Stauber (2000)
									Reproduction	NOEC	< 0.126[m]	
Hyalella azteca	La_2O_3 in HCl	S	7 d	N	T	124	7.2–9.0	24–25	Mortality	LC50	1.665	Borgmann et al. (2005)
				M	D	18	6.4–8.7			LC50	0.018	
Nematodes												
Caenorhabditis elegans (j)	$LaCl_3$	SR	72 h	N	D	–	–	20	Brood size	EC50	1.970	Zhang et al. (2010)
										NOEC	0.139	
									Growth	NOEC	0.695	
									Egg number	NOEC	1.389	
Caenorhabditis elegans (a)	$La(NO_3)_3$	S	24 h	M	T	–	–	20	Mortality	LC50	1.352	Tatara et al. (1998)
Annelids												
Lumbriculus variegatus	$LaCl_3$	S	96 h	M	T	53–71	5.9–6.7	20.4–22.8	Mortality	LC50	18.8	Bangert (2013b)
										NOEC	9.9	
Fishes												
Melanotaenia duboulayi	$LaCl_3$	S	96 h	M	D	40–48	6.5–8.1	23.0–24.5	Immobilization	EC50	< 0.600	Stauber and Binet (2000)
Melanotaenia duboulayi	La (P)	S	96 h	M	D	40–48	6.9	–	Immobilization	EC50	> 0.127	Stauber (2000)
Oncorhynchus kisutch	$LaCl_3$	S	96 h	N	T	25–36	7.0 ± 0.2	10	Mortality	TL_m[n]	1.130	Peterson et al. (1974)
Oncorhynchus mykiss	La (P)	S	96 h	M	D	128	7.1–8.4	15 ± 2	Mortality	NOEC	> 63.3[l]	Watson-Leung (2009)
Onchorynchus mykiss (egg)	-	SR	28 d	M	–	104	7.0–7.8	–	Mortality	LC50	0.02	Birge et al. (1979)
Onchorynchus mykiss (fry)	La (P)	S	96 h	M	T	30–40	7.5	17 ± 1	Mortality	NOEC	< 0.50[h]	Martin and Hickey (2004)
Danio rerio	-	SR	96 h	M	T	210	6.4–8.2	–	Mortality	LC50	23.0	Den Ouden (1995)[k]
Danio rerio	La_2O_3	S	96 h	N	T	250	7.3–7.8	24 ± 1	Mortality	LC50	> 100.0[j]	Bazzon (2000)
Cyprinus carpio	$LaCl_3$	SR	21 d	MA	D	218	6.3–8.2	19.5–21.0	Mortality	LC50	> 5.0	Bogers (1995b)
										NOEC	0.26	

NOELR – no observable effect loading rate , TL_m – mean tolerance limit.

[a] j – juvenile, a – adult.
[b] La(P) – application of Phoslock®, a lanthanum-modified clay used as water treatment technology for remediation of eutrophied waterbodies. La concentration in leachates was measured/calculated.
[c] S – static, SR – static with renewal of medium.
[d] h – hours, d – days.
[e] N –nominal, M – measured, I – initial, A – average, T – total, D – dissolved, uf – ultrafiltered.
[f] EC50 (LC50, IC50) - half maximal effective (L – lethal, I – inhibitory) concentration, EC10 - concentration that causes an effect in 10% of the organisms, NOEC – no observed effect concentration,
[g] Effect concentration recalculated as mg lanthanum per liter, if necessary.
[h] Estimated from graph or data.
[i] Concentration given as MI, since measured one at end of test mostly < LOD (limit of detection).
[j] Limit test conducted with saturated solution.
[k] Data from secondary literature quoted in Sneller et al. (2000) and Ng et al. (2011).
[l] Dissolved La concentration series not consistent.
[m] La concentration recalculated from the 100% leachate via dilution steps.
[n] Endpoint reported for 24 h exposure instead of 96 h.

effects of $La(NO_3)_3$ on the common duckweed (*Lemna minor*) were found only until La concentration had reached 1389 mg La L^{-1}, as indicated by a decrease of total chlorophyll content as well as a rise of MDA and H_2O_2-production. Several enzyme activities within the antioxidant defense systems as well as the redox metabolite glutathione (GSH) were already significantly increased at 695 mg La L^{-1}. This could be interpreted as a typical early response to abiotic stress (Ippolito et al., 2010). Very similar results were conducted in an earlier study with *L. minor* from Ippolito et al. (2007).

4.1.3. Crustaceans

Invertebrates are the taxonomic group with the largest number of studies and broadly dominated by crustaceans. At the same time these organisms showed the highest sensitivity towards La-ions dissolved from $LaCl_3$ (Table 3).

The LC50 of *Daphnia carinata* (acute 48 h test) in three media of different composition were reported as 1.180, 0.049 and 0.043 mg La L^{-1} at a water hardness of 160, 98 and 22 mg $CaCO_3$ L^{-1}, respectively (Barry and Meehan, 2000). These findings support the strong relation between La toxicity and water hardness, total Ca-content as well as medium composition. Water hardness modified the toxicity, as La^{3+} competes with Ca^{2+} for binding sites in biological systems (Evans, 1983) and leads to increasing mortality with decreasing water hardness. In addition, a shortage of available food could have affected the toxicity: Major components of Daphnia water are sodium, chloride and to a lesser extent $Ca(OH)_2$ and $CaCO_3$. Significant precipitation of La-complexes at medium hardness may have affected algae used as food in daphnia tests. The chronic toxicity was even higher with an NOEC of 0.039 mg La L^{-1} derived from a study over 21 d in ASTM hard water (hardness classification in accordance with United States Geological Survey, http://water.usgs.gov/owq/hardness-alkalinity.html). Mortality and a delay in age of maturity were the most sensitive endpoints. The latter one could lead to reduced reproduction. At medium hardness, high mortality was also observed, but no reliable NOEC could be derived because measured concentration steps had not been in ascending order. Barry and Meehan (2000) concluded that La is probably incorporated in *D. carinata* mainly via the carapace competing with Ca^{2+} for calcium binding sites and induces disturbance during the moult cycle.

A different test organism (freshwater amphipod *Hyalella azteca*) showed a similar relation between water hardness and toxicity (Borgmann et al., 2005). Borgmann et al. observed a higher toxicity on *H. azteca* in soft water than in hard water with LC50s of 0.018 and 1.665 mg La L^{-1}, respectively. The latter value was derived from nominal total concentrations while the former from measured dissolved ones, therefore an underestimation of toxicity in hard water is possible.

In a 21-d reproduction study with D. magna exposed to $LaCl_3$-solutions, Bogers (1995a) derived an LC50 of 0.552 mg La L^{-1} for parental mortality and an NOEC of 0.100 mg La L^{-1}. Reproduction as an endpoint had an EC50 > 0.620 mg La L^{-1}. The experiment was conducted in M7-medium, which contains the chelating agent EDTA and very high water hardness (250 mg $CaCO_3$ L^{-1}). After each renewal of the test-medium (72 h) the measured La concentration declined exponentially during the first 48 h, probably due to precipitation of La^{3+} with carbonate and sulfate and adsorption to algae. The La concentration was calculated as the geometric mean from the measurements.

Lürling and Tolman (2010) performed a 14-d study with *D. magna* in moderately hard water exposed to $La(NO_3)_3$-solutions in the presence and in the absence of phosphate (0.33 mg L^{-1}). In P-free medium the number of offspring in the third brood as total number per female was reduced at the highest La concentration of 1.0 mg La L^{-1}. The NOEC of overall reproduction in P-free medium was 0.33 mg La L^{-1} as nominal and 0.099 mg La L^{-1} as measured concentration. Neither significant mortality nor precipitation was observed. In P-containing medium, high precipitation occurred and stronger effects were reported but without significant mortality. The number of offspring, however, was significantly reduced in all three broods and the somatic growth of *D. magna* was lower than in P-free medium at highest La amount. The derived NOEC for reproduction was also 0.33 mg La L^{-1} given as nominal concentration, since the measured ones were not reported. In a parallel short assay, Lürling and Tolman also investigated the effect of La (1.0 mg La L^{-1}) on the food algae *Scenedesmus obliquus*. In P-containing medium strong precipitation occurred and the biovolumes were significantly lower than those in controls and in P-free medium with and without lanthanum. The authors suggested that La forms complexes with phosphate oxyanions ($H_2PO_4^-$, HPO_4^{2-}) which form aggregates and adsorb to algal surfaces, leading to extensive sedimentation. Consequently, the reduced availability of algal food probably caused the adverse effects on growth and reproduction of *D. magna* in P-containing medium. In contrast to most other studies with daphnids no significant mortality occurred until 1.0 mg La L^{-1} and reproduction was the most sensitive endpoint (Lürling and Tolman, 2010). One reason could have been the shorter time of exposure (14 d) in comparison with other chronic tests, which could have masked a potentially higher toxicity. As shown in the experiment from Bogers (1995a) mortality of *D. magna* occurred after more than 14 days of exposure and at low La concentrations. Secondly, the applied medium contained Na_2-EDTA (5.0 mg L^{-1}), which is able to complex with lanthanum and consequently could have altered bioavailability and toxicity of La, as described by Loureiro et al. (2011) for other metals. On the other hand, the M7-medium applied by Bogers (1995a) contained phosphate, EDTA in lower concentrations (2.5 mg L^{-1}) and high water hardness. While the last two are expected to reduce toxicity, phosphate could have enhanced it by initiating food shortage through precipitation of La with phosphate and algae as described before.

Further tests in soft water resulted in higher effect levels of $LaCl_3$ for *Daphnia magna*. Mean tolerance limits (TL_m) for *D. magna* were 1.59 mg La L^{-1} after 72 h and 0.91 mg La L^{-1} after 96 h (Petersen et al., 1974), with values recalculated from reported total nominal $LaCl_3$-concentration. By far the lowest sensitivity had *D. magna* in hard water with unclear starting substance in the study of Den Ouden (1995); quoted from Sneller et al. (2000) (secondary reference, no additional information available). Limit tests with saturated solutions of lanthanum carbonate ($La_2(CO_3)_3$) or lanthanum oxide (La_2O_3) showed no acute toxicity to *D. magna* (Seyfried, 2007a, 2007b; Höger, 2009), probably due to very low water solubility.

Two studies with *Ceriodaphnia dubia* were performed in soft water, one with $LaCl_3$ (Stauber and Binet, 2000) and another with Phoslock® leachates (Stauber, 2000). Both studies yielded high sensitivity in a 7-d exposure with LC50 values of 0.51 and 0.82 mg La L^{-1}, while NOECs for reproduction were 0.05 and < 0.13 mg La L^{-1}, respectively. In contrast to the very similar endpoints after a 7-d exposure, the LC50 values for *C. dubia* after a 48-h exposure to $LaCl_3$ and Phoslock® leachates differed by two orders of magnitude. To assess the impact of colloids on the toxicity of leachates, Stauber (2000) compared leachates filtered through 0.45 μm and through 0.1 μm, the latter to remove colloids from the fluid. The experiments, both with very similar La concentrations in the leachates, resulted in higher toxic responses of *C. dubia* in the ultra-filtered fraction. Therefore, the author concluded that toxicity of leachates was not caused by colloids, rather the ultra-filtration may have reduced the survival of *C. dubia* by removal of necessary colloids.

Table 4
Effect concentrations and selected exposure conditions for freshwater species exposed to sediment. Small lines (-) indicate missing or incomplete information, gaps ( ) refer to information from the same study in the previous row.

Species	Compound[a]	Exposure method[b]	Exposure time[c] 28 d 28 d 38 d 10 d 21 d 14 d	Exposure data[d]		Medium[e]	Hardness [mg $CaCO_3$ L^{-1}]	TOC[f] [%]	pH-value [-]	Temperature [°C]	Endpoint, biological	Endpoint, statistical[g]	Effect conc.[h] [mg La kg^{-1}]	Reference
Nematodes														
Caenorhabditis elegans	$LaCl_3$	S	96 h	N	T	Art. sed.	101[i]	2.1	–	19.7 – 20.2	Reproduction	EC50	241	Höss (2013)
												NOEC	50	
											Growth	NOEC	> 500	
Annelids														
Lumbriculus variegatus	$LaCl_3$	S	28 d	N	T	Art. sed.	355 – 535	2.9	7.5 – 8.4	18.8 – 20.3	Living worms	EC50	1272[j]	Bangert (2013a)
												NOEC	239[j]	
											Biomass	EC50	1272[j]	
												NOEC	598[j]	
Insects														
Chironomus riparius	$LaCl_3$	S	28 d	N	T	Art. sed.	269 – 606	1.9	7.8 – 8.2	20 ± 1	i.a. Emergence ratio	NOEC	> 1318[j]	Dietzmann (2010)
Chironomus zealandicus	La (P)	S	38 d	M	T	mud, sand	123 – 202	–	7.8 – 8.4	18.4 – 20.7	i.a. Emergence ratio	NOEC	> 1830	Clearwater (2004)
Chironomus dilutus	La (P)	S	10 d	M	T	Nat. sed.	122 – 179	–	8.1 – 9.1	23 ± 2	Mortality & growth	NOEC	> 0.880 mg/L[k]	Watson-Leung (2009)
Hexagenia spp.			21 d				101 – 125		8.1 – 8.5			NOEC	> 0.007 mg/L[k]	
Crustaceans														
Hyalella azteca	La (P)	S	14 d	M	T	Nat. sed.	145 – 208	–	8.0 – 8.6	23 ± 2	Mortality & growth	NOEC	> 1.79 mg/L[k]	Watson-Leung (2009)

[a] La(P) – application of Phoslock®, a lanthanum-modified clay used as water treatment technology for remediation of eutrophied waterbodies. La concentration in leachates was measured/calculated.
[b] S – static.
[c] d – days.
[d] N – nominal, M – measured, T – total.
[e] Art. sed. – artificial sediment, Nat. sed. – natural sediment.
[f] TOC: total organic carbon.
[g] EC50 – half maximal effective concentration, NOEC – no observed effect concentration.
[h] Effect concentration recalculated as mg lanthanum per liter, if necessary.
[i] Calculated from medium composition.
[j] Results as nominal concentrations, because measured ones varied less than 20% from nominal.
[k] La concentration measured in overlying water.

Table 5
Effect concentrations and selected exposure conditions for marine species. Small lines (-) indicate missing or incomplete information, gaps) refer to information from the same study in the previous row. Table structure is according to Ng et al. (2011) with modifications.

Species	Compound	Exposure method[a]	Exposure time[b]	Exposure data[c]		Salinity [‰]	pH-value [-]	Temperature [°C]	Endpoint, biological	Endpoint, statistical[d]	Effect conc.[e] [mg La L^{-1}]	Reference
Bacteria												
Aliivibrio fischeri	$La(NO_3)_3$	S	30 min	N	D	–[f]	5.5	–	Luminescence	EC50	5.56[g]	Weltje (2002)
Aliivibrio fischeri	$La(NO_3)_3$	S	15 min	N	D	–[f]	5.5	15	Luminescence	EC50	235.2	McCloskey et al. (1996)
Microalgae												
Skeletonema costatum	$LaCl_3$	S	72 h	N	T	32–35	8.0	25	Growth rate	EC50	4.055	Tai et al. (2010)
Crustaceans												
Acartia tonsa	–	S	48 h	–	–	28[h]	6.4–8.1[h]	–	Mortality	LC50	1.040	Bowmer et al. (1992) in Maas-Diepeveen and Botterweg (1993)
Sea urchins												
Paracentrotus lividus (embryos)	La_2O_3 in HNO_3	S	72 h	N	T	35	8.2	18 ± 1	Developmental defects	EC50	0.833	Oral et al. (2010)
			5 h						Cytogenetic effects	NOEC	> 0.417	
Paracentrotus lividus (sperm)	La_2O_3 in HNO_3	S	1 h	N	T	35	8.2	18 ± 1	Fertilization rate	NOEC	0.417	
									Offspring quality	NOEC	> 1.389	
Fishes												
Poecilia reticulata	–	SR	96 h	–	–	28[h]	6.9–8.1[h]	21–25[h]	Mortality	LC50	47.0	Hooftman et al. (1992) in Maas and Botterweg (1993)

[a] S – static, SR – static with renewal of medium.
[b] min – minutes, h – hours.
[c] N – nominal, T – total, D – dissolved.
[d] EC50 (LC50) – half maximal effective (L – lethal) concentration, NOEC – no observed effect concentration.
[e] Effect concentration recalculated as mg lanthanum per liter, if necessary.
[f] According to Weltje (2002) the applied medium reflects freshwater speciation conditions with an ionic strength between freshwater and seawater.
[g] Estimated from graph.
[h] Data from secondary literature quoted in Sneller et al. (2000) and Ng et al. (2011).

A differentiation of sensitivities between the cladocerans is challenging due to the large varieties in study design. Medium composition could have a great impact on metal toxicity as shown by Guilhermino et al. (1997) who examined responses of *D. magna* exposed to different metals. Furthermore, cladocerans exhibit interspecies differences in their sensitivity to calcium deficiency (Tan and Wang, 2010), which may be triggered by low Ca-content in the medium as well as the concentration of competing ions like La^{3+}. Comparing La toxicity data only under consideration of water hardness, *D. carinata* seems to be the most sensitive cladoceran (Barry and Meehan, 2000). Slightly less sensitive was *C. dubia*, though only observed in soft water (Stauber 2000), while *D. magna* demonstrated lower sensitivity in moderately and very hard water, respectively (Bogers, 1995a; Lürling and Tolman, 2010). This observation only partially coincides with results from diverse acute assays examining metal toxicity towards invertebrates. In these studies not only *C. dubia* showed a distinctly higher sensitivity than *D. magna* (e.g. von der Ohe and Liess, 2004; Bossuyt et al., 2004), but also than *D. carinata* (Cooper et al., 2009).

4.1.4. Nematodes and annelids

The nematode *Caenorhabditis elegans* has a short life cycle, which makes it possible to determine ecological relevant endpoints within 72–96 h. *Caenorhabditis elegans* exposed to $LaCl_3$ in liquid medium (Zhang et al., 2010) possessed a sensitivity similar to that of the crustaceans *D. magna* and *C. dubia* in long term studies, but no mortality occurred. Inhibition of growth and brood size were the most sensitive parameters with NOECs of 0.695 and 0.139 mg La L^{-1}, respectively, and an EC50 value of 1.97 mg La L^{-1} for reproduction. At low concentrations up to 0.139 mg La L^{-1} significant stimulation of growth and egg number occurred. A negative impact on the availability of the food source *E. coli* could be ruled out, since the range of tested La concentrations had not led to significant agglomeration of the bacteria. In addition, elemental mapping in *C. elegans* showed a dose-dependent uptake of lanthanum with the highest concentrations above the excretory pore, indicating that bioaccumulation occurs mainly via ingestion of La adsorbed by *E. coli*. The huge amount of La in the nematodes led to a distinct elemental imbalance, *e.g.* with a decline in concentrations of Ca, K and Zn.

A second study with *C. elegans* yielded a 24-h LC50 of 1.35 mg La L^{-1} as total concentration (Tatara et al., 1998). Simultaneously, a modeling exercise was performed to predict the relative toxicity of various metal ions. By means of regression analysis the first hydrolysis constant and the covalent index were proposed as the main parameters for a two-variable model, indicating the highest metal ion affinity to intermediate and soft biochemical ligands, which contain O or N and S donor atoms, respectively. A calculation of metal speciation with MINTEQA2 predicted a quota of free metal ions (98% for La ions); however, no improvement of the model fit was achieved.

Much lower toxicity was observed in a 96 h study conducted with the annelid *Lumbriculus variegatus*, in which Bangert (2013b) reported a NOEC of 9.9 mg La L^{-1} and a LC50 of 18.8 mg La L^{-1}.

4.1.5. Fishes

Several adverse effects on fishes and amphibians have been observed during La exposure, particularly on nervous systems, excretory organs and smooth muscles (detailed overview in Das et al. (1988)). For example, $LaCl_3$ affected the kinetic properties of acetylcholinesterase in the nervous system of the electric eel (*Electrophorus electricus*). In low ionic strength medium, La^{3+} activated the enzyme rapidly, resembling cellular ions like Ca^{2+} and Mg^{2+}, while inactivating the enzyme during ongoing exposure at low and high ionic strength (Tomlinson et al., 1982). La^{3+}-solution ($\geq$0.1 mmol La L^{-1}) changed the sensitivity of the electroreceptors of the skin in the catfish (*Kryptopterus* sp.) by inhibiting responses after anodal stimulus onset. Ions added to the solution like Ca^{2+} or Na^{+} did not change this inhibition (Roth, 1982).

Some examinations have been done on potential beneficial effects of lanthanum regarding toxicity of heavy metals. In an in-vitro study Hong et al. (2007) figured out that the destruction of intestinal DNA caused by Hg^{2+} could be mitigated by La^{3+}. In addition, La^{3+} has been shown to decrease the uptake of Cd in gill epithelial cells from *O. mykiss* (Verbost et al., 1987). In contrast to these findings, there was no such effect reported in a similar study by Block and Pärt (1992).

To date, only few toxicity studies with fishes have been performed. These studies exhibited a wide range of sensitivities with early life stages, being the most sensitive across organisms. A very low LC50 of 0.02 mg La L^{-1} was determined by Birge et al. (1979) for eggs from rainbow trout (*O. mykiss*) in a 28 day study with moderately hard water. Much lower toxicity was observed in parallel studies with respect to eggs from goldfish and narrow-mouthed toad, but neither endpoints were reported, nor the used starting substance. These results could possibly indicate species-specific sensitivity of developmental stages of vertebrates. Martin and Hickey (2004) tested fish fry from *O. mykiss* in a 96 h toxicity assay with Phoslock® leachates in soft water. Effect concentrations were given as dilution percentages of elutriates with values of 8.7% (LC50), 3.4% (LC20) and $<$6.25% (NOEC). Only very few La concentrations were stated though a graphical estimation for the lowest dilution step (6.25% elutriate) leads to a NOEC of approximately $<$0.5 mg La L^{-1} as assumed mean total concentration. A further test with fish fry yielded in reduced La toxicity, attributable to a high phosphorus concentration (2.5 mg L^{-1}).

The highest sensitivity among juvenile fishes in acute tests was exhibited by the rainbow fish (*Melanotaenia duboulayi*) exposed to $LaCl_3$ in soft water. The lowest applied La concentration of 0.60 mg La L^{-1} led to 100% mortality (Stauber and Binet, 2000), whereas, the coho salmon *Oncorhynchus kisutch* was less sensitive with a TL_m of 1.13 mg La L^{-1} after 24 h, also at low hardness (Petersen et al., 1974), and the zebrafish (*Danio rerio*) had the lowest sensitivity (LC50 of 23.0 mg La L^{-1}) in very hard water (Den Ouden, 1995). However, both of these endpoints are stated as total concentrations.

Results from a 21 day study with the common carp (*Cyprinus carpio*) exposed to $LaCl_3$ were ambiguous. The reported endpoints were an LC50 value $>$5.0 mg La L^{-1} and an NOEC of 0.26 mg La L^{-1} based on average measured concentrations in very hard water (Bogers, 1995b). At the highest concentration of 6.51 mg La L^{-1} 100% mortality occurred during the first days due to acute toxicity. Further mortality was only observed in the second highest concentration at day 12 and was related to a higher La recovery. This was probably caused by a different pH adjustment during medium renewal. Therefore, the derivation of the LC50 and NOEC remain uncertain.

In a study with *M. duboulayi* exposed to Phoslock® leachates in soft water, the highest tested La concentration (0.13 mg La L^{-1}) led to an imbalance of 25% without significance (Stauber, 2000). Much higher La content in eluates from Phoslock® (63.3 mg La L^{-1}) caused no toxic effect to the rainbow trout *O. mykiss* in moderately hard water (Watson-Leung, 2009). However, these data are less reliable because La concentrations were not measured, rather taken from a parallel study with *D. magna* in which the same dilution steps were used and the concentration series was not consistent (see above).

There could be species-specific differences as well as an impact of water hardness to the toxic effects towards fish and their early development stages as shown for several other metals (e.g. Pascoe

et al., 1986; Ebrahimpour et al., 2010; Pourkhabbaz et al., 2011). Due to the limited number of studies with lanthanum and numerous restrictions on reliability, further studies should be conducted.

4.2. Toxicity of lanthanum in freshwater sediments (Table 4)

Benthic organisms are likely to be exposed to La through sediments due to the high adsorption of La to sediment particles (Tijink and Yland, 1998; Weltje et al., 2002b) and to fine particulate organic matter (FPOM) (Schaller, 2013). Uptake depends mainly on the grain size of contaminated particles. However, uptake alone does not necessarily cause any harm since strongly bound contaminants first have to become bioavailable e.g. in the gastrointestinal tract of sediment feeders where the low pH alters physicochemical parameters.

Three out of five studies conducted with sediments use $LaCl_3$ as La-source while the other experiments were performed with Phoslock® (Table 4). The most sensitive sediment organism was the nematode *Caenorhabditis elegans* exposed via spiked sediment in a 96 h static test according to ISO guideline 10872 (Höss, 2013). The test was conducted in medium with moderate water hardness. The endpoints for reproduction were determined as 50 mg La kg^{-1} and 241 mg La kg^{-1} for NOEC and EC50, respectively, while the measured concentration of the NOEC was reported as 38.8 mg La kg^{-1}. The growth of *C. elegans* was not affected up to the highest concentration. In a 28 day study with the sediment feeding freshwater oligochaete *Lumbriculus variegatus* according to OECD guideline 225, the most sensitive endpoint was the NOEC of 239 mg La kg^{-1} for the number of living worms (Bangert, 2013a). This La content in artificial sediment corresponded with a measured La concentration in pore water and overlying water of about 0.17 mg La L^{-1} and 0.033 mg La L^{-1}, respectively. The EC50s for biomass and worm numbers were each 1272 mg La kg^{-1}. The endpoints were derived from nominal concentrations, since the measured ones were less than 20% lower. In contrast to these two results, first instar larvae from the hexapod *Chironomus riparius* were substantially less sensitive. The highest tested concentrations in sediment of 1318 mg La kg^{-1}, which corresponds approximately to 0.20 mg La L^{-1} in pore water, exhibited no toxicity with respect to emergence ratio and development rate (Dietzmann, 2010). In the last two studies, the measured hardness was very high compared to the nominal one, which could have affected the toxicity of lanthanum. However, it also could have been an analytical artefact due to the high La amount in the medium.

The Phoslock® studies did not show any toxicity at the tested concentrations. While in the experiment with midge larvae *Chironomus zealandicus,* La content in sediment and overlying water was reported (Clearwater, 2004), the other results were only given with regard to La concentration in water (Watson-Leung, 2009).

4.3. Toxicity of lanthanum in marine water (Table 5)

In contrast to the number of freshwater studies, very few tests were conducted with marine organisms and none were found for sediment or chronic studies. Weltje (2002) tested the sensitivity of the marine bacterium *Aliivibrio fischeri* (formerly: *Vibrio fischeri*) on lanthanum in a medium which reflects freshwater conditions (details in Table 5). Inhibition only occurred at high concentrations with an EC50 of 5.56 mg La L^{-1}. With increasing exposure time the EC50 decreased and at low concentrations hormesis occurred, which both could be related to a slow binding or uptake of La into the cells. A speciation with CHEAQS of total dissolved lanthanum at the effective concentration resulted in 79% free La^{3+}, about 20% $La(NO_3)^{2+}$ and less than 0.01 % complexes of La-OH and La-CO_3, respectively. Since no clear assignment of La species could be ruled out, the total dissolved concentration was proposed to express toxicity. Further, it was supposed that the toxic effect on bacterial metabolism was induced by the binding of La to oxygen-containing ligands on cell walls and membranes. According to a study from Takahashi et al. (2005) with natural microbial mats these ligands on bacterial cell walls are mainly phosphate and carboxylate groups. In comparison to Weltje (2002) a much higher EC50 for *A. fischeri* (235.2 mg La L^{-1}) were derived by McCloskey et al. (1996), probably due to a shorter exposure time. And in addition, a lower proportion of free La^{3+}-concentration (19%) was calculated with MINTEQA2.

Among the tested marine organisms early life stages of sea urchins *Paracentrotus lividus* possesses the highest sensitivity (Table 5). The toxic responses of embryos towards exposure of La^{3+}-solution were developmental defects during embryogenesis with an EC50 of 0.83 mg La L^{-1}, but no cytogenetic effects were observed up to highest nominal concentration of 0.42 mg La L^{-1} (Oral et al., 2010). Moreover, an exposure to 1.39 mg La L^{-1} significantly inhibited sperm fertilization rate of *P. lividus* (NOEC 0.42 mg La L^{-1}), whereas the quality of offspring larvae with regard to developmental defects was not affected. In the same study, cerium was found to be more toxic with high embryonic mortality, suggesting different modes of action for La(III) and Ce(IV). Tai et al. (2010) exposed diatoms (*Skeletonema costatum*) to 13 individual lanthanide salts and to a mixture of these in the same concentration range. The algae cells demonstrated very similar toxic response in each approach indicating that there was no differentiation by *S. costatum* between the individual lanthanides. It was supposed that this might be a special pattern of unicellular organisms in contrast to higher ones. The detected EC50 for lanthanum was 4.05 mg La L^{-1} and lies in the broad range of effect concentrations for freshwater algae. The calanoid copepod *Acartia tonsa* was more sensitive than the algae with a 48-h LC50 of 1.04 mg La L^{-1} (Bowmer et al., 1992; quoted in Maas-Diepeveen and Botterweg (1993)), which is in the same order of magnitude as the EC50 for *D. carinata* in hard water. The lowest sensitivity among the marine species was exhibited by the guppy *Poecilia reticulate* with an acute LC50 of 47 mg La L^{-1} (Hooftman et al., 1992; quoted in Maas-Diepeveen and Botterweg (1993)), which is also higher than the most effect concentrations for freshwater fishes.

A comprehensive comparison of differences in sensitivity between marine and limnic species is not possible due to the insufficient database for marine species. Nevertheless, the results of the acute tests may indicate approximately similar or slightly lower sensitivity for marine organisms. This assumption would be in accordance with research comparing toxicities of different heavy metals, where freshwater organisms respond mostly with higher sensitivity to various degrees than marine ones, probably because of larger amounts of free metal-ions and increased bioavailability at lower salinity (Wheeler et al., 2002; Hall and Anderson, 1995).

4.4. Transfer from laboratory to field

The only information which is available on La toxicity under 'natural' conditions is related to Phoslock® applications. As stated above, a wide range of physicochemical properties can alter the La speciation. Moermond et al. (2001) proposed, that the free La ion will be reduced in natural freshwaters by adsorption to humic substances. Consequently, the toxicity is probably reduced. For example, in two Phoslock® assays with batches of river water single La concentrations up to 15.0 mg La L^{-1} exhibited no toxic effect on *M. duboulayi*, while much lower concentrations applied in a standard medium were toxic (Stauber and Binet 2000).

Furthermore, no adverse effects on crustaceans are expected in combination with medium to high water hardness (Lürling and Tolman 2010). On the other hand, at low alkalinity and low phosphate concentrations toxic effects may occur (Spears et al., 2013). As reported by Pablo et al. (2009); quoted in Gibbs et al. (2011) juvenile *M. duboulayi* and *C. dubia* died in reservoir water that had been taken three days after a Phoslock® application. Over eight weeks of post treatment, toxic effects occurred towards the crustaceans, which probably were caused by the release of La from Phoslock® granules in combination with natural soft water. A three-year fish health monitoring during a Phoslock® application in a lake observed a decline in fish health during the first year, indicated by deviations in hematology, spleen and gill histopathology in rainbow trout and common bullies. In the second year, changes in some physiological parameters (e.g. female spleen size, significant decline in plasma chlorine) were recorded and mainly attributed to differences in reproductive timing and mean sizes of organisms (Landman and Ling, 2006). Significant variations in comparison with population from the untreated lake were recorded in the third year, e.g. hematocrit numbers in female trout, plasma ions Ca^{2+} and Cl^{-} (Landman et al., 2007). The latter may be related to the lanthanum exposure, since La could influence the plasma ion transport in gill cells (Perry, 1997; Eddy and Bath, 1979). However, differences in lake conditions, seasonal fluctuations and allometry make it difficult to attribute those potentially long-term effects directly to lanthanum. Therefore, further examination of chronic exposure would be useful (Landman and Ling, 2006).

5. Deriving environmental criteria for lanthanum

This review showed that information on the toxicity of lanthanum and which factors affect it is still scarce. Increasing emission of lanthanum to the environment due to its use in various applications, however, requires the formulation of a protective threshold value, which may need to be revised in future as more information is gathered. In this chapter, we will discuss the possibilities to derive environmental quality criteria for sediment and water, and discuss the current challenges.

5.1. Bioavailability of La-species

As with other metals, the free ion (La^{3+}) is considered the most bioavailable lanthanum species, followed by hydroxides (Moermond et al., 2001). Molecular or ionic mimicry have been suggested as processes that enable uptake of non-essential, cationic metal species across membranes. Cations thereby mimic an essential element and are mistaken by its structural transport pathway (see Bridges and Zalups (2005) for a review on molecular and ionic mimicry). Trivalent lanthanide ions (Ln^{3+}), for example, resemble calcium ions in several of their chemical properties: They bind ionically, have no significant covalent binding, and are about the same size. Due to the higher charge to volume ratio, Ln^{3+} have a much higher affinity for binding sites on proteins and are known to substitute Ca^{2+} (as well as Mg^{2+}, Fe^{3+}, Mn^{2+}) (Evans, 1983). There has been a controversial discussion whether La^{3+} is capable of crossing the cell membrane. Previously, authors assumed, that La^{3+} exhibited its effects exclusively by displacing Ca^{2+} from the cell membrane, thus interfering with Ca-dependent functions (Evans, 1983). More recently, evidence gathers that uptake of La^{3+} into cells is possible (Wang et al., 2014; Li et al., 2008).

5.2. Impact of confounding factors on the toxicity of lanthanum

Confounding factors such as water hardness (Ca^{2+}, Mg^{2+}), alkalinity (HCO_3^-, CO_3^{2-}), pH, and dissolved organic carbon (DOC) affect toxicity by changing the activity of the bioavailable species and therewith influence the interaction between toxicant and biological membrane.

5.2.1. Alkalinity respective water hardness

Several studies identified higher LC50 values with elevated $CaCO_3$-concentrations (Barry and Meehan, 2000; Borgmann et al., 2005; Moermond et al., 2001). This may be due to enhanced competition for Ca-binding sites on membrane proteins, or it could be a consequence of increasing formation of biologically unavailable La-carbonates causing a decrease of the concentration of those lanthanide species that seem to be bioavailable, La^{3+} and $LaOH^{2+}$ (Moermond et al., 2001). These observations could suggest formulation of different environmental quality criteria for different ranges of water hardness similar to the EQS for cadmium (European Commission, 2006). However, data are currently not sufficient to formulate hardness-dependent EQS. Fig. 1 depicts all well documented results (evaluated with regard to Klimisch et al. (1997) to be at least “reliable with restrictions”) with LC50 values over all $CaCO_3$ concentrations comprising data for crustaceans, fish, and annelids (see also Table 3). A reliable relationship between $CaCO_3$ and lanthanum with regard to toxicity can thus not be generalized over different organism groups.

5.2.2. pH and dissolved organic matter

Complexation of La in natural waters depends primarily on pH followed by the concentration of dissolved organic matter and presence of competitive cations. Modeling studies assuming the world average river water and a DOC concentration of 5 mg L^{-1} showed that La^{3+} (and sulfate complexes) will dominate in acidic waters (pH < 5.4), and carbonate species will dominate at pH > 7.9 (Tang and Johannesson, 2003). At circumneutral pH, lanthanum could be bound primarily to organic matter solution complexes. However, strong binding sites on e.g. humic substances would probably be outcompeted by Fe, Al and other cations under natural conditions, leaving only abundant weak binding sites to provide ligands for lanthanum. In addition, carbonate ions will probably outcompete light molecular weight DOC at circumneutral to alkaline pH (Tang and Johannesson, 2010).

With regard to the environmental quality, two conclusions need to be drawn from this: (a) the concentration of the bioavailable species La^{3+} will be relatively low at pH 7 but quickly increasing with acidity; (b) as the concentration of La^{3+} is strongly influenced by confounding factors, regional properties should be taken into account when performing a risk assessment.

5.3. Suggestions for environmental quality criteria

5.3.1. The calculation of PNEC using assessment factors

A Predicted No Effect Concentration (PNEC) is a regulatory value used in risk assessment that indicates a concentration under which risks to the environment are unlikely. PNECs are usually derived from ecotoxicological data by dividing NOEC or EC-values by an assessment factor that indicates the uncertainty behind the available database. The European Technical Guidance Document on Risk Assessment suggests assessment factors (AF) for a PNEC in an aquatic environment, which are also used in the REACH process. For metals, different AFs are adopted for freshwater and for marine effects assessment. Even though metal availability in marine waters tends to be lower as mentioned in Section 4.3, AFs for deriving quality standards are higher than those used for freshwater. This reflects the higher uncertainty when extrapolating EQS from a limited number of marine test species or from tests with freshwater organisms to the marine ecosystem with its high biodiversity (European Commission, 2011).

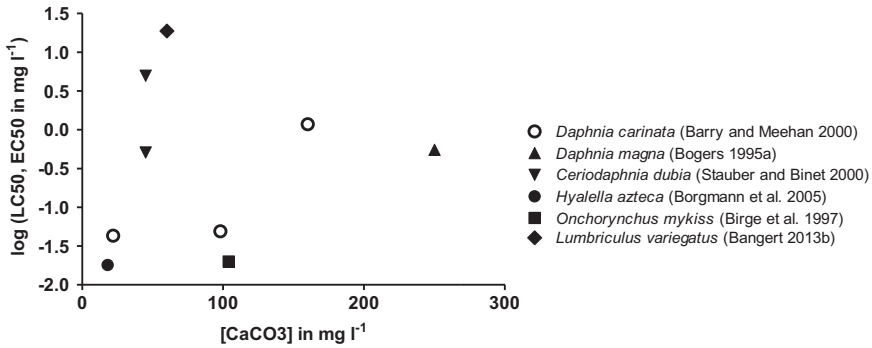

Fig. 1. Relationship between logarithmic values of inhibition concentrations (in mg L^{-1}; LC50: filled symbols; EC50: open circles) and water hardness for all well documented tests and over the whole $CaCO_3$ range. Data sources are indicated in the legend.

In this review, we derive only quality criteria for the freshwater community due to the small number of available tests with marine organisms (see Table 5).

As detailed in Table 3, NOECs for lanthanum are available for three species across trophic levels. According to the Technical Guidance Document (European Commission, 2003), this allows use of an assessment factor of 10 if the tested species can be considered sensitive. The lowest NOEC is used. NOEC-data chosen to derive the PNEC are 0.26 mg L^{-1} (fish: *Cyprinus carpio*, Bogers, 1995a), 0.13 mg L^{-1} (microalgae: *Selenastrum capricornutum*, Stauber and Binet, 2000), and 0.04 mg L^{-1} (crustacea: *Daphnia carinata*, Barry and Meehan (2000)). Applying an assessment factor of 10, a PNEC of 4 μg L^{-1} would be achieved as water quality criterion based on the NOEC for *D. carinata*. While this is a low value, it is not exceptionally low. Other results have been published on the basis of measured data, which are in the same range (NOEC 0.05 mg L^{-1} for *Ceriodaphnia dubia*, Stauber and Binet (2000); LC50 0.018 mg La L^{-1} for *Hyalella azteca*, Borgmann et al. (2005); LC50 0.02 mg La L^{-1} for *O. mykiss*, Birge et al. (1979)).

For sediments, the Technical Guidance Document gives slightly different conditions for selecting the AFs. Based on the summary of reliable data in Table 4, three long-term tests with species, that represent different feeding conditions, are available. Hence, an assessment factor of 10 is used. The chosen NOEC-values are 50 mg kg^{-1} (nematodes: *Caenorhabditis elegans*,Höss, 2013), 239 mg kg^{-1} (annelid: *Lumbriculus variegatus*, Bangert (2013a, 2013b)), and >1318 mg kg^{-1} (crustacea: *Chironomus riparius*, Dietzmann (2010)). A $PNEC_{sediment}$ of 5 mg kg^{-1} is derived.

5.3.2. The added-risk approach (Crommentuijn et al., 1997; Struijs et al., 1997)

This approach takes into account that organisms adapt to natural background concentrations of metals in their environment. Consequently, the "maximum permissible additions" (MPA) are calculated. These are similar to PNECs and must be established by testing non-adapted, sensitive organisms. In order to derive the "maximum permissible concentration" (MPC) (effects-oriented) the MPA is added to the background concentration (Cb). The "negligible concentration" (NC) (target value) is calculated by dividing the MPA by 100 and adding the median of the background concentration (Cb).

Accurate information on background concentrations is critical for this method, but also often difficult to get. One potential database is the geochemical atlas of Europe (FOREGS), which also compiled La-concentrations (http://weppi.gtk.fi/publ/foregsatlas/article.php?id=15). They range from <0.002 to 16 μg L^{-1} in stream water (median: 0.034 μg/L) and from 1.3 to 553 mg/kg in stream sediment (median: 31.9 mg kg^{-1}), depending on the local geology. The European Commission recommends using an added-risk approach (ARA) if the 90th percentile background value, calculated from the FOREGS data base, is higher or similar to the quality standard (European Commission, 2011). For La, these are 0.5 μg L^{-1} and 63.1 mg kg^{-1} for stream water and sediment, respectively. Thus, using an ARA for water would not be useful. For sediments, however, an ARA would prevent setting quality criteria below a geological background concentration.

Exemplarily, an added risk approach is applied in Table 6, using the median values of FOREGS as background concentrations. These correspond to upper La-concentrations in the West part of Germany (FOREGS, http://weppi.gtk.fi/publ/foregsatlas/maps_table.php).

As expected, the MPC for fresh water would still be 4 μg L^{-1}. Sneller et al. (2000) had calculated the MPC in freshwater to be 10.1 μg L^{-1} based on three studies that fulfilled the criteria of documenting the measured rather than the nominal La-concentration in the test systems. At the time of his review, these were the only chronic data available. Since then, 12 studies on the effect of lanthanum on freshwater organisms have been published, one of them being the study of Barry and Meehan (2000) with a NOEC of 0.04 mg L^{-1} for *Daphnia magna*. However, due to the wide range of background concentrations, a PNEC of 4 μg L^{-1} may be too low in some areas and should be taken as an incentive for further studies and region-specific assessments. In addition, more information on freshwater toxicity is needed to increase the reliability of the quality criterion.

In order to assess the hazard for sediments, the three tests mentioned above to derive the PNEC on the basis of the AF-method were taken into account and a threshold value (MPC) of 36.9 mg kg^{-1} was derived (Table 6). As sufficient data were not available in 2000, Sneller et al. had calculated the risk on the basis of equilibrium partitioning and achieved much higher MPA-values of 23 g kg^{-1} and 4.6 g kg^{-1}, depending on the applied partition coefficient K_d (Sneller et al., 2000).

5.3.3. Species sensitivity distribution (SSD)

The species sensitivity distribution is a statistical extrapolation method based on the assumption that the distribution of species sensitivity follows a theoretical distribution function. The minimal requirements to perform a reliable SSD are stated in the Technical Guidance Document for Risk Assessment (European Commission, 2003): at least 10 NOECs for different species covering at least 8 taxonomic groups are necessary. In this study, NOEC from "reliable" studies according to the Klimisch-criteria (Klimisch et al., 1997) that are based on measured concentrations are available for 6 species from 4 taxonomic groups. More well documented studies with organisms from other taxonomic groups than Daphnia and fish, supplying NOEC data and measured La-concentrations in the dissolved phase during the tests would help providing more

reliable water quality criteria by additionally calculating an SSD. Care must also be taken, however, to account for the potential impact of confounding factors (see Section 5.2.) such as different alkalinity or pH.

One advantage of using an SSD for defining quality criteria would be the integration of different test data into the final assessment instead of always taking the lowest NOEC

5.3.4. Biotic ligand model (BLM)

Setting up a biotic ligand model would be a possibility to provide water and sediment quality criteria because it addresses bioavailability issues. BLMs are currently available for Cu, Ag, Ni, Pb, and Zn and have been used for regional risk assessment. They take into account (a) the concentration of toxic metal species, (b) the binding of the toxic metal species to the biotic ligand, and (c) the toxic response as a consequence of the metal-ligand binding. Quantification of the underlying processes is among the challenges in setting up a BLM as recently reviewed by Smith et al. (2015). Other authors voiced more principle concerns: the disregard of exposure routes other than uptake from the aqueous phase in BLMs (Ahlf et al., 2009). Nevertheless, development of a biotic ligand model for lanthanum would improve understanding of toxicokinetic processes and increase confidence in the regional risk assessment. A suitable test candidate to develop such a model could e.g. be *Daphnia carinata*. Crustacea are relatively sensitive to La and first experiments by Barry and Meehan (2000) on the effect of $CaCO_3$ showed a decreasing toxicity with increasing carbonate concentration (see also Fig. 1).

6. Conclusion on water and sediment quality criteria for lanthanum

The number of papers on the ecotoxicity of lanthanum has steadily increased over the last 20 years. Compared to other metals, however, information on toxicity especially to La-contaminated sediments is still scarce. For derivation of quality criteria, we considered only well described results and NOEC values that were based on measured concentrations as opposed to nominal concentrations, preferably determined in the dissolved phase. We could compile enough data to derive PNECs for water and sediment, applying assessment factors of 10, resulting in a proposed water quality criterion of 4 $\mu g\,L^{-1}$. A moderate background concentration was considered for sediments to derive a maximal permissible concentration of 36.9 $mg\,kg^{-1}$. This approach has some drawbacks: It is still based on a relatively small number of papers and its use for regional risk assessment is limited: environmental conditions will largely influence the abundance of toxic species, which has to be taken into account site-specifically. Current developments in passive sampling for the water phase but also for sediments (reviewed in Peijnenburg et al. (2014)) could provide opportunities for relating labile La-fractions in the environment to toxicity. Consequently, we suggest the derived values only as preliminary criteria, bound to change as more data will be published. We strongly recommend the development of a biotic ligand model for lanthanum.

Table 6
Calculation of quality targets by the added-risk approach.

Matrix	Cb (Europe)	MPA or PNEC	MPC	NC
Freshwater	$< 0.002\ \mu gL^{-1}$ –16 μgL^{-1} Median: 0.034 μgL^{-1}	4 $\mu g\,L^{-1}$	4 $\mu g\,L^{-1}$	0.074 $\mu g\,L^{-1}$
Sediment	1.3–553 $mg\,kg^{-1}$ Median: 31.9 $mg\,kg^{-1}$	5 $mg\,kg^{-1}$	36.9 $mg\,kg^{-1}$	32 $mg\,kg^{-1}$

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