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Behaviour and speciation of lanthanides during standardized ecotoxicity tests with *Daphnia magna*: implications and recommendations for hazard and risk assessment

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ABSTRACT

Lanthanides (LNs) are a group of 14 elements with steadily increasing economical importance due to their multiple uses in technologies essential for sustainable ecological, digital and energetic transitions. Although knowledge on LN ecotoxicology has greatly improved over the last decade, uncertainty persists with regard to their actual hazard and risk in freshwater environments. In particular, only limited information is available on i) the actual relationships between LN speciation vs. ecotoxicological responses in standardized laboratory tests and ii) the existence of regular and predictable patterns in LN ecotoxicity along the LN series. The present paper provides the first report on the ecotoxicity of all lanthanides (except Pm) for the freshwater crustacean *Daphnia magna* along with an unprecedented level of detail on LN speciation in the exposure medium.

Experimental data show that exposure concentrations can decrease by up to 95 % over the test duration, with the percentage decrease being inversely related with LN atomic mass. Thermodynamic speciation calculations confirm the possible formation of insoluble species, mainly LN carbonates. However, the corresponding theoretical solubility limits do not fully agree with measured concentrations at the end of the tests. Experimental verification of exposure concentrations (as a minimum at the beginning and end of laboratory tests) remains therefore mandatory to reach proper conclusions as to the ecotoxicity of each LN. A decreasing trend in ecotoxicity can actually be observed along the LN series when temporal changes in the exposure concentrations are properly accounted for. However, this trend remains dependent on exposure time and selected exposure metrics. This and other caveats

42 must be considered in future research to reach a community-based consensus for the proper
43 hazard and risk assessment of LN towards daphnids and other aquatic organisms.

44
45 **Keywords:** aquatic ecotoxicity, elemental speciation, *Daphnia magna*, critical raw materials, hazard
46 assessment

47 1. Introduction

48 The transition from a global economy dominated by fossil fuels to one based on renewable energy
49 sources and the increasing digitalization of our society will both lead to a more intensive use of several
50 mineral resources that are collectively termed critical raw materials (Bobba et al., 2020; IEA, 2021, 2023).
51 Rare Earth Elements (REY), which include lanthanides (LN), Yttrium and Scandium, are needed in a large
52 number of strategic, interlinked technologies and sectors such as wind energy generation, electric
53 mobility (fuel cells and traction motors), robotics, drones, information and communication technologies
54 at large, and medical applications (Bau & Dulski, 1996; Bobba et al., 2020). The increasing demand for REY
55 has raised a) geopolitical issues in relation to supply chains (Bobba et al., 2020; IEA, 2021, 2023), b)
56 prospections for new resources across the globe (Dushyantha et al., 2020; Pell et al., 2021), c) concerns
57 about the disruption of their natural biogeochemical cycles (Hissler et al., 2016; Kulaksız & Bau, 2013;
58 Lerat-Hardy et al., 2019; Louis et al., 2023; Martin et al., 2021), and d) concerns about the insufficient
59 knowledge as to their potential environmental and human health risks (Blinova et al., 2020; Gonzalez et
60 al., 2014; Malhotra et al., 2020).

61 Specific challenges arise when assessing REY ecotoxicity. The test media and experimental conditions
62 (notably pH values) used in (standardized) ecotoxicity testing cause lanthanides to precipitate as insoluble
63 chemical species such as carbonates, phosphates and hydroxides (Blinova et al., 2018; Gonzalez et al.,
64 2014; Kang et al., 2022; Lachaux et al., 2022). The formation of such precipitates leads to variable
65 exposure conditions during ecotoxicity tests, which makes the choice of exposure metrics particularly
66 critical when deriving concentration vs. response relationships for hazard and risk assessment. Proposed
67 solutions include modification of standard media to avoid, in principle, the formation of precipitates
68 (Aharchaou et al., 2020; Blinova et al., 2018; El-Akl et al., 2015; Ma et al., 2016; Revel et al., 2023; Vukov
69 et al., 2016) or the choice of exposure metrics based on analytically measured concentrations at the end
70 of the tests or based on geometric means between initial and final filterable concentrations (Lachaux et
71 al., 2022; Vukov et al., 2016). However, modifications in standard procedures should be consensus-based
72 not to sacrifice reliability, *sensu* Roth and Ciffroy (2016), for relevance (note that we mean no criticisms to
73 the scientific validity of the studies having adopted this approach). Furthermore, modification of test
74 medium does not necessarily avoid the formation of colloidal-sized precipitates at circumneutral pH
75 values (El-Akl et al., 2015; Revel et al., 2023). Meaningful and informative comparisons among studies on
76 LN ecotoxicity must therefore give the utmost consideration to LN behavior and speciation in the different
77 test media and experimental conditions (Gonzalez et al., 2014).

78 *Daphnia magna* is a well-studied model filter-feeder used in standardized ecotoxicity testing (ISO,
79 2012; OCDE, 2004). However, information on its responses following exposure to REY remains quite
80 limited with a few acute ecotoxicity studies on selected LN (Blinova et al., 2018; González et al., 2015;
81 Lachaux et al., 2022; Ma et al., 2016; Revel et al., 2023) and a handful of works on chronic ecotoxicity,
82 transgenerational effects and life-history traits (Blinova et al., 2018; Blinova et al., 2022; Deng et al., 2022;
83 Galdiero et al., 2019; Lüring & Tolman, 2010; Shu et al., 2023). Studies on the effects of selected LN
84 mixtures are also available and suggest that LN mixtures could follow a concentration addition model for
85 mixture ecotoxicity (Lachaux et al., 2022; Romero-Freire et al., 2019). However, to the best of our
86 knowledge, there is no peer-reviewed investigation published to date that compares the effects of the full
87 LN series including its 14 elements on *D. magna*.

88 Because lanthanides exhibit regular variation in their physico-chemical properties from Lanthanum
89 (La) to Lutetium (Lu), ecotoxicologists have been looking for similar predictable patterns in ecotoxicity
90 along the LN series or for ecotoxicological predictions based on physico-chemical properties (Le Faucheur
91 et al., 2021). The presence of ecotoxicological trends along the LN series implies that the effects of
92 individual LN and their mixtures could be predicted from studies on selected LN. Apart from its

93 fundamental importance, this scenario would result in considerable time and money savings without
94 compromising reliability and relevance of ecotoxicological results; a highly desirable situation for both
95 fundamental and applied research in this field. The few studies examining at least ten LN have identified
96 both increasing and decreasing trends in their ecotoxicological effects along the LN series (Blaise et al.,
97 2018; Borgmann et al., 2005; Lin et al., 2022; Manusadzianas et al., 2020; Weltje, 2002). Except for Weltje
98 (2002), these observations require further confirmation because of missing or incomplete information on
99 LN speciation in the exposure medium, a key factor when looking for trends along the LN series (Gonzalez
100 et al., 2014).

101 The present study provides the first report on the acute ecotoxic effects of all LN to the model species
102 *D. magna* according to the norm ISO 6341 (2012). The behavior and speciation of LN in the exposure
103 medium are examined with an unprecedented level of detail to i) provide reliable and relevant data for
104 hazard and risk assessment, ii) verify the existence of ecotoxicity trends along the complete LN series for
105 this model organisms, and iii) summarize evidence-based recommendations to ensure maximum
106 reliability and relevance in future research on the ecotoxicity of LN.

107 Experimental results show that a statistically significant linear relationship exists between the atomic
108 mass and the solubility of LN in the standard ISO 6341 test medium, implying that reliable ecotoxicological
109 endpoints must explicitly account for changes in LN concentration over the test duration. On the other
110 hand, ecotoxicological trends along the LN series appear dependent on exposure time and the selected
111 exposure metrics, highlighting the need for the definition of shared experimental and reporting
112 procedures across the research community on this aspect. The most critical and pressing issues include
113 further research on LN speciation in ecotoxicological test media and, for risk assessment purposes, in
114 natural waters along with understanding the bioavailability and ecotoxicological potential of different LN
115 chemical species.

116 2. Methods

117 2.1. Chemicals

118 All lanthanides salts (chloride or nitrates) were purchased from Sigma-Aldrich and had a minimal
119 purity of 99% (Table S1). Chemicals for preparing the test medium for acute tests with *Daphnia magna*
120 were also purchased from Sigma-Aldrich. Concentrated hydrochloric acid (HCl Suprapur 30%) and
121 concentrated nitric acid (HNO₃ 67%, Prolabo) were from VWR. Ultrapure water for
122 washing/preconditioning of plasticware and preparing test medium and LN stock/working solutions was
123 obtained from a Veolia Purelab® Chorus apparatus.

124 2.2. Ecotoxicity testing with *Daphnia magna*

125 Parthenogenetic specimen of *D. magna* were reared in Lefebvre-Czarda (LC)-Volvic medium (Table S2)
126 at 20 °C and under a 16h light : 8 h dark photoperiod (light intensity 35 μmol/s/m²). The growth medium
127 was changed three times a week and daphnids were fed an algal mixture of *Chlorella vulgaris*,
128 *Pseudokirchneriella subcapitata* and *Scenedesmus subspicatus* (2.5, 5, and 2.5 × 10⁶ cells/day/daphnia,
129 respectively) after each medium renewal.

130 Acute immobilization tests (48 h) were performed according to international guideline NF EN ISO 6341
131 (2012) at 20 ± 2 °C in the dark. Daphnids less than 24 h old were used in all tests and were obtained from
132 parent organisms aged from two to six weeks. The composition of the standardized ISO 6341 medium
133 was: CaCl₂ × 2H₂O (294 mg/L), MgSO₄ × 7H₂O (123 mg/L), NaHCO₃ (64.7 mg/L), and KCl (5.75 mg/L).

134 In range-finding tests (data not shown), daphnids were exposed to a series of seven dilutions of all LN
135 (except the radioactive Pm) at concentrations ranging from 0.05 to 45 mg/L of the corresponding salt (see
136 Table S3 for details and the equivalent elemental concentrations). This range had to be extended up to
137 1,750 mg/L of LN salts to identify the appropriate test concentrations for the definitive tests with La, Nd,
138 Sm, Tb, Dy, Ho, Er and Tm (Table S3). Preliminary tests were performed at an initial pH of 7.8 units, as
139 recommended by the ISO 6341 norm, and of 6.5 units to reduce the visible precipitation of lanthanides
140 carbonate species without compromising organisms' survival. In the preliminary tests performed at the
141 initial pH value of 7.8, observed mortality did not span the 0–100% range required for optimal EC_x
142 estimations. Definitive tests were therefore carried out only at an initial pH of 6.5 units.

143 In definitive tests, minimum and maximum nominal exposure concentrations (expressed as elemental
144 values) were 0.7 to 15 mg/L and 20 to 70 mg L⁻¹, respectively. A dilution series of nine or ten
145 concentrations plus one control were used for each element (Table S4). Test tubes were preconditioned
146 for 24 h with the corresponding test solutions to minimize adsorption losses on test vials. The
147 preconditioning solutions were discarded before starting the experiments. Four replicate exposures (10
148 mL total volume) with five organisms each were used for all test concentrations. Immobilization of
149 daphnids was evaluated after 24 and 48 h of exposure. Two independent definitive tests were performed
150 for each element. The pH of exposure solutions was measured in control tubes at t = 0 (assuming
151 homogenous initial pH for all exposure concentrations) and again in control tubes and selected exposure
152 concentrations at t = 48 h (see section R.1). Potassium dichromate was used as a positive control with EC₅₀
153 24 h values between 0.6 and 2.1 mg/L of K₂Cr₂O₇ as recommended by the ISO 6341 norm (2012).

154 2.3. Analytical verification of exposure concentrations in the test medium

155 Analytical determinations were carried out by Inductively Coupled Plasma – Mass Spectrometry (ICP-
156 MS, Nexion 350x, Perkin Elmer). The following isotopes were measured: ¹³⁹La, ¹⁴⁰Ce, ¹⁴¹Pr, ¹⁴⁶Nd, ¹⁴⁷Sm,
157 ¹⁵³Eu, ¹⁵⁷Gd, ¹⁵⁹Tb, ¹⁶³Dy, ¹⁶⁵Ho, ¹⁶⁶Er, ¹⁶⁹Tm, ¹⁷³Yb, ¹⁷⁵Lu. Rhenium (¹⁸⁷Re) was used as internal standard.
158 Limits of detection (LOD) and quantification (LOQ) ranged from 0.1 to 0.8 µg/L (Table S5). LOD Analytical
159 and procedural blanks were prepared and analyzed using the same analytical procedure as for samples.
160 The accuracy of the whole analytical protocol was validated using international certified material (BCR-
161 668- mussel tissues) from LGC standards. The recovery of LN ranged from 105 to 116 % (Table S5).

162 Actual exposure concentrations were analytically verified at t = 0 and 48 h for total (unfiltered)
163 concentrations and at t = 0, 5, 24 and 48 h for filterable concentrations. Filtrations were performed with
164 0.45 µm syringe filters (Millex 33 mm diameter, mixed cellulose esters – MCE; Millipore, reference
165 SLHA033SB, lot R7HA27577). The day before use, filters were washed with 10 mL of diluted (10% v/v) HCl,
166 rinsed three times with 10 mL of ultrapure water and stored at 4 °C in the dark in a zip-bag with a few
167 drops of MilliQ water to prevent drying of the membranes. Filtered and unfiltered solutions were
168 collected in 15 mL falcon tubes previously preconditioned in two baths of diluted 10% v/v HNO₃ followed
169 by two baths of milliQ water. The soaking time was 24 h in each baths. Except for t = 0 h, all solutions for
170 analytical measurements were incubated in the presence of daphnids as described for ecotoxicity tests.
171 The first 2 mL of filtered solutions were discarded and any living daphnids or visible debris were
172 eliminated from the unfiltered samples before transfer into the falcon tubes. All samples were acidified at
173 1% v/v with concentrated nitric acid and stored at 4 °C in the dark pending analysis. Analyses at t = 0 and
174 48 h were performed in duplicate for both total and filterable concentrations. Measurement precision
175 was estimated using the formula:

$$176 \quad (1) \quad Precision = \sqrt{abs\left(\frac{m_1 - m_2}{2}\right)}$$

177

178 where m_1 is the first replicate measurement, m_2 is the second replicate measurement and abs is the
179 absolute value of the difference.

180 Analytical verifications were carried out on solutions initially amended with a concentration
181 corresponding to the 24 h EC₅₀, hereinafter C_{EC50}, determined in the first round of definitive test. Tubes for
182 the analytical verification of LN concentrations were incubated in parallel with the second definite tests
183 and pH values were verified at t = 0 and 48 h for selected concentrations (see sections R.1 and R.2). For
184 selected elements Lanthanum (La), Cerium (Ce), Gadolinium (Gd) and Ytterbium (Yb), total and filterable
185 concentrations were measured also in solutions amended with the minimum (C_{min}) and maximum (C_{MAX})
186 test concentrations (Table S4). These additional measurements were performed in duplicate at t = 0, 24
187 and 48 h using solutions where daphnids were initially added (except at t = 0 h). The pH was checked in all
188 the C_{min} and C_{MAX} solutions immediately before filtration and/or transfer to falcon tubes for analysis.
189 Procedures for filter cleaning and removal of debris from unfiltered solutions were as previously
190 described.

191 **2.4. Speciation of lanthanides in the test medium**

192 Speciation calculations were performed using VisualMinteq (VM) version 3.1. The precipitation of
193 carbonate and hydroxide complexes was allowed as ‘possible solid phases’. The default VM database
194 specifies values for carbonate solubility products only for La, Neodymium (Nd), Samarium (Sm), Europium
195 (Eu), Gd, Dysprosium (Dy) and Yb. Additional calculations were therefore performed using the carbonate
196 solubility products determined by Firsching and Mohammadzadei (1986) who provided values for all
197 lanthanides except Ce (Table S6). The value reported by Li et al. (2004) was used for $Ce_2(CO_3)_3$ solubility.
198 Input temperature was fixed at 20 °C, medium alkalinity was specified as 0.831 meq/L $CaCO_3$ and the
199 Debye-Hückel equation was used for activity correction. Calculations were performed in pH range 5 to 9
200 using increments of 0.2 units and for nominal concentrations from 10 ng/L ($5.7-7.2 \times 10^{-11}$ M) to 50 mg/L
201 ($2.9-3.6 \times 10^{-4}$ M). The upper and lower limit of the molar concentration ranges refer to La and Lu,
202 respectively. The nominal concentration range used for speciation calculation covered the range of tested
203 and measured concentrations in the present study. For each element, theoretical solubility limits were
204 estimated from speciation calculation by subtracting the percentage of precipitated concentrations from
205 the corresponding nominal values.

206 Speciation was also modelled for solutions amended with concentrations corresponding to the 24 h
207 EC_{50} obtained in the first round of definitive tests for each element. In this case, the elemental
208 concentration for VM runs was entered as the time-weighted mean (TWM) of the 24 h C_{EC50} to account
209 for the concentrations decreases observed over the test duration (see the Results section for details). The
210 TWM was calculated from the experimentally measured concentrations at 0 and 24 hours using the
211 formula (OECD, 2008):

212 (2)
$$TWM = \frac{Conc_{t(x)} - Conc_{t(x+1)}}{\ln(Conc_{t(x)}) - \ln(Conc_{t(x+1)})}$$

213 where: $Conc_{t(x)}$ is the measured concentration at $t = 0$; $Conc_{t(x=1)}$ is the measured concentration at 24;
214 \ln is the Napierian logarithm of the measured concentrations at any time ‘t’.

215 Because TWM concentrations are mathematical estimates, the corresponding pH values to specify for
216 VM calculations were estimated as follows. Changes in pH were monitored between 0 and 48 h for
217 several concentrations of all tested elements (Table S7). Except for Praseodymium (Pr), linear
218 relationships existed between pH at 48 h and LN nominal concentrations. These relationships were used
219 to estimate the expected pH values for the calculated TWM concentrations and for the concentrations
220 measured at $t = 24$ and 48 h (Table S8). In the case of Pr, the pH value of the concentration closer to the
221 TWM EC_{50} was used. It will be shown later that pH changes were minor between 24 and 48 h.

222 **2.5. Data analysis and statistics**

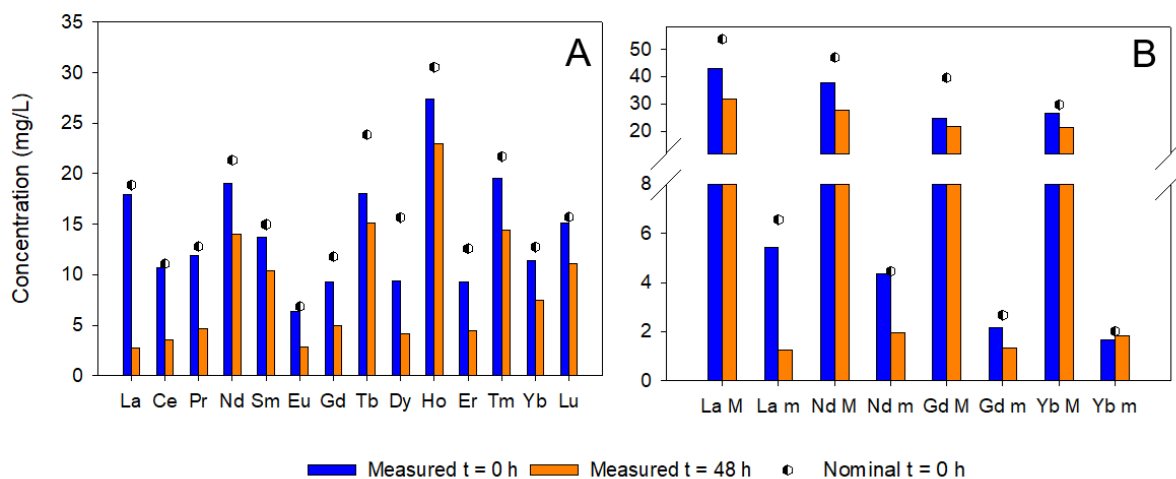
223 The presence of statistically significant linear relationships between variables was verified using the
224 standard Pearson least squares method and a robust MM estimation method that is less sensitive to
225 outliers and non-normally distributed errors (Susanti et al., 2014; Venables & Ripley, 1999). The letters
226 MM indicate that the estimation is of the maximum likelihood type, but do not form an acronym. Rather,
227 they refer to the type of estimation procedure as explained in Susanti et al. (2014). Linear relationships
228 were obtained with R version 3.6.0 (R Core Team 2019 R Core Team, 2019. R: A Language and
229 Environment for Statistical Computing. R Foundation for statistical computing, Vienna. [https://www.R-](https://www.R-project.org)
230 [project.org](https://www.R-project.org)). Graphs were prepared using Sigma Plot (version 14).

231 **3. RESULTS**

232 **3.1. Total concentrations in the test medium**

233 Measured levels of LN in control solutions were always below the corresponding analytical detection
234 limits (Table S5). The relative standard deviation (RSD) for replicate measurements of total LNs
235 concentrations was less than 10% at $t = 0$ and usually within 30% at $t = 48$ h. Total concentrations at $t = 0$
236 were within 20% of the expected nominal values except for solutions amended with Dy at C_{EC50} where
237 measured values were 60% of the expected ones (Fig. 1 and Table S9). This discrepancy, possibly due to
238 dilution errors, does not affect the objectives of the present paper nor the data interpretation presented

239 below. At the end of the tests (48 h), total concentrations in solutions initially amended with C_{EC50} were
 240 within 25% of initial values for Nd, Tb, Ho, Tm, Sm and Lu, but had decreased by more than 40% for the
 241 other elements (Fig. 1A and Table S9). Total concentrations also decreased by more than 50% in medium
 242 aliquots spiked with C_{min} of La, Nd, and Gd (6.55, 4.44 and 2.67 mg/L, respectively), but remained
 243 relatively constant for Yb (2.0 mg/L). In solutions spiked with C_{MAX} , total concentrations (La = 53.5, Nd =
 244 47.0, Gd = 39.4 and Yb = 29.6 mg/L) showed little variation over 48 h (Fig. 1B, Table S9).

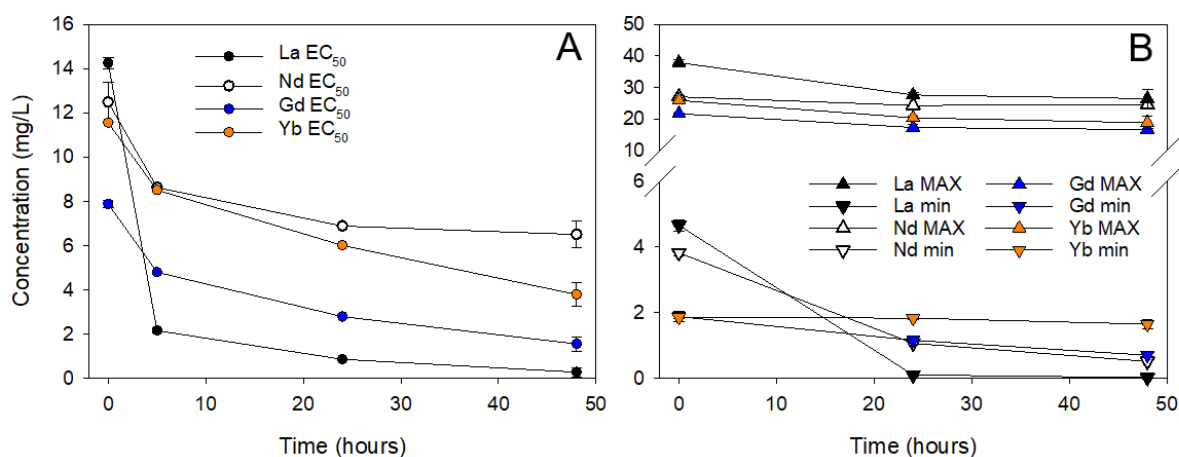


245

246 Figure 1. (A) Total concentrations of lanthanides (LN) measured at 0 and 48 hours in solutions
 247 initially amended with LN concentrations equal to the corresponding EC_{50} for *D. magna*. (B) Same as
 248 panel A for solutions initially amended with the maximum (LN M) and the minimum (LN m)
 249 concentrations of La, Nd, Gd and Yb used in ecotoxicity tests. Nominal values expected at t = 0h are
 250 indicated for comparison purposes in both panels.

251 3.2. Filterable concentrations in the test medium

252 In solutions amended with C_{EC50} , filterable concentrations decreased by 50–98% over the test duration
 253 according to three temporal patterns as described in figure 2A for selected elements and in table S9 and
 254 Figure S2 for the entire LN series. In pattern one (La and Ce), filterable concentrations decreased by more
 255 than 80% within 5 h from the start of the incubation and fell below 5% of the initial values after 48 hours.
 256 In pattern two (Pr, Sm, Eu, Gd, Er, Dy, Yb), the concentration decrease was less rapid and reached 70–95%
 257 after 48 hours. In pattern three (Nd, Tb, Tm, Ho, Lu), the overall concentration decrease was less than
 258 50% with little changes between 24 and 48h. After 48 h, the differences between total and filterable
 259 concentrations were less than 2-fold for Nd and the heavier REE (Tb, Dy, Ho, Er, Tm, Yb, Lu), but between
 260 3- and 34-fold for the lighter REE. The small differences for heavier REE suggest that these elements were
 261 either more soluble than the lighter REE or formed precipitates that were not retained by the 0.45 μ m
 262 filters. At C_{min} , the behavior of La, Nd, Gd and Yb essentially agreed with the observations at C_{EC50} , while
 263 filterable concentrations remained within 30% of the initial values for C_{MAX} scenarios (Fig. 2B, Table S9).



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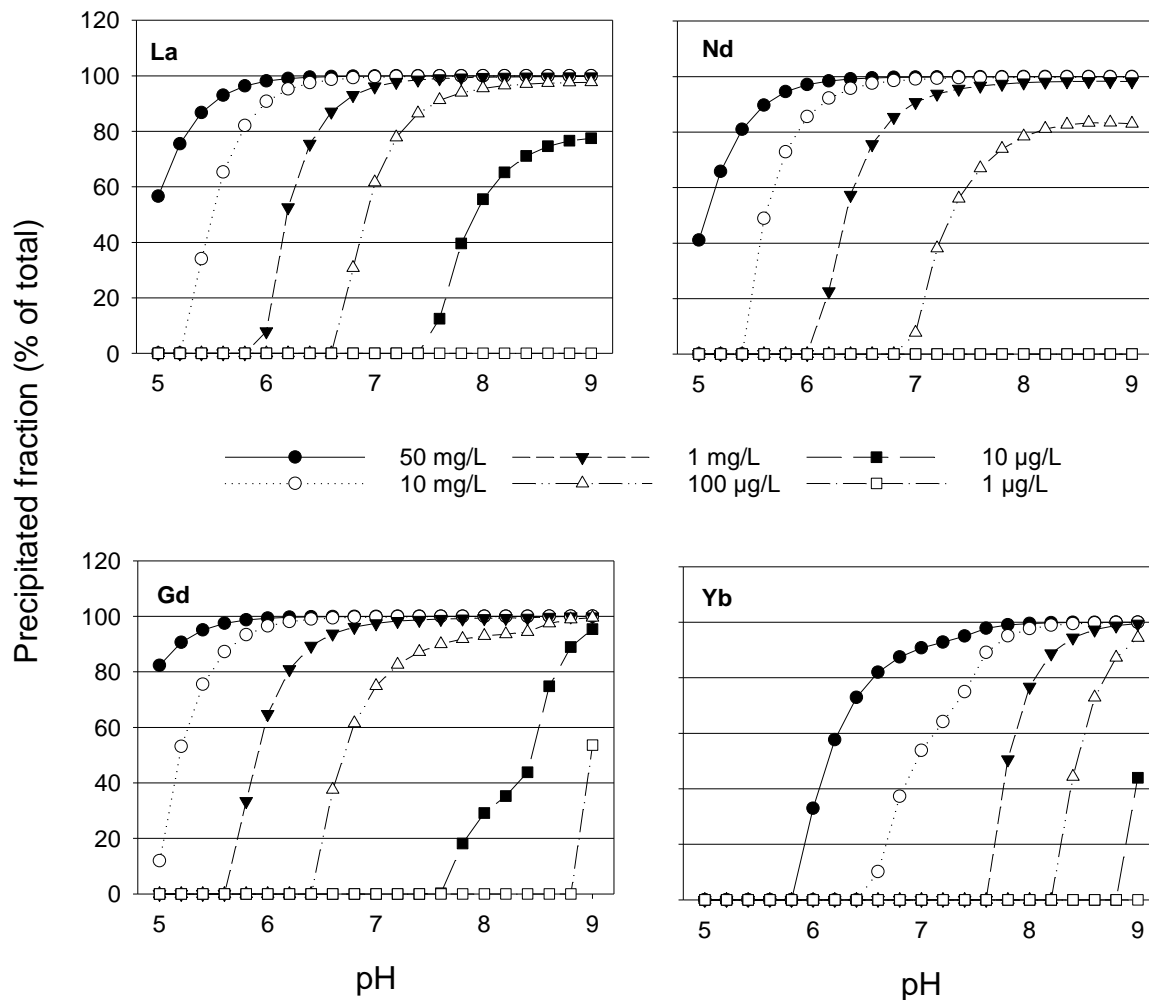
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Figure 2. (A) Temporal changes in the filterable concentrations (< 0.45 μm) of La, Gd, Nd, Yb for solutions initially amended with lanthanides concentrations equal to the corresponding EC₅₀ at 24 h. The selected elements are representative of the three different behaviors across the whole lanthanides series (see text for details and Table S9 and Fig. S2 for full results). (B) Same as (A), but for solutions initially amended with maximum (MAX) and minimum (min) tested concentrations.

270 **3.3. Theoretical solubility of lanthanides in the test medium**

271 The present section will focus on speciation results obtained using the carbonate solubility product
272 (K_{SP}) established by Firsching and Mohammadzadei (1986), except for La and Ce. In the case of La, using
273 the K_{SP} of Firsching and Mohammadzadei (1986) clearly overestimated La solubility compared with
274 experimental results. The default K_{SP} in the VisualMinteq (VM) database was therefore preferred (Table
275 S6). An indicative K_{SP} for $Ce_2(CO_3)_3$ was taken from Li et al. (2003), because no value for Ce was available in
276 Firsching and Mohammadzadei (1986).

277 In the pH range from 6.0 to 7.8 (covering the values measured in ecotoxicity tests, Table S7),
278 formation of insoluble carbonate species was predicted for all LNs and for concentrations as low as 10
279 μg/L (Fig. 3). Formation and precipitation of hydroxides, $LN(OH)_3$, was also predicted for Er, Tm, Yb and Lu.



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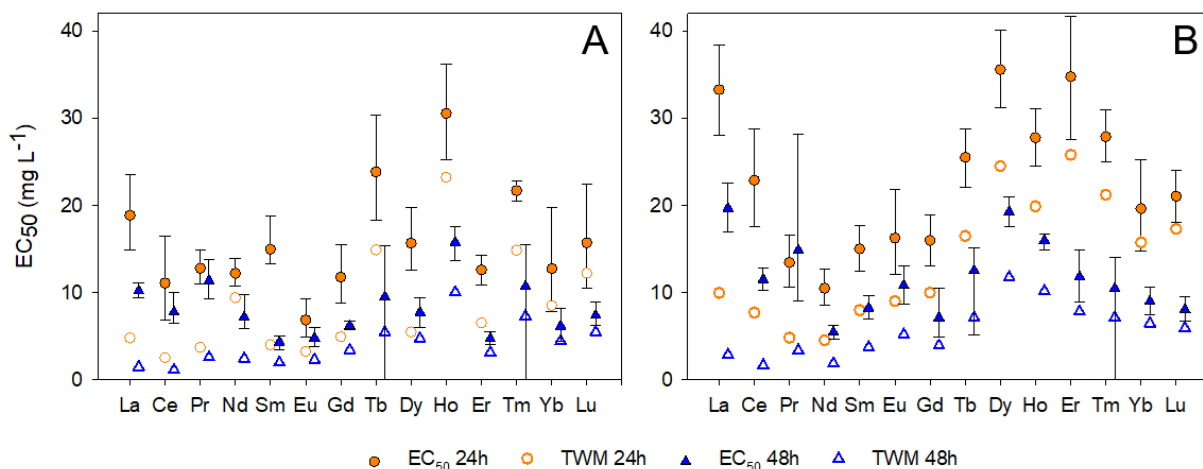
Figure 3. Theoretical solubility of La, Nd, Gd and Yb as a function of pH in ISO 6341 medium for acute toxicity testing with *Daphnia magna*. Model calculations were performed for theoretical concentration from 1 µg/L to 50 mg/L. No precipitation was predicted in theoretical solutions amended with 10 and 100 ng/L (plots not shown).

285 3.4. Lanthanides ecotoxicity

286 In the first round of definitive test, nominal EC₅₀ ranged from 6.84 to 30.5 mg/L and from 4.70 to 15.7
287 mg/L after 24 and 48 h of exposure, respectively (Fig. 4a; Table S10). To account for the decrease in LN
288 concentrations over time (section 3.1), the TWM EC₅₀ were calculated as follows. For the 24h TWM EC₅₀,
289 the experimental data presented in section 3.1 (i.e., the filterable concentrations at t = 0 and t = 24 h)
290 were directly entered into equation 2. For the 48h TWM EC₅₀, the LN concentrations at 48h were
291 estimated using equation 5 assuming initial concentrations equal to the nominal 48h EC₅₀ (see Table S11
292 for a detailed explanation of the procedure and for calculation results). Note that the experimental
293 measurements at 48h (section 3.1) could not be used for this purpose, because they refer to medium
294 aliquots initially spiked with concentrations equal to the 24h EC₅₀. For comparison purposes, the same
295 procedure was also performed for the 24h TWM EC₅₀ estimated using equation 4 (Table S11).

296 The TWM 24h EC₅₀ calculated using experimental values differed from the nominal EC₅₀ by more than
297 2-fold for La, Ce, Pr, Sm, Eu, Gd and Dy (Fig. 4A). The 24h TWM EC₅₀ estimated using equation 4 were
298 within 20 % of those obtained using experimental data for La, Pr, Eu, Tb, Ho, Tm, Yb, Lu and within a
299 factor of two for the remaining elements except Nd (Table S11). Differences between nominal and TWM
300 48h EC₅₀ were more than 2-fold for La, Ce, Pr, Nd, Sm and Eu (Table S11). The observations confirm that
301 TWM correction would avoid underestimating the ecotoxicity of La, Ce, Pr, Sm, Dy and, to a lesser extent,
302 Eu and Gd (Fig 4A). For the second round of definitive tests, 24h and 48h EC₅₀ ranged from 10.5 to 35.6

303 mg/L and 5.4 to 19.7 mg/L, respectively (Table S10, Fig. 4B). The TWM corrections were performed using
 304 equations 6 and 7 (Table S11), leading to results and conclusions equivalent to those discussed for the
 305 first round of tests.

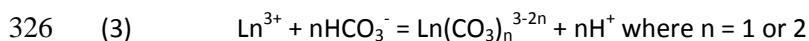


306
 307 Figure 4. Nominal and Time-Weighted Mean (TWM) EC₅₀ values for specimen of *Daphnia magna*
 308 exposed to lanthanides for 24 or 48 h. (A) first series of definitive tests and (B) second series of
 309 definitive tests. Bars represent 95% confidence intervals for nominal EC₅₀ (estimation not possible
 310 for TWM). Values for 24 and 48 h have been slightly offset for graphical representation purposes.

311 4. DISCUSSION

312 4.1. Temporal changes in total LN concentrations

313 In the present study, total LN concentration at t = 0 h were in good agreement with expected values,
 314 but showed an unexpected decrease at the end of the test for several LN (Fig. 1 and Table S9). We cannot
 315 exclude that the decrease in total LN concentrations could partly originate from adsorption losses onto
 316 the tubes walls despite preconditioning of the test tubes. However, daphnids can actively ingest LN
 317 precipitates forming into the test medium and contribute to the observed losses, although the extent of
 318 such ingestion is element-dependent (Revel et al., 2023). The effect of LN addition on the pH of the test
 319 medium (Table S7) also determines the observed behavior at C_{EC50} and C_{min}. Because test tubes were open
 320 to the atmosphere, medium pH increased by 0.5–1.0 pH units in most tubes over the test duration (Table
 321 S7). A similar situation was observed for tubes amended with C_{min} of La, Nd, Gd and Yb, while addition of
 322 C_{MAX} of the same elements resulted in pH values remained close to the initial value of 6.5 (Table S7). An
 323 inverse relationship between LN concentrations and pH was observed (Table S8) and reflects the
 324 formation of Ln₂(CO₃)₃ complexes in test solutions along with the release of protons according to the
 325 following equilibrium (Luo & Byrne, 2004):



327 As for alkaline waters in equilibrium with atmospheric CO₂ (Luo & Byrne, 2004), carbonate complexes
 328 are expected to dominate LN speciation regardless of the added concentrations. The formation and
 329 subsequent precipitation of such complexes consume the HCO₃⁻ / CO₃²⁻ ions present in the test medium,
 330 reduce its buffering capacity, shift its pH toward more acidic values via the release of protons (equation 3)
 331 and eventually increase LN solubility at high concentrations (see section 3.3). At the end of the test, pH
 332 differences can exceed one unit across the exposure range (Table S7), indicating that LN speciation is not
 333 homogenous for all exposure concentrations. The ecotoxicological significance of such variability remains
 334 to be ascertained and will be further discussed in section 3.4.

335 4.2. Temporal changes in filterable LN concentrations

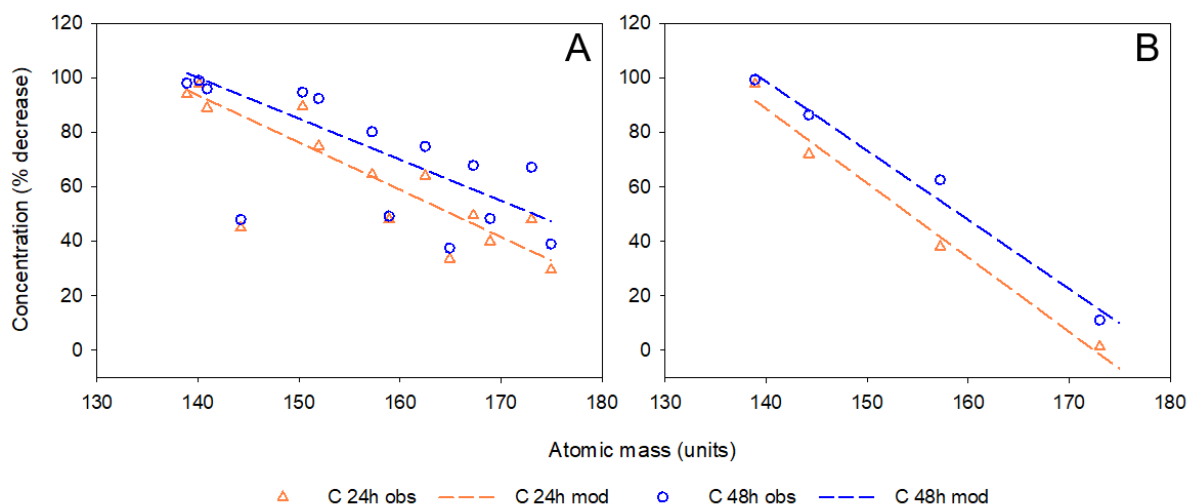
336 The decrease in filterable concentrations was always more marked than the corresponding total ones,
 337 suggesting the presence of insoluble LN particles large enough to be retained by the pores of 0.45 μm
 338 filters (see also section 3.3). Inverse linear correlations (equations 4 to 7) existed between the decrease in
 339 filterable concentrations at 24 and 48 h (expressed as % of initial concentrations) and LN atomic masses in
 340 solutions amended at C_{EC50} and C_{min} (Fig. 5). Robust MM regressions showed a better fit compared with
 341 conventional partial least-squares regressions for the C_{EC50} scatterplots, while the performance of the two
 342 regressions was equivalent for C_{min} (data not shown). For the sake of clarity, only robust MM regressions
 343 will be presented and discussed.

344 (4) $\%Loss C_{EC50_24hMM} = (-1.7353 \pm 0.2517) \textit{ atomic mass} + (337 \pm 40) \quad R^2 = 0.70$

345 (5) $\%Loss C_{EC50_48hMM} = (-1.5065 \pm 0.3772) \textit{ atomic mass} + (311 \pm 59) \quad R^2 = 0.54$

346 (6) $\%Loss C_{min_24hMM} = (-2.7296 \pm 0.2438) \textit{ atomic mass} + (471 \pm 38) \quad R^2 = 0.98$

347 (7) $\%Loss C_{min_48hMM} = (-2.5407 \pm 0.2461) \textit{ atomic mass} + (454 \pm 38) \quad R^2 = 0.98$



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352 Figure 5. (A) Scatterplots of percentage decrease in lanthanides concentrations vs. atomic mass at
 353 24 and 48 h in solutions initially amended with LN concentrations equivalent to the corresponding
 354 C_{EC50} and (B) to the minimum tested concentration C_{min} . Dotted lines are the corresponding linear
 355 fits (robust MM regressions — equations 4 to 7). Note that a 100% decrease means a filterable
 356 concentration equal to zero after 24 or 48h, while a 0% decrease means that concentrations did not
 357 change over time. See text and Figure S1 for the actual meaning of modelled values above 100% or
 358 below 0.

359 The better goodness-of-fit at 24 h reflects the presence of elements showing little concentration
 360 decrease between 24 and 48 h (i.e. pattern three in Figs. 2 and S2). Regression slopes were higher for
 361 solutions amended with C_{min} (equations 6 and 7) than with C_{EC50} (equations 4 and 5). These results
 362 indicate that i) the concentrations of lanthanides decreased faster in solutions amended with C_{EC50} than
 363 with C_{min} and ii) the differences in concentration decrease between C_{min} and C_{EC50} progressively became
 364 more important from La to Lu (see Fig. S1 for details and examples). In solutions amended with C_{EC50} , the
 365 observed percentage decrease in Nd concentrations (atomic mass = 144.24) was markedly lower than
 366 expected at both 24 and 48h (Fig. 5). We do not have a definite explanation for Nd behavior, but we
 367 notice that El-Akl et al. (2015) reported the formation of Nd-colloidal particles with an approximate size of
 368 60 nm in a non-complexing medium test medium for freshwater algae. Particles of such sizes can probably
 369 pass through the pores of standard 0.45 μm filters. However, it remains unclear while only Nd would form

370 such small-sized particles compared with other LN. Some modelled % losses fall outside the 0–100 %
371 range; i.e. the actual boundaries for experimental observations. These model artifacts do not invalidate
372 the clear trend in increasing LN solubility from La to Lu in the ISO 6341 test medium for acute ecotoxicity
373 testing with *D. magna*. The proposed linear models can be used to optimize analytical efforts to check for
374 exposure concentrations in ISO test medium for *D. magna* over the test duration (at least for
375 concentration up to C_{EC50} and with the possible exception of Nd).

376 Although decreasing total or filterable LN concentrations have been previously reported in
377 standardized test media for *D. magna* or *Daphnia* spp. (Barry & Meehan, 2000; Blinova et al., 2018;
378 González et al., 2015; Lachaux et al., 2022; Ma et al., 2016; Vukov et al., 2016), the present study provides
379 the first data of the different kinetics in concentration decrease across the whole LN series. Overall, LN
380 solubility appears to be time and concentration dependent and a detailed follow up of changes in
381 exposure concentrations over test duration is needed to correctly interpret LN ecotoxicity data. Caution is
382 also required to understand the impact of adding large quantities of LN to the test medium. Indeed, LN
383 concentrations remained within $\pm 30\%$ of the initial values in solutions amended with C_{MAX} for La, Nd, Gd
384 and Yb; contrary to what observed for C_{EC50} and C_{min} (Figure 2A, B). Furthermore, the pH in solutions
385 amended with C_{MAX} remained around the initial value of 6.5 units or slightly decreased over time, again in
386 contrast with observations of C_{EC50} and C_{min} where pH increased to about 7.5 units over the test duration
387 (Table S7 and S9). To the best of our knowledge, these are the first results considering the changes in pH
388 during standardized ecotoxicity test with *D. magna* following protocol ISO 6341 (2012). These findings
389 could also bear relevance for correct interpretation of chronic ecotoxicity tests such as the *Daphnia*
390 *magna* reproduction test (OCDE, 2012). Depending on the tested LN, exposure concentration can
391 decrease by up to 80% of initial values in five hours; a span much shorter than the 48 h among medium
392 renewal usually adopted in chronic tests with *D. magna*.

393 **4.3. Theoretical solubility of LN**

394 At the initial pH for the definitive ecotoxicity tests (range from 6.4 to 6.6, Table S7), all LN
395 concentrations were above the corresponding theoretical solubility except for the C_{min} of Er, Tm, Yb and
396 Lu (Table S12). The decrease in total and filterable LN concentrations over time (Fig. 1, Table S9) therefore
397 agreed with the modelling results. However, the agreement between modelled and observed LN solubility
398 was far from perfect, reflecting the limitations of thermodynamic speciation models for our experimental
399 matrix and conditions.

400 In solutions spiked with C_{EC50} , measured filterable concentrations at $t = 24$ and 48 h were consistently
401 higher than the corresponding theoretical solubility values in the pH range from 6.6 to 7.4 (Table S12).
402 The pH range 6.6–7.4 covers the corresponding values estimated from concentration–pH relationships in
403 solutions initially spiked with C_{EC50} (Table S8). The discrepancies between theoretical and measured
404 concentrations could simply indicate that the system had not yet reached equilibrium at the end of the
405 experiments. This explanation holds for La, Ce, Pr, Sm, Eu, Gd, Dy, Er, Tm and Yb. The filterable
406 concentrations of these elements continuously decreased between 0 and 48 h (Fig. 2) and the trend could
407 have continued beyond 48 h. On the other hand, the non equilibrium explanation does not apply to Nd,
408 Tb, Ho, Tm and Lu whose filterable concentrations plateaued after 24 h while remaining above the
409 corresponding theoretical solubility limits (Fig. 2). One possibility is that the measured filterable
410 concentrations of these elements included colloidal-sized precipitates small enough to pass through the
411 filter pores. The presence of colloids could have increased the apparent solubility of these elements
412 compared with VM calculations that do not consider the particle size of the precipitates. Finally, the
413 conditional nature of VM modelling parameters could also contribute to the observed differences for all
414 LNs (Rodríguez de San Miguel et al., 2023).

415 The reasoning developed for solutions amended with C_{EC50} also applies to experiments using C_{min} for
416 La, Nd, Gd and Yb. In solutions amended with C_{MAX} for the same elements, all daphnids died within 24 h
417 and pH values at $t = 48$ h had dropped below the initial value of 6.5 (Table S9). Both factors likely
418 contributed to the stability of filterable concentrations in these solutions (Fig. 2) even if the added LN
419 levels initially exceeded the corresponding theoretical solubilities and precipitation could be expected
420 (Fig. 3 and Table S12). Besides low pH values, the death of daphnids likely released different organic
421 molecules into test solutions, possibly increasing LN solubility (Lachaux et al., 2022).

422 **4.4. Comparison of different exposure metrics for lanthanides ecotoxicity**

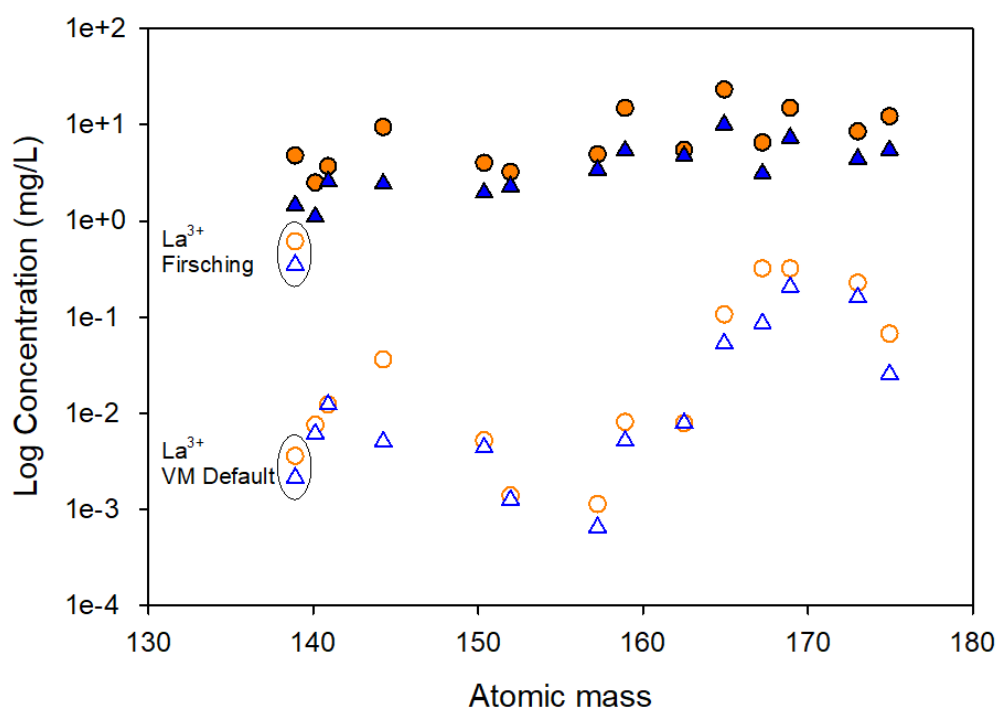
423 The two rounds of tests gave equivalent results (i.e., overlapping 95% confidence intervals of nominal
424 EC_{50}) for Pr, Nd, Gd, Tb, Ho, Tm, Yb, Lu and, at 24 h only, Sm (Table S10). In all other cases (La, Ce, Eu, Dy,
425 Er, and, at 48 h only, Sm), EC_{50} were higher in the second round of definitive tests than in the first one
426 (Table S10, Fig. 4). Except for Eu (see below), we surmise that these differences were caused by the higher
427 pH values of the exposure solutions during the second round of tests (Table S7).

428 In both experiences, pH values were measured at $t = 0$ h in control solutions (assumed to be
429 representative of all exposure solutions at the beginning of the tests) and at 48 h for selected
430 concentrations (Table S7). Measurements of pH after 24 h of exposure were not systematically performed
431 during definitive tests to avoid additional stress to daphnids. However, available data showed limited pH
432 variability between 24 and 48 h (Table S9).

433 Statistically significant inverse linear relationships were found between the measured pH values at 48 h
434 and the initial LN concentration in the test medium (Table S8). These linear relationships were used to
435 estimate the pH value in hypothetical aliquots of test media spiked with the corresponding nominal EC_{50}
436 (Table S8). Because pH controls the solubility of $Ln_2(CO_3)_3$, a higher pH value at the end of the test (data
437 in Table S7) implies i) a larger and probably faster decrease in the actual exposure concentrations over the
438 test duration (see sections 3.2 and 3.3) and hence ii) higher EC_{50} values in the second round of definitive
439 tests. The pH explanation does not hold for Eu whose exposure solutions showed lower pH values for the
440 higher EC_{50} in the second test series (Table S7 and S8). We acknowledge that the proposed simple
441 explanation does not account for kinetics processes and for confounding processes linked to the presence
442 of daphnids in the exposure solutions.

443 Besides the formation of insoluble precipitates, expressing the EC_{50} in terms of free Ln^{3+}
444 concentrations in the dissolved fraction can provide further insight into the ecotoxicity of LNs and
445 increase the reliability and relevance of concentration–response relationships. Estimation of Ln^{3+}
446 concentrations was done for TWM EC_{50} values using the same assumptions described in section 3.3 for
447 the choice of stability constants for $Ln_2(CO_3)_3$ precipitation. These estimations will be presented only for
448 the first series of definitive tests.

449 In absolute terms, Ln^{3+} based EC_{50} were between 1 to 10 $\mu\text{g/L}$ for La, Ce, Sm, Eu, Gd, Tb and Dy and in
450 the tens to hundreds of $\mu\text{g/L}$ for the remaining elements. Differences between Ln^{3+} and TWM-based EC_{50}
451 were between 1 and 3 orders of magnitude at both 24 and 48h of exposure (Fig. 6). The actual
452 ecotoxicological significance of such estimations depends on how well the constants used in the
453 thermodynamic models are representative of the true LN speciation in the test medium. For example,
454 estimates of free La^{3+} concentrations were three orders of magnitude higher when using the $La_2(CO_3)_3$
455 solubility product reported by Firshing et al. (1986) compared with the default value in the VisualMinteq
456 database (Fig. 6). Further work is needed to experimentally measure the free Ln^{3+} concentration in
457 exposure medium.



● TWM 24h (mg/L)
 ▲ TWM 48h (mg/L)
 ○ Ln³⁺ 24h (mg/L)
 △ Ln³⁺ 48h (mg/L)

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Figure 6. Comparison between 24h and 48h Time Weighed Mean (TWM) EC₅₀ expressed as total filterable concentrations and free Ln³⁺ concentrations. Free Ln³⁺ concentrations were estimated using VisualMinteq (see section 3.3 for details). Calculations for free lanthanum (La³⁺) are presented using two different La₂(CO₃)₃ solubility products to invite caution when making ecotoxicological inference using modelled La³⁺ values (see text for details).

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Considering the important quantities of LN salts added to the test medium (Table S3) and the tendency of test medium to get more acidic at high levels of added LN salts, it is important to verify the possible contribution of these two factors (pH and counterions added along with LNs) onto the survival of *D. magna*. Available reports (Chen et al., 2012) and online article abstracts (El-Deeb et al., 2011; Zhuang, 1994) suggest that effect of low pH become visible at values below 5.5 units, lower than those observed in the present study. In the case of the NO₃⁻ and Cl⁻ ions, the maximum concentration added along with LN were 76 mg/L and 46 mg/L, respectively (information on the specific counterion for each LN salt can be found in section 2.1). In the case of nitrates, LC50 reported in the literature for *D. magna* are in the range 323–611 mg/L N-NO₃⁻, i.e., 1,430–2,705 mg/L NO₃ (Scott & Crunkilton, 2000). In the case of chlorides, LC50 depends on the specific salt added to the test medium. Potassium chloride (KCl) has the lowest reported 48h LC50 of 660 mg/L, which corresponds to 314 mg/L of Cl⁻ (Mount et al., 1997). Based on this information, the toxic effects observed in the present study can be ascribed to exclusively to the added LN.

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The EC₅₀ values based on nominal values (Fig. 4 and Table S10) agree with those observed in previous studies with daphnids and other crustaceans (see the recent data compilation reported in Table S5 of Lachaux et al. (2022)). Comparison based on measured LN concentrations or on modelled free ion concentrations are less straightforward because of the methodological differences among the studies containing such information. In the case of Nd, Gd, and Yb, our TWM EC₅₀ at 48 h (Table S11) are within the 95% confidence intervals of the values reported by Lachaux et al. (2022) who used the same test medium and analogous methodologies. However, our estimations for EC₅₀ based on modelled free-ion concentrations (Fig. 6) are three orders of magnitude lower than those of Lachaux et al. (2022) because of different assumptions in model calculations. In particular, we allowed the precipitation of Ln₂(CO₃)₃ solids in the test medium and subtracted the precipitated concentrations from the total ones before calculating

487 the free-ion concentrations. Both approaches can be acceptable depending on the experimenter's choice
 488 as to the complexation and solubility constants in the speciation model (see sections 2.x and 3.9 for
 489 further discussion). Blinova et al. (2018) did observe a marked decrease in La, Ce, Pr, No, and Gd
 490 concentrations in standard artificial freshwater (OCDE, 2004), but did not attempt to calculate 48h EC₅₀
 491 based on measured concentrations. Vukov et al. (2016) reported a 48 h EC₅₀ of 0.49 mg/L Dy for *D. pulex*
 492 based on the concentration measured at the end of the test. This value is 10- to 20-fold lower than the
 493 48h TWM EC₅₀ of the present study (Table S11). However, it compares favorably with the filterable Dy
 494 concentration of 2 mg/L that remained in our exposure medium after 48 hours (Table S9). Shu et al.
 495 (2023) reported 24 h and 48 h EC₅₀ of 16.2 and 2.3 mg/L, respectively, for *D. magna* exposed to La
 496 according to OCDE guideline 202 (OCDE, 2004). These values referred to analytically measured filterable
 497 La concentrations at t = 0 (after 2h of equilibration following the initial La spike). They are higher than our
 498 EC₅₀ based on TWM (Table S11), but difficult to compare with nominal values considering the tendency of
 499 La concentration to rapidly decrease upon addition to the test medium (Fig. 1). Finally, Ma et al. (2016)
 500 substituted NaHCO₃ with NaOH in the test medium for *D. magna* and successfully avoided carbonate
 501 precipitation when testing the ecotoxicity of Ce. As a result, the filterable (0.22 μm) Ce concentration
 502 showed little variation between the beginning and the end of the test. Their 48h EC₅₀ of 1.5 mg/L (based
 503 on measured concentration) is in excellent agreement with our 48h TWM EC₅₀ of 1.11 mg/L (1st series)
 504 and 1.64 mg/L (2nd series) (Table S11), showing that correction for concentration decrease can improve
 505 data comparability across studies. We are not aware of other studies providing EC₅₀ based on free ion
 506 concentrations for *D. magna* or other daphnids, apart from the mentioned comparison with Lachaux et al.
 507 (2022).

508 4.5. Trends in EC₅₀ along the lanthanides series

509 Ecotoxicologists are constantly seeking for the presence of regular, predictable variations in EC₅₀ along
 510 the LN series, in analogy with the predictable changes in physico-chemical properties such as ionic radius
 511 and ionization potential. Regular ecotoxicological patterns would allow to focus research efforts on a few
 512 representative lanthanides from which relevant information could then be derived for the whole series.

513 In the present study, nominal EC₅₀ values did not show any clear trend along the LN series after 24 or
 514 48h of exposure (Fig. 4). On the other hand, linear relationships could be derived between the atomic
 515 mass of lanthanides and the EC₅₀ values expressed as TWM (equations 8 to 12, see Table S13 for the
 516 statistical significance of regression coefficients and calculation details). For 24 h exposure in the first
 517 series of experiments, two relationships were derived; one using TWM values calculated from equation 2
 518 with analytically measured concentration at 0 and 24 h as inputs (equation 8) and one using TWM
 519 estimated from equation 4 (equation 9). On average, the predicted values differed by 30–40 % from the
 520 input TWM values, with differences larger than 50% for many elements (Table S14).

$$521 \quad (8) \quad TWM_{24h(1stSeries_Exp)} = (0.2582 \pm 0.115) \textit{ atomic mass} + (-32.0 \pm 18.1) \quad R^2 = 0.29$$

$$522 \quad (9) \quad TWM_{24h(1stSeries_Mod)} = (0.3010 \pm 0.0898) \textit{ atomic mass} + (-37.5 \pm 14.1) \quad R^2 = 0.48$$

$$523 \quad (10) \quad TWM_{48h(1stSeries)} = (0.136 \pm 0.0413) \textit{ atomic mass} + (-17.4 \pm 6.5) \quad R^2 = 0.48$$

$$524 \quad (11) \quad TWM_{24h(2ndSeries)} = (0.4516 \pm 0.1013) \textit{ atomic mass} + (-56.9 \pm 15.9) \quad R^2 = 0.62$$

$$525 \quad (12) \quad TWM_{48h(2ndSeries)} = (0.1720 \pm 0.0489) \textit{ atomic mass} + (-21.3 \pm 7.7) \quad R^2 = 0.51$$

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 530 Expressing TWM EC₅₀ in terms of free ion concentrations resulted a clear M-shaped pattern at both 24
 531 and 48 h (Fig. 6). This pattern resembles the *tetrad effect* linked to the progressive filling of *f* orbitals
 532 along the lanthanides series (McLennan, 1994) and is also similar to the changes in the energy of
 533 electronic configuration from La to Lu (Schinzel et al., 2006). In particular, La, Gd and Lu have the largest
 534 differences between the energy of the highest occupied and lowest occupied molecular orbital and form
 535 the most stable complexes, which agrees with their higher ecotoxic potential (lower Ln³⁺ EC₅₀) compared
 536 with adjacent elements (Fig. 6). However, the solubility products used in the present study (Fig. S3) also
 537 showed a M-shaped trend when plotted against the atomic mass of the corresponding elements.

538 Otherwise stated, the pattern observed in Ln³⁺ EC₅₀ may simply be a model artifact linked to speciation
539 calculation. Methodological developments are clearly necessary to obtain experimental measurements of
540 LN speciation in ecotoxicological test media and verify the true meaning of this M-shaped pattern in Ln³⁺
541 EC₅₀.

542 Few studies examined the ecotoxic effects of the whole LN series and they reached contrasting results
543 (Table 1). Data from Blinova et al. (2018) provide the most relevant comparison for the present study and
544 suggest a linear decreasing trend for 48 h LC₅₀ to *D. magna* based on nominal values (La > Ce > Pr > Nd ≈
545 Gd). However, a strong decrease in LN concentration was reported over the test duration and the trend
546 based on measured concentration could not be validated based on the information provided in the paper.
547 Similarly, 21 d chronic LC₅₀ did not show any trend (La ≈ Gd > Ce ≈ Pr ≈ Nd). Decreasing ecotoxicity along
548 the LN series has been reported for *Hyalella Azteca*, *Hydra attenuata* and *Danio rerio* based on nominal
549 concentrations (Table 1). However, the heaviest lanthanides did not conform to the observed trends for
550 *H. azteca* and *H. attenuata* (see footnotes in Table 1). These findings (*i.e.*, a decrease in ecotoxicity along
551 the LN series) agree with the observations of the present study, but the comparisons cannot be
552 considered fully conclusive due to the missing analytical verification of exposure concentrations in these
553 previous works (Table 1).

554 At the opposite, increasing ecotoxicity along the LN series was reported for the charophyte alga
555 *Nitellopsis obtusa* (Manusadzianas et al., 2020) and the bacterium *Aliivibrio fischeri* (Weltje, 2002) (Table
556 1). In the very simple medium (0.355 M NaNO₃) used for testing with *A. fischeri*, free Ln³⁺ were predicted
557 to be the dominant species and showed the same trend as total dissolved concentrations (nominal
558 values). However, total dissolved and free Ln³⁺ concentration will likely have different patterns in more
559 complexing media, especially those containing phosphates or carbonates. Gonzalez et al. (2014) warned
560 about establishing trends in the absence of detailed and complete information on LN speciation in the
561 various test media used for different organisms. Until minimum analytical requirements are adopted by
562 the whole ecotoxicological community, it will remain elusive to establish meaningful and generally valid
563 ecotoxicity trends along the LN series.

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Table 1. Summary of studies examining trends in ecotoxicity along the lanthanides series to aquatic organisms. ↓ or ↑ indicate a decreasing or increasing trend in ecotoxicity along the lanthanides series, respectively. [LN] measured refers to analytical verification of exposure concentration; Y, yes; N, no.

| Elements | Model organism | Trend (Y/N) | [LN] measured | Medium composition | Reference |
|--|---|---|---------------|--|-----------------------------|
| La, Ce, Pr, Nd, Gd | <i>Daphnia magna</i> | Y [§] (acute, nominal), ↓ N (chronic) | Y | Acute test: OECD (2004) Chronic test: Lake Water (pH 7.5 ± 0.2, DOC 10.6 mg/L C) | Blinova et al. (2018) |
| All LN | <i>Danio rerio</i> | Y, ↓ | N | According to OECD 203 (2019) | Lin et al. 2022 |
| La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Er, Lu (and Y) | <i>Hydra attenuata</i> | Y [#] , ↓ | N | Hydra medium CaCl ₂ , TES, pH 7 | Blaise et al. (2018) |
| All LN | <i>Hyalella azteca</i> | Y, ↓ [§] | Y | Soft water | Borgmann et al. (2005) |
| All LN except Pr, Ho, Yb | <i>Vibrio fischeri</i> | Y, ↑ | N | 0.355 M NaNO ₃ , pH 5.5 | Weltje (2002) |
| All LN except Ho, Tm, Yb | <i>Nitellopsis obtusa</i> | Y, ↑ | N | Artificial Pond Water KCl, NaCl, CaCl ₂ and HEPES (pH 7.5) | Manusadžianas et al. (2020) |
| All LN except Ho, Tm, Yb | <i>Thamnocephalus platyurus</i> | N | N | Standard freshwater NaHCO ₃ , CaSO ₄ , MgSO ₄ and KCl | Manusadžianas et al. (2020) |
| All LN | Cell lines of <i>Danio rerio</i> and <i>Onchorynchus mykiss</i> | N | Y | Mixed medium | Fleurbaix et al. (2022) |
| La, Ce, Gd, Ho | <i>Danio rerio</i> | N [§] | Y | Standard dilution water CaCl ₂ , MgSO ₄ , NaHCO ₃ , KCl | Kang et al. 2022 |
| All LN | <i>Hyalella azteca</i> | N | N | Tap water | Borgmann et al. (2005) |
| All LN | <i>Chlorella vulgaris</i> | N | N | K ₂ HPO ₄ , KH ₂ PO ₄ , (NH ₄) ₂ SO ₄ , KNO ₃ (pH just below 7) | Den Dooren de Jong (1965) |
| All LN | <i>Skeletonema costatum</i> | N | N | f/2 medium without EDTA: NaNO ₃ , NaH ₂ PO ₄ , trace elements and vitamins (pH 8.0) | Tai et al. (2010) |

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§, The existence of trends has been examined by the authors of the present study, but was not mentioned in the original publication.
, only for 24 d LC₅₀ (not for shorter exposure time); #, if Er and Lu excluded from the regression; §, if Tm, Yb and Lu excluded.
§, Tm, Yb, Lu do not follow the trend

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603 4.6. Proposal for a unified working framework for hazard and risk assessment of lanthanides

604 The results of the present study highlight a number of caveats that should be addressed to improve
605 the reliability and relevance of laboratory studies on LN ecotoxicity. The proposed list of caveats (Table 2
606 and text below) considers only issues directly linked to the results and approaches used in the present
607 study and does not claim to be exhaustive.

608 *Caveat # 1. Formation of insoluble LN species during ecotoxicity testing*

609 The ecotoxicological community is already well aware of the tendency of LN to form insoluble
610 precipitates in ecotoxicological test media, especially in the presence of carbonates or phosphates
611 (Blinova et al., 2018; Lachaux et al., 2022; Ma et al., 2016). Formation of Ce-bearing colloidal particles has
612 been reported even in a non-complexing medium (0.01 M NaHEPES + 10^{-5} M $\text{Ca}(\text{NO}_3)_2$) spiked with
613 approx. 5 $\mu\text{g/L}$ of Ce at pH between 6 and 8, with 40 to 70 % of the total concentration being retained by a
614 3kDa centrifugal ultrafiltration device (El-Akl et al., 2015). It is therefore advisable to consider that
615 insoluble LN species will form in any medium and take the necessary analytical steps to verify this
616 hypothesis (Table 2, point #1). The use analytical verifications based on total concentrations (i.e.,
617 unfiltered samples) should however be discouraged because they do not distinguish between soluble and
618 (nano)particulate LN species (Vukov et al., 2016). Furthermore, soluble species and precipitates do not
619 necessarily contribute to ecotoxicity in the same way (Table 2, point # 3). The norm ISO14442 (ISO, 2006)
620 provides useful recommendations that are applicable to the hazard assessment of elements tending to
621 form insoluble precipitates such as LN.

622 Further research should also better characterize the particle size distribution of LN precipitates,
623 because filtration at 0.45 or 0.22 μm will not detect the presence of colloidal precipitates smaller than the
624 filter cut-off. Based on Single-Particle ICP-MS, El-Akl et al. (2015) estimated an average size of 60 nm for
625 Ce particles formed in an exposure medium for short-term uptake experiments with *Chlamydomonas*
626 *reinhardtii*. It is highly likely that part of the filterable concentrations reported in the present and previous
627 studies actually include a certain proportion of particles having passed through the filter pores.

628 Measurements of pH values (ideally at multiple times during exposures) provide valuable additional
629 information to i) ensure that LN speciation is similar across the chosen range of exposure concentrations
630 in individual studies and ii) facilitate comparisons across studies. Even in a complexing medium such as
631 the ISO 6341 used in the present study, the decrease in filterable LN concentrations was almost
632 suppressed when the quantity of added LN salt was high enough to keep the pH at values below 6.5 units
633 over the duration of the test (Fig. 1). Finally, modifications of exposure media are a possible alternative to
634 avoid the formation of LN precipitates and even increasing the environmental relevance of the results
635 (Blinova et al., 2018; Ma et al., 2016). These options would not eliminate the need for a thorough
636 preliminary verification of LN precipitation in the chosen matrix across the range of exposure
637 concentrations. Indeed, substituting NaCl for NaHCO_3 in ISO medium 6341 (i.e., the medium used in the
638 present study without modification) did not prevent La and Gd filterable concentrations from decreasing
639 by 50–98 % (La) and 40–70% (Gd) over the exposure period of 48 h (Revel et al., 2023). On the other hand,
640 Ma et al. (2016) apparently avoided the formation of Ce precipitates larger than 0.22 μm by substituting
641 NaOH for NaHCO_3 in the same medium. Medium modifications should therefore be standardized among
642 research groups to ensure that data across studies are comparable. A similar reasoning should ideally
643 apply also to the procedures to determine filterable LN fractions (Horowitz, 2013; Vignati et al., 2006;
644 Weyman et al., 2012).

645 *Caveat # 2. Variable exposure conditions for test organisms over the test duration*

646 The results of analytical verification (see caveat # 1) will determine the choice of the appropriate
647 exposure metric to calculate ecotoxicological endpoints. In principle, evaluation of LN ecotoxicity should
648 not be based on i) nominal or measured concentrations at the beginning of the test, or ii) total
649 concentrations that may contain a mixture of soluble and precipitated LN species (Vukov et al., 2016);
650 present study). Both choices can lead to a marked underestimation of ecotoxic effects (Fig. 4). Measured
651 concentrations at the end of the test would be a conservative alternative when exposure concentrations
652 decrease over time. However, we recommend either TWM or geometric mean values as the best options.
653 In the specific case of the test medium ISO 6341 (2012) for *D. magna*, future studies may rely on

654 equations 4 to 7 to estimate LN concentrations at the end of the tests and provide EC_{50} estimates as TWM
655 (present study) or geometric mean concentrations (Lachaux et al., 2022).

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Table 2. Caveats, recommendations and open issues for properly testing LN ecotoxicity to *Daphnia magna* and aquatic organisms in general. The recommendations are applicable to other ecotoxicological media where LN precipitation may occur. Open issues indicate possible priorities for future research and consensus-building (also see Table S15 for a more detailed presentation of each caveat). TWM, Time-Weighted Mean; LN, lanthanides.

| # | Caveats | Recommendations / Possible approaches | Open issues |
|---|--|--|--|
| 1 | Formation of insoluble chemical species in the test medium | Provide appropriate analytical verification of filterable exposure concentrations. Verification of pH values very useful. | Presence of colloidal particles undetected by filtration. Speciation differences across the range of exposure concentration. Definition of standard non-complexing media. |
| 2 | Changeable exposure conditions for test organisms | Derive EC _x using experimentally measured filterable concentrations and TWM or geometric means. | Relative contribution of soluble and particulate LN species to observed ecotoxic responses. Technical developments to measure LN bioavailable concentrations in test medium. |
| 3 | Unknown and contrasting ecotoxicological roles of precipitates | Modify test medium to avoid formation of precipitates. Verify the absence of precipitates by <i>e.g.</i> , ultrafiltration or single-particle ICP-MS. | Contribution of precipitated species to ecotoxicity. Accumulation of precipitates in the gut of filter-feeding organisms during tests. |
| 4 | Use of free ionic LN concentrations as an improved exposure metrics | Remember assumptions and limitations of thermodynamic speciation models. | Untested assumption that only Ln ³⁺ contribute to toxicity. Dynamic aspects of LN speciation. |
| 5 | Conditional character of stability and solubility constants in thermodynamic speciation models | Strive to combine speciation calculation and experimental verification of model predictions. | Developing techniques for direct determination of LN speciation in test media. |
| 6 | Ecotoxicity trends along the LN series may be artefacts related to methodological limitations and experimental choices | Do not establish trends in the absence of minimum verification of exposure concentrations (see # 1 and 2) and Table 1. | True trends require determination of the actual LN bioavailable fraction. |
| 7 | Inappropriate comparison between exposure metrics from ecotoxicity testing and environmentally measured levels | Clearly report what is being compared. Consider the implications of the different exposure metrics from ecotoxicity testing in terms of possible underestimation or overestimation of the risk. | Matrix effects on LN speciation remains to be fully understood. Field-based studies using DGTs may provide hints on LN bioavailability in natural conditions. Reporting conventions to be defined. |

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670 From a fundamental point of view, the simultaneous presence of particulate and soluble LN species
671 (and the changes in their relative abundances during the tests) deserve further investigations as to their
672 respective contributions to the observed ecotoxic effects. In particular, it is not possible to establish
673 beyond doubt if biological responses are caused solely by the free ionic LN species whose concentrations
674 will vary during the tests and may be only a tiny fraction of total or filterable ones (Fig. 6). Using Diffusive
675 Gradients in Thin Films (DGTs) could help in measuring the time-averaged labile LN species that are
676 considered good proxies of the corresponding bioavailable fraction (Gu et al., 2023; Paller et al., 2019).
677 This approach would not address the possible contribution of LN precipitates to the observed ecotoxic
678 responses, though.

679 *Caveat # 3. Unknown ecotoxicological role of precipitates*

680 Revel et al. (2023) recently observed that particle formation was accompanied by different effects and
681 tissue distributions in daphnids exposed for 48 h in medium aliquots initially amended with soluble La and
682 Gd in the same concentration range. As discussed in *caveat #1*, both elements formed insoluble
683 precipitates albeit La did so to a greater extent. Micro- and nano-XRF analysis showed that La
684 concentrated almost totally in the digestive tract, while Gd was apparently taken up and distributed
685 across different tissues. Only Gd caused a clear ecotoxicological response in the exposed organisms with
686 48h EC₅₀ of 13.9 mg/L (nominal value) or 8.22 mg/L (filterable concentration at the end of the test);
687 comparable with the present study. The absence of La ecotoxicity suggests that precipitates were not
688 available for uptake by internal organs, while the observed Gd effects cannot be univocally ascribed to
689 soluble or precipitated forms.

690 Identifying the possible role of precipitates in LN ecotoxicity is related, but not equivalent, to
691 understanding the ecotoxicity of nanoparticulate LN forms. LN-bearing nanoparticles are engineered
692 materials of known composition and primary particle-size distribution. This contrasts with the formation
693 of precipitates following addition of soluble LN salts into the test medium. LN precipitates have variable
694 composition, *i.e.*, different types of precipitates can be present at the same time, and unknown particle
695 size distribution. Their concentration may also change over the test duration depending on the stability of
696 exposure conditions and on the solubility of the precipitates. Specific experimental approaches are
697 required to identify the presence of precipitates and their possible contribution of precipitates to LN
698 ecotoxicity in standard laboratory tests (Table 2).

699 Alternatively, exposure media could be aged after spiking with soluble LN forms and the precipitates
700 removed by filtration, ultrafiltration or centrifugation before ecotoxicity testing in analogy to approaches
701 proposed in the ecotoxicity of engineered nanoparticles (Sørensen & Baun, 2015). Results from the
702 present study suggest that formation of particles larger than 0.45 µm (nominal cut-off) becomes
703 progressively less important along the LN series (Figs. 1 and 2). However, the time to reach stable
704 filterable concentrations varies among LN (Fig. 1), which may complicate studies on the effects of LN
705 mixtures. The choice of the appropriate filter cut-off also requires further information on the particle size
706 distribution of the precipitates. Such consideration may equally apply to chronic ecotoxicity testing
707 because theoretical calculations suggest that the solubility limits could be as low as a few tens of
708 micrograms per liter depending on specific elements and medium pH (Fig. 3 and Table S12). These
709 solubility limits are comparable to, or lower than, the lowest chronic ecotoxicity values reported by Shu et
710 al. (2023) and Lüring and Tolman (2010) for La (59 µg/L and 100 µg/L, respectively in artificial media), but
711 higher than Ce and Er concentrations of 1 µg/L used by Galdiero et al. (2019) to study multigenerational
712 effects. Comparison with the chronic values determined by Blinova et al. (2018) for La, Ce, Pr, Nd and Gd
713 (range 300 – 490 µg/L) is hindered by the use of a natural lake water at pH 7.5 and containing 10.6 mg/L
714 of dissolved organic carbon.

715 *Caveats # 4 and 5. Using modelled free ion concentrations as an improved exposure metric*

716 According to the scientific underpinnings of the biotic ligand model (BLM), ecotoxicological responses
717 are controlled by the bioavailable elemental fraction that binds to specific biological ligands. The
718 bioavailable fraction is mostly controlled by the the free ion concentration although contributions from
719 other elemental species are possible (Campbell & Fortin, 2013). While suitable analytical techniques are
720 being explored (Janot et al., 2021; Leguay et al., 2016; Nduwayezu et al., 2016), free ion concentrations
721 for LN are usually estimated using thermodynamic speciation models. This approach facilitates

722 comparisons across studies using different exposure media and provides ecotoxicity estimation more
723 relevant for risk assessment. However, it has some conceptual limitations that researchers should
724 understand to avoid overstressing the environmental significance and implications of experimental
725 results (Table 2, points # 4 and 5).

726 The choice of Ln^{3+} as a metric of exposure assumes that only free ions contribute to the observed
727 ecotoxic effects. In support of this assumption, MacMillan et al. (2018) found good overall relationships
728 between the modelled ΣREE free ion concentrations and REE accumulation by indigenous zooplankton in
729 Canadian lakes. On the other hand, studies with a variety of model organisms provide contrasting
730 evidence as to the bioavailability of Ln-containing particles formed in ecotoxicological media following the
731 addition of soluble LN forms (Aharchaou et al., 2020; El-Akl et al., 2015; Revel et al., 2023; Vukov et al.,
732 2016). The problem is exacerbated when comparing Ln^{3+} concentrations in ecotoxicological media and in
733 natural waters.

734 Although insoluble precipitates can dominate LN speciation in the laboratory, LN in natural waters can
735 be strongly associated with colloids and occurring as complexes with dissolved natural organic matter
736 (Janot et al., 2021; Marsac et al., 2021; Martin et al., 2021; Pinheiro & Rotureau, 2023). Thermodynamic
737 speciation calculations in the presence of natural organic matter still suffer from conceptual shortcomings
738 that could lead to erroneous estimations of Ln^{3+} in natural waters (Tesfa et al., 2022; Town et al., 2019).
739 Similarly, speciation calculation in a given standard ecotoxicological medium (or across ecotoxicological
740 media) will yield different results depending on the stability constants chosen for modelling by the
741 experimenters as in the case of Lachaux et al. (2022) vs. the present study. The choice to allow or not for
742 the precipitation of insoluble species during speciation modelling (provided that the necessary solubility
743 products are available) can also affect the comparability of free ion based metrics across different studies.
744 Theoretical solubility limits can also vary markedly depending on the choice of solubility values for the
745 possible precipitate species. In the present study, solubility limits could differ by over 10-fold when
746 comparing calculations using the 'Firsching' and the 'Default VM' databases for carbonate solubility (Table
747 S12), notably in the case of La. Finally, estimation of free ion concentrations based on nominal or total
748 concentrations and filterable concentrations at the beginning of the test should be avoided for the same
749 reasons discussed in caveat #1.

750 *Caveat # 6. Identifying meaningful trend along the LN series*

751 The previous caveats show that defining a generally valid ecotoxicological trend along the LN series
752 remains elusive at the current state of knowledge, but also provide some hints to ensure that future
753 research provides valid results for verifying the actual existence of such trends. In particular, results from
754 studies not providing minimum analytical information on exposure concentrations (Table 1) should be
755 considered of limited reliability for hazard and risk assessment purposes until further verification. Trends
756 based on average, measured exposure concentrations (or free ion concentrations derived from such
757 measurements) provide better information, but are also subject to further screening as more knowledge
758 on LN speciation and bioavailability becomes available in both standardized test media and natural
759 waters.

760 The results of the present study do not end the quest for the presence or absence of a regular,
761 generally valid ecotoxicological patterns along the LN series in relation to their acute ecotoxicity toward
762 *Daphnia magna*. They do however show a clear trend in the concentration decrease (Fig. 5), suggesting
763 the best approaches to avoid underestimating LN ecotoxicity, especially in the case of light LN. The
764 speciation calculation and discussion of the corresponding caveats provide a new starting point for future
765 research on these topics. The necessary improvements in the hazard and risk assessment frameworks for
766 LN are the subject of forthcoming work.

767 *Caveat # 7. Comparing laboratory-derived exposure metrics with natural concentrations*

768 Risk assessment is based on the comparison between the EC_{50} derived from laboratory studies (hazard
769 assessment) with the measured ambient concentrations in the case of site-specific investigations or
770 probable environmental concentrations to establish environmental quality standard on a wider scale
771 (European Commission, 2019). At the current state of knowledge, the utmost care is required to avoid
772 both overestimation and underestimation of the potential risks arising from (increasing) concentrations of
773 LN following anthropogenic impacts (Table 2). Laboratory exposure metrics derived from nominal

774 concentrations (or concentrations measured at the beginning of the tests) would clearly underestimate
775 risk. At the opposite extreme, comparing properly derived EC₅₀ with total elemental concentrations in
776 natural water would likely overestimate the actual risk because LN bound to environmental particles will
777 be considered equivalent to the dissolved (bioavailable) fraction. Studies attempting risk assessment
778 should therefore be germane as to the analytical details of the concentrations being compared. An
779 intriguing possibility would be to base risk assessment on comparisons of time-averaged, DGT-labile
780 concentrations measured in both laboratory media and natural freshwater by extending approaches
781 proposed for in situ ecological risk in sediments (Gu et al., 2020; Gu et al., 2022).

782 **5. Concluding remarks and way forward**

783 Reliable exposure vs. response relationships are the foundation of hazard and risk assessment.
784 Understanding the dynamic and complex speciation of LN is therefore a missing cornerstone in
785 standardized ecotoxicity tests for these elements. In the absence of such information, it is not possible to
786 choose the appropriate metric to link exposure to LN with the measured biological even in controlled
787 laboratory conditions. Given the difficulties in obtaining stable exposure concentrations of LN in many test
788 media, one may even question the ability of standardized methods to provide reliable results on the
789 ecotoxicity of LN to aquatic organisms. However, similar issues would equally apply to New Approach
790 Methodologies (NAM) such as in vitro screening, and to any test method unless they adopt test media
791 allowing a thorough control of LN speciation. In our opinion, addressing the caveats discussed in section 4.6
792 will provide stronger basis for mutual acceptance of data across studies and help to reconcile
793 standardized tests with the much more complex environmental reality (Vignati, 2021). Similarly,
794 ecotoxicity trends along the LN series will remain conditional (i.e., dependent on the chosen exposure
795 metric and exposure time, among the other variables) until precise information becomes available as to the
796 LN form(s) capable of interacting with test organisms.

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804 **Data, scripts, code, and supplementary information availability**

805 Data and supplementary information are available online: <https://doi.org/10.57745/NW0GF9>
806 (Vignati et al., 2023)

807 **Conflict of interest disclosure**

808 The authors declare that they comply with the PCI rule of having no financial conflicts of interest in
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