

1 **Tissue distribution and trophic magnification of trace elements in**
2 **typical marine mammals in Bohai and north Yellow Seas**

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14 **Tissue distribution and trophic magnification of trace elements in**
15 **typical marine mammals in Bohai and north Yellow Seas**

16 **Abstract**

17 A total of 20 stranded spotted seals (*Phoca largha*) and 9 stranded minke whales
18 (*Balaenoptera acutorostrata acutorostrata*) were collected from Liaodong Bay
19 and the northern part of the Yellow Sea to investigate the tissue distribution (liver,
20 kidney, heart, lung, and muscle), risk, and trophic magnification of 13 trace
21 elements (TEs, Hg, As, Cd, Co, Cr, Cu, Mn, Ni, Pb, Se, Sn, V, Zn). The 13 TEs
22 were all detected in all spotted seal and minke whale tissue samples, with mean
23 concentrations ranging from 0.041-136.3 mg/kg dry weight (dw) and 0.022 to
24 152.6 mg/kg dw, respectively. Zn was the dominant contaminant in all tissues for
25 both spotted seals and minke whales. There was tissue-specific distribution of TEs
26 in both marine mammals, and the TEs tended to accumulate in internal organs.
27 Significant positive correlations were found in the body length of the spotted seals
28 and minke whales among some of the TEs, especially for Cd in the internal organs.
29 Gender-dependent distribution of the TEs was not obtained for the spotted seal.
30 Ecological risk evaluation for spotted seals and minke whales suggested that
31 greater concern should be given to Hg, As, and Se. Based on the TE concentrations
32 detected in this study and trophic levels determined by stable carbon and nitrogen
33 isotopes, trophic level-associated biodilution was obtained for As, Cd, Co, Cu, Mn,
34 Pb, Se, Sn, and V in the spotted seal, while Zn displayed a significant
35 biomagnification trend with increasing trophic levels. In the case of the minke
36 whale, As, Cd, Co, Mn, Pb, Se, and V displayed significant biomagnification trends
37 with increasing trophic levels.

38 **Keywords:** spotted seal; minke whale; trace elements; trophic magnification;
39 tissue distribution; risk evaluation

40 **1 Introduction**

41 Marine mammals such as cetaceans and pinnipeds are often considered sentinel species
42 as their health and population changes can act as an indicator of the current or potential
43 negative effects on the marine ecosystem (Hazen et al., 2019; Maxwell et al., 2013).
44 Cetaceans and pinnipeds play an important role in maintaining the structure, composition,
45 and function of marine ecosystems (Sanganyado et al., 2021). They regulate the
46 spatiotemporal flow of mass and energy in the ocean and archive in their fat deposits
47 critical trophic data from multiple spatiotemporal scales (Hazen et al., 2019). In addition,
48 cetaceans and pinnipeds are long-term inhabitants of marine environments and long-lived
49 apex predators which makes them susceptible to environmental threats such as marine
50 pollution (Desforges et al., 2016). Therefore, understanding the impact of marine
51 pollution on cetaceans and pinnipeds is important since a decline in their health and
52 population may disrupt critical ecosystem functions and services of marine ecosystems.

53 Spotted seals (*Phoca largha*) and mink whales (*Balaenoptera acutorostrata*
54 *acutorostrata*) are typical marine mammals that inhabit tropical, temperate, and polar
55 regions (Burns, 2009; Risch et al., 2019). Spotted seals inhabit ice floes during the
56 breeding season and open ocean or shores in the summer season. In contrast, mink whales
57 breed throughout the year and do not have clear seasonal migration patterns like other
58 baleen whales. Juvenile spotted seals feed on krill and crustaceans while adults feed on
59 small schooling fish such as arctic cod, capelin, and herring (Burns, 2009). However,
60 mink whales are opportunistic feeders that eat crustaceans, krill, plankton, and small
61 schooling fish (Risch et al., 2019). The International Union for Conservation of Nature's
62 Red List of Threatened Species ranked spotted seals and mink whales as least concern,
63 meaning they were at a low risk of extinction (IUCN, 2020). However, in China, spotted
64 seals and mink whales are considered class-I protected animals because of increasing

65 threats from climate change, habitat loss, poaching, noise, traffic, and marine
66 pollution(Wang et al., 2021).

67 The Bohai and northern Yellow Seas in China are important habitats of spotted seals and
68 mink whales. Of the eight known breeding grounds of spotted seals worldwide, Liaodong
69 Bay, in northern parts of Bohai Sea, is the southmost and has hundreds of adults raising
70 their cubs there during winter seasons (Hu et al., 2013; Wu et al., 2022). However, the
71 Bohai Sea has several offshore oil platforms that often contribute to the discharge of
72 anthropogenic pollutants in the ocean (Wang et al., 2022). High median concentrations
73 of trace elements such as Cr (27.07 mg kg⁻¹), Cu (10.35 mg kg⁻¹), Zn (38.90 mg kg⁻¹), Pb
74 (21.16 mg kg⁻¹), and As (9.78 mg kg⁻¹) were found in sediments from Liaodong Bay
75 (Wang et al., 2020). Additional studies demonstrated that these trace elements
76 accumulated in clams (Liu et al., 2020), oysters (Liu et al., 2021), and fish (Guo et al.,
77 2016).

78 In spotted seals, Cd (0.09-2.18 mg kg⁻¹), Hg (0.10-2.62 mg kg⁻¹), and As (0.01-0.13 mg
79 kg⁻¹) were found in the liver and Cd (7.76 mg kg⁻¹) and Hg (0.90 mg kg⁻¹) were found in
80 the kidneys (Dehn et al., 2006a). Dehn et al. (2006) found that trace elements (TEs) had
81 higher concentrations in the liver, lower in the muscle, and sex had no significant effect
82 on TE distribution. The biomagnification factors of Hg were found to be higher than 1 in
83 the liver and kidney of spotted seals, as well as those for renal Cd, indicating
84 biomagnification of these two TEs in the internal organs in spotted seals. A recent study
85 found that As, Hg, Se, Cd, and Pb widely occur in the meat of minke whales from the
86 Northeast Atlantic Ocean, with concentrations ranging from 0.002 to 0.65 mg/kg wet
87 weight, and Cd levels were found to increase with increasing body length (Maage et al.,
88 2017). Hence, spotted seals and minke whales may accumulate TEs through the

89 surrounding environment or food chain due to their long lifespan and high trophic level.
90 However, there is a knowledge gap on the trophic magnification of TEs in spotted seals
91 and minke whales and their food webs. Therefore, the objectives of this study were 1) to
92 investigate the tissue distribution of TEs in spotted seals and minke whales, 2) to evaluate
93 the risk of TEs on spotted seals and minke whales, and 3) to characterize the trophic
94 magnification of TEs in the food web of spotted seals and minke whales. To the best of
95 our knowledge, this is the first systemic study on the tissue distribution and trophic
96 magnification of TEs in both spotted seals and minke whales, which could expand our
97 knowledge on TE trophic transfer in marine mammals and their food chains.

98 **2 Materials and Methods**

99 *2.1 Chemicals and reagents*

100 The TE standards were purchased from Perkin Elmer (PerkinElmer, USA). Rhodium (Rh)
101 was purchased from O2Si (Charleston, SC, USA) and was used as an internal standard to
102 overcome the matrix effect during detection. Nitric acid and hydrogen peroxide were UPS
103 grade and were purchased from Jinrui (Suzhou Crystal Clear Chemical Co., Ltd, Suzhou,
104 China). Certified reference material (CRM) TMQC0005 (BBS27) (salmon) was obtained
105 from the National CRM Center of China. Milli-Q water was used throughout the study.

106 *2.2 Sample collection and preparations*

107 A total of 20 individual stranded spotted seals and 9 stranded minke whales from
108 Liaodong Bay and the northern part of the Yellow Sea were investigated in this study.
109 Spotted seals and minke whales were collected from 2015 to 2020. Muscle, kidney, liver,
110 heart, and lung samples were collected from stranded individual samples, while the prey
111 items of marine mammals were collected between 2016 and 2017 in the same area

112 (38°28'8.86" - 38°58'33.81" N, 120°31'26.58 - 122°17'50.02" E). The biological
113 information of the collected samples was recorded according to the national standard
114 method of China: Specifications for oceanographic survey - Part 6: Marine biological
115 survey (GB/T 12763.6-2007, in Chinese). The biological information of the investigated
116 marine mammals is given in Table S1 in the Supplementary materials (SM). The spotted
117 seals and minke whales collected in Liaodong Bay, China, were authorized under the
118 Ministry of Agriculture and Rural Affairs of the People's Republic of China, permit
119 number: 1376. This study was conducted under a permit issued by the Liaoning Fisheries
120 Administration Bureau, Liaoning Province, China (approval number:
121 LSYXFZ20111105).

122 Approximately 0.3 g of the freeze-dried marine mammal tissue sample or food web
123 sample was digested using 2 ml H₂O₂ and 5 ml HNO₃ by a microwave digestion system
124 (YiYao, TOPEX 40, China) and then reconstituted in 10 mL with Milli-Q water. Before
125 analysis, the samples were filtered with a 0.22 µm syringe-driven filter.

126 **2.3 Trace elements analysis**

127 Analysis of TEs was performed according to the method described by Liu et al. (2018).
128 Briefly, As, Cd, Co, Cr, Cu, Mn, Ni, Pb, Se, Sn, V, and Zn were analyzed using ICP–MS
129 (PerkinElmer, NEXION 300X, USA). Standard mode (STD) was applied to analyze Cd,
130 Pb, and Sn, while As, Co, Cr, Cu, Mn, Ni, Se, V and Zn were determined by kinetic
131 energy discrimination mode (KED). Hg was analyzed using an atomic fluorescence
132 spectrometer (JiTian, AFS-921, China). The settings of ICP–MS were as follows: RF
133 power 1200 W, plasma gas (argon) flow rate 15 L/min, nebulizer gas flow rate 0.94
134 L/min, analog stage voltage -1900 V, pulse stage voltage 950 V, scan mode peak hopping,
135 MCA channels 1, dwell time 50 ms, integration time 1000 ms, and readings were taken

136 as triplicates. The main parameters for the atomic fluorescence spectrometer were a lamp
137 current of 30 mA, photomultiplier tube voltage of 270 V, reading time of 7 s, and delay
138 time of 0.5 s.

139 **2.4 Trophic level determination**

140 Stable carbon and nitrogen isotopes of the selected marine mammals and other organisms
141 were detected using an isotope ratio mass spectrometer (Delta V Advantage, Thermo,
142 USA) in our previous study (Tian et al., 2018), and the results and abbreviations are
143 shown in Table S2 in the SM. Trophic levels (TL) were calculated using the following
144 equation (Sham et al., 2020), and the results are given in Table S2:

$$145 \text{ TL}_{\text{consumer}} = 2 + (\delta^{15}\text{N}_{\text{consumer}} - \delta^{15}\text{N}_{\text{baseline}})/\text{TEF}$$

146 where $\delta^{15}\text{N}_{\text{consumer}}$ is the $\delta^{15}\text{N}$ value of the investigated organisms in this study (Table S2),
147 $\delta^{15}\text{N}_{\text{baseline}}$ is the $\delta^{15}\text{N}$ value of adductor muscle of *Chlamys farreri*, 5.8‰, and TEF is the
148 trophic enrichment factor, 3.4‰.

149 **2.5 Trophic magnification factor calculation**

150 The following formulas were used to calculate the trophic magnification factor (TMF) of
151 the TEs in the marine food web (Sham et al., 2020):

$$152 \text{ Log}_{10}[\text{TE}] = a + b \times \text{TL}$$

$$153 \text{ TMF} = 10^b$$

154 where [TE] is the concentration of the element in the prey item and muscle of the spotted
155 seal or minke whale (mg/kg dw); TL is the trophic level; and b is the slope of the
156 regression equation.

157 **2.6 Risk assessment**

158 The molar ratio of Se/Hg was calculated using the following formula:

159
$$\text{Se/Hg} = (C_{\text{Se}}/78.96)/(C_{\text{Hg}}/200.59)$$

160 where C_{Se} and C_{Hg} are Se and Hg concentrations in the same tissue, and 78.96 and 200.59
161 are the atomic weights of Hg and Se, respectively. For risk evaluation, the reference dose
162 (RfD) and toxicity reference value (TRV)-based risk quotient (RQ) were employed in this
163 study, and the maximum allowable concentration (MAC) was calculated using the
164 formulas below (Hung et al., 2004):

165
$$\text{MAC}_{\text{RfD}} \text{ or } \text{MAC}_{\text{TRV}} = (\text{RfD or TRV} \times \text{BW} \times \text{AT})/(\text{IR} \times \text{FI} \times \text{EF} \times \text{ED})$$

166
$$\text{RQ} = C_{\text{TEs}}/ \text{MAC}_{\text{RfD}} \text{ or } \text{MAC}_{\text{TRV}}$$

167 Where BW is body weight of spotted seal or minke whale, 100 or 3000 kg in this study;
168 AT represents average time, 14600 days (365 day/year \times 40 years) for spotted seal and
169 18250 (365 day/year \times 50 years) for minke whale, respectively; IR is ingestion rate, 5 and
170 150 kg/day (5% of body weight), respectively for spotted seal and minke whale; FI is
171 fraction ingested from pollution source, 0.9; EF is exposure frequency, 365 day/year; ED
172 is exposure duration, 40 and 50 years, respectively for spotted seal and minke whale. The
173 RfD values were cited from the USEPA in the Integrated Risk Information System
174 (<http://www.epa.gov/iris>). The TRV values used in this study were calculated by the no
175 observable adverse effect level (NOAEL) obtained on test mammals (rat, mouse, and
176 mink) reported by Sample et al (1996) and were calculated using the following formula
177 (Hung et al., 2004):

178
$$\text{TRV} = \text{NOAEL}_t \times (\text{BW}_t/\text{BW}_r)^{0.25}$$

179 where $NOAEL_t$ is the NOAEL for the test mammal; BW_t is the body weight for the test
180 mammal; and BW_r is the body weight for the spotted seal or minke whale in this study.
181 The parameters used for risk evaluation in the current study are given in Tables S3 and
182 S4 in the SM, and the calculated MAC_{RfD} and MAC_{TRV} are shown in Tables S3 and S4 in
183 the SM.

184 **2.7 *Quality control and quality assurance***

185 Procedural and reagent blank samples were performed throughout the study. Zn and
186 manganese Mn were found in both procedural and reagent blanks but accounted for less
187 than 0.05% of the lowest acquired data in this study and thus could be negligible. The
188 results in this study were not blank corrected. Satisfactory recoveries were obtained for
189 the CRM samples, with TE recoveries ranging from 91.1% to 114.7% (Table S5). Two
190 standard solutions ($0.5 \mu\text{g L}^{-1}$ for Hg and $5 \mu\text{g L}^{-1}$ for the remaining TEs) were analyzed
191 with each batch of 20 samples. The accuracy and precision of the instrumental analysis
192 were reported as recoveries, and the relative standard deviations are shown in Table S6
193 and ranged from 93.7% to 103.7% and from 2.7% to 6.5%, respectively.

194 **2.8 *Statistical analysis***

195 Statistical analysis was performed using SPSS 21.0. Descriptive statistics and box charts
196 were used to characterize the levels of TEs in the marine mammals and food web samples.
197 Data sets of TE concentrations were normally distributed when natural logarithm
198 transformed (Kolmogorov–Smirnov test), and ln-transformed data were used in the
199 parametric statistical analysis. Briefly, a Pearson correlation model was employed to
200 analyze potential relationships among various parameters. Independent samples t tests
201 and LSD tests were applied to analyze the difference in TE levels in different tissues.
202 Statistical tests were considered significant when $p < 0.05$.

203 3 Results and Discussion

204 3.1 Tissue distribution of the selected TEs

205 3.1.1 Spotted seal

206 The statistical concentrations of the TEs in different tissues (muscle, kidney, liver, heart,
207 and lung) of the 20 selected spotted seals are shown in Fig. 1, and detailed information is
208 given in Tables S7 to S11 in the SM. Briefly, the selected 13 TEs were detected in all
209 spotted seal tissues with mean concentrations of 0.041-136.3 mg/kg dw. The levels of Co
210 were the lowest with mean concentrations ranging from 0.018 to 0.077 mg/kg dw; in
211 contrast, Zn was the predominant element in all five tissues, with mean concentrations up
212 to 173.9 mg/kg dw in the liver. Generally, a tissue-specific distribution of TEs was found;
213 TEs tended to accumulate in internal organs, and the total TE concentrations in the five
214 tissues from highest to lowest were in the order of liver > kidney > heart > muscle > lung.
215 In the case of specific TEs, pulmonary As and Zn were significantly lower (LSD, $p <$
216 0.05) than those in the other tissues, while renal Pb and Cd were significantly higher
217 (LSD, $p <$ 0.05) than those in the other tissues. Hepatic, renal and cardiac Co, Cu, Mn
218 and Se were significantly higher (LSD, $p <$ 0.05) than those in the muscle, while hepatic
219 and renal V displayed higher levels (LSD, $p <$ 0.05) than those in the muscle. However,
220 muscular Cr was significantly higher (LSD, $p <$ 0.05) than those in the liver and kidney,
221 while muscular Ni displayed higher levels (LSD, $p <$ 0.05) than that in the liver. Similar
222 distribution trends were found in different tissues in spotted seals for Cd and Hg (Dehn
223 et al., 2006b, 2006a). However, Cu was mainly found in the internal organs of the spotted
224 seals in this study, while Cu accumulated in the muscle of the spotted seals from Alaska
225 (Dehn et al., 2005). Overall, only two studies reported TE levels in spotted seals, and wet

226 weight-based concentrations were used in previous studies; therefore, they could not be
227 compared with the data from this study and merit further study.

228 3.1.2 *Minke whale*

229 The levels of the TEs in different tissues (muscle, kidney, liver, heart, and lung) of the
230 selected 9 minke whale are given in Fig. 2, and detailed information is displayed in Tables
231 S7 to S11 in the SM. Similar to spotted seals, 13 selected TEs were detected in all mink
232 whales with concentrations ranging from 0.003 to 242.7 mg/kg dw. Muscular V
233 concentrations (0.036 mg/kg dw) were the lowest, while Zn (48.05-152.6 mg/kg dw) was
234 the predominant element in all five tissues. There was tissue-specific distribution with
235 TEs preferentially accumulating in internal organs. The total TE concentrations tissues in
236 ascending order was liver > kidney > heart > lung > muscle. In terms of specific TEs,
237 hepatic, renal and cardiac As, Co, Cu, Se and Zn were significantly higher (LSD, $p <$
238 0.05) than those in the muscle, while muscular Cd, Mn and V were significantly lower
239 (LSD, $p <$ 0.05) than those in the kidney and liver. However, Hg, Cr, Ni, Pb and Sn did
240 not show a significant distribution in the investigated tissues from the selected minke
241 whale. The mean concentrations of Mn, Zn, Cu, Pb, and Co in the liver of the minke
242 whale in this study were comparable to those from the Antarctic; however, hepatic Cd
243 and Hg were orders of magnitude lower than those from the Antarctic (Honda et al.,
244 1987).

245 3.2 *Differences in TE accumulation with different body lengths and sexes*

246 3.2.1 *Spotted seal*

247 Briefly, some TE concentrations showed significant positive correlations with the body
248 length of the spotted seals, including muscular Cd (Pearson correlation coefficient (PCC)

249 = 0.503, $p = 0.028$), renal Hg (PCC = 0.569, $p = 0.017$), renal Cd (PCC = 0.840, $p =$
250 0.000), hepatic Cd (PCC = 0.677, $p = 0.003$), hepatic Se (PCC = 0.551, $p = 0.022$), hepatic
251 V (PCC = 0.487, $p = 0.047$), pulmonary Cd (PCC = 0.644, $p = 0.005$), and pulmonary Se
252 (PCC = 0.612, $p = 0.009$), but significant negative correlations were observed among
253 muscular Cu (PCC = -0.750, $p = 0.000$), renal Cu (PCC = -0.506, $p = 0.038$), hepatic Cu
254 (PCC = -0.521, $p = 0.032$) and body length. No significant correlations were found among
255 the investigated TE levels of the five spotted seal tissues and sex.

256 3.2.2 *Minke whale*

257 Similar to spotted seals, some TE concentrations exhibited significant positive
258 correlations with body length of the minke whales, including muscular As (PCC = 0.712,
259 $p = 0.048$), hepatic Cr (PCC = 0.873, $p = 0.023$), cardiac Cd (PCC = 0.758, $p = 0.029$),
260 cardiac Se (PCC = 0.713, $p = 0.047$), cardiac Sn (PCC = 0.743, $p = 0.035$), pulmonary
261 Hg (PCC = 0.891, $p = 0.003$), pulmonary As (PCC = 0.804, $p = 0.016$), pulmonary Cd
262 (PCC = 0.800, $p = 0.017$), pulmonary Co (PCC = 0.713, $p = 0.047$), and pulmonary Mn
263 (PCC = 0.817, $p = 0.013$). Due to the small number of individual male minke whales
264 (only two specimens), the correlation between gender and TE levels of the minke whale
265 was not analyzed. Overall, the negative correlation coefficients of TE levels with body
266 length could be partially explained by biodilution as a result of animal growth, while the
267 positive correlation coefficients of TE levels with body length suggested that the rate of
268 bioaccumulation of TEs was faster than that of biodilution (Zhang et al., 2017).

269 3.3 *Risk assessment*

270 The RQ values of the investigated TEs were calculated for the spotted seals and minke
271 whales based on MAC_{RFD} and MAC_{TRV} described above in two exposure scenarios (50th
272 and 95th represent average and high exposure scenarios), and the results are given in

273 Table 1. Generally, the RfD-based RQ values were higher than those for TRV-based RQ
274 values for both spotted seal and minke whales, largely because RfD is used for human
275 health evaluation and stricter than those from toxicological studies on mammals. In
276 spotted seals, more than half of the MAC_{RfD} -based RQ values exceeded 1, including Hg,
277 As, Cr, Cu, Se, and Zn. The highest risk was observed in the two exposure scenarios,
278 indicating potential toxicological risk to spotted seals. Greater concern should be given
279 to Hg, As, and Se because MAC_{TRV} -based RQ values exceeded 1 in average and high-
280 exposure scenarios. Similar to the spotted seals, the RQ values based on MAC_{RfD} of Hg,
281 As, Cd, Cr, Cu, Se, and Zn in minke whales exceeded 1, suggesting potential toxicological
282 risk to minke whales. Among them, As was the primary pollutant. In the case of MAC_{TRV} -
283 based RQ values, Hg, As, and Se exhibited potential risk to minke whales in both average
284 and high exposure scenarios and merits more attention.

285 It should be noted that As exists mainly in organic form in marine mammals and
286 organisms and is relatively nontoxic (Kubota et al., 2003); therefore, the risk might be
287 overestimated for both spotted seals and minke whales. Cd can influence the immune
288 system and reproduction and cause cancer (Shankar et al., 2021; Zwolak, 2020). The
289 source of Cd in marine mammals is from both land-based and offshore discharges (Fraga
290 et al., 2018), and this study found that Cd accumulation in some tissues was significantly
291 positively related to the body length of the investigated spotted seals and minke whales,
292 especially in internal organs, and the MAC_{RfD} -based RQs of Cd exceeded 1. Therefore,
293 the health risk of Cd to spotted seals and minke whales is worth noting and needs further
294 study. In the case of essential elements Cu and Zn, these two element concentrations in
295 all of the investigated tissues of spotted seals and minke whales were within the
296 acceptance ranges (12-120 mg/kg dw for Cu and 80-400 mg/kg dw for Zn) (Hung et al.,
297 2007, 2004), suggesting that the investigated spotted seals and minke whales are basically

298 healthy. Trivalent Cr is an essential element for mammals, but hexavalent Cr is toxic to
299 biology and is found to cause tissue damage, irritative lesions of the skin and respiratory
300 tract and cell-mediated allergic reactions. Some hexavalent chromium compounds also
301 induce tumors. However, most Cr in marine animals is trivalent and usually does not pose
302 a health risk to consumers (Yilmaz et al., 2017). Therefore, the risk of Cr to minke whales
303 might be overestimated, and more studies should be conducted to illustrate the chemical
304 speciation of Cr in minke whales. Se is necessary for organism growth, and the levels of
305 Se in the current study were far lower than the essential limitation (120 mg/kg dw) (Law,
306 1996); hence, the risk of Se to the spotted seal and minke whale mainly belongs to chronic
307 selenosis, which might result in feed intake reduction, growth retardation, liver cirrhosis,
308 and even induce genotoxicity, embryotoxicity, immunotoxicity, and cytotoxicity (Lv et
309 al., 2021). Therefore, further study should be conducted to identify which risk would be
310 posed by long-term accumulation of Se in spotted seals and minke whales. Hg, As, and
311 Cd have attracted more attention due to their high toxicity at low concentrations; however,
312 Se has antioxidant properties that play a special detoxification mechanism to these
313 pollutants, including competing binding sites, forming nontoxic complexes, and
314 activating the Nrf2 pathway (Zwolak, 2020), especially for Hg. Previous studies have
315 documented that a molar ratio of Se/Hg less than 1 indicated an exposure risk posed by
316 Hg (Berry and Ralston, 2008). Overall, the molar ratios of Se/Hg in all of the tissues of
317 the investigated spotted seals and minke whales were larger than 1, indicating that Se
318 could largely counteract the harmful effects of Hg in these two marine mammals.
319 However, based on the current study, MAC_{TRV}-based RQ values of Hg for the two marine
320 mammals exceeded 1, which indicated that the investigated spotted seals and minke
321 whales have potential risk exposure to Hg and needs further attention.

322 3.4 Trophic magnification of TEs

323 The concentrations of the TEs in food webs of the spotted seal and minke whale were
324 reported in our previous study (Tian et al., 2021), and the average concentrations of the
325 TEs in each class of prey are given in Table S12 in the SM. The TMF values of TEs from
326 the food web of spotted seals and minke whales investigated in this study are shown in
327 Table 2. Only muscular TE levels were used to calculate TMFs in this study to minimize
328 the effects of different TE levels on different tissues, especially for internal organs,
329 because some TEs, such as Pb and Cd, are mainly stored in the liver and kidney (Hu et
330 al., 2021). For spotted seals, based on the current study, trophic level-associated
331 biodilution was obtained for As, Cd, Co, Cu, Mn, Pb, Se, Sn, and V, while Zn displayed
332 a significant biomagnification trend with increasing trophic levels. However, Hg, Cr, and
333 Ni did not exhibit obvious trophic transfer trends. In the case of the minke whale, As, Cd,
334 Co, Mn, Pb, Se, and V displayed significant biomagnification trends with increasing
335 trophic levels, while the other investigated TEs did not exhibit obvious trophic transfer
336 trends.

337 Both biodilution and biomagnification of As with increasing trophic levels were found in
338 previous studies (Trevizani et al., 2018), but As biodilution was the primary process in
339 aquatic food webs and presented a biodilution trend in global marine food webs (Sun et
340 al., 2020). However, organic As, which readily biomagnifies than the inorganic As, is
341 often the predominant form in marine organism. Therefore, As might be readily
342 biomagnified by minke whales since they have broader diet different kinds of diets
343 compared to spotted seals (Du et al., 2021). A recent study documented that
344 environmental (e.g., latitude and temperature) and ecological factors (e.g., trophic
345 structure composition) can substantially influence the biomagnification process of As and
346 Se. In addition to the level of bioaccumulated concentration, biomagnification depends

347 on the biology, ecology and physiology of the organisms (Córdoba-Tovar et al., 2022).
348 Cu and Mn can be excreted by high trophic level species efficiently and are regulated by
349 homeostasis, which might partially explain the results of biodilution of Cu and Mn in
350 spotted seal obtained in the current study (Hu et al., 2021). Trophic transfer of Cd in
351 aquatic food chains is controversial, and trophic transfer of Cd in marine food webs was
352 observed in a previous study, with biodilution in higher trophic organisms and
353 biomagnification in lower trophic organisms, which was in line with this study (Espejo
354 et al., 2018). Pb is known to be transferred inefficiently through marine food webs,
355 probably because its form presented in aquatic organisms is difficult to absorb (Nfon et
356 al., 2009). Therefore, biodilution might occur with the growth of marine mammals, such
357 as spotted seals in this study. Trophic transfer of Co and V and their transfer mechanisms
358 have rarely been reported by previous studies and need further study. Although we have
359 found trophic magnification of Zn, there is much debate on whether Zn can be transferred
360 at the trophic level and needs further study (Hu et al., 2021). Based on the current study,
361 different trophic transfers of most TEs were found, which might be partially explained by
362 the different dietary habits and physical structures of these two marine mammals. The
363 spotted seal has only one stomach, while the minke whale has three stomachs. As filter
364 feeders, minke whales mainly prey on large zooplankton (65%), small pelagic fishes
365 (30%), and miscellaneous fishes (5%) and occupy a lower trophic level than spotted seals
366 (Pauly et al., 1998). In contrast, the main food source of spotted seals is fish. They like to
367 prey on pelagic and mesopelagic fishes, as well as cephalopods and shrimp (Tian et al.,
368 2018). In general, trophic biomagnification or biodilution of TEs in marine food webs is
369 affected by various factors, such as food web length and environmental and biological
370 factors, and hence inconsistent results might be obtained, even for the same predator
371 (Córdoba-Tovar et al., 2022).

372 **4 Conclusions**

373 Thirteen TEs were 100% detected in all of the investigated tissues of 20 stranded spotted
374 seals and 9 stranded minke whales, and the TEs tended to accumulate in internal organs,
375 especially the liver and kidney. Body length can affect the accumulation of TEs in the
376 two marine mammals, and both positive and negative effects have been observed.
377 However, the TE levels displayed insignificant sex-specific differences. More than half
378 of the investigated TEs posed health risks to the two marine mammals based on the
379 current study, especially for Hg, As, and Se. Therefore, long-term monitoring of TEs is
380 required to discover the adverse effects of TEs on marine mammals in depth. Trophic
381 transfer of TEs was evaluated for the first time for spotted seals and minke whales. For
382 the spotted seal in this study, As, Cu, Mn, Ni, Pb, and V underwent biodilution, while Zn
383 underwent biomagnification. In the case of the minke whale, As, Cd, Co, Mn, Pb, Se, and
384 V undergo biomagnification. The rest of the TEs underwent no obvious biodilution or
385 biomagnification for either spotted seal or minke whale.

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390

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533

534 **Table 1.** The risk quotient (RQ) of halogenated organic contaminant calculated at 50th
535 and 95th percentile.

536 **Table 2.** Trophic magnification factor (TMF) for the investigated trace elements of the
537 two marine mammals.

538 **Figure 1.** Nonparametric probability distribution of the TEs levels and molar ratio of
539 Se/Hg in the tissues of the spotted seals (the top and bottom of each box represent 75th
540 and 25th percentiles, respectively; the top and bottom of each whisker represent 5th and
541 95th percentile, respectively; line across inside of each box represents median; the small
542 square represents the mean value, and diamond beyond whiskers means outliers).

543 **Figure 2.** Nonparametric probability distribution of the TEs levels and molar ratio of
544 Se/Hg in the tissues of the minke whales (the top and bottom of each box represent 75th
545 and 25th percentiles, respectively; the top and bottom of each whisker represent 5th and
546 95th percentile, respectively; line across inside of each box represents median; the small
547 square represents the mean value, and diamond beyond whiskers means outliers).