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Original article

The Effect of Gadolinium and Lanthanum on the Mortality of *Daphnia magna*

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Abstract

Rare earth elements (REEs) have been recently identified as emergent contaminants because of their numerous and increasing applications in technology. The impact of REEs on downstream ecosystems, notably aquatic organisms, is of particular concern, but has to date been largely overlooked. The purpose of this study were to generate toxicological information regarding these poorly studied Gadolinium and Lanthanum elements to determine the current risk associated with these elements. The results of this work indicate notable D. magna mortality in high concentration of La and Gd. The highest mortality rate was determined as 100% at 100 mg/L concentration for both La and Gd at the end of the 24hour . At the end of the 48 hours, the highest mortality rate for both La and Gd was observed at 100 mg/L concentration. No mortality was determined at 48 hours at a concentration of 10 mg/l Gd. 100% mortality was observed for two elements at 50 and 100 mg/L concentrations at 72 hours. in the natural living water no death was seen in this time period. The findings from our study also indicate that Gd is more toxic than La. Due to this mortality effect of La and Gd to D. magna, it will be important for the ensuring continuity of the ecosystem to monitor especially aquatic environments and to treat them with appropriate treatment methods from contaminated environments.

Keywords: Gadolinium, Lanthanum, Daphnia magna, Mortality

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INTRODUCTION

The main reason why the causes of accidents due to environmental risks have been largely disregarded until last years is that intense increase in demands on a global scale. In fact, with continued industrial applications of REEs due to increased mineral demand and use, as well as imprecise discharge of contaminats containing these materials into the receiving bodies, concentrations of REEs can reach extreme levels in receiving environments (Freitas et al., 2020), For these reasons, problems of exceeding recorded levels in natural water, which are generally in the range of a few ng/L to a few µg/L, can pose a threat. (Verplanck et al., 2001).

The main reason why light and heavy REEs show toxicity differences in organisms is that they are metal groups with similar chemical properties to REEs freshwater ecosystem (Cui et al., 2012). REEs have significant effects on the high temperature strength as well as the creep resistance of alloys and they improve magnesium corrosion resistance (Willbold et al., 2015). In the science of ecotoxicology, there has been an increase in studies focusing on the measurement and assessment of the effects of pollutants at the biochemical and molecular level (Gonzalez et al., 2014), because these studies require important knowledge about the affected biological and chemical methods revealing the mode of action of toxic substances, as well as identify important environmental stress factors. They also detect (Connon et al., 2012). However, the available information on the behavior of rare earth elements in aquatic and soil ecosystems and their other roles in the ecological cycle is insufficient to comment on the risks associated with high limits of these elements (Cobelo-García et al., 2015). REEs as alloying elements in biodegradable metals have attracted a great deal of attention due to their unique atomic structure and properties (Li et al., 2021).

Lanthanum is the first element of the (La) lanthanides (or lanthanoids), This series ranges in atomic numbers from 57 to 71, from lanthanum to lutetium (Holden and Coplen, 2004). Looking at the geochemical cycles of lanthanides, the increase in global production and deterioration with the use of human beings are striking. The ecotoxicities of these elements are still not fully characterized (Gonzalez et al., 2015).

The atomic properties of the lanthanide groups are quite similar to each other. (Greenwood and Earnshaw, 1997). According to the configuration properties of them, it is possible to divide the lanthanides into two basic groups. These groups range from lanthanum to europium (LaeEu) as the light lanthanides and from gadolinium to lutetium (GadeLu) as the heavy lanthanides.

According to the literature studies, although the cases exposed to lanthanide pollution are generally few, there is a need to obtain a general opinion about the behavior of lanthanides in the ecological cycle, their biochemical accumulation and their mechanism of action on nature in order to confirm the risks associated with the existing anthropogenic releases to the environment in recent studies (Gonzalez et al., 2014).

While zooplankton such as Daphnia are an essential component of ecosystems in freshwater, there is a predator-prey relationship to phytoplankton, and these zooplankton are also a very important food source for larger predators. Daphnias unmatched characteristics like short life period and reproductive time, large habitat, easy cultivation and touchiness to foreign materials have made Daphniathese livings the optimum model organism for the investigation of the ecology, physiology and toxicology of water habitats (Liu et al., 2020).

According to Sousa et al. (2020), OECD, ASTM, US EPA accepts Daphnias as model organisms for various chronic and acute toxicity measurement protocols. Jing et al. (2021) revealed aout that *Daphnia magna* is one of the crustaceans that have a significiant role in ensuring ecological stability in fresh waters.

The aim of this study is to evaluate the mortality rate of two lanthanides, lanthanum and gadolinium, by using *D. magna* bioassays, to obtain toxicological information about these less studied elements and to reveal the current risk associated with these elements.

MATERIALS and METHODS

Chemicals

Lanthanum and Gadolinium used in this study were purchased from Bostonchem (Boston, MA).

The test organism used in the study and mortality assays

D. magna used as a test organism obtained from stock culture at environmental toxicology laboratory in Munzur University. Optimum temperature and photoperiod conditions were created in our laboratory so that the usual life processes of water fleas can be continue. Hence it was ensured that the self-death rate of water fleas in stock conditions was minimized. For the water fleas to survive their daily nutritional needs were regularly provided, natural life water is also oxygenated continuously for 24 hours by air pumps. In addition, some of the water was renewed periodically with preconditioned water.

For mortality assessment, five experimental groups were designed. Firstly, 250 mL of Natural Living Water (NLW) from stock culture as control group and 10-30-50-100 mg/L of Lanthanum or Gadolinium solutions (total volume 250 mL) filled into polycarbonate containers and 10 daphnia individuals were added the all containers.

No feed was added to the organisms used for testing during the experiment. Experiments were performed in triplicate for all living groups. At the end of 24, 48 and 72 hours, the number of dead water fleas in each container was determined and the mortality rate of these daphnias was calculated as a percentage at the end of each period (Babu et al., 2015).

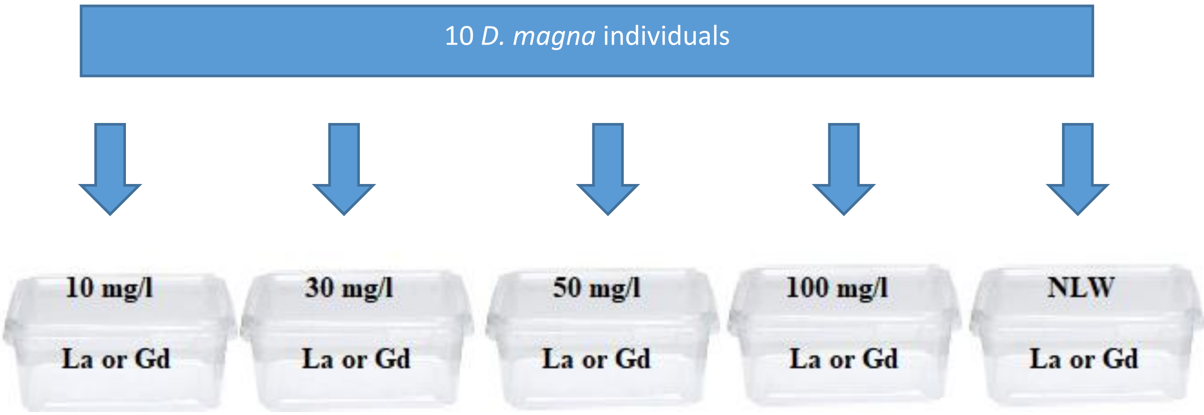

Fig. 1. The mortality setup, NLW: Natural Living Water

Statistical analyses

SPSS version PASW Statistics 18 was used for statistical analysis. One-way ANOVA and Duncan's multiple range tests were employed to evaluate the statistical differences in the all concentrations in the same elements ($^{abc}P<0.05$).

RESULTS and DISCUSSION

The toxicity of lanthanides can also increase with increasing atomic numbers, as seen in previous literature working with prediction models based on their chemical properties (Wolterbeek and Velburg, 2001). The ecotoxicity of the lanthanides is generally inferior to that of other metals widely evaluated in ecotoxicology (eg, Cd, Pb) when compared in the light of similar practical studies. In addition, interspecies variations have been found due to changes in metal bioavailability under different exposure environments, different uptake times, or different basic physiological characteristics with respect to the organism (Rainbow et al., 2002).

At 24 hours, the highest mortality rate was determined as 100% at 100 mg/L concentration for both La and Gd. It was determined that mortality increased statistically significant depending on the increase in concentration for La (P<0.005). No mortality was detected in the natural living water and the applications of 10 and 30 mg/L Gd concentrations within 24 hours (Fig. 2)

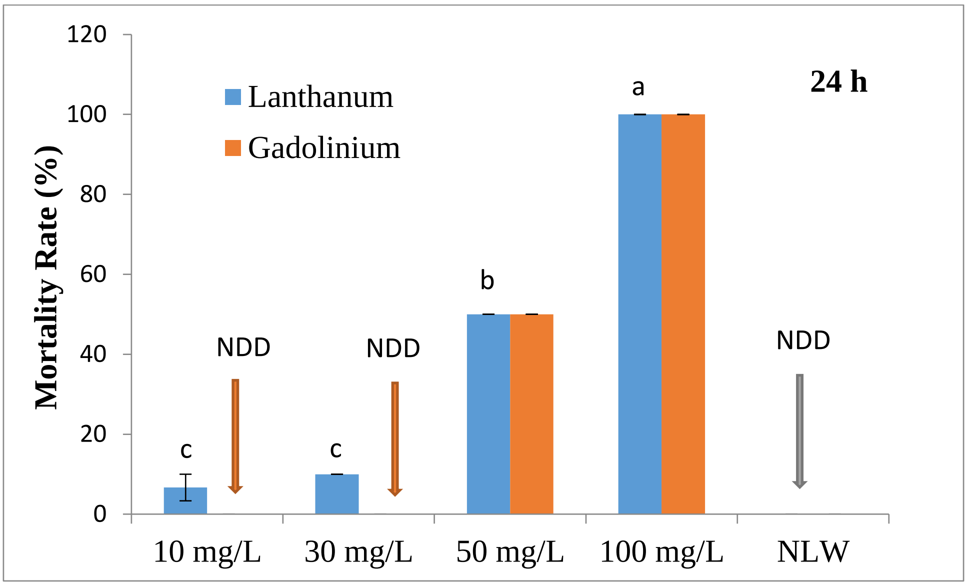

Fig. 2. *D. magna* mortality rates at 24th hour, NLW: Natural Living Water, NDD: Not Dead Determined. The different letters ([abc]P<0.005) on the bar indicates that statistically differences amoung concentrations in same element (La or Gd) according to Duncan's multiple range test).

At 48 hours, it was determined that La caused an increase in mortality rate due to the increased concentration. While no mortality was observed in the natural water environment, the highest mortality rate for both La and Gd was observed at 100 mg/L concentration. At a concentration of 10 mg/l Gd, no mortality was determined at 48 hours (Fig. 3)

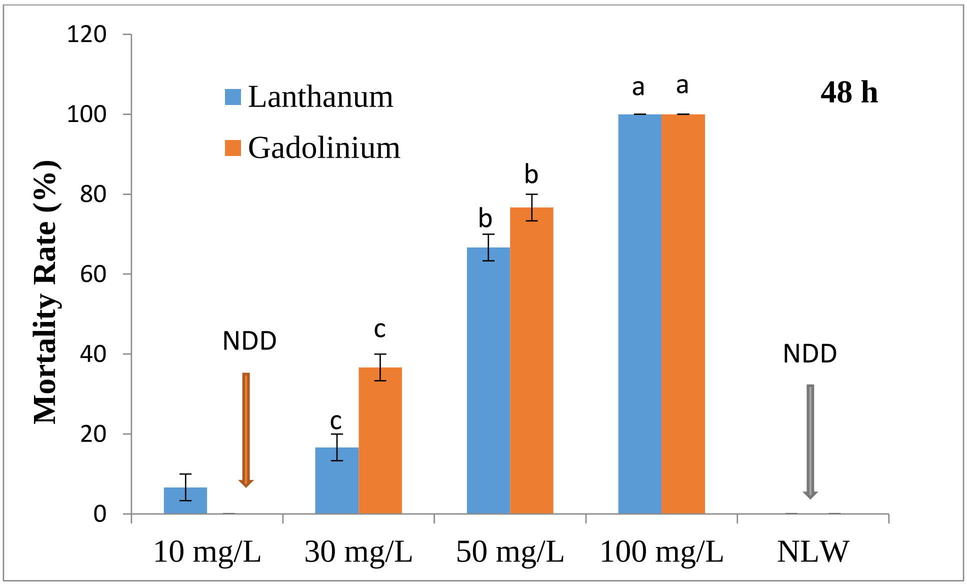

Fig. 3. *D. magna* mortality rates at 48th hour, NLW: Natural Living Water, NDD: Not Dead Determined. The different letters ([abc]P<0.005) on the bar indicates that statistically differences amoung concentrations in same element (La or Gd) according to Duncan's multiple range test).

At 72 hours, 100% mortality was observed for both elements (La and Gd) at both 50 and 100 mg/L concentrations. No death was seen in the natural living water environment at 72 hours. There were no deaths for Gd at 48 hours, with a mortality rate of approximately 17% at 72 hours (Fig. 4)

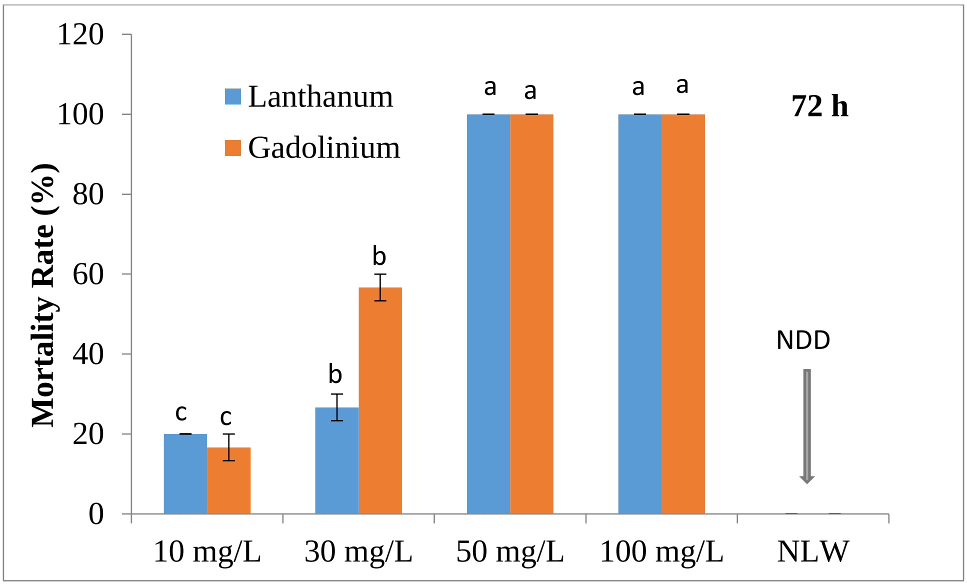

Fig.4. *D. magna* mortality rates at 72th hour, NLW: Natural Living Water, NDD: Not Dead Determined. The different letters ($^{abc}P<0.005$) on the bar indicates that statistically differences amoung concentrations in same element (La or Gd) according to Duncan's multiple range test).

In some experiments with water fleas, subjects such as lethal effect, reproduction and the destructive consequences of any chemical substance on biochemical parameters are among the research topics in general. The most preferred studies are experiments to determine the lethal effects (Tkaczyk et al., 2021). Bustamante and Miramand (2005) obtained a similar finding when they compared the tissue concentration and partitioning of La, Nd and Ce lanthanides among other trace elements in *Chlamys varia*. According to the results of the study, it was determined that at the subcellular level, lanthanides were associated with organelles, membranes or granules, especially in the digestive gland, but no dissolution occurred in the cytoplasm.

Although we determined the toxic effect of La or Gd on *D. magna* in our study, Zhou et al. (2004) reported that a direct toxic effect of La on the food alga is not expected as La can promote growth of phytoplankton. Additionally, Jin et al. (2009) revealed that these elements were toxic only at high concentrations. In another study similar to this one, Fujiwara et al. (2008) found that lanthanides were more toxic than Cd, Co or Cr and less toxic than Cu compared to the toxicity of other common metals.

CONCLUSION

The results of this work indicate notable *D. magna* mortality in high concentration of La and Gd. The findings from our study also indicate that Gd is more toxic than La. However, the increased lanthanum discharge into the receiving bodies due to their use in many industrial areas involves the establishment of a protective outset assess value that have to to be revised as more information becomes available in the future. In addition, due to this mortality effect of La and Gd to aquatic organism, it will be important for the ensuring continuity of the ecosystem to monitor especially aquatic environments and to treat them with appropriate treatment methods.

Conflict of interest: No potential conflict of interest was declared by the authors

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