Chemosphere xxx (2016) xxx-xxx

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com

Characteristics of water and ion exchange of *Elodea nuttallii* cells at high concentrations of lanthanides

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ARTICLE INFO

Article history:
Received 29 April 2016
Received in revised form 9 September 2016
Accepted 12 September 2016
Available online xxx

Handling Editor: Martine Leermakers

Keywords:
Membrane permeability
Lanthanides
Rare-earth elements (REE)
Aquaporins
NMR-Diffusometry
Elodea nuttallii

ABSTRACT

Changes of diffusive permeability of membranes of *Elodea nuttallii* cells following a short-term (60 min) treatment with high concentrations of lanthanides were recorded by the ^{1}H NMR-diffusometry and conductometry methods. The 1-h infiltration of segments of *Elodea nuttallii* internodes in 10 mM solutions of nitrates of La, Nd and Lu resulted in the increased leakage of electrolytes from cells, but has no effect on a water diffusive permeability of membranes. In samples subjected to a 30 min pretreatment with a water channel inhibitor $HgCl_2$ the water diffusive permeability of membranes (P_d) drops down under the influence of lanthanides, as well as an outcome of electrolytes. To explain the observed effects the change of spontaneous curvature of membrane lipid layer has been taken into consideration. The interaction of lanthanides with lipids of plasmalemma leads to the negative spontaneous curvature of lipid layer at which membrane channels are unclosed. Blocking of the ionic and water channels by mercury ions compensate the effect of change of spontaneous curvature of lipid layer.

1. Introduction

An increased application of lanthanides in industry and agriculture, and, hence, a growing extraction of rare earth element (REE) containing minerals leads to amplification of concentration of elements of this group in the environment (Kulaksız and Bau, 2013). The majority of REEs is adsorbed by soil particles, but approximately 10% remain solvable (Pang et al., 2001). These solvable lanthanides can migrate through soil, getting to ground waters, and invoking the pollution of rivers and lakes. The extensive use of gadolinium in medical researches has led to the increase of its concentration in lakes, drowned rivers, neritic and groundwater, and also in tap water (Bau et al., 2006; Kulaksız and Bau, 2013, 2007; Lawrence, 2010; Möller et al., 2002; Morteani et al., 2006; Rabiet et al., 2009).

Submersed aquatic plants, including *Elodea nuttallii*, play a key role in the functioning of freshwater ecosystems being natural sorbents of heavy metal ions (Jeppesen et al., 1998). The sorption capacity of cell walls of *Elodea nuttallii* causes a high tolerance of this plant to mercury, cadmium and lanthanum (Larras et al., 2013; Zhang et al., 2015). Biological effects of metals appear after filling of sorption capacity of cell wall and are caused by interaction of metals with cell membranes.

The main function of plasma membranes is the regulation of water-ion homeostasis of a cell. It is obvious that the secondary-water plants would firstly modify the permeability of plasma membrane in the 'above-ground' organs to conform to the ion change caused by the altering of their inhabitancy place. Mineral nutrition of submersed macrophytes in most cases is provided by whole surface of a plant, whereas the root system can function only as an anchoring organ. Secondly, they adapted water exchange processes to the absence of one of the main driving forces - the hydrostatic pressure created by transpiration. It is known that in the absence of a pressure gradient water flow through membrane is determined by osmosis and described by the following equation (Steudle, 1994; Zimmermann and Steudle, 1998):

$$Jw = P\left(C_{in} - C_{ex}\right) \quad (1)$$

where P – membrane permeability coefficient, C_{in} and C_{ex} – concentration of osmotically active molecules inside and outside the cell.

The intercellular water exchange depends on the amount and functional activity of water channel proteins, known as aquaporins, and the permeability of lipid bilayer of cell membrane (Li et al., 2014; Maurel, 1997; Maurel et al., 2015). Currently it is pointed out that lipids play an important role in regulation of cellular metabolism not only on the biochemical level, but also through the changes of physical parameters of membranes. It is known that an increased cholesterol content in membranes of animal cells has a negative influence on water conductivity of aquaporins which is caused by a decreased lateral mobility of lipids in membrane bilayer (Tong et al., 2013, 2012).

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http://dx.doi.org/10.1016/j.chemosphere.2016.09.044
0045-6535/

In the majority of researches the main indicator of biological activity of lanthanides is the disbalance of various biochemical processes - development of oxidative stress, weakening of photosynthetic pigments, disruption of absorption of nutrients (Zhang et al., 2015). But the change of water permeability of cellular membranes was out of focus. Therefore the main objective of the present work is the assessment of the effect of lanthanide-membrane interaction on the integral water permeability of cellular membranes of *Elodea nuttallii* and the revealing of the underlying mechanism.

2. Materials and methods

2.1. Plant material and metal treatment

Vegetative shoots of *Elodea nuttallii* were grown in 5% Hoagland-Arnon solution in controlled laboratory conditions (illumination intensity - 114 μmol/m^2/s, a 14 h photoperiod, 25°C/20°C day/night temperature). After removal of leaves the shoots were cut into segments (15–20 mm length) and vacuum infiltrated at a pressure of 10 Pa during 60 min in: a) a nutrient solution for a Control; or one of the following lanthanide-containing 10 mM solutions: b) $La(NO_3)_3$ (La^{3+} 1.4 g L^{-1}); c) $Nd(NO_3)_3$ (Nd^{3+} 1.44 g L^{-1}); d) $Lu(NO_3)_3$ (Lu^{3+} 1.74 g L^{-1}).

To inhibit the functioning of water conducting channels the segments were vacuum infiltrated in $HgCl_2$ 100 μM (Hg^{2+} 20 mg L^{-1}) solution for 30 min prior to the infiltration with one of the lanthanide-containing solution or nutrient solution. In such a case the resulted overall duration of infiltration was 90 min.

2.2. Determination of lipid peroxidation

The level of lipid peroxidation in the segments of shoots (0.2 g) was determined by thiobarbituric acid reaction according to Heath and Packer (1968) just after the infiltration in control or one of lanthanide solutions. The concentration of MDA was calculated using 155 mM cm^{-1} as extinction coefficient in terms of nmol g^{-1} fresh weight. Measurements were performed on spectrophotometer Unico-2800 UV/VIS (USA) at wave length of 532 nm, as well as at 600 nm for an adjustment of nonspecific absorption (Hodges et al., 1999).

2.3. Determination of barrier properties of membranes

The barrier properties of cellular membranes were assessed by the extent of electrolyte release from the 0.2 g segments of shoots (Kholodova et al., 2005). After infiltration the segments were shaken for 15 min in 10 ml of distilled water – to remove any extracellular electrolytes and remnants of the cells damaged upon cutting. The segments were quickly dried with filter paper and placed into clean tubes with 20 ml of deionized water (Millipore Milli-Q, Germany), with their subsequent incubation during 120 min at 20°C. The concentration of electrolytes after the incubation indicated the extent of membrane leak. To extract the remaining electrolytes, the sections were boiled for 30 min in a new portion of water and then shaken for at least an hour. Electroconductivity of extracts was measured using a PWT (HI 98308) conductometer (HANNA Instruments, Germany). The extent of membrane leak was calculated as a percentage of the electrolytes released after the 1st, 60-min, incubation to the total cellular electrolytes extracted.

2.4. Cytoplasmic streaming

The rotational protoplasmic motion was registered by detecting the chloroplast motion velocity. The method of synchronous tracking (Vorob'ev et al., 2002) was used to register the chloroplast motion. The measurements were carried out on the cells of the leaf rear layer where the central rib begins at room temperature. There were no any signs of plasmolysis detected under lanthanide treatment.

2.5. Determination of water permeability of membranes by pulsed field gradient NMR

After infiltration the segments were gently wiped with a filter paper. 20–25 arranged in parallel segments were placed into a glass test-tube for NMR measurements. Experiments were carried out at 25°C on the time-domain ^1H NMR-analyzer "Spin Track" (Resonance Systems Ltd., Yoshkar-Ola, Russia) operating at 19.1 MHz and equipped with the permanent magnet. A three-pulse stimulated echo sequence with pulsed field gradient was used to measure the translational diffusion coefficient of water (Tanner, 1970). The pulsed magnetic field gradient was applied perpendicularly to the test tube. Thus the water self-diffusion in a cross direction of the segments (radial transport) was observed.

During the experiments the attenuation of spin echo signal as a function of the strength of magnetic field gradient pulse (g) changing up to 3 T/m with fixed values of the pulse duration (δ) of 350 μs and the diffusion time t_d of 700 ms was registered. An initial part of signal attenuation plot (at $g \to 0$) was fitted with Eq. (2) resulting in a mean water diffusion coefficient (D)

$$A(g)/A(0) = \exp\left[-\gamma^2\delta^2 g^2 t_d D\right] \quad (2)$$

where $A(0)$ is the echo amplitude in the absence of the magnetic field gradient; γ is the proton gyromagnetic ratio.

At t_d equal to 700 ms, the displacement of water molecules becomes comparable with the transverse size of *Elodea nuttallii* internodal cells which was measured to be about 50 μm. Thus, the measured diffusion coefficient come close to D_∞ (the diffusion coefficient in the long diffusion time limit $t_d \to \infty$) (Fig. 1), and can be interpreted in terms of tortuosity (commonly used for porous structures) or in terms of permeability that is more suitable for a system with semipermeable membranes (Sibgatullin et al., 2010, 2007). A model of parallel semipermeable planes (Crick, 1970) was used to calculate the value of diffusive water permeability of membranes P_d

$$\frac{1}{D_\infty} = \frac{1}{D_0} + \frac{1}{P_d \cdot R} \quad (3)$$

with D_0 the bulk water diffusion coefficient at $t_d = 0$ and R the distance between the membranes. To take into account the actual geometry of the cells the correction coefficient was applied to the diameter of the cell.

2.6. Statistics

Statistical analysis was accomplished on OriginPro 9.0 (OriginLab). The data obtained are represented as the mean of three independent experiments with standard deviation. The confidence of the dif-

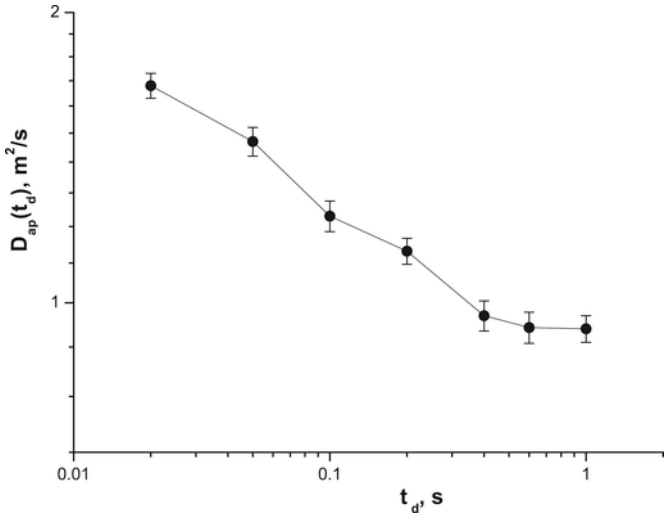

Fig. 1. Typical dependence of apparent water diffusion coefficient as a function of diffusion time in *Elodea nuttallii* internodal cells measured after vacuum infiltration.

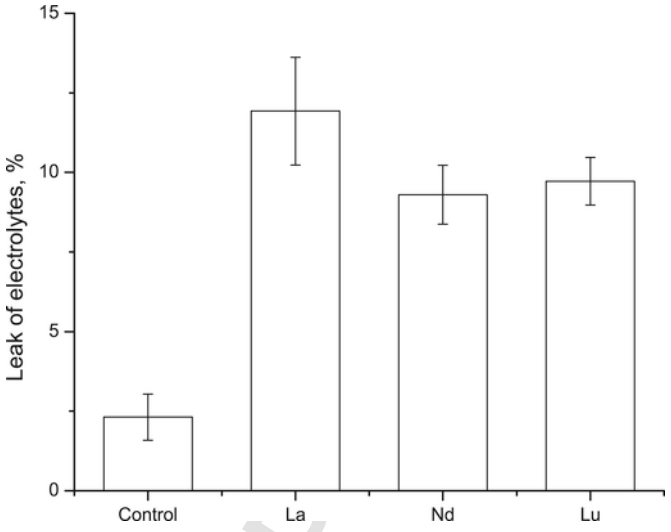

Fig. 3. Effect of lanthanides on the leakage of electrolytes from *Elodea nuttallii* cells (mean ± SD, n = 3). Percentage of the total content of electrolytes of cells.

ference between two values was estimated by a standard Mann-Whitney test ($p < 0.05$).

3. Results

One hour infiltration of samples in lanthanide solutions has not led to a noticeable change of the signal attenuation plot compared to the control samples subjected to the infiltration in a nutrient solution (Fig. 2). However, it has resulted in 4–5 times higher leakage of electrolytes from *Elodea nuttallii* cells (Fig. 3).

According to Equation (1) the driving force of water flow through a membrane is the concentration gradient of osmolites. The leakage of electrolytes weakens this gradient, but does not affect the resistance of membrane to a water exchange. It is the barrier function of membranes that creates limitation for diffusive transfer of water molecules resulting in a change of the rate and shape of signal attenuation plot in the diffusion experiment (Sibgatullin et al., 2010; Snegireva et al., 2006).

Two pathways of transmembrane transfer of water are known: transport through aquaporins and through lipid bilayer of membrane. Mercury chloride is a commonly used inhibitor of aquaporin functioning (Chaumont and Tyerman, 2014). It binds to the thiol group of cystein residues located in the pore region of channel protein. It is logically to assume that while the aquaporins are fixed in closed state the effect of phospholipid-lanthanide interaction on water transmembrane transfer through lipid bilayer can be revealed in diffusion experiments.

Fig. 4 presents signal attenuation plots of diffusion experiment obtained with samples preliminarily infiltrated in mercury chloride solution (100 μM). As was expected, the infiltration of samples in mercury chloride has led to a decrease in mean diffusion coefficient of water compared to control. The influence of lanthanides against

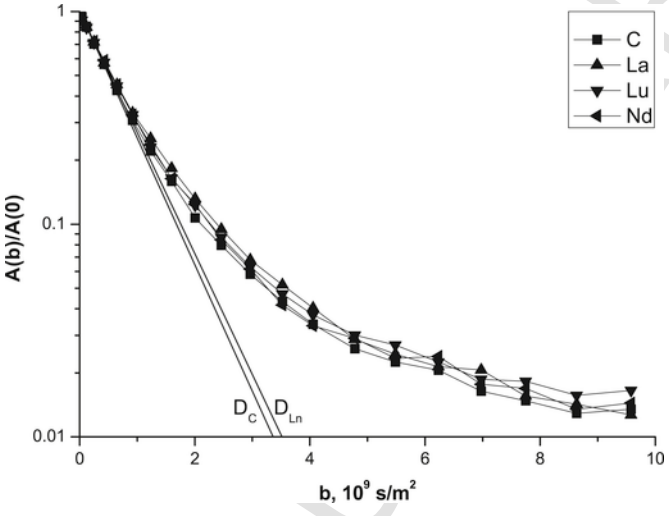

Fig. 2. Signal attenuation plots of diffusion experiment obtained with samples infiltrated in La, Lu and Nd containing solutions. D_C and D_{Ln} stand for lines indicating the initial slope of the plot (so the measured mean diffusion coefficient) of control and lanthanide treated samples correspondingly. The difference between D_C and D_{Ln} is less than the error of diffusion experiment.

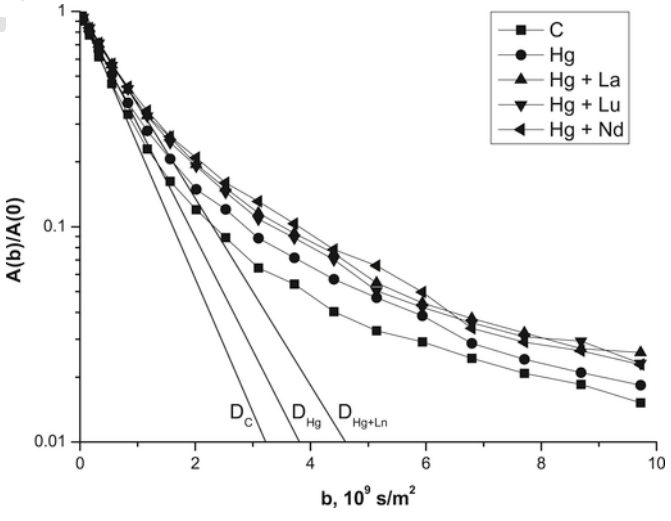

Fig. 4. Signal attenuation plots of diffusion experiment obtained with samples preliminarily infiltrated in mercury chloride solution (100 μM). D_C, D_{Hg} and D_{Hg+Ln} stand for lines indicating the initial slope of the plot (so the measured mean diffusion coefficient) of control, $HgCl_2$ infiltrated and consecutive treatment with $HgCl_2$ and lanthanides correspondingly.

the background of the mercury chloride treatment resulted in even larger inhibition of transmembrane water transfer (Fig. 4).

The MDA content of samples infiltrated with $HgCl_2$ has shown some increase of lipid peroxidation compared to control whereas the lanthanide treatment itself neither add nor diminish the MDA content of mercury treated samples (Fig. 5) as well as the MDA content of control samples (data not shown).

The mercury pretreatment prevents the lanthanide mediated increase in a leakage of electrolytes (compare Fig. 6 and Fig. 3). It is probably caused by the interaction of mercury with sulfhydryl groups of channel proteins responsible for ion exchange (not only aquaporins).

Against the absence of distinctions in the lipid peroxidation level (Fig. 5) a variant with mercury treatment (alone) and variants of consecutive treatment with mercury and lanthanides are reliably differed in the measured water diffusion coefficient (Fig. 4).

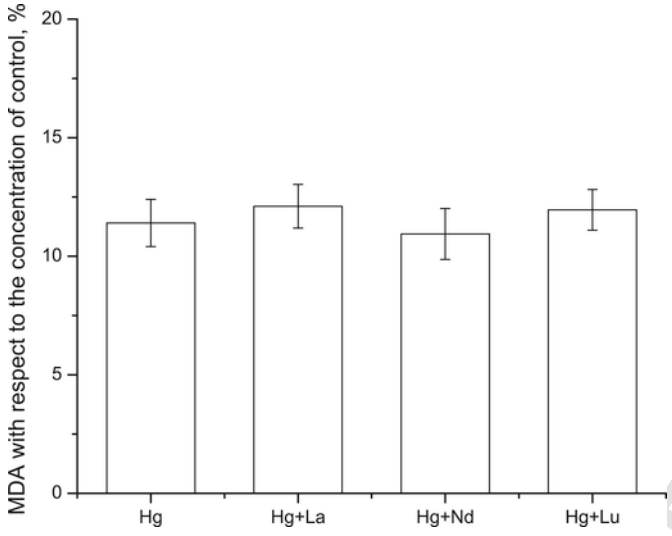

Fig. 5. The relative increment of MDA content compared to control in $HgCl_2$ infiltrated samples and samples consecutively treated with $HgCl_2$ and lanthanides.

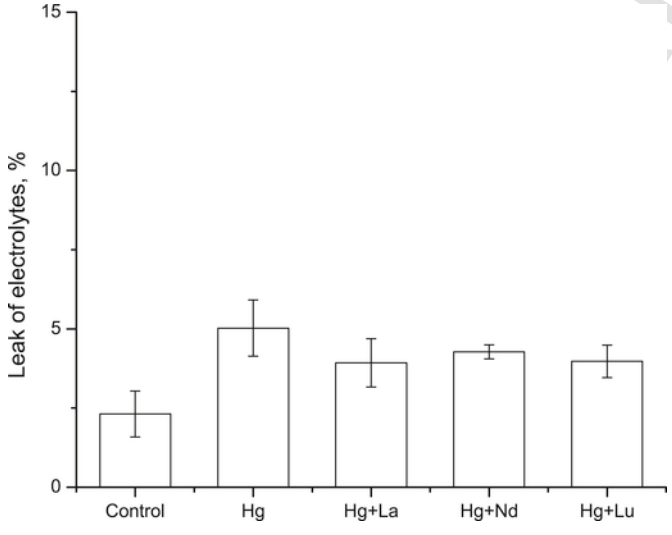

Fig. 6. Joint influence of mercury and lanthanides on a leakage of electrolytes from *Elodea nuttallii* cells.

The water diffusive permeability of membranes was calculated on the basis of the diffusion measurements. A significant decrease of permeability in response to a consecutive treatment with mercury and lanthanides was observed (Table 1).

Suppression of hydraulic conductivity of *Arabidopsis* roots by mercury chloride treatment was measured to be 35–65% of control (Sutka et al., 2011). In our experiments the P_d was reduced by 20.3% by a mercury treatment. In cases of consecutive treatment with mercury and lanthanides (Hg + La, Hg + Nd and Hg + Lu) the reduction was 40.2; 42.5; and 37.6% correspondingly.

At values of membrane water permeability of the order of 10^{-6} m/s and higher the contribution of unstirred layers (also called Nernst diffusion layers) to the control of transmembrane water transfer rate becomes apparent (Kotyk and Janáček, 1970). As shown earlier the change of velocity of cytoplasmic streaming in *Elodea* leaf cells affects the rate of transmembrane water exchange through the change of a thickness of unstirred layers (Vorob'ev et al., 2002). To test whether the difference in measured water permeability of membrane is caused by the contribution of unstirred layers the chloroplast motion velocity was measured. However, the treatment of *Elodea nuttallii* leaves with lanthanides in our experiments has not led to a reliable change of velocity of cytoplasmic streaming that was measured to be 9.4 ± 2.3 μm/s at least during 2 h of treatment.

4. Discussion

It is commonly supposed that the effect of rare earth elements is caused by their competition with divalent cations for the binding sites of organic molecules (Hu and Ye, 1996; Tyler, 2004). The experimentally observed effects of rare earth elements can be divided in two groups. The first one consists of the prolonged effects caused by the entering of ions inside the cell. Penetration of rare earth elements is facilitated by endocytosis and takes up to 15 h (Wang et al., 2014). The second group of effects (short-term effects) is caused by the interaction of rare earth elements with structures of membrane. The interaction of gadolinium with cation-sensitive receptor in cells of rat kidney invoked an increase of endocellular concentration of Ca^{2+} with the subsequent activation of Cl^- channels (Riccardi et al., 1995). Lanthanum leads to a four times increase in a leakage of potassium from cells of wheat roots (Kataoka et al., 2002). On the other hand there are evidences of the decrease of membrane permeability caused by the formation of stable complexes of REEs with phospholipides (Dong et al., 1993; Ni, 1995; Qiao et al., 1993). A linkage of REE ions with phospholipides of membranes is more preferable and assumes the replacement of ions of calcium from places of linkage (dos Remedios, 1981; Squier et al., 1990; Westman and Eriksson, 1979).

The data on blocking of calcium channels by lanthanum ions in cells of maize seedlings testify to the interaction of lanthanides with membrane proteins (Gong et al., 1997). It can be assumed that aquaporins are affected by lanthanides in the same way as ion channels. Unfortunately the possibility of direct influence of lanthanides on functional activity of aquaporins has not met an appropriate discussion yet. However the decrease of conductivity of aquaporins can be

Table 1
The water diffusion permeability of membranes of cells of *Elodea nuttallii* internodes after infiltration with solutions (mean ± SD, n = 3).

Solutions	Control	Hg	Hg + La	Hg + Nd	Hg + Lu
P_d, 10^{-5} m/s	3.06 ± 0.19^a	2.44 ± 0.24^b	1.83 ± 0.13^c	1.76 ± 0.23^c	1.91 ± 0.18^c

Note: means followed by the same letter are not significantly different at $p < 0.05$.

a consequence of lanthanide mediated increase of endocellular concentration of calcium (Riccardi et al., 1995). It is known that the increase of cytosolic concentration of calcium stabilizes the closed conformation of aquaporins involving the residues His-193 in the loop D, the Ser-115 in the loop B, and the N-terminal Asp-28 and Glu-31 (Chaumont and Tyerman, 2014; Frick et al., 2013b).

It was supposed that the lanthanide treatment would reduce the rate of transmembrane water exchange in *Elodea* cells. Firstly, due to the blocking of aquaporins in analogy to calcium channels. Secondly, due to the decrease of aquaporin conductance in response to the increase of cytosolic concentration of calcium. Thirdly, due to the increase of resistance of lipid bilayer for transmembrane water exchange as a consequence of the increase of viscosity of membrane lipid bilayer (Tong et al., 2013, 2012). In this case a decrease in a leakage of electrolytes would be observed (Shen and Yan, 2002; Tian, 1990).

Seeing that the increase in the leakage of electrolytes (Fig. 3) is not accompanied by changes in signal attenuation plot (Fig. 2) (and so water permeability of membrane) under high concentration lanthanide treatment, the above-stated assumption is subjected to question.

In the majority of researches the osmotic water permeability (P_f) of oocytes and liposomes (Fetter et al., 2004; Frick et al., 2013a) or hydraulic conductance (L_p) of part of a plant (Knipfer and Fricke, 2011) were used as the main indicators of the aquaporin activity. Water diffusive permeability of membrane (P_d) measured by the pulsed field gradient NMR technique was also used to determine the activity of aquaporins, e.g. in the inhibitory analysis with mercury chloride (Ionenko et al., 2006; Velikanov et al., 2015).

It was expected that the use of mercuric chloride as an inhibitor of the protein channel conductance would show the effect of lanthanides on the transmembrane water exchange. Indeed, against the action of mercury the maximum reduction of apparent water diffusion coefficient was observed in variants with lanthanides (Fig. 4). Therefore lanthanides reduced water permeability of the lipid component of the membranes.

The decrease of mean diffusion coefficient of water can be a consequence of metal-induced oxidative stress caused by the disbalance between the production and elimination of reactive oxygen species (ROS) (Kovačik et al., 2010; Opdenakker et al., 2012). It has been recently shown that the increase of lipid peroxidation caused by oxidative stress is followed by the drop of P_d of membranes in maize root cells (Velikanov et al., 2015). Many metals are capable to induce production of ROS (Körpe and Aras, 2011; Shahid et al., 2014). It is known that a prolonged effect of lanthanum chloride on *Elodea nuttallii* was expressed in the development of oxidative stress, weakening of photosynthetic pigments and disturbance of absorption of nutrients (Zhang et al., 2015). Mercury inhibits the activity of proteins due to its affinity with sulfhydryl groups (Pourrut et al., 2011). If the infiltration with mercury chloride induces the oxidative stress then the intensification of lipid peroxidation will be expected (Wahsha et al., 2012).

It is possible that the decrease of measured water diffusion coefficient in Hg + Ln variants (Fig. 4) is due to the growth of lipid peroxidation. The mercury treatment has led to a nearly equal increase of MDA content in all variants of the experiment (Fig. 5). Thus the lipid peroxidation can't be the main reason for the decrease of water diffusion coefficient in Hg + Ln variants.

Effects of mercury were as follows: the blocking of aquaporins (Fig. 4) and the decrease of electrolyte leakage, probably due to the inhibition of ion channels (Fig. 6). The diffusion experiments with mercury treatment revealed the effect of lanthanides on the lipid component of membrane. Herewith, when the mercury is not applied the lanthanide treated samples are indistinguishable from control by water diffusion (Fig. 2), but show more than once higher ion permeability compared to control (Fig. 3).

In order to explain the obtained results the concept of spontaneous lipid layer curvature (Pera et al., 2015) can be involved. According to the presented data the interaction of lanthanides with lipids of plasma membrane increases the viscosity of a lipid layer and enhances its negative spontaneous curvature. In this case the probability of an open state of the protein channel becomes higher, than that in membranes with zero spontaneous curvature of lipid layer (Sobko et al., 2006). As a consequence of an "opening" of ion channels the increased leakage of electrolytes is observed (Fig. 3).

Perhaps a change in spontaneous curvature of the lipid layer can cause the observed activation of water conductance of SoPIP2; 1 of the mercury treated liposomes while the aquaporin activity was blocked by mercury *in planta* (Frick et al., 2013a).

Hydroponically grown geophytes show reduced reaction to mercury treatment compared to the soil grown plants pointing to the reduced role of aquaporins in a transmembrane water exchange (Levin et al., 2007). It is not surprising that the contribution of aquaporins to the water permeability of membranes of internodal cells of *Elodea nuttallii* is only about 20% of total (Table 1), the rest being the contribution of a lipid bilayer. The P_d of lipid bilayer decreases by 25 ± 2% under the influence of REE. Such reduction of P_d should be reflected in the signal attenuation plot of the diffusion experiment. However, it was not registered experimentally. The absence of difference in diffusion attenuation plots (Fig. 2) can be explained by the "opening" of aquaporins if one assumes that only a part of aquaporins is physiologically active in the control samples. The validity of this hypothesis is endorsed by the observation of difference in day and night water flow (60% versus 40% of total correspondingly) in maize at the same content of PIP2 aquaporin (Lopez et al., 2003). Then the "opening" of inactive aquaporins as a consequence of a change of spontaneous curvature of lipid layer will compensate the reduction of water permeability of lipid bilayer.

The effect of mercury ions is explained in context of the proposed hypothesis. Linkage of mercury ions with SH groups of protein channels of the membrane transforms these channels into the "closed" state. Against this background the change of spontaneous curvature does not lead to the "opening" of channels. As a consequence the lanthanide treatment decreases the leakage of electrolytes (Fig. 6) and reduces the water diffusive permeability of lipid bilayer (Fig. 4).

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