Science of the Total Environment 650 (2019) 111–120

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Mercury mobility and effects in the salt-marsh plant *Halimione portulacoides*: Uptake, transport, and toxicity and tolerance mechanisms

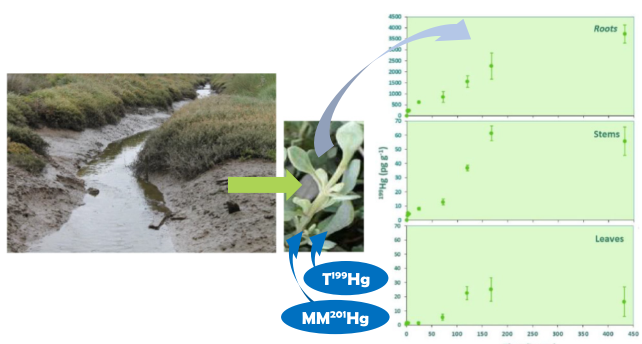
Maria Teresa Cabrita [a,*,1], Bernardo Duarte [b], Rute Cesário [a,c], Ricardo Mendes [a], Holger Hintelmann [d], Kevin Eckey [d,e], Brian Dimock [d], Isabel Caçador [b], João Canário [c]

[a] *Instituto do Mar e da Atmosfera (IPMA), Rua Alfredo Magalhães Ramalho, 6, 1495-006 Algés, Lisboa, Portugal*
[b] *MARE — Marine and Environmental Sciences Centre, Faculty of Sciences, University of Lisbon, Campo Grande, 1749-016 Lisbon, Portugal*
[c] *Centro de Química Estrutural, Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais, Lisboa 1, 1049-001 Lisboa, Portugal*
[d] *Water Quality Centre, Trent University, 1600 West Bank Drive, Peterborough, ON K9J 0G2, Canada*
[e] *Institute of Inorganic and Analytical Chemistry, University of Muenster, Schlossplatz 2, 48149 Munster, Germany*

HIGHLIGHTS

- Mercury mobility in *H. portulacoides* assessed by stable isotope enriched Hg and hydroponics.
- Mercury (THg, MMHg) is mainly accumulated into the roots of *H. portulacoides*.
- Direct translocation of THg and MMHg occurs from roots to aerial parts of the plant.
- Temperature and PAR influenced Hg content in stems and roots pointing to Hg release.
- Low levels of Hg can impact *H. portulacoides* photochemistry with prolonged exposure.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 8 April 2018
Received in revised form 23 August 2018
Accepted 24 August 2018
Available online 28 August 2018

Editor: D. Barcelo

Keywords:
Mercury
Methylmercury
Halimione portulacoides
Accumulation
Translocation
Photochemical responses
Salt marshes

ABSTRACT

The plant *Halimione portulacoides*, an abundant species widely distributed in temperate salt-marshes, has been previously assessed as bioindicator and biomonitor of mercury contamination in these ecosystems. The present study aims to assess uptake and distribution of total mercury (THg) and methylmercury (MMHg) within *H. portulacoides*, potential mercury release by volatilization through leaves, and toxicity and tolerance mechanisms by investigating plant photochemical responses. Stem cuttings of *H. portulacoides* were collected from a salt-marsh within the Tagus estuary natural protected area, and grown under hydroponic conditions. After root development, plants were exposed to $^{199}HgCl_2$ and $CH_3^{201}HgCl$, and sampled at specific times (0, 1, 2, 4, 24, 72, 120, 168 (7 days) and 432 h (18 days)). After exposure, roots, stems and leaves were analysed for total ^{199}Hg ($T^{199}Hg$) and $MM^{201}Hg$ content. Photobiology parameters, namely efficiency and photoprotection capacity, were measured in leaves. Both THg and MMHg were incorporated into the plant root system, stems and leaves, with roots showing much higher levels of both isotope enriched spikes than the other plant tissues. Presence of both mercury isotopes in the stems and leaves and high significant correlations found between roots and stems, and stems and leaves, for both THg and MMHg concentrations, indicate Hg translocation between the roots and above-ground organs. Long-term uptake in stems and leaves, leading to higher Hg content, was more influenced by temperature and radiation than short-term uptake. However, the relatively low levels of

* Corresponding author at: CEG/IGOT, University of Lisbon, Rua Branca Edmée Marques, 1600-276 Lisbon, Portugal.
E-mail address: tcabrita@campus.ul.pt (M.T. Cabrita).
[1] Present affiliation: Centro de Estudos Geográficos (CEG), Instituto de Geografia e Ordenamento do Território (IGOT), University of Lisbon, Rua Branca Edmée Marques, 1600-276 Lisbon, Portugal.

https://doi.org/10.1016/j.scitotenv.2018.08.335

both THg and MMHg in the aerial parts of the plant, which were influenced by temperature and radiation, support the possibility of mercury release by stems and leaves, probably via stomata aperture, as a way to eliminate toxic mercury. Regarding photochemical responses, few differences between control and exposed plants were observed, indicating high tolerance of this salt marsh plant to THg and MMHg.

1. Introduction

Mercury (Hg) is one of the most dangerous anthropogenic pollutants because of its high toxicity (Driscoll et al., 2013), and a major threat to coastal ecosystems mostly due to accumulation and biomagnification through food webs (Gworek et al., 2016). Mercury exists in many forms, and the most toxic ones are the organic mercury compounds, in particular methylmercury (MMHg), due to its high solubility in lipids, enhancing the potential for biological uptake and bioconcentration (Clayden et al., 2013). Methylmercury is made available by transformation of inorganic mercury (Hg(II)) through a complex set of biologically mediated chemical reactions under anaerobic conditions (Gworek et al., 2016; Randall et al., 2013). This organic form is a potent neurotoxin with harmful effects on reproduction and neural development in fish and mammals, representing most of the mercury content in contaminated fish and human bodies (Burgess and Meyer, 2008; Hong et al., 2012).

Although anthropogenic Hg emissions have decreased by half over the last decades (Obrist et al., 2018; Pacyna et al., 2001), mercury contamination is still a global issue due to the long-range transport of this persistent pollutant across several environmental compartments (Fitzgerald and Lamborg, 2003; Sonke et al., 2013). Biological mercury hotspots found worldwide are a major concern to human populations and the ecosystems on which they depend (Driscoll et al., 2013; Evers et al., 2007; Obrist et al., 2018). Salt marshes are among Earth's most productive (Barbier et al., 2011; Giblin and Weider, 1992; Odum, 1971) and highly relevant ecosystems supporting vital ecosystem functions (Costanza et al., 1997), such as primary productivity, nutrient, metal and metalloid biogeochemical recycling, wildlife habitat, and shoreline stabilization (Mitsch and Gosselink, 2000). When located near polluted areas, these ecosystems are receivers of municipal, industrial and agricultural waste (Anjum et al., 2014a; Caçador et al., 2009; Gupta and Chandra, 1998). Although the global estimates of 45,000 to 54,951 km^2 of salt marsh area (Greenberg et al., 2006; Mcowen et al., 2017; Pendleton et al., 2012) only correspond to about 0.07% of the total land surface, some salt marshes can act as sinks for metals and metalloids (Caçador et al., 1993, 1996; Hung and Chmura, 2006; Weis and Weis, 2004; Williams et al., 1994). Mercury inputs to waste are generally linked to effluents from metal production, pulp industries and chloralkali plants (Lindqvist et al., 1991). Whilst salt marshes can have an important role in reducing contamination of adjoining areas (Jacob and Otte, 2003), impairment of this function may occur as levels of contaminants rise. Once released into salt marshes, mercury can interact with both sediments and pore waters (Canário et al., 2005), and become available to the biota (Suntornvongsagul et al., 2007). Halophytes such as *Halimione portulacoides*, *Sarcocornia* sp. and *Spartina maritima*, which colonize and produce elevated biomass in salt marshes, retain metals/metaloids mostly during the growing season (Caçador et al., 2000; Duarte et al., 2010) and can influence the chemical speciation and mobility of contaminants by changing sediment redox conditions, pH and organic matter content (Castro et al., 2009; Jacob and Otte, 2003; Pedro et al., 2015). Studies on mercury in halophyte colonised salt marsh areas have consistently shown elevated THg and MMHg levels in the rhizosphere, compared to levels found in sediments (Canário et al., 2010), and limited transport of both forms into stems and leaves, (Anjum et al., 2011; Canário et al. 2010; Castro et al., 2009; Válega et al., 2008a, 2008b). These results suggest either reduced translocation to or weak retention of mercury species by aerial parts of plants, and/or Hg volatilization from these plant organs. In other plant species besides halophytes, most of the Hg content in foliar tissue has been found to come from the atmosphere, being more significant than Hg translocation from the roots (Ericksen et al., 2003; Frescholtz et al., 2003; Gustin et al., 2004; Laacouri et al., 2013; Mao et al., 2013; Marrugo-Negrete et al., 2016a; Tomiyasu et al. 2005). In addition to incorporation into leaves via atmospheric Hg deposition, Hg release from leaves during plant transpiration has also been observed (Weis and Weis, 2004; Windham et al., 2001). Continuous Hg emission from plants into the atmosphere, shown to be positively correlated with air temperature, suggests that Hg translocation within the plants may play a more important role than previously anticipated (Canário et al., 2017). However, the uptake mechanism into the roots and from these organs to the aerial parts of the plants is still not well understood.

Although some salt marsh halophytes are able to endure metal/metalloid contamination to a certain degree, excessive levels internalised in the plants can cause severe impairment of fundamental processes linked to protein and energy metabolism (Falchuk et al., 1979; Liu et al., 2013; Patra et al., 2004). In fact, metal/metalloid overload have been shown to trigger severe damage in the photosystem II (PS II) at the biophysical level (Anjum et al., 2016; Duarte et al., 2014; Santos et al., 2014). At the biochemical level, metal/metalloid-accrued increase in reactive oxygen species (ROS) can induce cellular redox homeostasis imbalance (e.g. Anjum et al., 2014b, 2016; Pietrini et al., 2003; Santos et al., 2014, 2015; Schroder et al., 2009). Tolerance mechanisms are developed by the plants in order to escape these harmful effects, for example, metal ions can be prevented from interfering with the cellular metabolism by either cell wall immobilization (Sousa et al., 2008; Wang and Greger, 2004) or chelation with specific peptides or organic acids (Hall, 2002; Yang et al., 2005). Despite these advances, a knowledge gap is noticeable regarding the mechanisms by which THg and MMHg enter and accumulate in plant tissues and how these toxic compounds are transported from roots to the aboveground plant parts. The present work investigates the uptake of mercury species into the roots of salt marsh plants and its subsequent translocation and accumulation by aerial parts (stems and leaves) of the plant, as well as the plants photochemical response to mercury contamination. The study was targeted at the salt marsh plant *Halimione portulacoides* and aimed at providing critical insight on (i) processes of uptake, translocation and distribution of THg and MMHg within the whole plant, and (ii) toxicity and tolerance mechanisms by investigating plant photochemical responses. In order to achieve these objectives, fully developed halophyte *H. portulacoides* plants, grown under hydroponic conditions and exposed to mercury stable isotopes, were monitored during a period of 18 days, for changes in (i) $T^{199}Hg$ and $MM^{201}Hg$ content in roots, stems and leaves, (ii) PS II electron transport activity, and (iii) electron transport chain (ETC) behaviour, in leaves. The salt marsh plant *H. portulacoides* was chosen because it is an abundant halophyte species colonizing salt marshes worldwide, grows well from cuttings, has been shown to accumulate mercury within its root system, and has been suggested as a potential biomonitor for mercury and metal contamination. Hydroponics have already been successfully used to investigate uptake and translocation of mercury species in different environmental compartments of wetland plants (Chattopadhyay et al., 2012; Cui et al., 2014; Rahn, 1973). In the present study, combination of the mercury stable isotope tracer method with hydroponic plant growing was applied, to allow consistent plant exposure to Hg species, thus avoiding