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Review

Trace elements in Mediterranean seagrasses: Accumulation, tolerance and biomonitoring. A review

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ABSTRACT

This study investigated the state of the art on trace elements in Mediterranean seagrasses, and their close environment (seawater and sediment). The analyzed species were *Posidonia oceanica*, *Cymodocea nodosa*, *Halophila stipulacea*, *Zostera marina* and *Zostera noltei*. All these species showed high tolerance to pollution and high capacity of accumulation of trace elements. Seagrasses also showed similar patterns of accumulation: the highest concentrations of As, Hg and Pb were found in the roots, whereas those of Cd, Cr, Cu, Mn, Ni and Zn were found in the leaves. Phytotoxic levels in seagrasses are unknown for most trace elements. The accumulation of trace elements in seagrasses is widely recognized as a risk to the whole food web, but the real magnitude of this risk is still uncertain. Seagrasses are known to act as trace element bioindicators, but this potential is still poorly valued for the creation of biomonitoring networks.

1. Introduction

Seagrasses are distributed worldwide and include as many as 60 different species, living in sandy and muddy coastal areas, from 0 to 100 m of depth, in all seas, except the Antarctic Ocean (Hemminga and Duarte, 2000). Seagrass ecosystems form complex food webs by supporting grazing and detrital food, and by providing habitats for many species of flora and fauna (Jackson et al., 2001; Bostrom et al., 2006). Moreover, seagrasses play an important role in global carbon and nutrient cycling, and provide many other ecosystem services such as sediment stabilization, coastal erosion prevention, and support for fish and invertebrate communities for human consumption (Costanza et al., 1997; Bortone, 2000; Cullen-Unsworth and Unsworth, 2013; Mtwana Nordlund et al., 2016). Like corals, seagrasses are facing a deep crisis and are declining worldwide due to several factors; the most relevant include wastewaters, dredging, nutrient enrichment, contaminated sediments, habitat destruction, invasive species, macroalgae blooms and overfishing (Short and Wylie-Echeverria, 1996; Orth et al., 2006; Lewis and Devereux, 2009; Han and Liu, 2014). In particular, trace elements are increasingly entering marine ecosystems, both from natural and anthropogenic sources (Halpern et al., 2008; Serrano et al., 2011). Trace elements play a critical role in marine ecosystem functioning: whereas some are non-essential and toxic to organisms (As, Cd, Cr, Hg, Pb), others act as fundamental micronutrients (Cu, Mn, Zn), provided that their concentrations do not exceed the toxicity threshold values

(Sunda, 1989; Stevenson and Cole, 1999). Trace elements may pose a serious risk to seagrass ecosystems because unlike organic pollutants, they are persistent in the environment and, once accumulated in the rhizosphere, they become more bioavailable to rooted plants. Bioaccumulation can result from trace elements transport in the rhizosphere and absorption onto soil organisms or passage through plants' plasmalemma at the root:soil interface (Robinson et al., 2005). Once concentrated in plant tissues, they begin to move up the food web, biomagnifying at higher trophic levels (Rainbow, 2007; Roberts et al., 2008).

This work aimed to review the state of the art regarding the accumulation capacity, the tolerance level, and the bioindication potential of trace elements in all five Mediterranean marine vascular plants: *Posidonia oceanica*, *Cymodocea nodosa*, *Halophila stipulacea*, *Zostera marina* and *Zostera noltei*. Trace element patterns in Mediterranean seagrasses have been thoroughly investigated in the last three decades (Warnau et al., 1995; Tranchina et al., 2005; Stanković et al., 2015), but most of these studies focused on the fate and effects of trace elements on a single species, and exceptionally on two (Catsiki and Panayotidis, 1993). Although various reviews of trace elements accumulated in seagrasses have been published (e.g. Lewis and Devereux, 2009), to our knowledge, this is the first review entirely focused on trace elements in Mediterranean seagrasses. This study aimed also to investigate whether phytotoxic thresholds in Mediterranean seagrasses have been identified for each trace element. Moreover, we discuss the magnitude of the

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Table 1
Trace elements in marine waters associated with the studied seagrasses. Concentrations [ppb] are expressed as range or mean values.

Seagrass	Locations	As	Cd	Cr	Cu	Hg	Mn	Ni	Pb	Zn	References
<i>P. oceanica</i>	Favignana Island (Italy)	-	0.20-0.37	0.12-0.32	1.15-3.11	-	-	-	1.61-3.00	3.92-10.0	Campanella et al. (2001)
	Ustica Island (Italy)	-	0.14-0.29	0.11-0.27	0.82-1.48	-	-	-	0.81-1.14	9.03-19.3	Conti et al. (2007)
	Tuscany, Sardinia, Corse (Italy, France)	-	6.00-16.0	152-616	-	-	-	197-1380	38.0-75.0	-	Lafabrie et al. (2007)
	Linosa Island (Italy)	-	0.33 ± 0.03	0.16 ± 0.02	2.34 ± 0.26	-	-	-	0.97 ± 0.15	13.0 ± 1.00	Conti et al. (2010)
<i>C. nodosa</i>	Sicily (Italy)	< 0.10-3.52	< 0.10-0.55	2.15-9.89	33.7-123	-	-	7.60-33.6	< 0.20-0.35	7.63-25.6	Bonanno and Di Martino (2017)
	Antikyra Gulf (Greece)	-	1.50	-	42.0	-	-	-	7.80	51.0	Malea and Haritonidis (1995)
	Aegean Sea (Greece)	-	0.16-0.47	19.3-58.7	1.92-4.15	-	0.10-0.29	2.85-6.50	0.90-1.50	0.09-1.40	Malea and Haritonidis (1999)
	Thessaloniki Gulf (Greece)	0.81-3.05	-	0.37-6.41	-	-	-	1.46-7.42	-	-	Malea and Kevrekidis (2013)
	Sicily (Italy)	1.25-3.10	0.74-0.90	4.74-6.85	63.5-87.4	-	-	12.6-19.0	0.64-0.80	9.65-15.2	Bonanno and Di Martino (2016)

effects on the food web associated with high levels of trace elements in seagrasses, and the current use of seagrasses for biomonitoring trace element pollution.

2. Materials and methods

2.1. Biology and ecology of Mediterranean seagrasses

Posidonia oceanica (L.) Delile, endemic to the Mediterranean Sea, forms dense mono-specific communities (meadows), with a bathymetric range of 0–40 m depth, along coastal areas of which it covers a total surface of c. 35,000 km², amounting to 1.5% of the Mediterranean waters (IUCN, 2016). *P. oceanica* meadows play a fundamental role in the ecology of Mediterranean ecosystems, not only because they are one of the main contributors to coastal primary production, but also because they provide spawning areas, nurseries, and permanent habitats for numerous plant and animal species, thus contributing to the creation of complex food webs (Hemminga and Duarte, 2000; Larkum et al., 2006; Vassallo et al., 2013). *Cymodocea nodosa* (Ucria) Ascherson, a coastal phanerogam of tropical origin, is restricted to the Mediterranean Sea and to some locations in the North Atlantic Ocean, from southern Portugal and Spain to Senegal, including the Canary Islands and Madeira (Green and Short, 2003). Similarly to *P. oceanica*, *C. nodosa* forms mono-specific meadows, or sometimes mixed with *Zostera noltei* Hornemann (Mazzella et al., 1993), in up to 40 m-deep waters, and can act as a pioneer species able to colonize bare sandy coastal areas (Borum and Greve, 2004). *Halophila stipulacea* (Forssk.) Ascherson is a seagrass native to the Indian Ocean that spread across the Mediterranean Sea after the opening of the Suez Canal (IUCN, 2010a). It forms dense populations, and prefers shallow coastal waters. Despite its invasive nature, *H. stipulacea* does not seem to pose significant risks to *P. oceanica* and *C. nodosa* meadows (Gambi et al., 2009). *Zostera marina* Linnaeus is a cosmopolitan seagrass, mainly distributed in the northern areas of the Atlantic and Pacific Oceans, with few relict populations in some locations of the Mediterranean Sea, such as the northern Adriatic Sea, the Aegean Sea, and some areas along the French and Spanish coasts (IUCN, 2010b). In turn, *Z. noltei* is less distributed worldwide, and can be mainly found off NW Africa, Atlantic and Baltic Europe (e.g. Portugal, Spain, Netherlands, Sweden), and in the Mediterranean Sea (IUCN, 2010c). Similarly to the other seagrasses, both *Zostera* species form mono-specific populations, but prefer shallow waters, down to 5–10 m of depth (Larkum et al., 2006; Valle et al., 2014).

2.2. Analysis of literature databases

We analyzed peer-reviewed articles from the 1990–2016 period using the Scopus and ISI Web of Science scientific databases. We excluded gray literature data (e.g. congress proceedings, local reports). The study areas of all consulted articles were restricted to Mediterranean locations. In our research, we selected the following keywords, appropriately combined: *Posidonia oceanica*, *Cymodocea nodosa*, *Halophila stipulacea*, *Zostera marina*, *Zostera noltei*, Mediterranean seagrasses, marine phanerogams, marine vascular plants, trace elements, heavy metals, accumulation, bioindication, biomonitoring. We then tabulated the concentrations of As, Cd, Cr, Cu, Hg, Mn, Ni, Pb, Zn, detected in water (ppb), sediments and seagrass tissues (ppm). We used these data to discuss the levels of trace element concentrations present in water, sediments and seagrasses, to assess the capacity of accumulation by seagrasses, and to identify possible differences of accumulation among various seagrass species and organ types.

3. Trace elements in coastal waters and seagrass rhizosphere

Previous studies showed that concentrations of trace elements in surface waters over seagrass ecosystems are generally more available than those of other chemicals. Our analysis found, in particular, that out

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