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Global decrease in heavy metal concentrations in brown algae in the last 90 years

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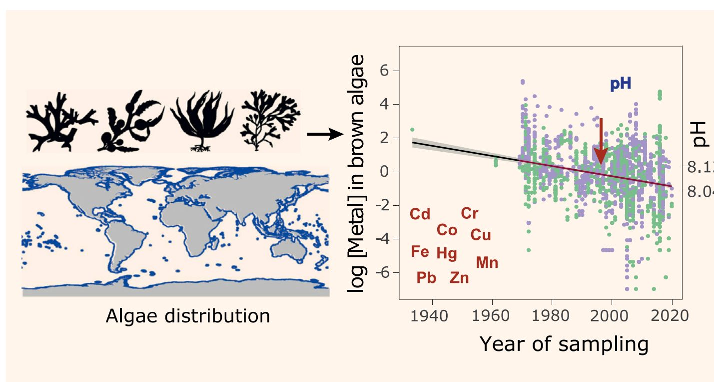
HIGHLIGHTS

- A decline in metal pollution in algae is widespread in coastal ecosystems worldwide.
- Decrease in algae concentrations may not also occur in seawater but in bioavailability.
- Decreases began from 70's coinciding with the implementation of environmental policies.
- Legislation and ocean acidification can impact on the heavy metal content in algae.

GRAPHICAL ABSTRACT



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ABSTRACT

In the current scenario of global change, heavy metal pollution is of major concern because of its associated toxic effects and the persistence of these pollutants in the environment. This study is the first to evaluate the changes in heavy metal concentrations worldwide in brown algae over the last 90 years (>15,700 data across the globe reported from 1933 to 2020). The study findings revealed significant decreases in the concentrations of Cd, Co, Cr, Cu, Fe, Hg, Mn, Pb and Zn of around 60–84% (ca. 2% annual) in brown algae tissues. The decreases were consistent across the different families considered (Dictyotaceae, Fucaceae, Laminariaceae, Sargassaceae and Others), and began between 1970 and 1990. In addition, strong relationships between these trends and pH, SST and heat content were detected. Although the observed metal declines could be partially explained by these strong correlations, or by adaptions in the algae, other evidences suggest an actual reduction in metal concentrations in oceans because of the implementation of environmental policies. In any case, this study shows a reduction in metal concentrations in brown algae over the last 50 years, which is important in itself, as brown algae form the basis of many marine food webs and are therefore potential distributors of pollutants.

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1. Introduction

Metals and metalloids have been discharged in large amounts into the marine environment as a result of human activities (e.g. agriculture, aquaculture, mining, industry, urban spills, etc.) and without adequate environmental control (Halpern et al., 2008; Islam and Tanaka, 2004; Lu et al., 2018; UNEP, 2004) since the Bronze Age (Davis Jr. et al., 2000), but especially since the industrial revolution. In addition, new sources such as 'electronic waste' have emerged (UNEP/GPA, 2006).

Chronic exposure to metals represents a real threat to marine organisms because of their high toxicity at sub-individual level and their persistence and biomagnification capacity (Tlili and Mouneyrac, 2021). Thus, the presence of high or even low concentrations for some metals (e.g. Cd, Pb and Hg) has ecological consequences for the structure and functioning of the entire ecosystem, seriously jeopardizing its integrity and undermining its ecological resilience (Halpern et al., 2008).

The potential risks associated with metallic pollution have been of particular concern for the sound management of coastal zones worldwide. States and organizations worldwide have been implementing a wide range of policies and measures for several years, trying to minimise the damage caused by metal pollution in the marine environment (Grip, 2016). However, the mitigating effects of the policies have been questioned (IPCC, 2021).

Besides metal pollution itself, other drivers of global change, interacting synergistically, can affect the bioavailability and bioaccumulation of metals by organisms, leading to a very complex scenario in the oceans. However, little attention has been paid to the impacts of these anthropogenic drivers on the oceans, and especially on the coastal environments (Duarte, 2014). The oceans are the largest reservoir in the world and have acted as sinks for around 40% of the anthropogenic CO_2 emitted in the past centuries (i.e. more than 118 ± 19 Pg), modifying the carbon dioxide-carbonate equilibrium in water and leading to ocean acidification (Broecker and Clark, 2001; Caldeira and Wickett, 2003; Sabine et al., 2004). Thus, ocean time-series observations indicate changes in the CO_2 system and the decrease in pH over years (Bates et al., 2014), and further acidification is expected in the coming years (Guinotte and Fabry, 2008; IPCC, 2021; Miller et al., 2009). Strong evidence indicates that ocean acidification increases the solubility and mobility of metals and affects their speciation in seawater (Gledhill et al., 2015; Hoffmann et al., 2012; Millero et al., 2009). However, acidification is not the only driver of global change that interacts with these pollutants: increasing water temperature, salinity and organic matter complexation can also modify the accumulation of metals by marine organisms. Based on the available data and the simulation scenario, it has been established that all of these drivers potentially contribute to increasing stress, making organisms more sensitive to even small perturbations caused by chemical stressors (Tlili and Mouneyrac, 2021).

Macroalgae are the dominant species in coastal areas worldwide and maintain the structure and integrity of these ecosystems (Smith et al., 2021). As primary producers at the base of the food webs, macroalgae are responsible for important ecosystem services such as habitat, food and shelter for a diverse community of associated organisms (Tait and Schiel, 2011; Taylor and Cole, 1994). However, macroalgae are negatively affected by metal pollution (Alestra and Schiel, 2015; Miao et al., 2013) and they can also potentially transfer contaminants to organisms that consume them, through biomagnification in marine food webs (Lee and Wang, 2001). Particularly, brown macroalgae (class Phaeophyceae) have been widely used in research studies to monitor metal pollution (e.g. Bonanno and Orlando-Bonaca, 2018; García-Seoane et al., 2018), because their high sorption capacity (Davis et al., 2003) and their ability to integrate high levels of pollutants from the environment (Phillips, 1990; Rainbow, 1995).

Globally, the Northeast Pacific is the area with the highest regional species richness of brown macroalgae of the order Laminariales, Tilopteridales and Desmanrestiales with hotspots of diversity also in the Western Pacific, the Atlantic regions from Greenland to Terranova, and along the Atlantic coast of Europe (Fragkopoulou et al., 2022). While for the order Fucales, the South Pacific is the richest area with hotspots in the Indian Ocean, in the northwest and southeast Pacific, in the North Atlantic, the southeast Mediterranean and the Black Sea. In contrast, higher latitudes such as the Arctic or the Baltic Sea, are areas with low species richness in general. Nonetheless, a study by Barrientos et al. (2020) in the Atlantic Ocean (northwest of the Iberian Peninsula) shows a decline in the number of intertidal red and brown seaweed species since 2014. Although these authors suggest that new data should be collected in the future to confirm this decreasing trend, they believe that water warming due to climate change may be affecting the distribution of seaweed at a regional scale. This conclusion was also reached by Piñeiro-Corbeira et al. (2018) who, through laboratory experiments with different macroalgae, found that water temperature is a driver of changes in abundance. Moreover, the increasing water temperature is also modifying the distribution of macroalgae, mainly in cooler-temperate waters (Kersting, 2016). Despite their worldwide distribution and ecological importance, unfortunately, few studies have reported temporal trends in metal concentrations in brown algae and have generally measured only short-term, regionally circumscribed series. Nonetheless, some authors have observed a surprising decrease in metal concentrations in brown macroalgae, under these limitations (4–7 years in a small region of the North Atlantic Ocean coast), since the beginning of the 21st century (García-Seoane et al., 2021; Viana et al., 2010).

The objective of this study was to determine whether the decrease in metal concentrations in brown algae is restricted to the aforementioned small region during the past two decades or whether it has occurred in other areas of the world at different times. Here, we present the most extensive assessment of metal concentrations in brown macroalgae sampled across the globe carried out to date (>15,700 data – sampling sites/years – from the period 1933–2020), to be used as a proxy for global long-term changes in marine metal pollution. This consistent database enables the reconstruction of detailed long-term trends (multidecadal time series) in Cd, Co, Cr, Cu, Fe, Hg, Mn, Pb and Zn concentrations in algae from observational records. Due to the scarcity of studies on the temporal trends in metal contamination in coastal ecosystems on a global scale (Lu et al., 2018), we report an important basis for global assessment of the effectiveness of environmental measures to reduce marine metal pollution. The study findings will serve to promote new governmental initiatives and environmental goals.

2. Material and methods

2.1. Literature search

Articles published worldwide concerning the metal contents of marine brown algae species (Class Phaeophyceae, Phylum Ochrophyta) were initially selected using the "Documents search" tool in the Elsevier abstract and citation database of peer-reviewed articles from scientific journals (SCOPUS; https://www.scopus.com/). Search syntax yielded articles published in English in the last 68 years (1952–2020) that met some of the following criteria in "article title, abstract and/or keywords": i) containing at least one element and/or its chemical symbol (*cadmium, chromium, cobalt, copper, iron, lead, manganese, mercury, zinc*); and ii) including some terms related to the nature of the elements (*metal, heavy metal*), to pollution monitoring (*bioaccumulation*, *accumulation, biomonitoring, monitoring, pollution, contamination*), and to algae (*algae, brown algae, macroalgae, macroalgal*, *seaweed*). The search result (9006 articles) was manually screened by reading the titles and abstracts, and 161 articles were finally selected. Additional publications were searched in the Google Scholar database (http://www.scholar.google.com/) by using the keywords "*metal, monitoring, pollution, brown algae*". Finally, reference lists of the selected articles were also checked. After discarding several studies that did not meet the desired criteria, e.g. they did not report the concentrations of the elements or the exact location of the sampling sites (either indicating the coordinates, place names or locations on a map or in the text), a total of 368 articles were finally accessed through the search platform, library exchange or by requests to the authors, and included in the database. Data published in annual reports, thesis and others were not considered.

2.2. Data collection

The information of interest for building the database, including "Year of sampling", "Species", "Locations (geographical coordinates)", "Element concentrations" and "Anthropogenic pressure of the sampling stations", was recorded in a data set, which is accessible in a Supplementary file. Some guidelines, described below, were considered for screening the information included in the articles.

2.2.1. Year of sampling

Most of the studies indicated the year when the samples were collected, but when omitted, the year of publication of the article was recorded. In some studies, several sampling surveys were carried out over the years but only a single mean value of the concentrations was reported. In this case, if the same sampling frequency was used over the years (i.e. sampling the same number of days/months in each year), a year in the middle of the time series was taken as the reference year (the latter in two-year sampling campaigns). In the same situation, but with a different sampling frequency, the year most frequently sampled was selected. In the studies with independent monthly values, the annual mean value was recorded.

2.2.2. Species

Scientific names of the species reported in the studies were checked against the taxonomic information included in the global algal database AlgaeBase (AlgaeBase, 2021; http://www.algaebase.org/), and the taxonomically accepted names were recorded. Information about scientific names of the species used in the literature consulted and scientific names currently accepted taxonomically is given in detail in a Supplementary file.

2.2.3. Geographical location

Most of the studies detailed the exact location of the sampling sites, either indicating the coordinates, the name of the sites or including a map. The geographical information programme Google Earth Pro (7.3.2 version) was used to map the points. The coordinate system used was Geographical Coordinates WGS84 (World Geodetic System 84). When sampling locations were indicated by the names of the locations (neither coordinates nor a map were shown), toponyms were searched in Google Earth Pro. When the studies provided sampling locations on land, the closest intertidal zone where brown algae could be found was recorded. When several locations were sampled in the same area but only a single mean concentration was given for all of them, the assigned location corresponded to a mean value of all the point coordinates. If the midpoint was located on land, the closest intertidal location was chosen. Exceptionally, in two of the articles reviewed (Carral et al., 1995; Viana et al., 2010), regional studies covering more than 100 sampling points were carried out in each case, but only regional global results were reported. Information on sampling points was therefore requested directly from the authors.

2.2.4. Element concentrations

In order to enable comparability between data within and between sampling sites, the basis on which the elemental concentrations are expressed must be stated. The choice of the basis was intended to satisfy several considerations: scientific validity, uniformity in groups of contaminants and minimum loss of data. As most of the studies expressed the elemental concentrations in μg g^{-1}, this unit was chosen to present the results in the database. In some cases (e.g. those using nmol g^{-1}), the original data were converted to the reference unit when possible. Only those concentrations expressed on a dry weight basis (DW) were considered. Data was extracted from figures using the WebPlotDigitizer web tool (Version 4.3, https://automeris.io/WebPlotDigitizer/). For concentrations expressed as a range (minimum value–maximum value), the mean value was used. For concentrations indicated as being below the limit of quantification of the analytical technique used (LOQ), the value given was replaced by 0.5 LOQ (Real et al., 2011). When concentrations for the same element were obtained by different analytical methods, a single mean value was recorded. In studies reporting disaggregated concentration values of different sections of the algae thallus, the mean value for all sections was recorded. The bulk data analysis includes the global available data and the statistical analysis confirmed their validity.

2.2.5. Anthropogenic pressure on the sampling sites

In order to prevent erroneous conclusions regarding overall trends in algal contamination, the different sampling sites were classified as belonging to areas affected by anthropogenic pressure (a priori polluted) and areas not affected by anthropogenic pressure (presumed to be free of contamination) on the basis of statements made by the authors or the presence of obvious nearby pollution sources such as urban settlements or power plants.

2.3. Data treatment and statistical analysis

Classification of areas affected and not affected by anthropogenic pressure is subject to some subjectivity, as there are no standardized criteria available for this purpose. The Mann−Whitney−Wilcoxon test was used to assess whether the classification was meaningful by comparing the concentrations of the main hazardous metals (i.e. Cd, Co, Cr, Cu, Fe, Hg, Mn, Pb and Zn) in algae collected in areas affected by anthropogenic pressure and those in algae collected in areas not affected by anthropogenic pressure. Significant differences were obtained for most of the elements in the different families of algae (i.e. Dictyotaceae, Fucaceae, Laminariaceae, Sargassaceae and Others), and generalized additive models (GAMs) were then used to analyse the temporal evolution of the ratio between sampling areas with anthropogenic pressure and the total number of sampled areas. Association between records of algae families and the different oceans was assessed with a chi-square test. To study global trends in algal pollution, GAMs of the logarithmic concentrations of these metals in the different families over the years were also used. The difference between the highest concentration value predicted by the model (excluding the last predicted point and those initial periods of ten years with less than five records) and the value at the last predicted point divided by the former was calculated, providing percentages of variation in metal concentrations for these periods that were considered significant if the 95% confidence intervals of the two points did not overlap. In addition, these values were divided by the number of years of these periods obtaining the percentage of annual variation.

As the trend of climate change related variables can affect the metal speciation, availability and mobility, metal concentrations in brown algae predicted by GAMs over the periods studied were obtained to allow comparison of the time series of each metal with the observed trends for different hydrographic variables over the entire water column (annual values), i.e.: global surface ocean pH (1985–2020), global average sea surface temperature (SST) anomalies (1993–2020), global heat content (1970–2017), and global vertical mean salinity anomalies (PSS) (1970–2017). Hydrographic data are available online from the Copernicus Marine Environment Monitoring Service (CMEMS, https://marine.copernicus.eu/) for pH and SST anomalies, and from the National Oceanic and Atmospheric Administration, National Centers for Environmental Information (NOAA, https://marine.copernicus.eu/) for heat and PSS. Non-parametric Spearman's rank correlation coefficients (ρ) were also calculated in order to determine the relationship between elemental concentrations predicted by GAMs and hydrographic data.

Finally, a non-metric multidimensional scaling (nMDS) ordination was conducted to explore groupings between the most represented families of brown algae (Dictyotaceae, Fucaceae, Laminariaceae and Sargassaceae) based on the patterns of similarity in metal concentrations. Because of the existence of missing values for the elements included in our data set in a significant number of records, the nMDS was performed maximizing the number of data for the elements more consistently measured across these families, based on the Bray-Curtis dissimilarity matrix constructed from non-transformed metal concentrations for Cd, Cu, Fe, Pb and Zn (n = 1013 records, 5065 individual data). The significance of dissimilarity in metal concentrations between the different assemblage clusters was assessed with ANOSIM statistics. Statistical analysis was carried out using R Software, version 3.6.2 (R Development Core Team, 2008). The "mgcv" (Wood, 2017) and the "vegan" (Oksanen et al., 2020) packages were used to derive the GAMs and compute the nMDS, respectively; "ggplot2" (Wickham, 2009) package was used to plot them. The "PerformanceAnalytics" (Peterson and Carl, 2018) package was used to calculate Spearman's correlations. ArcGIS 10.8 software was used to plot the maps.

3. Results

3.1. Distribution of algae families

Association between various families of brown algae and different oceans is shown in Fig. 1. The Dictyotaceae family is significantly linked to the Indian Ocean, the Mediterranean Sea and the South Atlantic Ocean (Fig. 1A), whereas the Fucaceae family is significantly linked to the North Atlantic Ocean (Fig. 1B); Laminariaceae family is significantly linked to the Pacific Ocean and the Antarctic Ocean (Fig. 1C) and the Sargassaceae family to the Indian Ocean, the Mediterranean Sea and the North Pacific Ocean (Fig. 1D). The other families are mainly associated with the Pacific Ocean, the Antarctic Ocean and the Arctic Ocean (Others in Fig. 1E). The previous associations will be considered in the following analysis, and the trends identified for the different families will be restricted to the afore-mentioned oceans.

3.2. Global trends in metal concentrations

The obtained GAMs for concentrations over time for the different metals and algae families are shown in Figs. 2–5 and Figs. S1–S5. In general, despite some oscillations over time, the concentrations of all metals tended to decrease, although these declines were not always linear or significant in all families. Thus, considering all the families together, significant decreases in concentrations of Pb (84%), Zn (79%), Cd (77%) and Cu (72%) have occurred since the 1970 s (Figs. 2-4, Fig. S2, Table S1), while decreases in concentrations of Mn (75%) and Hg (65%) occurred since the 1980 s (Figs. S1 and S4; Table S1), and in those of Cr (66%), Fe (64%) and Co (60%) since the 1990 s (Fig. 5; Figs. S3 and S5, Table S1). This represents an annual global decrease between 1.4% (in Cu) and 2.6% (in Fe). The order obtained by ranking the metals according to the overall percentage decrease did not correspond to the order based on the annual rates of decrease, as the lag in the period of decrease differs for the various elements considered.

The ratio between sampled areas affected by anthropogenic activities and the total area sampled was very variable and was not consistent with the decrease in metal concentrations (Fig. S6).

3.3. Climate change drivers related to global metal trends

Spearman's rank correlation coefficients between metal concentrations in brown algae predicted by GAMs and pH, SST, heat content and salinity are shown in Table 1 and Fig. 6. A strong significant positive correlation was observed between all elements and pH since 1985. Fig. 6A shows that after normalising the metal concentration values predicted by the GAMs and pH values, when plotted against time, the resulting shape for pH is extremely similar to that of Cd, Co, Cu, Mn and Pb (ρ ca. 1.00), while the trend for Fe and Cr is slightly concave (with lower ρ values, 0.91 and 0.94, respectively), and that of Zn and Hg is convex (with the lowest ρ values, 0.77 and 0.83, respectively) with respect to pH. In turn, since 1993, significant negative correlations were observed with SST, with most metals clearly following the same decreasing trend (ρ between −0.91 and −0.94), although without reacting to small variations of SST over time. However, correlation adjustment for Zn and Hg (ρ = −0.49 and −0.62, respectively) is again weaker because of the convex trend (Table 1, Fig. 6B). Regarding heat content, despite increasing the time window (1970–2017), the results obtained were similar to those for SST, showing a negative relationship with a good fit for most metals (ρ between −0.90 and −0.99), weaker for Fe, Hg, Zn and Cr (ρ between −0.31 and −0.89) (Table 1, Fig. 6D). However, salinity displayed a less clear pattern over time and, thus, the relationship between salinity and metal concentrations obtained were weaker. In addition, this relationship showed variable results, with some metals being positively (i.e. Pb, Cd, and Zn, ρ between 0.33 and 0.52) and others being negatively (Fe and Cr, ρ between −0.52 and −0.40) correlated with salinity since 1970, while Cu, Hg, Co and Mn showed no significant correlation (Table 1, Fig. 6C). These results suggest that ocean acidification and increasing seawater temperatures could be decreasing the bioconcentrated metals in brown algae tissues.

3.4. Trends in metal concentrations by algae family

Considering each individual algae family separately, no consistent pattern was observed when comparing the extent of decrease in element concentrations between families (see Figs. 2–5, Figs. S1–S5, Table S1). In the Dictyotaceae family there has been a significant decrease in concentrations of all metals considered (from 75% in Cu to 88% in Fe), except for Hg; since the early 2000 s, except for Cr and Mn, for which they began in the late 1970 s–early 1980 s (annual declines between 2.0% in Mn and 5.7% in Co). The Fucaceae family has also experienced significant decreases in concentrations of the metals considered, except Mn; however, these decreases began in the 1970–1990 s, ranging from 45% (Fe) to 91% (Co) (annual decreases ranging from 1.3% in Zn to 3.6% in Cr). In the Laminariaceae family, significant decreases were observed in concentrations of Fe, Zn, Cu and Pb, since 1947, and in Co and Cd, since the 1980 s and 2000 s, respectively. The decreases in concentrations range from 75% for Fe to 96% for Cu (with annual decreases ranging from 1.0% for Zn to 4.5% for Cd). In the Sargassaceae family, significant decreases were only observed for Fe (78%), Mn (79%) and Zn (46%) (annual decreases ranging from 1.7% for Mn to 4.6% for Fe). In the other families (Others), significant decreases were only observed in Mn concentrations (80%) (annual decrease of 1.6%).

Fig. S7 shows the result of the non-metric multidimensional scaling (nMDS) based on the concentrations of Cd, Cu, Fe, Pb and Zn found in the algae from the families Dictyotaceae, Fucaceae, Laminariaceae and Sargassaceae. Although no clear separation between clusters was observed due to the overlapping of the groups, the existence of higher concentrations of these metals in Laminariaceae, but especially in Fucaceae, could be observed. However, the ANOSIM results (Global R statistic = 0.151, $p > 0.05$) indicated that the metal composition was not significantly different among families.

4. Discussion

4.1. Global trends in metal concentrations

Long-term time series data revealed a significant global decrease (ranging from 60% to 84%) in the concentration of all metals considered since the early 1970 s, with annual rates of decline around 2%. However, these declines were not always linear and, in some cases, after an initial sharp decrease, a stabilisation or "damping" effect (Jepson et al.,

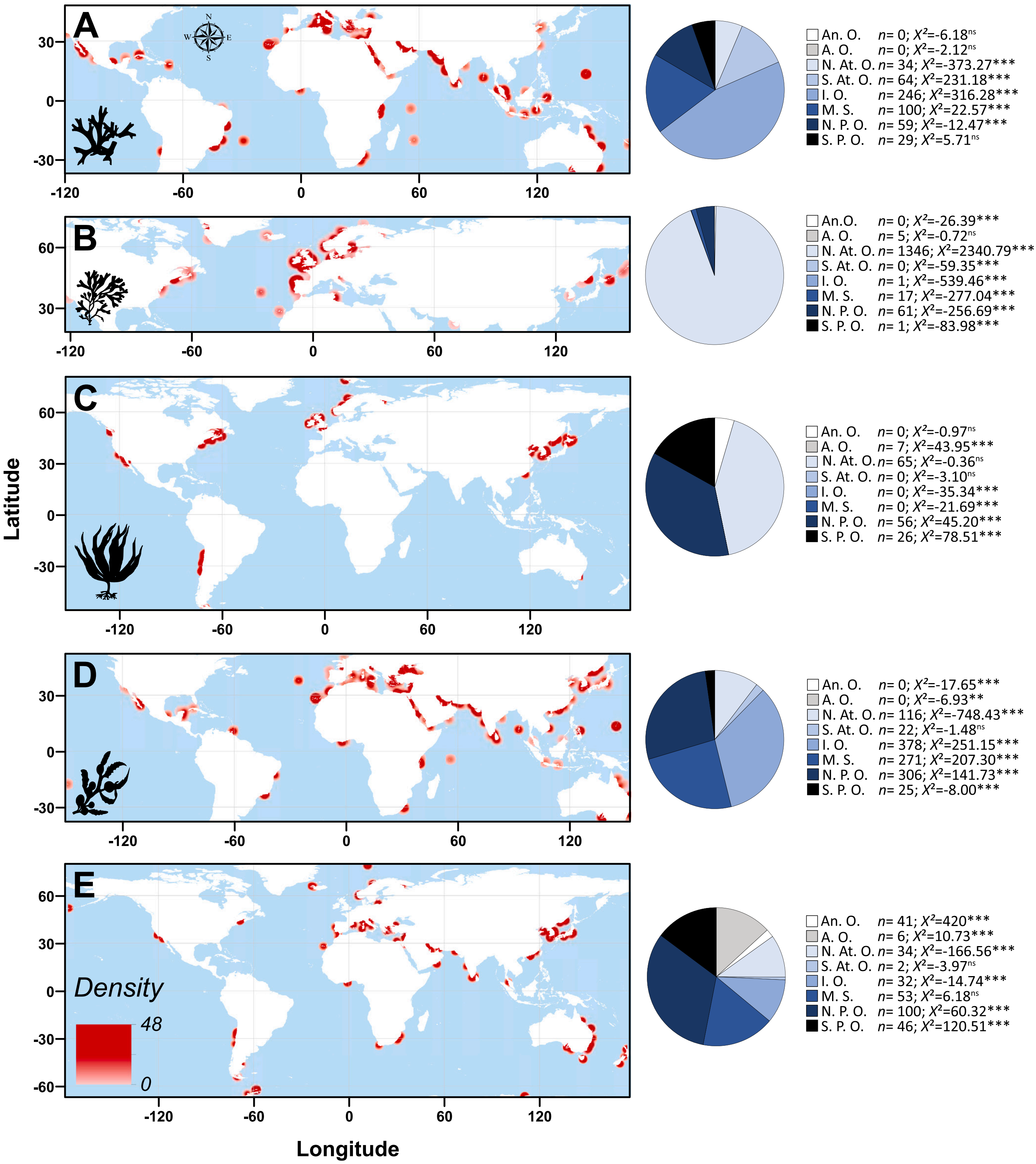

Fig. 1. Distribution of records in the seas and oceans for the different families of brown algae. Left: Kernel density maps of the sampling sites (sites / 0.01 geographic degree) where algae belonging to the following families were collected: A) Dictyotaceae (n, 532), B) Fucaceae (n, 1431), C) Laminariaceae (n, 154), D) Sargassaceae (n, 1118), and E) Others (Adenocystaceae, n = 7; Agaraceae, n = 4, Alariaceae, n = 46; Ascoseiraceae, n = 6; Bachelotiaceae, n = 2; Chordaceae, n = 15; Chordariaceae, n = 7; Cladostephaceae, n = 2; Desmarestiaceae, n = 36; Durvillaeaceae, n = 3; Ectocarpaceae, n = 8; Halosiphonaceae, n = 3; Hormosiraceae, n = 7; Ishigeaceae, n = 3; Lessoniaceae, n = 32; Neoralfsiaceae, n = 1; Phyllariaceae, n = 1; Ralfsiaceae, n = 1; Scytosiphonaceae, n = 106; Seirococcaceae, n = 2; and Stypocaulaceae, n = 19). Right: Pie charts for each family (see above), representing the number of sampling sites in each ocean/sea (An.O.: Antarctic Ocean; A.O.: Arctic Ocean; N.At.O.: North Atlantic Ocean; S.At.O.: South Atlantic Ocean; I.O.: Indian Ocean; M.S.: Mediterranean Sea; N.P.O.: North Pacific Ocean; and S.P.O.: South Pacific Ocean) and the $\chi 2$ value of the null hypothesis of an independent distribution of the families in the different oceans and their significance ($p > 0.01$: ns; $p < 0.01$: **; and $p < 0.001$: ***) obtained in each case. A negative sign before the $\chi 2$ value indicates a negative association, and no sign indicates a positive association. ns: not significant.

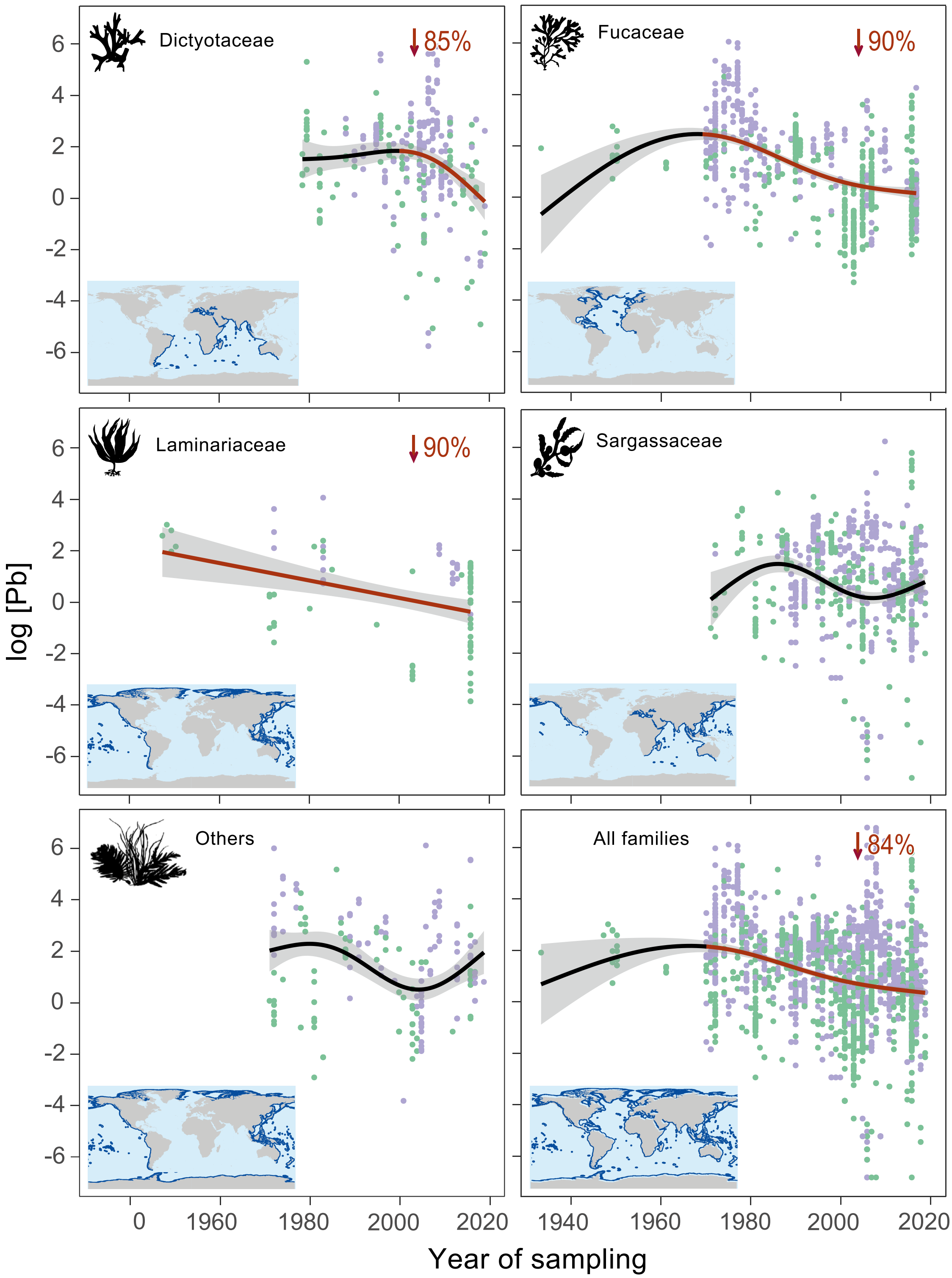

Fig. 2. Temporal changes in log Pb concentrations. Worldwide temporal changes in log Pb concentrations (μg g^{-1} DW) in samples of different families or group of families of brown algae (for Others; see Fig. 1 for more details), and those corresponding to all of the families together. The map inside each graph corresponds to the main area of distribution of each family in the compiled data set (see Fig. 1 for more details). The area coloured in dark blue on the map inside each graph corresponds to the main area of distribution of each family in the compiled data set. The solid black line represents the GAM fit, and the grey area represents the limits of the confidence intervals at 95%. Green dots indicate algae samples collected in areas without any anthropogenic pressure; purple dots indicate areas subjected to anthropogenic pressure. The red lines indicate the period of decline considered to calculate the percentage decline in concentrations, also shown in the figure with a downward arrow.

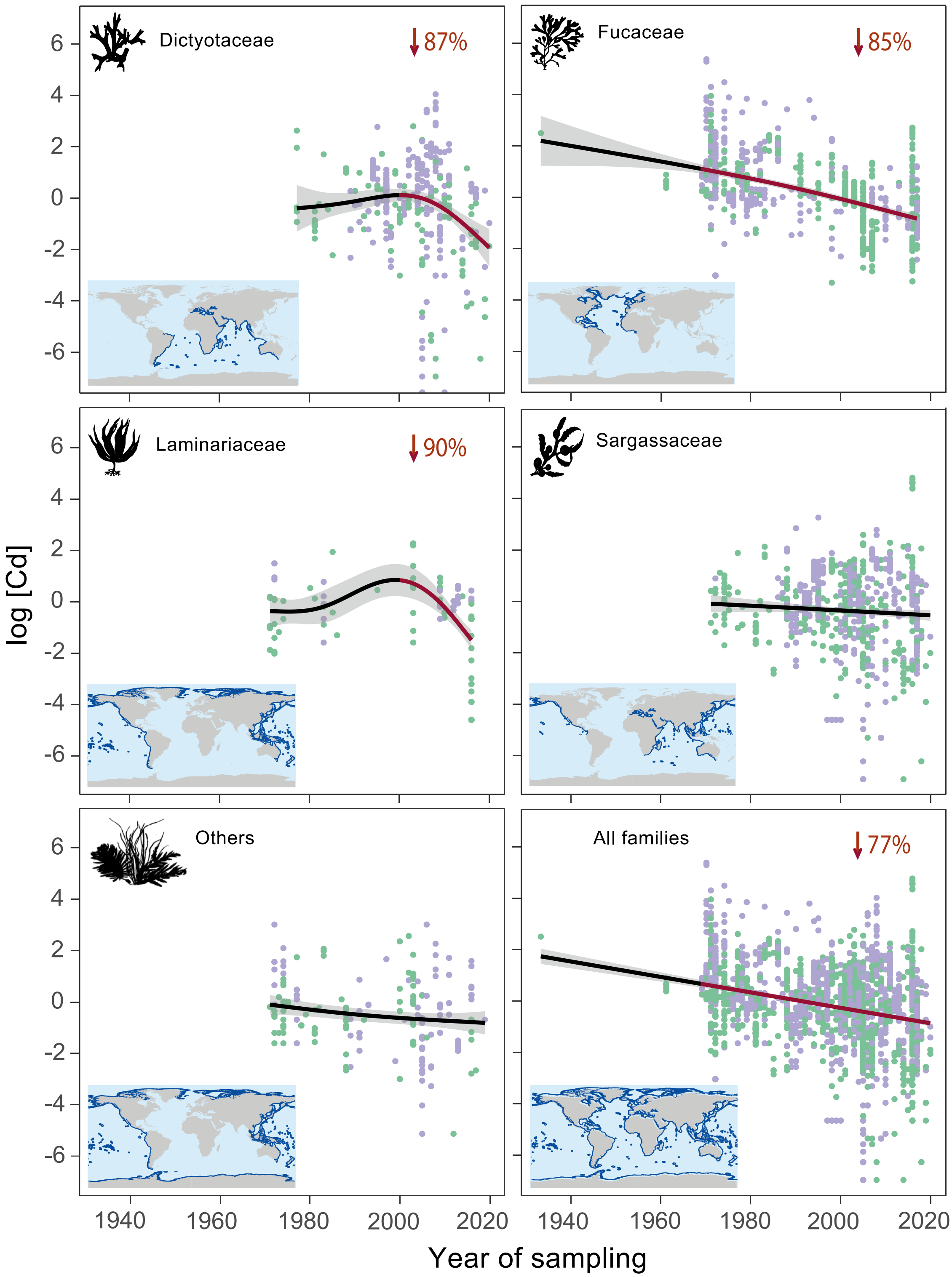

Fig. 3. Temporal changes in log Cd concentrations. Worldwide temporal changes in log Cd concentrations (μg g^{-1} DW) in samples of different families or group of families of brown algae (for Others; see Fig. 1 for more details), and those corresponding to all of the families together. The map inside each graph corresponds to the main area of distribution of each family in the compiled data set (see Fig. 1 for more details). The area coloured in dark blue on the map inside each graph corresponds to the main area of distribution of each family in the compiled data set. The solid black line represents the GAM fit, and the grey area represents the limits of the confidence intervals at 95%. Green dots indicate algae samples collected in areas without any anthropogenic pressure; purple dots indicate areas subjected to anthropogenic pressure. The red lines indicate the period of decline considered to calculate the percentage decline in concentrations, also shown in the figure with a downward arrow.

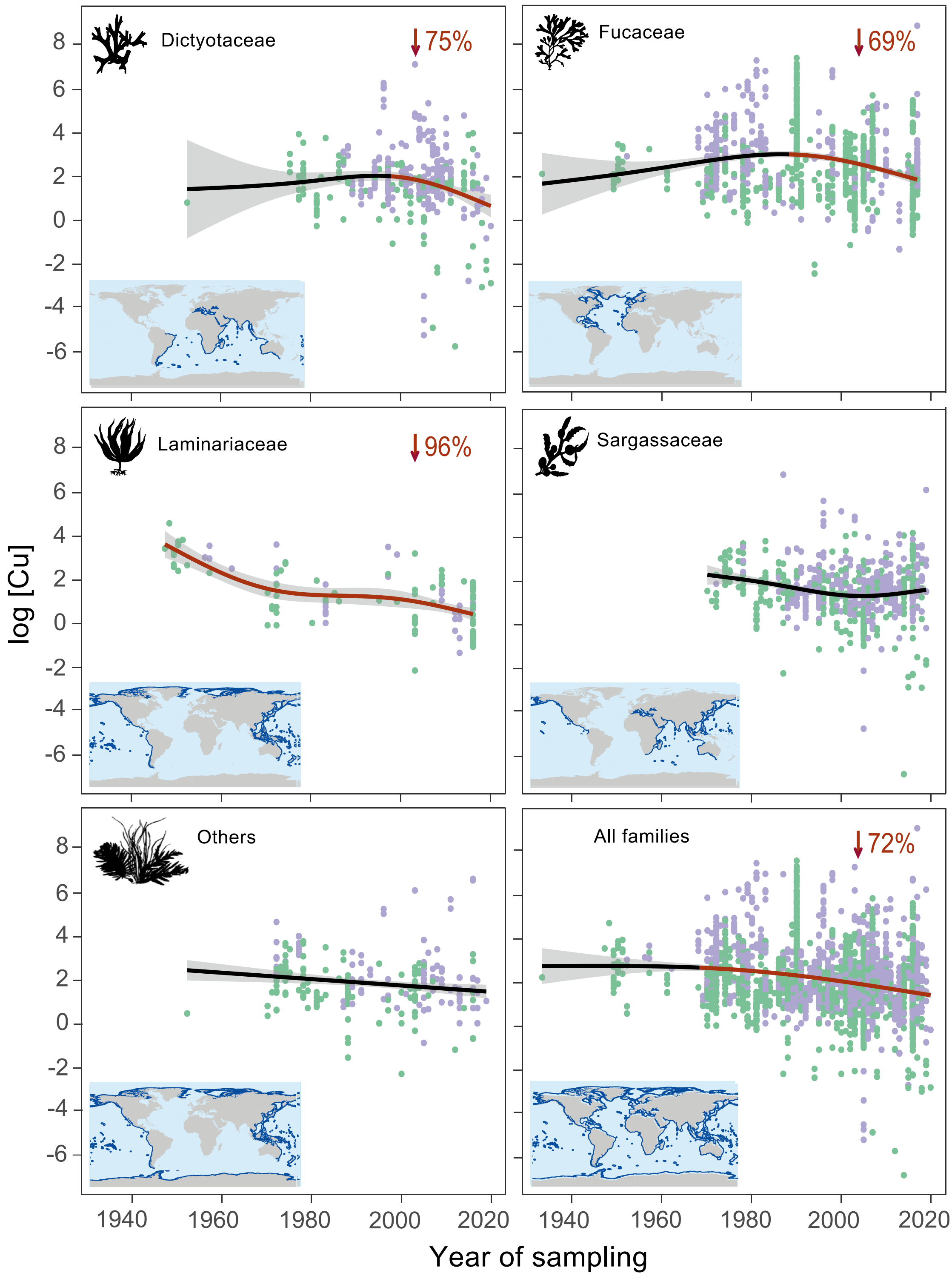

Fig. 4. Temporal changes in log Cu concentrations. Worldwide temporal changes in log Cu concentrations (μg g^{-1} DW) in samples of different families or group of families of brown algae (for Others; see Fig. 1 for more details), and those corresponding to all of the families together. The map inside each graph corresponds to the main area of distribution of each family in the compiled data set (see Fig. 1 for more details). The area coloured in dark blue on the map inside each graph corresponds to the main area of distribution of each family in the compiled data set. The solid black line represents the GAM fit, and the grey area represents the limits of the confidence intervals at 95%. Green dots indicate algae samples collected in areas without any anthropogenic pressure; purple dots indicate areas subjected to anthropogenic pressure. The red lines indicate the period of decline considered to calculate the percentage decline in concentrations, also shown in the figure with a downward arrow.

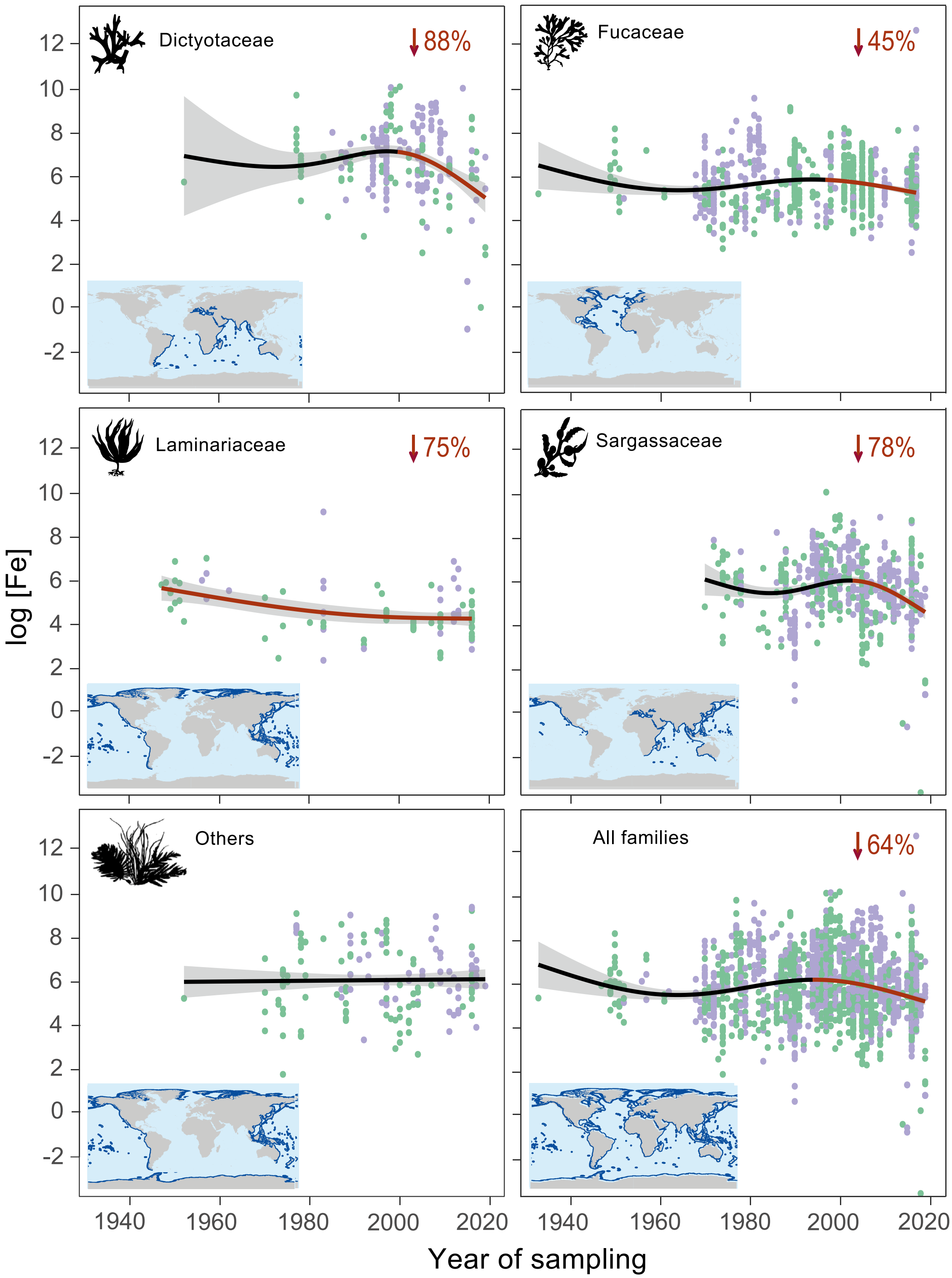

Fig. 5. Temporal changes in log Fe concentrations. Worldwide temporal changes in log Fe concentrations (μg g^{-1} DW) in samples of different families or group of families of brown algae (for Others; see Fig. 1 for more details), and those corresponding to all of the families together. The map inside each graph corresponds to the main area of distribution of each family in the compiled data set (see Fig. 1 for more details). The area coloured in dark blue on the map inside each graph corresponds to the main area of distribution of each family in the compiled data set. The solid black line represents the GAM fit, and the grey area represents the limits of the confidence intervals at 95%. Green dots indicate algae samples collected in areas without any anthropogenic pressure; purple dots indicate areas subjected to anthropogenic pressure. The red lines indicate the period of decline considered to calculate the percentage decline in concentrations, also shown in the figure with a downward arrow.

Table 1
Non-parametric Spearman's rank correlations between metal concentrations in brown algae predicted by GAMs over the periods studied and four hydrographic variables. pH: global annual surface ocean pH (yr^{-1}) relative to the period 1985–2020. SST: global annual average sea surface temperature anomalies (°C. yr^{-1}) relative to the period 1993–2020. Heat: global annual heat content (Joules) relative to the period 1970–2017. Salinity: global annual vertical mean salinity anomaly (PSS) relative to the period 1970–2017. The values of the Spearman's correlation coefficient (ρ) along with the significance level are shown: ($p < 0.001$, "***"); ($p < 0.01$, "**"); ($p < 0.05$, "*").

	Hydrographic variables			
Elements	pH	SST	Heat	Salinity
Cd	1.00 * **	-0.94 * **	-0.97 * **	0.33 * **
Co	0.99 * **	-0.94 * **	-0.90 * **	-0.02
Cr	0.94 * **	-0.94 * **	-0.53 * **	-0.40 * **
Cu	1.00 * **	-0.94 * **	-0.99 * **	0.26
Fe	0.91 * **	-0.91 * **	-0.31 *	-0.52 * **
Hg	0.83 * **	-0.62 * **	-0.89 * **	0.24
Mn	0.99 * **	-0.94 * **	-0.95 * **	0.06
Pb	0.97 * **	-0.94 * **	-0.94 * **	0.40 * **
Zn	0.77 * **	-0.49 *	-0.83 * **	0.52 * **

2016; Jepson and Law, 2016) has been identified from 1990 onwards (e.g. Hg, Zn). These variations were independent for each family, and it was not possible to identify any common pattern by ordering the elements according to the percentage decrease in concentration. This lack of a common pattern may be attributed to the narrow ranges of variability in the concentrations observed (e.g. in Dyctiotaceae, the decrease in the concentration of 7 elements, except for Cu and Hg, ranged between 82% and 88%).

Accordingly, other studies using brown algae showed the same trends. Kozhenkova et al. (2021) reported decreasing trends in metal concentrations in *Sargassum miyabei* and *S. pallidum* in the Sea of Japan. Likewise, significant decreases in *Fucus vesiculosus* (Fucaceae) on the NW Iberian coast, between 2001 and 2007, specifically for Al, Cd, Co, Fe, Hg, Ni and Zn (annual decrease from 5% to 10%) were detected (Viana et al., 2010); and even greater annual decreases (between 10% and 20%) were observed for Co, Fe, Hg, Ni and Zn between 2015 and 2019 (García-Seoane et al., 2021). Thus, the findings of the present study are consistent with these previous observations, despite the different nature of the approaches compared, i.e. large spatial-temporal scale with low resolution and non-standardized methodologies (present study) versus small spatial-temporal scale with high resolution using standard methods

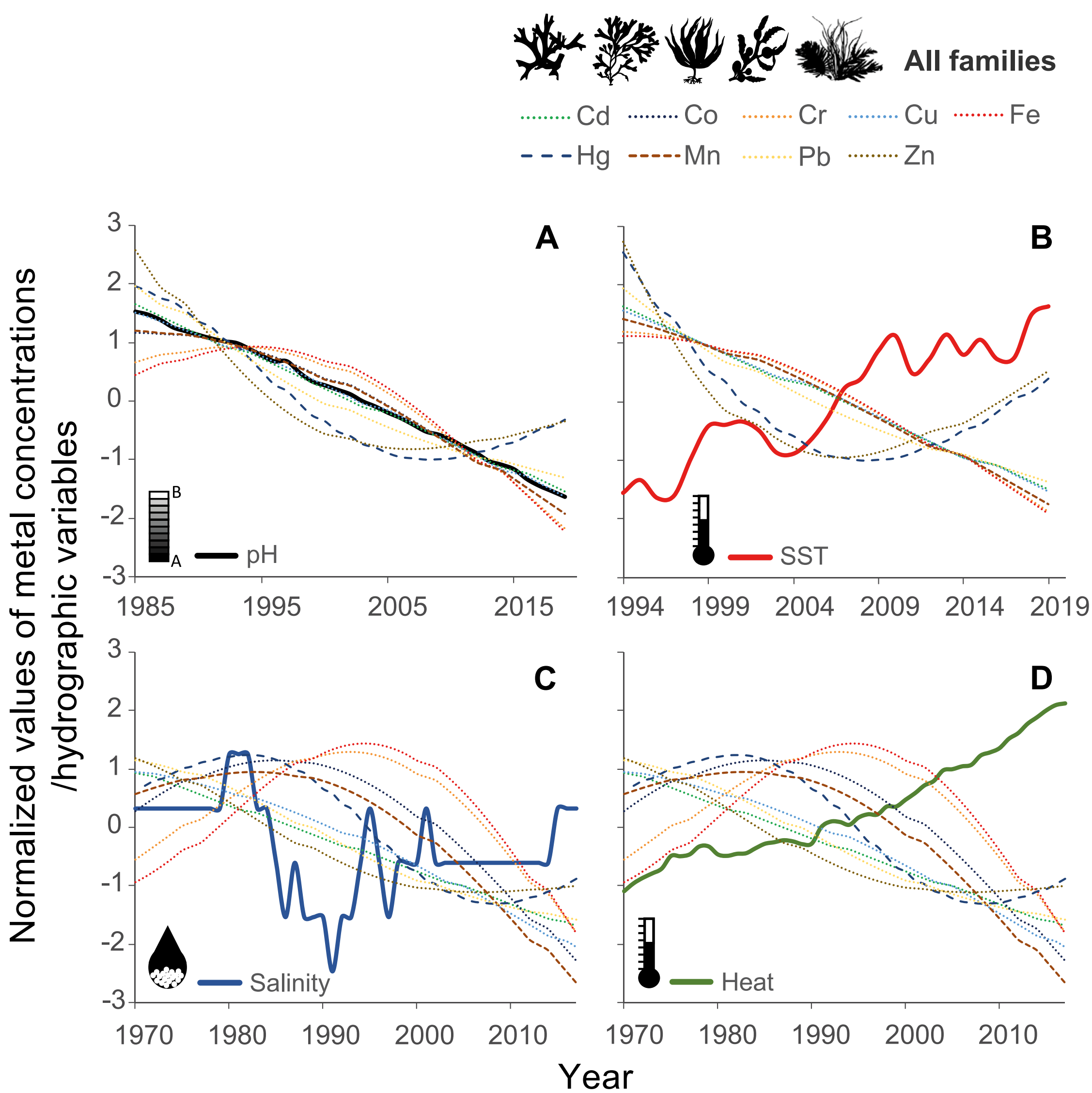

Fig. 6. Metal concentration values obtained in the GAM adjustments and subsequently normalised, and water variable data according to the periods of years available for these variables: A) pH: annual global surface ocean pH (yr^{-1}) from 1985 to 2020; B) SST: global annual average sea surface temperature anomalies (°C yr^{-1}) from 1993 to 2020; C) Salinity: annual global vertical mean salinity anomaly from 1970 to 2017; D) Heat: global annual heat content (Joules) from 1970 to 2017.

(regional studies).

However, in other organisms and in abiotic components of the oceans the results obtained were not homogeneous. Thus, significant decreasing trends in metal concentrations have been detected in bivalves and fish in the European Economic Area (EEA, 2003), in offshore sediments in the Cantabrian Sea (Garmendia et al., 2019), the China Sea (Yang et al., 2021), the North Sea (except for Zn, Le et al., 2021), and in coastal waters of South Africa (Wepener and Degger, 2012). In contrast, Dong et al. (2021) found that, globally, the levels of metals in sediments have not changed significantly over time, and those of Cd and Hg have even increased. Increases in metal concentrations have also been reported in mussel tissues in the North Sea (Mubiana, 2005), in marine sediments of the Aegean Sea (Sert, 2018) and in coral reefs in the China Sea and the Persian Gulf (Chen et al., 2010; Jafarabadi et al., 2017; Song et al., 2014). Finally, other studies found different direction trends depending on the metals and locations studied, as in the case of offshore sediments in the Persian Gulf (Nicolaus et al., 2022) or the franciscana dolphins in South America (Garcia-Garin, 2021). Although these results differ from those obtained in the present study, the different environmental compartments studied (i.e. sediment, animals, etc.) and the reduced spatial scale of most of them make these results compatible with the global downward trend and the high variability observed in our study.

4.2. *Trends in metal concentrations by algae family and region*

Regarding the different algae families, the detailed evaluation of the trends revealed some differences between groups, with the highest annual rates of decrease reached in the Dyctiotaceae family (from over 3–6%), almost doubling the rates in other families for elements such as Co, Cu, Pb and Zn. These differences may be explained by different reasons; firstly, the different bioconcentration capacity among species and/or genera. For example, the genus *Padina* (which accounts for >70% of our database records for the family Dyctiotaceae), includes some of the species with the highest capacity to concentrate metals (Jalali et al., 2002; Sheng et al., 2005) and may be somewhat more sensitive to major changes in environmental metals than other brown species. However, the nMDS performed in this study testing the different uptake capacities of the families considered (see Supplementary Fig. 7) was not significant. Secondly, since the families considered are restricted to certain oceans and seas, the different decreasing trends between families may reflect different changes in metal concentrations in the marine environment depending on where they are located.

4.3. *Underlying causes of the observed trends*

Previous sections showed a decrease in metal concentrations in brown algae consistent with findings in the existing literature. This decline can be explained by different causes such as a decrease in the ions bioavailability, adaptive mechanisms of the algae that diminish their ability to bioconcentrate metals, or a global reduction in metal concentrations in oceans.

4.3.1. *Climate change drivers*

Climate change invokes the increase of surface seawater temperature, salinity, heat content and ocean acidification, which rules the metals speciation and mobility. In this sense, strong significant correlations between pH and metals considered were found in this study (Fig. 6A, Table 1). Decreasing pH causes changes in the hydrogen, carbonate, and hydroxide ion concentrations in seawater, which affects: i) the adsorption of the ions by the protonation of chemical active sites of the algae cell walls, decreasing the number of available sites for the metals (González and Pokrovsky, 2014; Yee and Fein, 2001), and could explain the relationship between pH and the adsorption and uptake of metals found in brown algae (Haug, 1961; Lu et al., 2009); ii) the speciation of metals in solution (González-Dávila et al., 1995; González and Pokrovsky, 2014; Gledhill et al., 2015; Miller et al., 2014; Millero et al., 2009; Stockdale et al., 2016), increasing the free, bioavailable species of metals whose speciation is related to the above-mentioned ions; iii) complexation with organic matter as previously exposed in i) (Calace and Petronio, 2004; Cheng et al., 2020); iv) the sediment-water exchange of metals mainly reducing the metal sorption of metals to sediments (López et al., 2010); and v) the organism's metabolism and functioning that may modify the uptake of metals (e.g. changes in membrane permeability), although to our knowledge these changes are not properly studied in brown algae (Roleda and Hurd, 2012). While the first pH effect would reduce the levels of metals in the algae, the second, the third and the fourth would increase them, and the fifth is difficult to predict. Hence, the final effect of ocean acidification in metal concentrations in brown algae over time remains uncertain and will depend on the algae species and the metals considered, the pollution source and the geological composition of the sediments. Therefore, although the results suggest a strong relationship between pH and algae metal concentrations (Table 1, Fig. 6A), there is not enough information to state which fraction of the obtained decrease in metal concentration can be attributed to the observed decrease in pH (which in fact was limited, ca. 0.002 units.yr^{-1}, during the studied period). Other variables showing collinearity with pH, not considered here, could be also responsible for the decrease in metal concentrations in the algae.

Likewise, SST anomalies and heat content resulted significantly correlated with metal concentrations trends (Table 1, Figs. 6B and 6D). Temperature affects metal-algae interactions by changes in their metabolism and in the bioavailability of metals. Thus, increasing temperatures impact the particle residence in the euphotic zone and the redox chemistry of metals by implication of photooxidation (Breitbarth et al., 2010). However, robust studies and predictions are not yet available on this regard (Hoffmann et al., 2012).

Finally, vertical mean salinity anomalies displayed different correlations with algae metal concentrations, some of them being not significant (Table 1, Fig. 6C). Salinity can reduce the bioavailability of metals as they strongly bind to salts, a phenomenon known as "salting out effect" (Noyes et al., 2009). However, the salinity pattern over time was not clear and it is difficult to extract preliminary conclusions regarding this variable.

4.3.2. *Algae adaptive responses to metal pollution*

Another possible factor influencing the decreasing pattern of metal concentrations in algae could be the continued exposure to high metal concentrations in the environment. Thus, García-Seoane et al. (2020) have demonstrated that some *F. vesiculosus* populations exposed to long-term pollution show limited heavy metal uptake because of the adaptive response to metallic toxicity. This response includes the reduction of (García-Seoane et al., 2020): i) their growing speed which limits the concentration dilution by growth; ii) specific leaf area of algae causing the diminishing of the adsorption surface related to the algae mass; iii) alginate concentrations, which are the main compounds involved in algae bioconcentration capacity; and iv) the number or activity of cell membrane cation transporters. Moreover, exudation of organic compounds that complex metals decrease their concentration in brown algae (Andrade et al., 2006; Davis et al., 2003). Finally, it must be taken into account that changes in response to polluted-induced stress can operate in algae living in highly polluted sites, so it is unclear whether this fact could be important enough throughout the entire globe to explain the global decreases detected.

4.3.3. *Environmental policies affecting metal concentrations*

The observed decrease in metal concentrations in brown algae may reflect a decrease in marine metal pollution as a result of the environmental policies implemented to date. Indeed, the beginning of the decrease coincides with the first measures adopted in the Stockholm Convention (1972) (UN, 1972) and the International Convention for the Prevention of Pollution From Ships (1973) (IMO, 1973). Since then, a wide range of policies has been established, particularly since the 1990–2000 s, by the major global marine-related organizations and conventions within the United Nations system, coordinating intergovernmental responses against metal pollution, via environmental programmes and actions. Implemented measures include those taken by the UN Conference on Environment and Development (UNCED), the UN Convention on Law of the Sea (UNCLOS), the Intergovernmental Oceanographic Commission of UNESCO (IOC), the International Maritime Organization (IMO) and the United Nations Environment Programme (UNEP) (UN, 2013, 1992, 1982). Moreover, other regional marine-related organizations collaborate, especially in developed countries: the European Environment Agency (EEA), the U.S. Environmental Protection Agency (US-EPA) or the China State Environmental Protection Administration (SEPA).

Metal-specific measures implemented have been mostly developed for Cd and Pb (e.g. Battery Directive and Directive 2006/66/EC of the EU) and for Hg (e.g. Mercury Export Ban act -US EPA, 2008, EU Regulation 2017/852 and Minamata Convention on Mercury, 2013). In addition, the closure of most of the non-ferrous refining and smelting industries and coal-fired electricity generation plants together with the decrease in coal consumption and the implementation of effective waste treatment in developed countries have been produced. As a result, a 34% reduction in the release of trace metals to water from Europe's industries in the period 2010–2016 has been reported (EEA, 2018). Likewise, Canada has registered a decrease of Pb by 89% (907 t) between 1990 and 2020 and, in China, emissions of metals in waste water decreased 28% between 2016 and 2019. Moreover, the MSC-E Technical Report 1/2015 reported a total reduction of 78% in Pb, 53% in Cd and 23% in Hg between 1990 and 2012 for the EMEP region (Europe, Caucasus and Central Asia). Thus, it seems that the results obtained in this study can be explained to a large extent by the real reduction of metal pollution observed in the marine environment in developed countries. However, at the global scale, this reduction does not seem to be as clear, and there are even indications of an increase in pollution (e.g. Emissions Database for Global Atmospheric Research reported a significant global increase in Hg air emissions between 1970 and 2012). Since the vast majority of the data recorded in this study were collected in developed countries, an increase in the sampling effort in both developing and underdeveloped countries is essential.

5. Final remarks

The meta-analysis conducted showed robust decreases in metal concentrations (45–96%) for all the brown algae families considered, distributed throughout the World's oceans. Thus, the high variability obtained did not prevent the detection of consistent temporal changes. This variability is not only explained by differences in metal concentrations in the environment or by changing physico-chemical parameters such as pH, but also by the use of non-standardised methodologies within the collected studies (i.e. different algal species with varying size/age, different sampling times, different analytical techniques, lower analytical quality and lower number of samples in previous studies, etc.). The trends were quite synchronous and post-date global marine environmental protection actions, which could be the main cause of these temporal patterns, although decreasing pH and increasing SST and heat content could also explain them partially. Therefore, this study found, for the first time, a decline in the bioconcentrated metal levels of brown macroalgae for the last 40–50 years, and with it, a potential decline of metal concentrations in world's intertidal habitats. However, most of the records were located in North Atlantic Ocean, with other oceans such as the Arctic Ocean or the South Atlantic Ocean poorly represented (18 and 88 records respectively). Thus, conclusions drawn here must be applied primarily to the North Atlantic Ocean and monitoring efforts in other oceans should be increased. This data can be used as a starting point for future emission scenarios and to inform management decisions.

Competing Interest Declaration

The authors declare that they have no competing financial or non-financial interests that could have influence the work reported in this paper.

CRediT authorship contribution statement

J.R. Aboal, J.A. Fernández: Study conception and design. **J.R. Aboal, C. Pacín, R. García-Seoane, Z. Varela, J.A. Fernández**: Data mining. **J.R. Aboal, C. Pacín, R. García-Seoane**: Data analysis and figure design. **J.R. Aboal, C. Pacín, R. García-Seoane, Z. Varela, A.G. González, J.A. Fernández**: Interpretation and wrote the manuscript. All authors reviewed and approved the final version of the manuscript.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

All data are provided in a Supplementary file.

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Statement of "environmental implication"

Metallic pollution is of major concern because of the toxic effects and persistence of these pollutants in the environment. This contribution provides the first extensive meta-analysis of metal concentrations and their evolution (15,758 data compiled from 368 studies worldwide over the last century) in brown macroalgae. The findings revealed significant global decreases of Cd, Co, Cr, Cu, Fe, Hg, Mn, Pb and Zn since 1970, coinciding with the implementation of environmental policies. This information is essential to work on future legal regulations and provides some hope about the evolution of metal pollution in the oceans, severely threatened by global change.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jhazmat.2022.130511.

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