



PLANCLIMAC2

Iron distribution in the Macaronesian waters and in the coastal waters of Azores, Canary Islands, Cape Verde, Madeira and São Tomé and Príncipe

TECHNICAL REPORT

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Table of contents

Executive Summary	3
1. Introduction	6
2. Iron distribution.....	8
3. Iron speciation	10
4. Processes controlling trace metal and ligand distributions	12
5. Comparisons across regions	13
6. Knowledge gaps and future directions	14
7. Conclusion.....	15
References	15

Executive Summary

The Macaronesian archipelagos of the Azores, Madeira, the Canary Islands and Cape Verde, together with São Tomé and Príncipe in the eastern equatorial Atlantic, encompass contrasting oceanographic and biogeochemical environments. Across this region, trace-metal distributions are influenced by atmospheric deposition, ocean circulation, coastal and equatorial upwelling, volcanic and hydrothermal inputs, sediment resuspension, continental and riverine inputs, and biological recycling. These processes are particularly relevant for iron (Fe), an essential micronutrient involved in marine primary productivity and the ocean carbon cycle.

This report synthesises the current state of knowledge on trace metals across these regions, with a specific quantitative focus on dissolved iron (dFe) and its organic complexation by iron-binding ligands (L_{Fe}), for which sufficient regional information is available to examine broad spatial patterns. Published studies and observations from the GEOTRACES program are used to compare areas with contrasting iron sources and oceanographic conditions, as well as to identify key gaps in observations that are relevant to future research and environmental monitoring. Accordingly, the wider trace-metal context should be distinguished from the more detailed Fe-focused assessment presented here.

The available evidence shows pronounced regional variability in dFe. The Azores display comparatively low and relatively homogeneous surface dFe concentrations, consistent with their predominantly open-ocean setting and weaker influence from continental and Saharan dust sources. Madeira and the Canary Islands show intermediate conditions associated with the combined effects of Saharan dust deposition, island-related processes, volcanic inputs and the influence of Northwest African upwelling. Cape Verde exhibits greater variability, reflecting the interaction of strong Saharan dust inputs, proximity to the African margin, sedimentary and island-related sources, and dynamic ocean circulation.

São Tomé and Príncipe represents a substantially different equatorial setting. Available observations from the eastern equatorial Atlantic indicate potentially higher dFe concentrations and a marked coast-to-open-ocean gradient associated with continental inputs, equatorial upwelling and intense organic-matter recycling. This conclusion must, however, be interpreted cautiously: the dataset considered in this report does not provide direct dFe observations from the immediate coastal waters of São Tomé and Príncipe, and the nearest sampling location used in the comparison lies approximately 500 km south of the islands. The region therefore remains

a major geographical knowledge gap that could be attended in the frame of cooperation projects such as PLANCLIMAC2.

A second major finding concerns iron speciation. Where measurements are available, dFe is predominantly complexed by organic ligands, and ligand concentrations generally exceed dFe concentrations. This excess complexation capacity affects iron solubility, scavenging and potential bioavailability. Fe-binding ligand concentrations vary among the studied regions, whereas conditional stability constants show more limited regional variability, suggesting that comparable classes of iron-binding organic compounds may occur across contrasting environmental settings. At the same time, ligand observations remain absent or very limited in key areas, particularly the Azores and São Tomé and Príncipe.

The assessment demonstrates that the present observational basis is spatially and temporally incomplete. Seasonal variability, responses to episodic Saharan dust deposition, and the influence of coastal, riverine and mangrove environments remain insufficiently characterised. These limitations restrict the establishment of robust regional baselines against which future environmental and climate-related change can be assessed. For public authorities, the principal implication is therefore the need for a more coordinated and comparable observational framework across the territories considered by PLANCLIMAC2.

Priority actions for regional authorities and monitoring programmes.

1. Strengthen observations in poorly sampled regions, particularly São Tomé and Príncipe and the Azores, while improving coverage of coastal and island-influenced waters.
2. Increase temporal coverage through sustained observations and time-series measurements to distinguish long-term change from seasonal and episodic variability.
3. Harmonise sampling, quality-control and analytical approaches so that results can be robustly compared among territories and over time.
4. Combine dissolved Fe and Fe-binding ligand measurements with relevant physical, biogeochemical and biological indicators, and expand ligand characterisation where feasible.

Within PLANCLIMAC2, this synthesis provides a scientific baseline for identifying where current knowledge is sufficiently robust and where additional observations are most urgently required. Strengthening coordinated trace-metal monitoring across Macaronesia and São Tomé and Príncipe would improve understanding of marine biogeochemical variability and provide regional authorities with a stronger evidence base for long-term environmental assessment and climate-adaptation planning in eastern Atlantic islands and coastal ecosystems.

1. Introduction

The Macaronesian region (Azores, Madeira, the Canary Islands and Cape Verde) and the eastern tropical Atlantic (São Tomé and Príncipe), form an important transition zone between the subtropical and equatorial Atlantic Ocean. This region is characterised by strong latitudinal gradients in ocean circulation, nutrient availability, and biogeochemical processes (Arnone et al., 2022; Djakouré et al., 2017), making it particularly interesting for investigating the sources, distribution, and cycling of trace metals such as iron (Fe).

Ocean circulation plays an important role on biogeochemical conditions across this area. Along the Northwest African margin, the Canary Current and seasonally variable coastal upwelling driven by trade winds bring nutrient-rich subsurface waters into the euphotic zone and can influence trace-metal distributions, stimulating biological productivity and modifying surface trace-metal inventories (Arnone et al., 2022; Fitzsimmons et al., 2013). Mesoscale processes associated with island wakes, eddies, and frontal systems further redistribute trace metals horizontally and vertically, particularly around archipelagos such as the Canary Islands and Cape Verde (Sangrà et al., 2009). In contrast, the Gulf of Guinea, where São Tomé and Príncipe is located, is influenced by equatorial circulation, seasonal equatorial upwelling, and strong vertical mixing (Djakouré et al., 2017). This island is further characterised by riverine inputs and mangroves (Afonso et al., 2023). These processes, combined with high primary productivity and intense organic matter cycling, have an impact on the regeneration of trace metals in surface and subsurface waters (Hatta et al., 2015).

Iron is an essential micronutrient for phytoplankton and plays a central role in regulating primary productivity and the oceanic carbon cycle (Moore et al., 2001). Despite its abundance in the Earth's crust, iron occurs at very low concentrations in seawater due to its limited solubility, and it often limits or co-limits biological production in large regions of the Atlantic Ocean (Boyd and Ellwood, 2010). In seawater, up to 99% of the dissolved Fe (dFe) is complexed by organic ligands, which increase iron solubility (Rue and Bruland, 1995), reduce scavenging losses (Tagliabue et al., 2019) and control its bioavailability (Gerringa et al., 2006). Fe-binding ligands (L_{Fe}) can be classified according to their conditional stability constant $\log K^{cond}_{Fe \cdot L}$ and are generally divided into two categories based on their strength: strong ligands (L_1), with $\log K^{cond}_{Fe \cdot L} > 12$, and weak ligands (L_2), with $\log K^{cond}_{Fe \cdot L} < 12$ (Gledhill and Buck, 2012; Rue and Bruland, 1995). These ligands are linked to functional groups or organic molecules. For example, siderophores are classified as L_1 -type ligands (Rue and Bruland, 1995;

Witter et al., 2000), humic substances and polyphenols are L₂-type ligands (Hassler et al., 2025, 2011; Rico et al., 2013).

The region is exposed to multiple and contrasting Fe and L_{Fe} sources. Atmospheric dust deposition from Sahara represents a major external input of Fe and L_{Fe} to the eastern Atlantic, particularly affecting the Canary Islands and Cape Verde (Jickells et al., 2005; Rijkenberg et al., 2008). Upwelling and margin processes supply Fe and L_{Fe} from deep waters and sediments (Bundy et al., 2014; Sangrà et al., 2009), while volcanic islands contribute localised inputs, sediment resuspension, and island-mass effects (Arnone et al., 2022; Blain et al., 2001; González-Santana et al., 2024). In the equatorial Atlantic, continental and margin-derived sources further enhance Fe and L_{Fe} availability near São Tomé and Príncipe. Furthermore, the present riverine and mangrove systems can supply Fe and organic compounds to the ocean (Afonso et al., 2023; Hunter and Boyd, 2007).

While dFe distributions in the Atlantic Ocean have been increasingly documented through international programs such as GEOTRACES, the distribution and characteristics of L_{Fe} remain comparatively poorly constrained, particularly in the region influenced by island and equatorial regions. The coexistence of atmospheric, upwelling, volcanic, and continental sources across the Macaronesia and West African region therefore provides a natural laboratory to investigate how physical and biogeochemical processes regulate iron speciation.

The objective of this report is to synthesise available observations of dFe concentrations, iron-binding ligand concentrations, and ligand stability constants across the Macaronesian and West African region, including São Tomé and Príncipe as an equatorial endmember. Using GEOTRACES data and published studies, this work aims to identify broad spatial patterns, compare regions with contrasting iron sources, and provide a framework for interpreting iron speciation in support of the PLANCLIMAC2 project.

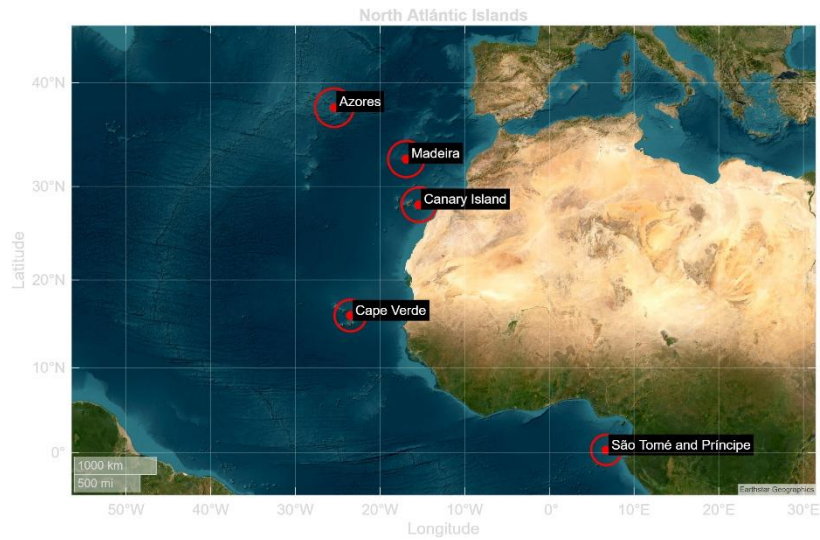


Figure 1: Map of the different areas of interest

2. Iron distribution

Dissolved Fe concentrations highlighted pronounced spatial variability across the Macaronesian and West African region, reflecting differences in external inputs, circulation, and biological activity (Fig. 2 and Fig. 3). GEOTRACES observations and regional datasets indicate that surface dFe concentrations typically range from 0.12 nmol L⁻¹ in oligotrophic open-ocean regions to 1.66 nmol L⁻¹ levels in areas influenced by dust deposition, upwelling, but increase to 47.74 nmol L⁻¹ in continental margins and coastal areas (Arnone et al., 2022; Fitzsimmons et al., 2013; Rijkenberg et al., 2008).

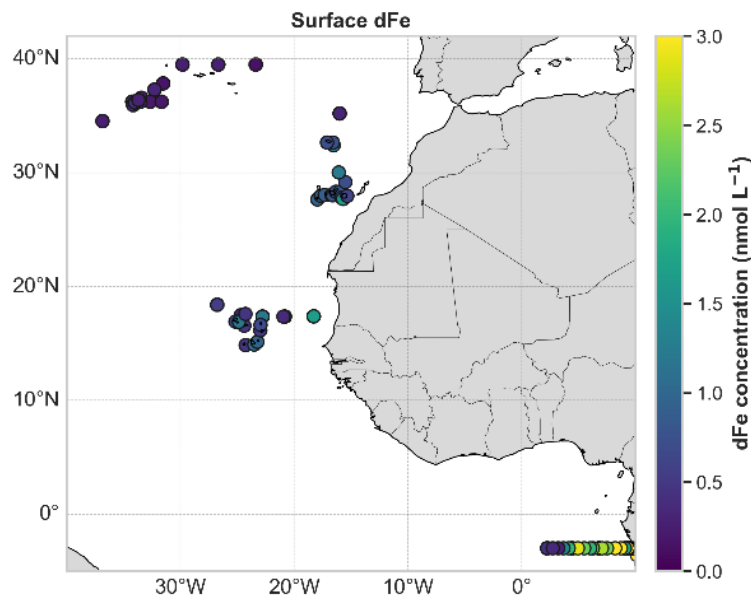


Figure 2: Representation of surface concentration of dFe in nmol L⁻¹

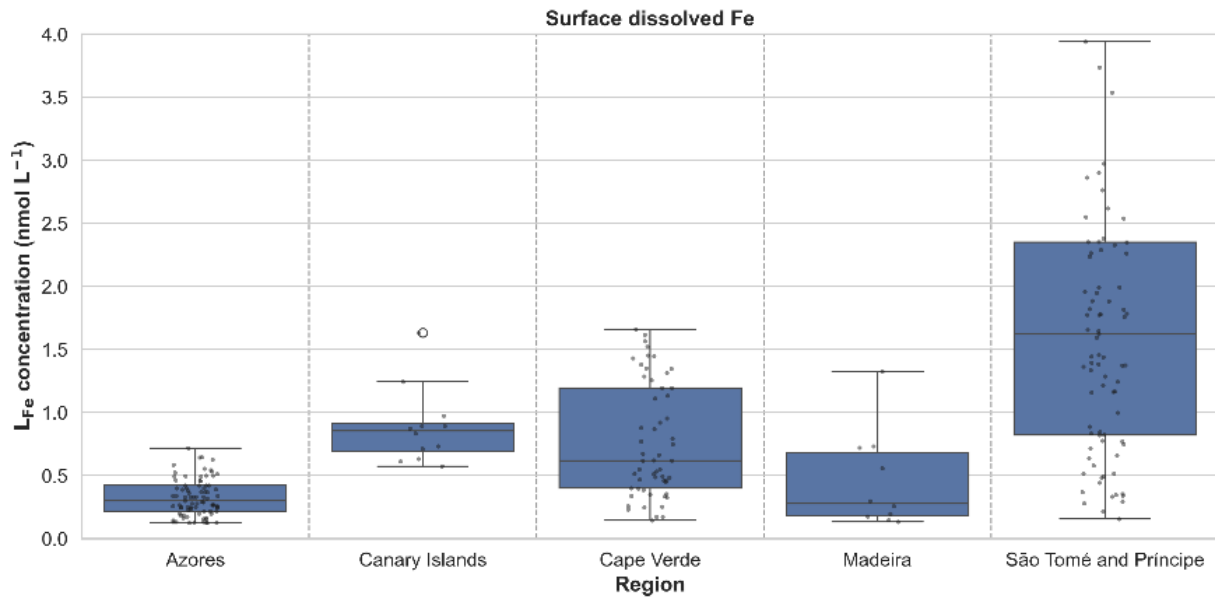


Figure 3: Boxplot of the dFe in nmol L⁻¹ in function of the region for surface waters

Surface waters (0-200 m) can display lower dFe concentrations than subsurface waters due to biological uptake and scavenging (Tagliabue et al., 2019), whereas remineralization of sinking organic matter releases Fe back into the dissolved pool and reduced scavenging at depth can contribute to higher dissolved Fe concentrations (Boyd and Ellwood, 2010; Gerringa et al., 2006).

Clear regional contrasts emerge within the Macaronesian archipelagos (Fig. 2). The Azores, located far from major continental and dust sources, highlight low and relatively homogeneous dFe concentrations (0.12-0.75 nmol L⁻¹), characteristic of open-ocean conditions (Fig. 3). In comparison, Madeira and the Canary Islands can reach higher dFe concentration (0.13-1.24 nmol L⁻¹), reflecting a balance between Saharan dust deposition, volcanic activity, island-mass effects, and upwelling along the Northwest African margin. These processes can enhance biological productivity and may contribute to spatial variability in dFe through biological uptake and recycling (Arnone et al., 2022). These regions show some spatial variability, but overall iron concentrations remain lower than those observed closer to continental sources.

Cape Verde stands out in the Macaronesian archipelago for its higher variability in dFe concentrations (0.14-1.66 nmol L⁻¹). This variability may reflect the combined influence of important dust deposition from Sahara, proximity to the African margin, and dynamic circulation patterns that enhance both iron inputs and removal processes. These concentrations

highlight the importance of localised sources such as sediment resuspension, island-mass effects and lateral transport (Arnone et al., 2022; Blain et al., 2001; Rijkenberg et al., 2008).

For São Tomé and Príncipe, the nearest sampling point was 500 km to the south, and this region has a distinct dFe distribution pattern compared to the subtropical Macaronesian archipelagos. Available observations from the eastern equatorial Atlantic suggest higher dFe concentrations, in surface stations influenced by continental or margin-derived inputs, (0.15-47.74 nmol L⁻¹) with a net gradient between the coast and the open ocean. The influence of equatorial upwelling, continental margin inputs, lateral transport, and enhanced regeneration associated with high biological productivity may contribute to this variability (Hatta et al., 2015; Ussher et al., 2010). Similarly, its equatorial location could present higher precipitation which could lead to higher sediment transport close to the coast. While strong biological uptake can rapidly deplete surface iron concentration during bloom conditions, sustained inputs from upwelling and remineralization maintain the dFe concentrations relatively high compared to oligotrophic subtropical regions. However, these observations should not be interpreted as direct measurements of the coastal waters of São Tomé and Príncipe, for which dedicated observations remain lacking.

3. Iron speciation

Iron speciation across the Macaronesian and West African regions is dominated by organic complexation, as illustrated by the ligand concentration and stability constant (Fig. 4, Fig. 5, and Fig. 6). Where ligand measurements are available, L_{Fe} concentrations generally exceed dFe concentrations, indicating a persistent excess of complexation capacity in surface waters (0-200 m). This pattern is consistent with observations from previous studies in the subtropical and tropical Atlantic, where more than 99% of dissolved iron is typically complexed by organic ligands (Fitzsimmons et al., 2015; Gerringa et al., 2006; Rijkenberg et al., 2008).

L_{Fe} concentrations observed highlight a regional variability (Fig. 4, 5, and 6). The highest L_{Fe} concentrations were observed at Cape Verde, with concentration range 0.28-2.66 nmol L⁻¹. Madeira and the Canary Islands have less data for surface water and have an intermediate position with lower concentration range 0.55-1.61 nmol L⁻¹. This spatial structure is similar to the distribution of dFe (Fig. 2 and Fig. 3), suggesting a coupling between dFe inputs and L_{Fe} production or supply in this region.

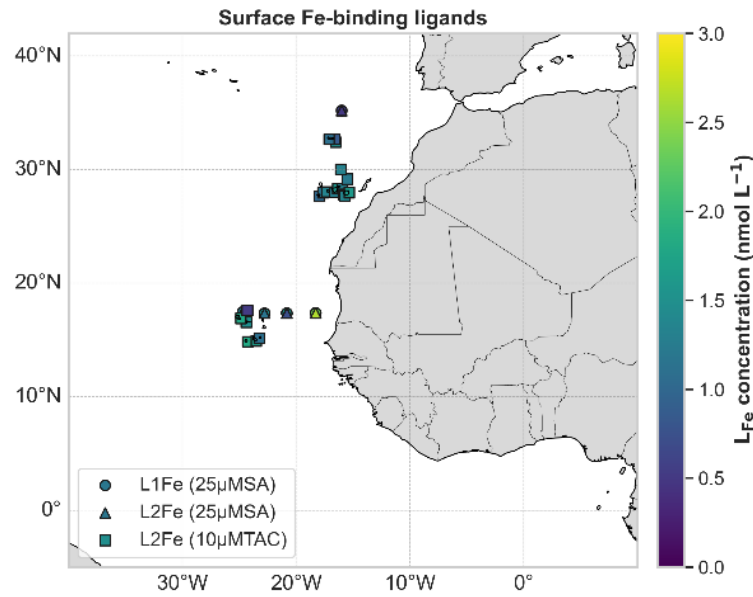


Figure 4: Representation of surface concentration of L_{Fe} in nmol L^{-1}

In the available Cape Verde dataset, the stronger ligand pool represents a substantial fraction of the measured ligand concentration (Fig. 5 and Fig. 6). Such strong ligand pools may include a range of biologically derived compounds, including siderophore-like molecules, exopolysaccharides and other organic compounds from degradation of organic matter, although ligand identity cannot generally be established from conditional stability constants alone (Fitzsimmons et al., 2015; Völker and Tagliabue, 2015).

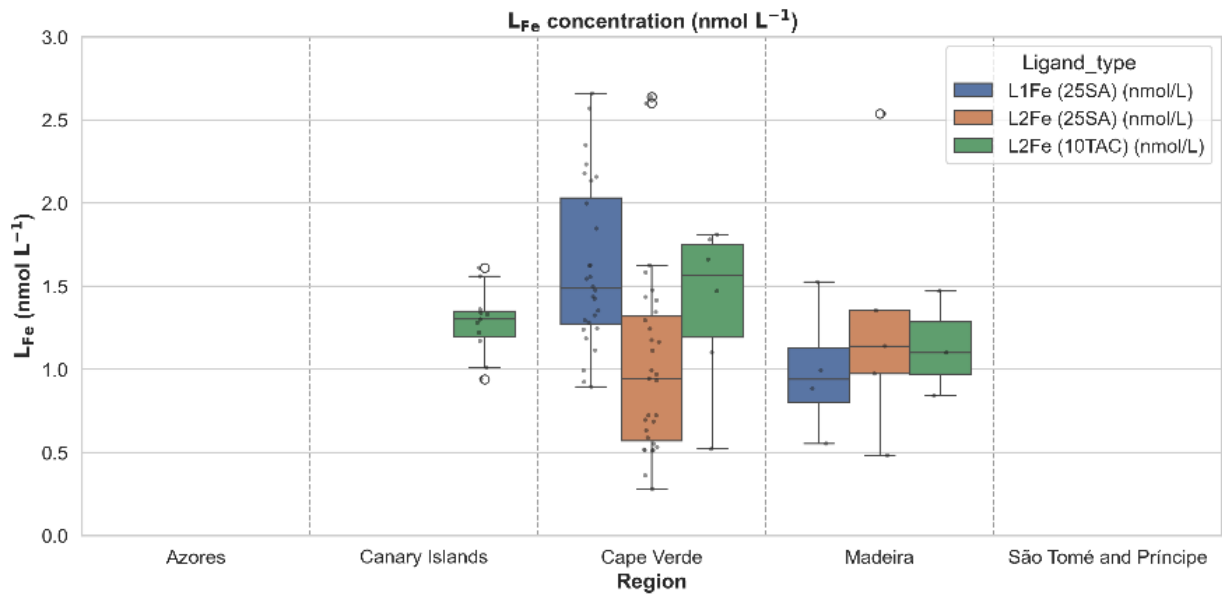


Figure 5: Boxplot of the L_{Fe} in nmol L^{-1} in function of the region for surface waters

Conditional stability constants ($\log K^{\text{cond}}_{\text{Fe}^{\text{II}}\text{L}}$) for the L₁-type ligands are similar for Cape Verde and Madeira, the two regions with data of ligands of this type 12.08-12.65 (Fig. 6). Furthermore, the L₂-type ligands measured with 2 types of artificial ligands (25 μM SA and 10 μM TAC), in the Canary Islands, Cape Verde and Madeira are remarkably uniform across regions (Fig. 6), with values typically ranging between 10.77 and 11.98. These values fall within the range reported for ligand pools associated with organic compounds such as phenolic (Hassler et al., 2011; Rico et al., 2013), humic substances (Hassler et al., 2025), and porphyrins (Witter et al., 2000). This limited variability suggests that, despite contrasting iron sources and environmental settings, similar ligand types dominate iron complexation throughout the region. Comparable $\log K^{\text{cond}}_{\text{Fe}^{\text{II}}\text{L}}$ values have been reported for Macaronesian coastal waters (Arnone et al., 2022), subtropical North Atlantic (Rijkenberg et al., 2008), and equatorial Atlantic (Hatta et al., 2015). The regions of the Azores and São Tomé and Príncipe were not documented for ligands.

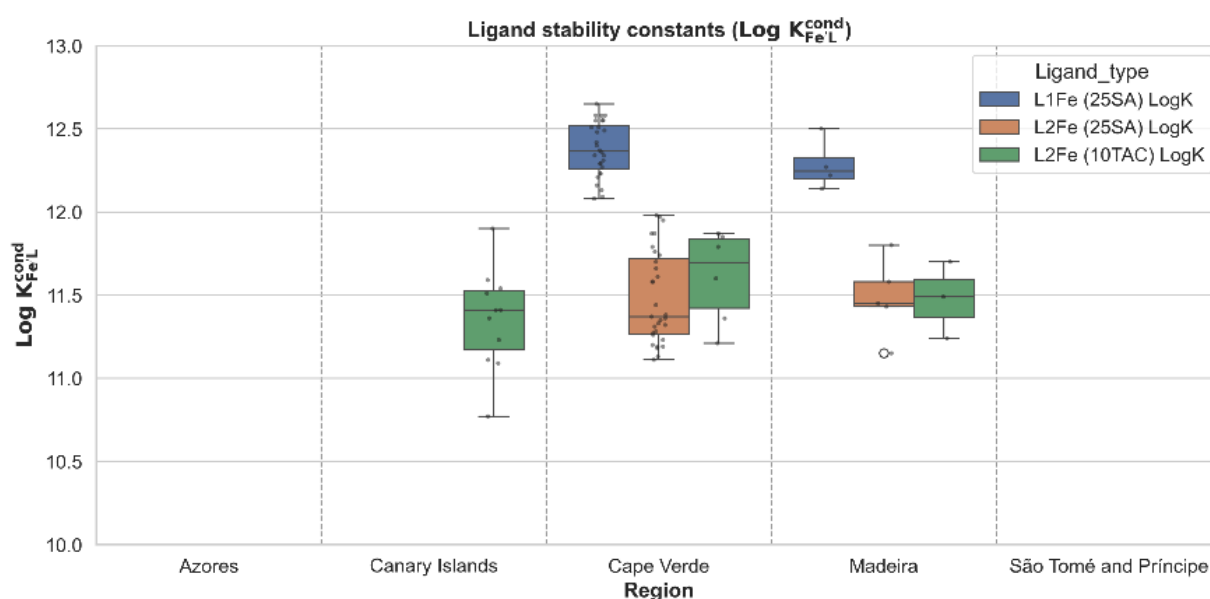


Figure 6: Boxplot of the $\log K^{\text{cond}}_{\text{Fe}^{\text{II}}\text{L}}$ in function of the region for surface waters

4. Processes controlling trace metal and ligand distributions

The observed distributions of $d\text{Fe}$ and L_{Fe} result from the interaction between physical transport, external inputs, biological activity, and chemical removal processes. In surface

waters, biological uptake by phytoplankton represents a major sink for dFe, rapidly depleting available iron during periods of high productivity. At the same time, biological processes act as a key source of organic ligands through exudation (González-Santana et al., 2024; Rico et al., 2013), grazing (Sato et al., 2007), viral lysis (Poorvin et al., 2011), and remineralization of organic matter (Gerringa et al., 2006; Hatta et al., 2015).

Atmospheric dust deposition is an important external source of iron for a major part of the Macaronesian region, particularly the Canary Islands and Cape Verde, which are frequently exposed to Saharan dust plumes (Arnone et al., 2022; Rijkenberg et al., 2008). Dust deposition provides an important external source of iron to the eastern North Atlantic. Dust-derived particles can also modify particle concentrations and therefore influence iron scavenging and speciation. Furthermore, volcanic activity can provide important, localised inputs of Fe to coastal waters, although much of the volcanic Fe may initially occur in particulate or colloidal forms (González-Santana et al., 2024). Hydrothermal activity can also contribute reactive Fe to the surrounding waters (Laes-Huon et al., 2016).

Upwelling along the Northwest African margin and in equatorial regions introduces deep waters rich in iron into the euphotic zone. These processes can modify both dFe concentrations and L_{Fe} distributions by bringing subsurface waters near Cape Verde into the euphotic zone and altering biological and chemical cycling. In contrast, the Azores region, weakly influenced by upwelling and dust deposition, exhibits lower dFe concentrations.

Scavenging processes (Tagliabue et al., 2019), including adsorption onto sinking particles and colloidal aggregation, represent a major loss pathway for dissolved iron. These processes are particularly efficient in regions with high particle loads, such as waters influenced by coast and island. Strong organic complexation mitigates scavenging losses by stabilizing iron in the dissolved phase, highlighting the central role of ligands in increasing the residence time of iron in the water column (Gledhill and Buck, 2012; Tagliabue et al., 2019).

5. Comparisons across regions

The boxplots reveal clear contrasts in dFe concentration, ligand abundance, and variability among the five considered regions (Fig. 3, Fig. 5, and Fig. 6). The Azores stand out as the most oligotrophic and homogeneous region, with lower dFe concentrations. This reflects their offshore location, weak influence from dust and continental sources, and relatively low biological productivity.

Madeira and the Canary Islands show intermediate characteristics, with moderate $d\text{Fe}$ and L_{Fe} concentrations. These regions are influenced by a combination of Saharan dust deposition, island-mass effects, and episodic upwelling, resulting in spatially heterogeneous but generally moderate iron availability.

Cape Verde exhibits the highest variability in both dissolved iron and ligand concentrations for the Macaronesia region. This variability likely reflects the combined influence of intense dust deposition, proximity to the African margin, and dynamic circulation patterns. The elevated ligand concentrations suggest an active biological response and sedimentary inputs that enhance iron complexation.

São Tomé and Príncipe represents a distinct equatorial endmember. Dissolved iron concentrations observed 500 km in the south are systematically higher than in the subtropical regions, consistent with strong continental influence, equatorial upwelling, and high rates of organic matter recycling. The influence of riverine, mangrove and continental inputs on Fe and Fe-binding ligand distributions remains an important knowledge gap for São Tomé and Príncipe.

6. Knowledge gaps and future directions

Despite progress through GEOTRACES programme and regional studies, significant gaps in knowledge remain. Spatial and temporal coverage of iron speciation data is inconsistent, particularly for L_{Fe} in the Azores and for both $d\text{Fe}$ and L_{Fe} in the equatorial region, including São Tomé and Príncipe. Seasonal variability, episodic dust events, impact of mangrove and short-term biological responses are poorly constrained for the Fe biogeochemical cycle.

The few ligand measurements provide limited information on ligand identity and origin. Further characterisation of Fe-binding ligands, including through voltammetric approaches, is needed to better constrain their distribution and chemical properties, and understand better the iron biogeochemical cycle in this region.

Time-series observations at key locations (e.g., CVOO, ESTOC, and near São Tomé) would be invaluable for capturing seasonal and interannual variability. Coordinated measurements of $d\text{Fe}$, L_{Fe} concentrations, and biological indicators are essential for improving our knowledge on iron biogeochemical cycle.

7. Conclusion

This synthesis highlights strong spatial variability in dFe concentrations and iron speciation across the Macaronesian and West African regions. Organic ligands dominate iron chemistry in all regions, maintaining most dissolved iron in a complexed and potentially bioavailable form. While ligand concentrations vary substantially between regions, stability constants remain relatively uniform, suggesting the widespread presence of similar ligand classes.

Regional contrasts reflect differences in iron sources, circulation regimes, and biological activity, with Cape Verde and São Tomé and Príncipe emerging as key regions of elevated iron concentrations.

These results highlight the central role of iron-binding ligands in regulating iron availability and the biogeochemical cycle in the eastern Atlantic. Similarly, the lack of available data underlines the need for increased observational efforts, particularly in equatorial region and island-influenced environments.

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