# TRANSPORT PATHWAYS OF SHELF SOURCE MICRONUTRIENTS TO THE SOUTHERN OCEAN

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#### **SUMMARY**

We use a numerical ocean model to evaluate the hypothesis that the continental shelves are significant sources of dissolved iron to the Southern Ocean. We simulate the distribution of passive tracers released from the 18 different continental shelf regions of the extra-tropical southern hemisphere oceans using an offline, eddy-permitting transport model. The circulation fields are taken from the Southern Ocean State Estimate, and we only simulate the transport of inert tracers focusing on the physical transport pathways. The resulting tracer fields are then compared with the remotely sensed ocean color data, revealing a remarkable resemblance between the distributions of shelf-source tracers and the climatological surface chlorophyll-a concentrations. We further analyze the spatial pattern of simulated tracer fields in relation to satellite ocean color data. Dynamic ocean features such as the Southern Ocean fronts and coastal waters are reflected in both the tracer model and the observed biological productivity. Our results support the overall importance of continental shelves as a potential source region for dissolved iron. The relative importance of different shelf regions is found to vary significantly depending on the relevant circulation features.

#### **CHAPTER 1**

#### INTRODUCTION

#### **Literature Survey**

Life has various impacts and needs; the chemical interactions between the abiotic sphere of the planet, and the biosphere are largely referred to as biogeochemical cycles. The field of biogeochemistry includes many natural processes, including the nutrient supply for low trophic level ocean organisms such as plankton (2,7,8). The factors behind the distribution of these organisms is not well understood (2,4). Since ocean life requires many nutrients to thrive, the distribution of each of these nutrients is important (6,4,7,8). Models are used to analyze and predict the impact that ocean physics has upon these nutrients, thus also upon the life therein (1,3).

The impact and nature of nutrients is a core problem in biogeochemistry. Carbon flux is often studied due to the importance that carbon has upon atmospheric chemistry and climate, as well as the direct link between carbon flux and the biological environment of the oceans (3). Changes in the amount and form of carbon in the ocean controls pH, thus also controls carbonation. There are a number of studies outlining the mechanisms through which carbon impacts these multiple facets of the ocean system, as well as analysis on the causes and extent of these changes and the associated feedback (3). Similarly, sulfur can reflect the condition of oceanic biology (8). Sulfur is partially indicative of an anoxic ocean, thus also could have co-linearity with iron chemistry. This paper analyzes the ocean variability during this time, but doesn't describe modern oceanic sulfur, or reflect directly on a iron-sulfur connection, though this analysis could lend to a solution.

A particular topic within biogeochemical study of oceanic nutrients is the study of oceanic iron. A comparative lack of information on iron in relation to other micro-

nutrients makes direct analysis difficult; as a result, the literature seems to be divided into small scale concept testing, and modeling. Iron is an important nutrient for biological processes, though it is not always sufficiently present, and can be a limiting factor in some oceanic ecosystems as a result of scarcity. One paper (2) connects iron limitation to algae and phytoplankton limitation, thus establishes a possible connection between iron and chlorophyll. The paper, however, does not attempt to explain impacts from circulation, or the nature of the iron pathways. The form, or speciation, of iron is important in understanding how it is used by the ecosystems in which it is used, as well as for understanding the propensity of the iron to precipitate out of the mixed layer. A review by Tagliabue and Volker describes the chemistry and physical framework associated with iron speciation (5). The model outlined by this paper provides a useful framework to augment a model for iron pathway analysis, although this may or may not be necessary for this particular application, or it may be able to be computed independently of the physical model. Iron's other chemical properties, such as oxidation state, are potentially important in respect to biology and persistence, as explored by Roy, Wells, and King (6); this paper explores iron, namely iron(II) in water with respect to depth in certain environments and establishes a clear significant connection in the areas studied. The paper suggests that certain variables would cause a model with an inert tracer and a collection of iron tracers to diverge; the extent of this divergence could, however, be negligible in particular models. Although the focus is much different, the focus upon estuaries by Buck et al (2007) could prove to be a useful insight on the impact of other variables upon the role iron has upon biotic activities (7). Overall, the iron literature suggests which adjustments should be done to the model if inert tracer modeling proves to be insufficient for the purposes of transport in the Southern Ocean.

Since we will use three-dimensional physical and chemical ocean modeling, the current methods associated with ocean modeling are an important baseline for building specialized models. General spatial ocean modeling is well understood, but not always

easy to implement. Many models create a large-scale box model to simulate the spatial distribution of tracers, mapping circulation patterns on the inter-box fluxes (1). These models are easy to implement, thus are usually uncomplicated and allow for addition or removal of different systems without impacting the model mechanisms. Modeling iron is done with or without any considerations of other physical/chemical properties of iron within a circulation model (4). The model we use will include considerations for these properties, so that accurate iron pathways can be found.

Due to the nature of the problem, analysis is critical; standard statistics and numerical analysis may be insufficient to analyze the results. Kernel methods and function optimization within machine learning are well understood and optimized, though these have not been well explored in the fields of biogeochemistry or oceanography (9,10). Since some variables may impact the interactions between other variables, methods ranging from Hidden Markov Models (HMM) to a custom kernel analysis can be used to determine the results.

#### **Background**

Biogeochemistry is a collective name for many of the processes which govern certain abiotic and biotic systems. It concerns the nature, sources, sinks, and impacts of different nutrients upon the planet. The nature of a nutrient usually refers to the chemical properties and relative abundance of a nutrient. The dichotomy of the scarcity levels of these nutrients results in the classification of macro and micro nutrients.

While some materials lack a meaningful source or sink region, many of the materials present in biogeochemical cycling have a source process or region. Some of these are sourced from high-productivity regions, some by anthropogenic processes, but many of them are sourced from geological processes, especially erosion/weathering in the case of ocean biogeochemistry (23). Since different regions have different and localized geologic

composition, the resulting chemical composition of the ocean in these regions can be diverse. Geologic and biologic subsystems exist within biogeochemistry.

Biological processes have profound impact upon biogeochemical cycling.

Organisms have some common needs, as is signified by an estimator such as the Redfield ratio (3). On a small scale, biological processes can remove a majority of certain substances, at the amount needed by the organisms. On a larger scale, the positioning of low trophic level organisms can fundamentally change the nature of nutrients on such a macro-scale. Higher-trophic level organisms or the destruction of other organisms can release nutrients which allows for organisms to be both a sink and a transport of nutrients (13). Biological processes can also alter the form of less stable nutrients, which allows for longer circulation and more broad transport of said nutrients (14). The sum of the effective biological processes perturbs the system in ways which are often difficult to predict, and often entirely predictable, depending on the nature of the exact process (17).

Chemical cycling and biological processes have profound impacts upon each other within biogeochemistry. Since different life forms have different needs, the presence or absence of a nutrient can dictate if a life form will be able to exist in a given area. This is often apparent when considering the high correlation of seasonality and distribution of biology (28). Likewise, this relationship often means that biological productivity can be an indication that the area is replete of the specific nutrients needed by the specific biology (17). However, a lack of biological productivity cannot be accurately related to a lack of nutrients, in the general case (24).

Many components of oceanography itself must be understood to understand the role which the ocean has upon this problem in particular. Oceanography is a broad field, yet the focus herein will be upon ocean chemistry and ocean dynamics.

Ocean chemistry is a superset of ocean biogeochemistry, as mentioned in the previous section. Some of the processes within ocean chemistry exhibit trends and patterns which

match other processes, or which may match processes or patterns about which little is

known. Sulfur, for example, has a well-known process cycle, in which organismal interaction is necessary for nutrient speciation, is sourced at the crusts, and undergoes notable oxidization changes (8). Manganese and aluminum have low oceanic solubility, and can be used to infer properties of biological uptake over time (18). Carbon, likewise, can be related to many other biological chemical process due to the abundance of the nutrient, and the near-universal relation between carbon and biological processes, via the implications of the Redfield ratio, (3) and also can be inferred to represent flux in other nutrient cycles (29). Copper experiences organic ligand based speciation within oceanic context (23).

Ocean Dynamics are the physical processes by which the ocean interacts with the earth, atmosphere, and itself. As a result, implementation ocean dynamics are vital and necessary in modeling nutrient cycling. On a large scale, currents, like the Antarctic Circumpolar Current (ACC) and Antarctic Surface Water (ASW) can be seen in nutrient distribution over long periods of time, while mesoscale eddies often can perturb the currents on smaller scales in both time and space, though they tend to be stochastic when multiple events are considered together for the purposes of tracers (19). To a certain extent, the currents form a semi predictable path set for tracers such as iron, (20) as depthwise processes such as upwelling can be predicted and inferred as a source (21,22). In the case of iron transport, specifically, ocean dynamics controls not only the distribution of the nutrient, but also the erosion and weathering processes which allow for the nutrient to enter the ocean (26). Dynamics follow seasonal and inter-annual patterns, as most notable in the tropics, but also present in the Antarctic (30). In the winter, mesoscale circulation is associated largely by landform impact on ocean dynamics (31).

Iron chemistry is an important independent consideration, as iron is the nutrient of concern. Iron behaves differently than other nutrients in a few notable ways; in modeling iron circulation, these considerations must at least be understood to properly assess importance and implication (4).

Oceanic iron arises from different sources in different forms in different locations. (15) Some of these sources are more significant than others; given regional considerations, often one or two iron sources compose a large majority of iron present. (12) One possible source for oceanic iron is from hydrothermal venting: these geologic features release heat, as well as iron and other nutrients, into the deep ocean (11). Wind and atmospheric processes may also result in iron deposition (17). Sediment may also be a fundamental source of oceanic iron in some conditions (33). Furthermore, the role of pathways in considering a regional iron source map is essential; even if no hydrothermal vents are present in a region, or atmospheric iron deposition is minimal, iron, as well as other nutrients, may migrate from another, seemingly disconnected, spatial region (20, 21).

The impact of iron in a given region is manifold and essential. Both regionally and globally, the biological impact of adding iron to otherwise nutrient replete water is sufficiently well understood (13). There are additional regional experiments on the southern ocean and Antarctic which further suggest significant impact and usage of iron as a nutrient in said region (16).

There are some essential chemical considerations specific to oceanic iron; in oxygen replete waters iron reacts via oxidation, which precipitates iron out in certain quantities. While certain eras of paleoceanography-predicted oceans lacked sufficient oxygen to precipitate out iron in large quantities, sedimentary banded iron formations show a change in the properties of the ocean and atmosphere over time. One consideration is that the chemical environment is in flux in regards to iron, though modeling these trends may be analogous to over fitting the model (25). Another consideration is iron speciation (33).

Iron speciation refers to the different forms which iron and iron-related compounds take (6). One major property difference between certain speciations of iron and unspeciated iron is a large difference in solubility (18). Although certain speciations

of iron do not interact with biology in the same manner of unspeciated iron, the differences are often negligible in large-scale (2).

#### State of the Problem

From previous studies, especially those with empirical measurements, there is a reasonable background about the nature of other nutrients; figure 2 shows the z-score normalized (standard deviation normalized) silicon (a) and nitrogen (b) distributions in the target area, the Southern Ocean. As a result of such extensive studies, and the relative abundance of data describing productivity at some resolution (figure 3), the areas where these nutrients are important in predicting productivity can be determined. Iron, however, lacks robust enough data to as assuredly make such a claim. Additionally, oxidation and precipitation of Iron make the problem of Iron more difficult to conclude directly.

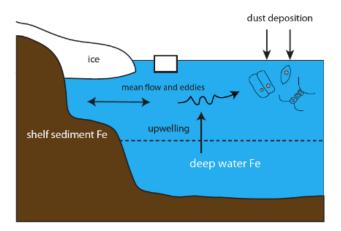


Figure 1: Schematic of iron sources in the Southern Ocean

The literature has some suggestions towards the nature of the problem. In regard to other nutrients, it is suggested that iron has a linear relationship with nutrients such as magnesium, which shows the strength of the importance of horizontal mixing for both.

(26). Horizontal mixing and advection is also shown to be greatly connected with chl-a concentration in at least the drake passage (22), so we should expect high connection between iron and chl-a in this region. In the Erebus bay, we see a similar connection between iron and aluminum, and a connection with sea ice and productivity in this area.

(17) Further areas, however, are not commented upon in such a regard; this study aims to provide a wider scope for these comparisons.

Some aspects of the other areas of the Southern Ocean are reflected upon in the literature. One paper suggests that 10-50% of iron present in Antarctic regions is connected to shelf subsurface pathways (33), as where in the Indian Ocean, the role of the deep layer depth, about 3 km, is expanded upon (11). Within the ACC, while a few stations show high productivity and low iron water content, most of the observations show either low iron and low productivity, or high iron and high productivity (25).

Some papers provide either theoretical or observational insight upon the nature of iron. It has been established that hydrothermal vents and terrestrial inputs are the primary sources of Iron (11). Surface transport can also be seen as an effective mechanism, but in a lower order of magnitude (12). From these considerations, and the nature of the Southern Ocean, it can be determined that a model focused in terrestrial inputs is a reasonable model for this problem.

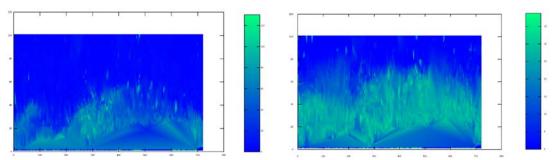


Figure 2: Annual mean oceanic Silicon (left) and Nitrogen (right) Z-score

#### Comparison

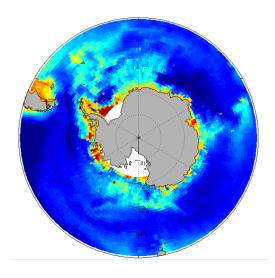


Figure 3: Ocean Color Data, 10 year average from SWAWiFS (log<sub>10</sub>)

Iron is an important micronutrient in chemical and biological oceanography due to the processes which depend on the quantity and form which iron takes in different locales. To determine the trends of iron, different techniques are used, namely analysis of existing data and creating models, and using simulations to determine potential changes in hypothetical situations. However, not many outlooks effectively integrate the advantages of both techniques of analysis and simulation. As an attempt to properly understand the problem and to analyze the solution output, this study uses machine learning to digest data to be used in the simulation, as well as the data output by the simulation to determine accuracy relative to empirical data. The simulation classifies different source areas of shelf related iron in the southern ocean and Ross Sea, using clustering geospatial clustering methods. The simulation treats iron as an inert tracer; each source extent being categorized per the cluster. The results are intended to determine the iron presence in the area, as well as to determine the extent of the link between iron and biological productivity. The different source regions are shown in figure 4.

Nutrient cycling and availability is important to many fields, especially biology and earth science. While some nutrients are relatively well understood, other nutrients,

such as Iron do not have such a comprehensive coverage from a robustness of data perspective. Iron is hypothesized to be a primary-producer limiting micronutrient, thus the balance of other nutrients can depend on iron presence or absence.

#### **CHAPTER 2**

#### METHODS.

#### **Model Description and Experimental Design**

A model is constructed to determine the nature and extent of Iron from sediment inputs across the Southern Ocean. The model is constructed out of the Southern Ocean State Estimate (SOSE), using the global circulation model via MIT (MITgcm). The model is a three dimensional time-dependent model, including seasonal and interannual processes in addition to advection-diffusion. The resolution is ½ of a degree squared over 25s to 78s, across all longitudes (2160x320). The model is run with a fifteen minute time step for ten years simulated time.

To determine the regional connection, the experiment is designed such that the sedimentary iron (30) can be used to model the biological productivity, given light limitation (20.) Due to the nature of the ocean color data present, however, light limitation is disregarded, and only surface ocean is considered in analysis.

In brief, the model runs upon sedimentary iron sources clustered on similarity, and the results are optimized to the color data. Each of the following sections focuses on one of these aspects.

#### Clustering

Data in large quantities, as opposed to insufficient amounts of data, allows for deeper analysis, even if the data present is not directly related to the problem itself. As the other aspects of the nature of environmental interactions are essential to understanding the exact problem, a primary analysis of some features can be used to specify aspects of input.

Some aspects of the environment have a great impact upon the later full analysis of the output of the model, so some separation is used as a consolidation of other features based upon mutual similarity; this is the basis for clustering.

Since the source regions may have different shelf release rates or other such important properties to consider in analysis, the sources are categorized by normalized variance in latitude, longitude, and depth using clustering. The classification results show similarity to continental divisions, and a deep/shallow subclassification therein. There are different algorithmic approaches to clustering; each of which may be used to conform to different considerations.

Clustering itself is a well understood and frequently used method of understanding, manipulating, and digesting data. The solution archetype is largely to split a large number of tuples into groups based upon some function of their attributes or the attributes of similar tuples (36). Two of the most used solution implementations are k-means and k-nearest-neighbors. These are unsupervised iterative algorithms, and often diverge in results, allowing for users to pick the one which best suits their problem.

The K-means algorithm works by assigning points to the centroid to which they are closest, and updates centroid position and cluster membership iteratively. This is particularly appropriate for cases that cooperate with dimensionality reduction, as Euclidean distance to centroid is the only measure used (36). K-nearest neighbor works by taking a majority vote of points with the lowest Euclidean distance to unlabeled points. This algorithm is more flexible, but requires some labeled points to start (34). Some other solution implementations that can be used or modified for solution sets are

single-linkage hierarchy and recursive range search. Single-linkage works by iteratively connecting close groups, eventually grouping everything together; meaningful results are found by evaluating the results at different iterations, or hierarchical levels (35).

Recursive range search works by adding all elements deemed "good" by a certain measure to a cluster; this method benefits greatly from user specified initial points (34).

Within the problem, some assumptions may be reasonable, such that areas close to each other may have similar properties (37). These seem to be the case for iron cycle modeling, where observational data is sparse and continental dust/runoff is a primary source of iron in the ocean. Since the model tracks the source region of all modeled iron throughout the simulation, the initial determination of source regions is essential to interpreting model output. Hydrology, namely pollutant tracing, has similar considerations, but instead of models used, observational data is used (37).

Currently, a manual merged k-means or a pure manual clustering method is used for splitting the source regions. This solves some problems with many out of the box techniques, such as assurance that no two continents have a common cluster, but ignores many more subtle characteristics of the land-forms, such as small islands (36). In designing a solution for biogeochemical model source clustering, a few of these considerations must be implemented.

The method proposed is to use a seeded recursive or iterative range search, followed by an algorithmic consolidation of the groups. To assure that continents and other large landforms have unique clusters, the minimum distance between such landforms is specified, and each cluster attains all points within that distance of a seeded point (34). This is run iteratively, until convergence, where each unique geospatial feature gets a

cluster. Afterwards, to consolidate, each cluster calculates an affinity measure for other groups, and merges with the one with the highest affinity, if the normalized affinity reaches a certain threshold.

To assure that the consolidation does not violate any of the requirements while still adding meaningful work, the affinity is determined per application; in this case, affinity should be a function of the sizes of both clusters, and the proximity. This assures that if either cluster is too large, a consolidation will not occur between them, and that groups clustered maintain a spatial coherence. Due to the nature of the background and experiment, there is reasonable justification to use a broad manual clustering method (9).

In this experiment, eighteen clusters are made, in respect to the nine areas in figure 4, with the additional nine areas being the deep-source areas of these same regions.

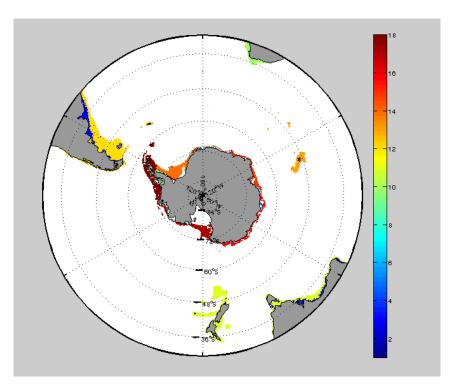


Figure 4: Dye Source Regions

#### **Optimization**

Since the different source areas have different attributes, they also have different contributions to the total output of iron in the region. As a result, the free variables introduced can be used as multipliers to the output flux of the tracers in each region. These different methods are used to attempt to establish the connection between Iron from shelf pathways and ocean productivity using these free variables.

The three optimization methods used were relative z-score matching, as reflected in figures 2 and 3, yet this seemed only to be useful to understand the nature of the data. As a result, linear optimization was used initially. However, as described in figure 5, the data is about normal in the log scale, the optimization was also applied to the log scale, as described by the cost functions of both of the optimization methods.

For the linear optimization, the function is simply

 $\epsilon = log_{10}(chl_a) - a_n log_{10}(c_n)$  , whereas for the nonlinear optimization in log space is

$$log_{10}(chl_a)=log_{10}\left(\sum_{n=1}^{18}a_nc_n\right)+\epsilon$$
 described by ; for both methods, the goal is to minimize  $\epsilon^T\epsilon$ .

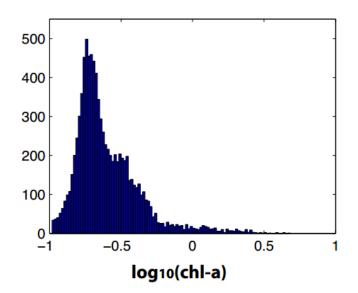


Figure 5: Observations of chl-a by proxy of color data (log10)

#### **CHAPTER 3**

#### RESULTS.

#### Dye simulation output

The model produces raw output from releasing the same dye amount in each active region at a constant rate. Figure 6 shows the result of this raw method. From the result, a few spatial patterns emerge, namely the presence of the "tail" and resulting gap due to the ACC. Furthermore, it shows some differences in coastal areas, most notably the variability in Antarctica, but also reflected in the difference between the east and west side of South America. Additionally, most islands seem to show a clear drift in a single direction.

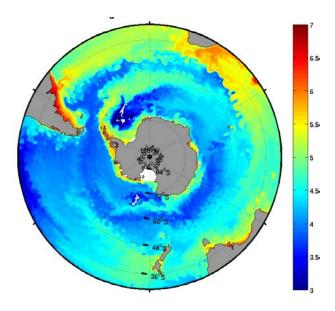


Figure 6: Unweighted sum of all tracers after 10 simulated years (log<sub>10</sub>)

When looking at each tracer individually, many key notable features, such as island drift present in tracer 4, and the strong tail off the Antarctic Peninsula in tracers 5 and 9. For the most part, these seem to show a strong decomposition in features from different source regions, as later discussed.

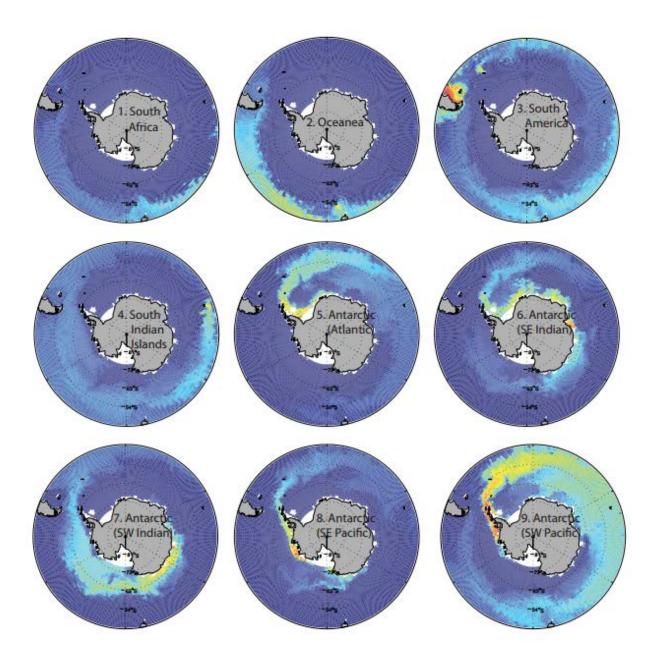


Figure 7: Unweighted result of each region-sourced tracer after 10 simulated years  $(\log_{10})$ 

Looking at the model from a histogram perspective, it shows rough similarity to the chlorophyll data, as shown in figure 8. Notable are the peak near the left side, the tail to the right, and the increase with respect to normal found to the slight right of the peak.

The difference in the increase with respect to normal between the two, and the longer/thicker right tail in the model data is a distinct concern.

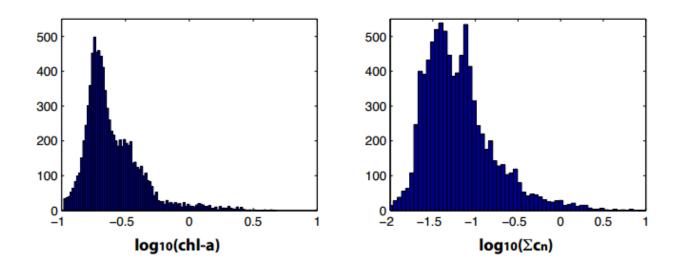


Figure 8: Comparison Between Figure 5 and the data in Figure 6 Histograms

Optimization

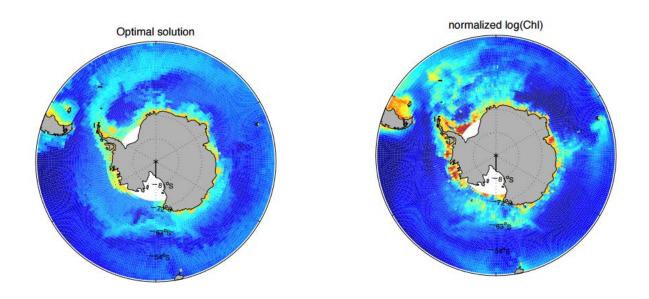


Figure 9: The result from the model after nonlinear optimization, in comparison with the data from figure 4, normalized.

In addition to the model, our optimization also produced interesting results. The optimization gave significant increases to the correlation coefficient between the model and the productivity data, to R=0.65 when using the nonlinear optimization, which resulted more favorably than the linear model, which gave R=0.45 for the same data sets. Visually, in the comparison in Figure 9, the model has the ability to show seemingly similar coastal trends for both islands and continents. The model does over predict the nature of the ACC, which seems not to be as pronounced in the data from Figure 3. The coefficients from the nonlinear model are shown in Figure 10.

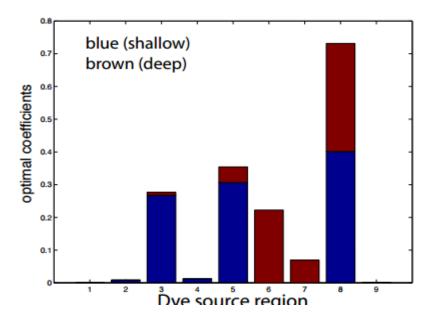


Figure 10: Weights from (figure 9) for each region from in figure 10. The height of each color represents its value.

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#### **CHAPTER 4**

#### DISCUSSION.

#### Validation

As a form of validation, some observations and trends in the literature will be compared with the differences shown in Figure 9. A simple observation which matches theory is the general pattern for the iron amount to be highest around land and island, and for this concentration to decrease with distance out (32). While observing this trend, the connection is not direct enough for this to be the only controlling factor, though it does support the hypothesis on iron sources. The northern part of the southern ocean seems to be slightly more responsive to input, which matches the model and data comparison, as the comparison seems more direct in more northern areas of the studied region (13). The Amundsen Sea's productivity is present in the model as predicted, but seems to extend further, into the Bellingshausen Sea, from the results (16). Of course, the large tail stemming from the Antarctic Peninsula in the model, despite its absence in the productivity data, is also in line with the other observations with regard to the Antarctic Peninsula. (20) Similarly, the trend in respect to islands is validated (30).

#### **Conclusions and Implications**

Given that many prominent features of the result are validated to both theory and observation, we can describe the implications of this study. The data in figure 10 can have multiple interpretations, one of which being the amount of iron in shelf sediment, and another the ability for the ocean to take up sediment. Furthermore, the coefficients may be made less physical by areas missing another nutrient making a source region seem less prevalent in productivity data, so a comparison to figure 2 or similar data is essential in interpreting the optimization results.

Perhaps one of the more interesting interpretations of the result from the model are the areas where the two subplots in figure 9 do not match. Features such as a shorter tail in the productivity data may reflect some of the limitations in the model, as well as other transport processes or sources, nutrients, or species. Additionally, while it may represent a disparity in color data with respect to productivity, this seems less likely than other explanations.

The approach of the model is intentionally simple, showing only shelf transport pathways. As a result, many relevant aspects have been excluded from the model. With regard to the problem of Iron, chemical impacts, other pathways, biological impacts, ice (18), decay, and other sources (11) have been neglected. With regard to productivity, other nutrients, light (28), and past productivity have been omitted. All of these omitted processes are important in understanding the system, and may be useful to include in future experimentation. However, it is important to note that this simple model was able to somewhat accurately link productivity to unreactive passive dyes from shelf regions alone. From this, we defend that the link between shelf iron and biological productivity is an essential mechanism in biogeochemistry.

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