Anthropogenic alteration of the nitrogen cycle in coastal waters: Case studies from the Mediterranean Sea and the Gulf of Mexico

Doctoral Program in Water and Environmental Engineering

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To Diego,

who shared this journey with me.

"Lock up your libraries if you like; but there is no gate,
no lock, no bolt that you can set upon the freedom of my mind."

A room of one's own - Virginia Woolf

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Abstract

Nitrogen (N) is one of the most important elements for life on Earth. Unfortunately, the unbalance caused to the N cylce is already causing dramatic damage to many ecosystems around the world. In coastal waters, the N processes are altered by anthropogenic activities such as the excessive use of fertilizers, urban development or energy production. These changes result in a series of consequences for the biodiversity and for human health, and could aggravate climate change. However, the mechanisms by which humans contribute to the unbalance of the N cycle in coastal waters has not been studied in detail and the consequences are still unclear.

The main objective of this research is to contribute to the evaluation of how anthropogenic activity changes the N dynamics in coastal waters. As such, the research investigates the activities by which humans modify the N processes, and focuses on how the N cycle is altered in coastal waters by both pollution and climate change. For this purpose, two study sites were selected: the Jucar River Basin District (JRBD) in the Northwestern Mediterranean Sea (Spain) and the Central Gulf Hydrological Region (CGHR) in the Southern Gulf of Mexico (Mexico). Each of these locations has different ecological and socio-economic characteristics, which allowed the evaluation of different aspects of the N processes.

The thesis is presented as a collection of four research articles, and each article focuses on the evaluation of a specific aspect of N in coastal waters. Similarly, throughout the articles different evaluation tools are developed, with the application of different techniques such as a simple biogeochemical model, artificial neural networks and grey systems theory. These tools are also an important contribution of the thesis, which could be applied in future studies to other regions of the world or to evaluate other processes of the N cycle.

The first article evaluates how nitrification in coastal waters is altered by anthropogenic pressures and close to urban settlements in the JRBD (Mediterranean Sea). Through the application of a simple biogeochemical model that simulates nitrite dynamics (intermediary compound) to nine coastal areas with similar characteristics but different anthropogenic pressures, an evaluation of the decoupling of the two steps of nitrification was carried out. The main conclusions indicate that anthropogenic pressures modify the nitrite peaks observed in winter driven by low temperatures. The research also concludes that the second step of nitrification (nitrite to nitrate transformation) is more sensitive to temperature, which entails that climate change may contribute to the decoupling of the two steps.

The second article evaluates the future trends of dissolved inorganic nitrogen (DIN) concentrations under climate change in the JRBD (Mediterranean Sea). The effect of meteorological variables on DIN concentrations was studied through the application of simple artificial neural networks trained with field data. Decreasing trends of nitrite and nitrate concentrations were observed throughout the 21st century under both climatic scenarios RCP 4.5 and RCP 8.5, mainly due to rising temperatures and decreasing rainfall, with major changes expected in winter. On the other hand, ammonium did not show any significant annual trend but it either increased or decreased during some months.

The third article develops a new method based on grey systems theory and Shannon entropy to derive useful information regarding N pollution in areas where only limited data is available. The method was applied to eight estuaries of the

CGHR (Gulf of Mexico) associated to mangroves. Two indexes were developed: the Grey Nitrogen Management Priority (GNMP) index and the Grey Land Use Pressure (GLUP) index. The two indexes were then confronted to validate the methodology. The results indicate that the urban development over beaches and mangroves is the leading cause of N pollution in the study area.

The fourth article is a spatiotemporal analysis of N pollution along two rivers discharging into a touristic coastal area of the CGHR (Gulf of Mexico) associated to mangroves. Through statistical techniques such as clustering analysis, the Mann-Kendall test and the Mann-Whitney W-test, an evaluation of the origine of N pollution and the temporal variations of the N compounds was performed. The results conclude than organic N concentrations are increasing along the coast, and the main potential source identified was the decomposition of the invasive species of water hyacinths in saline waters, which has completely covered the surrounding beaches and mangroves, enhanced by N pollution.

Overall, the main conclusions are that both pollution and climate change alter the N cycle in coastal waters by modifying N processes such as nitrification, the seasonal variations of N concentrations and by destroying the coastal ecosystems. The differences in ecological and socio-economic characteristics of the two study sites played a significant role in the pressures and impacts of anthropogenic activities, as well as in the methods that could be used to evaluate N pollution. Moreover, the methods developed, i.e. the mechanistic model for the evaluation of nitrification, the use of artificial neural networks to evaluate the impact of meteorological variables on N compounds under climate change and the grey systems methodology developed, can be applied to other coastal regions to evaluate the anthropogenic alteration of the N cycle worldwide. Future research should also focus on the evaluation of the overall impact of anthropogenic activities on N in coastal waters, including all the processes involved in the N cycle. Finally, the effects on humans and the ecosystems need to be evaluated in detail in order to propose prevention measures and avoid pushing the system into an unstable environmental state with catastrophic consequences.

Resumen

El nitrógeno (N) es uno de los elementos más importantes para la vida en la Tierra. Sin embargo, la actividad antrópica está causando un grave desequilibrio sobre el ciclo del N y provocando daños importantes a muchos ecosistemas en todo el mundo. En aguas costeras, los procesos del N se ven alterados por actividades tales como el uso excesivo de fertilizantes, el desarrollo urbano o la producción de energía. Como consecuencias, esto provoca una pérdida de biodiversidad, pone en riesgo la salud humana, y podría agravar los efectos del cambio climático. Sin embargo, los mecanismos por los cuales los seres humanos contribuyen a este desequilibrio no se han estudiado en detalle y las consecuencias aún no se conocen con claridad.

El objetivo principal de esta investigación es contribuir a la evaluación de cómo la actividad antrópica cambia la dinámica del N en aguas costeras. Como tal, se investigaron las actividades por las cuales se modifican los procesos del N, enfocando el estudio en cómo el ciclo del N es alterado en aguas costeras por la contaminación y el cambio climático. Con este propósito se seleccionaron dos lugares de estudio: la demarcación hidrográfica del Júcar (JRBD) en el Noroeste del Mar Mediterráneo (España) y la Región Hidrológica del Golfo Central (CGHR) en el Sur del Golfo de México (México). Cada uno de estos lugares tiene diferentes características ecológicas y socio-económicas, lo que permitió la evaluación de diferentes

aspectos del nitrógeno.

La tesis se presenta como un compendio de cuatro artículos de investigación, y cada artículo se centra en la evaluación de un aspecto específico del N en aguas costeras. De manera similar, a lo largo de los artículos se desarrollan diferentes herramientas de evaluación con la aplicación de diferentes técnicas, tales como un modelo biogeoquímico, redes neuronales artificiales y teoría de sistemas grises. Estas herramientas también son una contribución importante de la tesis, y podrían aplicarse en futuros estudios a otras regiones del mundo o en la evaluación de otros procesos del ciclo del N.

El primer artículo evalúa cómo la nitrificación en aguas costeras se ve alterada por las presiones antrópicas y cerca de los asentamientos urbanos en el JRBD (Mar Mediterráneo). Mediante la aplicación de un modelo biogeoquímico simple que simula la dinámica del nitrito (compuesto intermedio) a nueve áreas costeras con características similares pero diferentes presiones, se evaluó el desacoplamiento de los dos pasos de la nitrificación. Las principales conclusiones indican que las presiones antrópicas modifican los picos de nitrito observados en invierno debido a las bajas temperaturas. La investigación también concluye que el segundo paso de la nitrificación (transformación de nitrito a nitrato) es más sensible a la temperatura, lo que implica que el cambio climático puede contribuir al desacoplamiento de estos dos pasos.

El segundo artículo evalúa las tendencias futuras de las concentraciones de nitrógeno inorgánico disuelto (NID) bajo los efectos del cambio climático en el JRBD (Mar Mediterráneo). El efecto de las variables meteorológicas en las concentraciones de NID se estudió mediante la aplicación de redes neuronales artificiales simples entrenadas con datos de campo. Se observaron tendencias decrecientes de las concentraciones de nitrito y nitrato a lo largo del siglo XXI bajo los escenarios climáticos RCP 4.5 y RCP 8.5, principalmente debido al aumento de las temperaturas y a la disminución de las precipitaciones, con cambios más significativos en invierno. Por otro lado, el amonio no mostró ninguna tendencia anual significativa, pero se observaron aumentos o disminuciones durante algunos meses.

En el tercer artículo se desarrolla un nuevo método basado en la teoría de los sistemas grises y la entropía de Shannon para obtener información útil sobre la contaminación por N en áreas donde los datos disponibles son limitados. El método se aplicó a ocho estuarios del CGHR (Golfo de México) asociados a manglares. Se desarrollaron dos índices: el índice gris de prioridad de gestión de nitrógeno (GNMP) y el índice gris de presión de uso de la tierra (GLUP). Los dos índices fueron comparados para validar la metodología. Los resultados indican que el desarrollo urbano sobre playas y manglares es la principal causa de la contaminación de N en el área de estudio.

El cuarto artículo es un análisis espacio-temporal de la contaminación de N a lo largo de dos ríos que desembocan en una zona turística costera del CGHR (Golfo de México) asociada a manglares. Mediante técnicas estadísticas como el análisis de cluster, la prueba de Mann-Kendall y la prueba W de Mann-Whitney, se realizó una evaluación del origen de la contaminación de N y las variaciones temporales de los compuestos de N. Los resultados concluyen que las concentraciones de N orgánico están aumentando a lo largo de la costa, y la principal fuente potencial identificada fue la descomposición de la especie invasora de lirio acuático en aguas salinas, que ha cubierto completamente las playas y manglares circundantes potenciado por la contaminación de N.

El conjunto de la investigación concluye que tanto la contaminación como el cambio climático alteran el ciclo del N en aguas costeras al modificar elementos importantes del N como la nitrificación, las variaciones estacionales de las concentraciones de N o los ecosistemas costeros. Las diferencias en las características ecológicas y socioeconómicas de las dos zonas de estudio desempeñaron un papel decisivo en las presiones e impactos de las actividades antrópicas, así como en los métodos que pueden usarse para evaluar la contaminación. Además, los métodos desarrollados, es decir, el modelo mecanicista para la evaluación de la nitrificación, el uso de redes neuronales artificiales para evaluar el impacto de las variables meteorológicas en los compuestos de N bajo el cambio climático y la metodología de sistemas grises desarrollada, pueden aplicarse a otras regiones costeras para evaluar la alteración antrópica del ciclo del N a nivel mundial. Futuras investigaciones también deberían centrarse en la evaluación del impacto global de las actividades antrópicas sobre el N en aguas costeras, incluidos todos los procesos involucrados en el ciclo del N. Finalmente, los efectos sobre la salud humana y los ecosistemas deben evaluarse detalladamente para proponer medidas de prevención y evitar llevar al sistema a un estado ambiental inestable con graves consecuencias.

Resum

El nitrogen (N) és un dels elements més importants per a la vida en la Terra. Desafortunadament, el desequilibri provocat sobre el cicle del N està causant danys importants a molts ecosistemes a tot el món. En aigües costaneres els processos del N es veuen alterats per activitats antropogèniques com ara l'ús excessiu de fertilitzants, el desenvolupament urbà o la producció d'energia, amb conseqüències negatives per a la biodiversitat o la salut humana, i podran agreujar els efectes del canvi climàtic. No obstant això, els mecanismes pels quals els éssers humans contribueixen al desequilibri del cicle del N en aigües costaneres no s'han estudiat detalladament i les conseqüències encara no es coneixen amb claredat.

L'objectiu principal d'aquesta investigació és contribuir a l'avaluació de com l'activitat antropogènica canvia la dinàmica del N en aigües costaneres. Com a tal, s'investiguen les activitats per les quals es modifiquen els processos del N, i s'enfoca en com el cicle del N és alterat en aigües costaneres per la contaminació i el canvi climàtic. Amb aquest propòsit es van seleccionar dos llocs d'estudi: la demarcació hidrogràfica del Xúquer (JRBD) al Nord-oest (NO) de la Mar Mediterrània (Espanya) i la Regió Hidrològica del Golf Central (CGHR) al Sud del Golf de Mèxic (Mèxic). Cadascun d'aquests llocs té diferents característiques ecològiques i socioeconòmiques, la qual cosa va permetre l'avaluació de diferents aspectes del nitrogen.

La tesi es presenta com una col·lecció de quatre articles d'investigació, i cada article se centra en l'avaluació d'un aspecte específic del N en aigües costaneres. De manera similar, al llarg dels articles es desenvolupen diferents eines d'avaluació amb l'aplicació de diferents tècniques, com ara un model biogeoquímic, xarxes neuronals artificials i teoria de sistemes grisos. Aquestes eines també són una contribució important de la tesi, que podran aplicar-se en futurs estudis a altres regions del món o en l'avaluació d'altres processos del cicle del N.

El primer article avalua com la nitrificació en aigües costaneres es veu alterada per les pressions antropogèniques i prop dels assentaments urbans en el JRBD (Mar Mediterrània). Mitjançant l'aplicació d'un model biogeoquímic simple que simula la dinàmica del nitrit (compost intermedi) a nou àrees costaneres amb característiques similars però diferents pressions, es va avaluar el desacoblament dels dos passos de la nitrificació. Les principals conclusions indiquen que les pressions antropogèniques modifiquen els pics de nitrit observats a l'hivern a causa de les baixes temperatures. La investigació també conclou que el segon pas de la nitrificació (transformació de nitrit a nitrat) és més sensible a la temperatura, la qual cosa implica que el canvi climàtic pot contribuir al desacoblament d'aquests dos passos.

El segon article avalua les tendències futures de les concentracions de nitrogen inorgànic dissolt (NID) pel canvi climàtic en el JRBD (Mar Mediterrània). L'efecte de les variables meteorològiques en les concentracions de NID es va estudiar mitjançant l'aplicació de xarxes neuronals artificials simples entrenades amb dades de camp. Es van observar tendències decreixents de les concentracions de nitrits i nitrats al llarg del segle XXI tant sota l'escenari climàtic RCP 4.5 com RCP 8.5, principalment a causa de l'augment de les temperatures i a la disminució de les precipitacions, amb canvis més significatius a l'hivern. D'altra banda, l'amoni no va mostrar cap tendència anual significativa, però es van observar augments o disminucions durant alguns mesos.

En el tercer article es desenvolupa un nou mètode basat en la teoria dels sistemes grisos i l'entropia de Shannon per a obtindre informació útil sobre la contaminació per N en àrees on les dades disponibles són limitats. El mètode es va aplicar a huit estuaris del CGHR (Golf de Mèxic) associats a manglars. Es van desenvolupar dos índexs: l'índex gris de prioritat de gestió de nitrogen (GNMP) i l'índex gris de pressió d'ús de la terra (GLUP). Els dos índexs van ser comparats per a validar la metodologia. Els resultats indiquen que el desenvolupament urbà sobre platges i manglars és la principal causa de la contaminació de N en l'àrea d'estudi.

El quart article és una anàlisi espacio-temporal de la contaminació de N al llarg de dues rius que desemboquen en una zona turística costanera del CGHR (Golf de Mèxic) associada a manglars. Mitjançant tècniques estadístiques com l'anàlisi de clúster, la prova de Mann-Kendall i la prova W de Mann-Whitney, es va realitzar una avaluació de l'origen de la contaminació de N i les variacions temporals dels compostos de N. Els resultats conclouen que les concentracions de N orgànic estan augmentant al llarg de la costa, i la principal font potencial identificada va ser la descomposició de l'espècie invasora de jacints d'aigua en aigües salines, que ha cobert completament les platges i manglars circumdants potenciat per la contaminació de N.

El conjunt de la investigació conclou que tant la contaminació com el canvi climàtic alteren el cicle del N en aigües costaneres en modificar els processos del N com la nitrificació, les variacions interanuals de les concentracions de N i la destrucció dels ecosistemes costaners. Les diferències en les característiques ecològiques i socioeconòmiques de les dues zones d'estudi van exercir un paper decisiu en les pressions i impactes de les activitats antropogèniques, així com en els mètodes que poden usar-se per a avaluar la contaminació. A més, els mètodes desenvolupats, és a dir, el model mecanicista per a l'avaluació de la nitrificació, l'ús de xarxes neuronals artificials per a avaluar l'impacte de les variables meteorològiques en els compostos de N sota el canvi climàtic i la metodologia de sistemes grisos desenvolupada, poden aplicar-se a altres regions costaneres per a avaluar l'alteració antropogènica del cicle del N a nivell mundial. Futures investigacions també hauran de centrar-se en l'avaluació de l'impacte global de les activitats antropogèniques sobre el N en aigües costaneres, inclosos tots els processos involucrats en el cicle del N. Finalment, els efectes sobre la salut humana i els ecosistemes han d'avaluar-se detalladament per a proposar mesures de prevenció i evitar portar al sistema a un estat ambiental inestable amb greus conseqüències.

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List of Abbreviations

AE	Absolute error
AEMET	National meteorological agency (Spain)
ANN	Artificial neural network
AOA	Ammonium oxidizing archaea
AOB	Ammonium oxidizing bacteria
BOD	Biological oxygen demand
CEDEX	Center for studies and experimentation of public works (Spain)
CGHR	Central Gulf hydrological region
CIW	Coastal inshore waters
CO_2	Carbon dioxide
COD	Chemical oxygen demand
CONAGUA	National commission of water (Mexico)
DIN	Dissolved inorganic nitrogen

DNRA	Dissimilatory nitrate reduction to ammonium
EPA	Environmental protection agency
GLUP	Grey land use priority
GNMP	Grey nitrogen management priority
GoM	Gulf of Mexico
HAB	Harmful algal bloom
HMWB	Heavily modified water bodies
HNO_3	Nitric acid
IPCC	Intergovernmental panel on climate change
JRBD	Jucar river basin district
LME	Large marine ecosystem
MAP	Mediterranean action plan
MedGIG	Mediterranean intercalibration group
MEDPOL	Mediterranean pollution assessment and control programme
MS	Mediterranean Sea
N	Nitrogen
N_2	Dinitrogen
NH_3	Ammonia
NH_4^+	Ammonium
NH_2OH	Hydroxylamine
NO	Nitric oxide

NO_x	Nitrogen oxides
N_2O	Nitrous oxide
NO_2	Nitrogen dioxide
NO_2^-	Nitrite
NO_3^-	Nitrate
NOAA	National ocean and atmospheric administration (United States)
NOB	Nitrite oxidizing bacteria
NOH	Nitroxyl
P	Phosphorous
PNACC	National plan for climate change (Spain)
RBD	River basin district
RCP	Representative concentration pathway
RMSE	Rooted mean squared error
SAP	Strategic action plan
SGD	Submarine groundwater discharge
SIMPA	Integrated precipitation simulation model
TDA	Transboundary diagnosis analysis
TN	Total nitrogen
WFD	Water framework directive
WWTP	Wastewater treatment plant

CHAPTER 1

Background

Extensive review of the key background literature.

1.1 The nitrogen cycle

1.1.1 The global nitrogen cycle

Nitrogen is a common element found in living organisms and an essential requirement for plant growth (Galloway et al., 2004). As such, the global N cycle is a key component of the Earth's biogeochemistry and nitrogen has a critical role in controlling primary production (Gruber, Galloway, 2008). Large flows of nitrogen circulate from the atmosphere to the land and the oceans, mainly through biological nitrogen fixation (Fowler et al., 2013). Then, the microorganisms found in soil and water transform nitrogen into a large variety of inorganic and organic molecules which finally return to the atmosphere through denitrification (Fowler et al., 2013). A schematized simplification of the global N cycle can be seen in Figure 1.1.

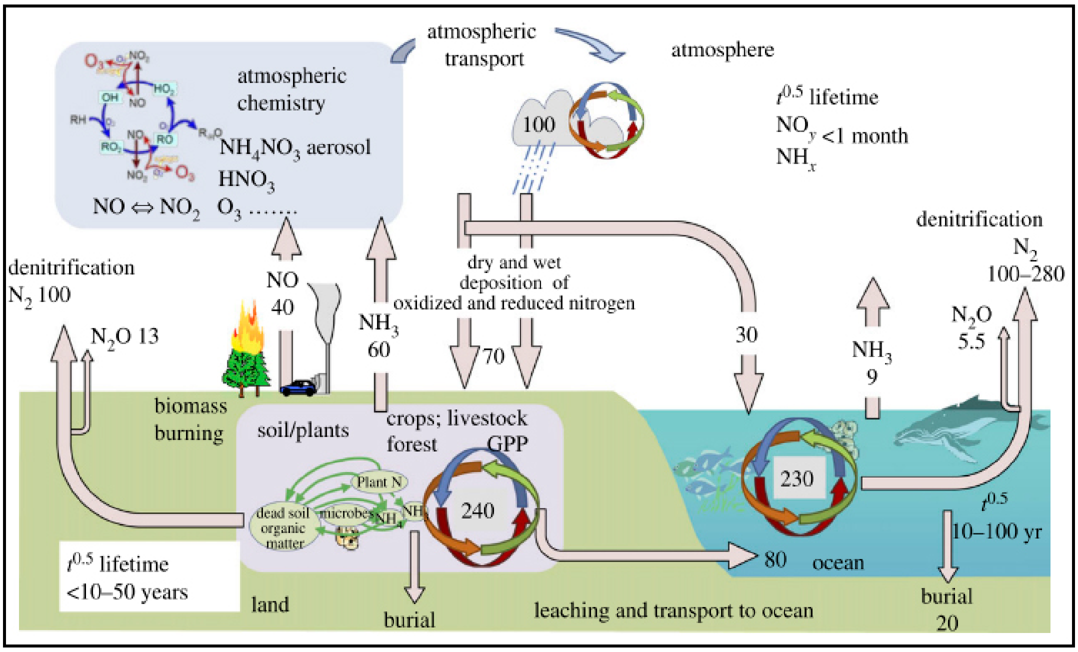

Figure 1.1: Processes and fluxes ($TgN.yr^{-1}$) of the global N cycle. Source: Fowler et al. (2013).

In the atmosphere, dinitrogen (N_2) is the most abundant gas, while nitrogen oxides (NO_x) play a key role in oxidation processes, as well as in the photochemical production of ozone (Fowler et al., 2013). Nitrous oxide (N_2O) is an important gas for the radiative balance of the Earth, representing a strong contribution to the greenhouse gas effect. Lighting is also an important process of reactive nitrogen in the atmosphere, by which the stable N_2 is transformed into nitric oxide (NO), then oxidized to nitrogen dioxide (NO_2) and nitric acid (HNO_3) and finally deposited into land and aquatic ecosystems (Galloway et al., 2004).

In land processes, the N biogeochemical cycle is also highly influential. Nitrogen fixation, the main process regulating the flux of nitrogen from the atmosphere to the soil, is an important mechanism for plant growth (Fowler et al., 2013). Nitrogen can leach from terrestrial ecosystems mainly carried away by freshwater, and finally reach the ocean (Gruber, Galloway, 2008).

1.1.2 Nitrogen processes in marine waters

Nitrogen in marine systems can be found both in gaseous, dissolved and particulate form, as well as in organic or inorganic forms (Statham, 2012). The forms of nitrogen of greatest interest in marine waters are dinitrogen (N_2), nitrate (NO_3^-), nitrite (NO_2^-), ammonium (NH_4^+) and organic nitrogen. Some small amounts of N_2O can also be found. N_2 is the most common form of nitrogen in the ocean with an estimated 95% of the total N (Voss et al., 2013), due to its high partial pressure in the atmosphere and to its stability (Romero Gil, 2003). A large amount of the nitrogen exists as organic nitrogen, either as part of the living biomass, dead biomass or as dissolved organic nitrogen, which includes a large variety of compounds such as aminoacids (Statham, 2012). NH_4^+ is the most reduced form of nitrogen and is therefore generally considered as the preferred species for phytoplankton growth (Romero Gil, 2003).

All these forms of nitrogen are biochemically interconvertible by marine organisms either to obtain energy or to synthesize structural components (Capone et al., 2008). Through oxidation-reduction reactions controlled by the prevailing physicochemical conditions and carried out by autotrophic and heterotrophic microorganisms, nitrogen passes from -3 to +5 valence states (Herbert, 1999). The main nitrogen processes are schematized in Figure 1.2 and presented below.

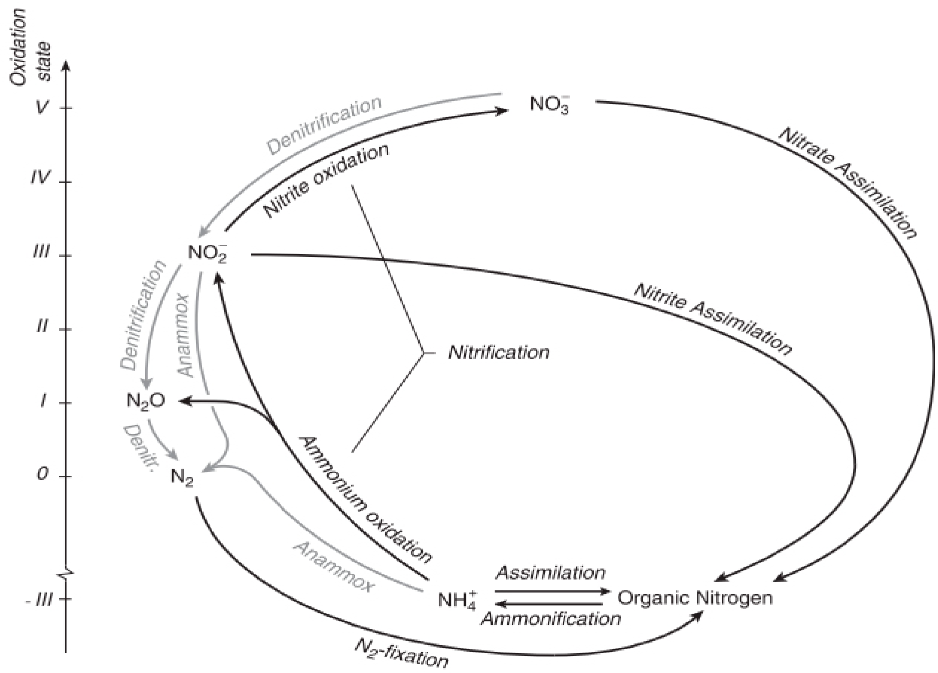

Figure 1.2: Major processes of the marine N cycle. Processes in grey occur in anoxic conditions. Source: Capone et al. (2008).

Nitrogen fixation

N_2, the most abundant form of nitrogen in marine waters, is generally not bioavailable. Nitrogen fixation is the biological reduction of N_2 into ammonium which can be subsequently used for cell production (Arrigo, 2005).

$$N_2 + 2H^+ + 3H_2 - > 2NH_4^+ \tag{1.1.1}$$

Nitrogen fixation is carried out by certain prokaryotes which possess the enzyme nitrogenase; however those responsible for most of the fixation in natural waters are certain species of cyanobacteria (Herbert, 1999). Many parameters can limit nitrogen fixation, such as temperature, light, oxygen concentrations, turbulence or salinity (Capone et al., 2008).

Nitrification

Nitrification is the biological oxidation of ammonium to nitrate performed by some chemoautotrophic bacteria and archaea to produce energy (Voss et al., 2013). It is generally described as a two-step process: oxidation of ammonium to nitrite by ammonium-oxidizing bacteria (AOB) and ammonium-oxidizing archaea (AOA), and oxidation of nitrite to nitrate by nitrite oxidizing bacteria (NOB) (Kim, 2016).

$$NH_4^+ + 1.5O_2 -> 2H^+ + H_2O + NO_2^- \tag{1.1.2}$$

$$NO_2^- + 0.5O_2 -> NO_3^- \tag{1.1.3}$$

Hydroxylamine (NH_2OH), nitroxyl (NOH) and nitrous oxide (N_2O) are intermediary compounds in nitrification (Kim, 2016), which only occurs at aerobic conditions. Some parameters affect the rate of nitrification such as pH, temperature, ammonia and nitrite concentrations, dissolved oxygen, suspended solids, and organic and inorganic compounds (Bowie et al., 1985). This process links the reduced and oxidized forms of nitrogen, and provides nitrate for denitrification (Herbert, 1999).

Denitrification

Under anaerobic conditions, nitrite and nitrate can be used as electron donors by certain heterotrophic facultative anaerobic bacteria (Kim, 2016). Nitrite is formed as an intermediate with the principal end-product being dinitrogen. The complete denitrification process can be expressed as:

$$NO_3^- + 2e^- + 2H^+ -> NO_2^- + H_2O \tag{1.1.4}$$

$$NO_2^- + 3e^- + 4H^+ -> 0.5N_2 + 2H_2O \tag{1.1.5}$$

Denitrification only occurs at very low oxygen concentrations and it is a fundamental process to reduce nitrogen concentrations (Herbert, 1999). N_2O, which is a powerful greenhouse gas, is an intermediary compound in denitrification. This process is one of the main mechanisms by which nitrogen is removed from the ocean to the atmosphere (Kim, 2016).

Ammonification

Ammonification is the transformation of non-living organic nitrogen to ammonium. This process involves several mechanisms including bacterial decomposition. Depending on the structure of the organic molecules, ammonification can be a simple or a complex reaction (Herbert, 1999).

Anammox

Anammox (anaerobic ammonium oxidation) is a process of the nitrogen cycle discovered in 1995. Ammonium is oxidized to nitrogen gas under anaerobic conditions, using NO_2^- as oxidizing agent (Kim, 2016). In contrast to denitrification, anammox is used for energy production (Capone et al., 2008).

$$NH_4^+ + NO_2^- -> N_2 + H_2O \tag{1.1.6}$$

Dissimilatory nitrate reduction to ammonium

Dissimilatory nitrate reduction to ammonium (DNRA), also known as nitrate ammonification, is the reduction of nitrate to ammonium under anoxic conditions (Kim, 2016). It is carried out by some microorganisms which use nitrate as electron sink (Lam, Kuypers, 2011).

$$NO_3^- + 2H^+ + 2e^- -> NO_2^- + 2H_2O \tag{1.1.7}$$

$$NO_2^- + 6e^- + 8H^+ -> NH_4^+ + 2H_2O \tag{1.1.8}$$

Nitrogen assimilation

Nitrogen is an essential element for phytoplankton growth, and is therefore assimilated into biomass in the upper layers of the ocean (euphotic zone) (Capone et al., 2008). In 1934, Alfred Redfield noticed that the ratio of carbon, nitrogen and phosphorus C:N:P in marine systems was controlled by phytoplankton in a fixed ratio of 106:16:1 (Arrigo, 2005). While ammonium is the preferred form of nitrogen due to its lower oxidation state, other forms such as nitrate or nitrite are also assimilated into biomass (Zouiten et al., 2013). Nitrogen has been long believed to be the limiting nutrient for phytoplankton growth in most marine areas (Paerl, 2018), although the concept of a nutrient co-limitation (Arrigo, 2005) has gained increasing attention in the last decades.

When phytoplankton dies, nitrogen is released back through detritus decomposition and remineralized to inorganic forms. Part of the dead detritus sinks to the deep waters, and ocean recirculation brings back the remineralized inorganic nitrogen to the euphotic zone where they can be reused for phytoplankton growth (Capone et al., 2008). This nutrient loop is essential for the Earth's climate, as the nutrient availability in the photic zone allows phytoplankton growth with subsequent carbon uptake (Capone et al., 2008).

Athmospheric deposition

Atmospheric deposition is a transport process by which atmospheric nitrogen is delivered to the sea through air masses. It can occur both as wet deposition, associated to rainfall, or as dry deposition (Pacyna, 2008). It is the main source of nitrogen in the open ocean (Voss et al., 2013).

1.1.3 Nitrogen in coastal waters

Freshwater inputs

In coastal waters, rivers are the major source of nitrogen (Voss et al., 2013), but most of the river transported N does not reach the open ocean (Capone et al., 2008). Submarine water discharges from coastal aquifers are also an important source of nutrients to some coastal areas (Voss et al., 2013). These freshwater inputs enhance primary production, deriving in a high phytoplankton biomass (Statham, 2012), which is often dependent on temporal patterns in riverine exports (Capone et al., 2008). Consequently, the nitrogen processes in coastal waters differ considerably form the open ocean, where the sources of nitrogen are limited.

Sediments

Due to the low depths found in coastal waters, benthic fluxes from the sediment are often a relevant source of nitrogen to the water column (Voss et al., 2013). When the organic matter deposited in the sediment decomposes, a nutrient exchange occurs through diffusion from the sediment to the water column. As such, the strong benthic-pelagic coupling enhances primary production (Capone et al., 2008). At the surface of the sediment, an excess of organic matter can lead to anoxic conditions (Sospedra et al., 2015). Sediments are also habitat for a great number of microorganisms, invertebrates and plants, which are an integral part of the N cycle (Capone et al., 2008).

Coastal upwelling

Wind-driven coastal upwelling results in high nitrogen inputs to the upper coastal waters, enhancing the primary production. Deep waters are generally rich in nitrate, which stays unavailable for phytoplankton until coastal upwelling pushes it back to the photic zone (Capone et al., 2008). The upwelling depends on the wind patterns and on water stratification, and therefore varies from region to region (Capone et al., 2008).

Coastal ecosystems

Coastal ecosystems include areas of distinct structure and high biodiversity, such as seagrass meadows, mangroves, kelp forests, estuaries, coral reefs or salt marshes. All these ecosystems have particular N cycling and are among the most productive ecosystems in the world (Capone et al., 2008). For example, seagrass meadows obtain a large proportion of their nitrogen requirement from nitrogen fixation, which makes this process an important component of the biogeochemistry of macrophytes in coastal environments (Capone et al., 2008). Mangroves and other wetlands lay between the land and the sea, having a determining influence on the global N cycle (Gonçalves Reis et al., 2017). They promote nutrient recycling (Holguin et al., 2001) and are regarded as nutrient filters (Geedicke et al., 2018). Mangroves also play a significant role as carbon stocks known as "blue carbon", and provide resilience for coastal ecosystems (Adame et al., 2018), which tranform N and deliver it to coastal waters (Gonçalves Reis et al., 2017). In estuaries, the hydrodynamics play an important role in N processes, and nitrate is the predominant nitrogen form due to its stability under well oxygenated conditions (Statham, 2012). However, coastal ecosystems are often fragile, and due to their proximity to the land and to human activities, the N cycle in coastal regions is the most affected by anthropogenic pressures (Pesce et al., 2018).

1.2 Anthropogenic pressures on the N cycle in coastal waters

The alteration of the N cycle has already surpassed the threshold known as the "planetary boundary", which establishes the limit considered safe for humanity (Rockström et al., 2009). In fact, nitrogen is feared to be "the next carbon" (Battye et al., 2017). The highly dynamic character of the marine N cycle makes it especially sensitive to substantial changes (Capone et al., 2008). In the last decades, many processes have contributed to the unbalance of the natural N processes in coastal waters amongst which the following can be highlighted for their relevance: food production, energy production, urban development and climate change.

1.2.1 Food production

The anthropogenic alteration of the N cycle started many years ago, mainly driven by Fritz Haber's patent "synthesis of ammonia from its elements" and the derived Haber-Bosch process to produce fertilizers (Erisman et al., 2008). The role of chemical fertilizers is essential to increase crop production and feed the growing global population, but the abusive and inefficient use has carried many environmental consequences (Prabakaran et al., 2018). The cascading effects of fertilizer production from atmospheric nitrogen fixation include greenhouse gas emissions, biodiversity loss and water pollution. Today, the overall anthropogenic nitrogen fixation is so large that it is estimated to double the natural sources (Fowler et al., 2013).

Concurrently, a large increase in nitrogen-fixing crops such as legumes (e.g. soybeans) occurred during the 20th century, with an estimated increase of ten-fold since 1960 (Battye et al., 2017). Soybeans are mainly used for animal feed, which only convert a small fraction of the nitrogen to proteins, excreting the rest as urea or other forms of organic nitrogen. Thus, the increase in animal population for human consumption derives in higher N excretion which often ends up in natural waters (Battye et al., 2017). The land clearing for agriculture, such as the large areas of deforestation in the Amazon rainforest in the last decades, also contribute to the alteration of N processes (Boucher et al., 2011). In China for example, the imports of soybeans from Brazil have increased a 2,000% since 2000 due to its rapidly growing meat demand (Fuchs et al., 2019).

The anthropogenic nitrogen fixation for food production as led to many marine environmental problems such as eutrophication (Gruber, Galloway, 2008). Much of the nitrogen in fertilizers ends up in natural waters and in coastal zones, causing excessive primary production and driving anoxic events (Rockström et al., 2009). In the last decades, nitrogen pollution to coastal systems has rapidly increased, largely due to industrial agriculture and the intensive fertilizer application (Boucher et al., 2011). Additionally, the use of fertilizers, together with septic systems, has caused an increasing nitrate pollution in groundwater which ultimately reach marine waters (Galloway et al., 2004). As such, the future trends of nitrogen in coastal waters is highly dependent on the global demand for food, dietary choices and agricultural management practices (Sinha et al., 2019).

Finally, aquaculture is an important source of N pollution to many coastal environments (Camargo, Alonso, 2006; Do-Thu et al., 2011) which is rapidly expanding worldwide (including mariculture) (Capone et al., 2008). Most of the aquaculture operations depend on food supply and fertilization to sustain fish productivity, which translates into a high amount of nitrogen leaching to the surrounding waters (Capone et al., 2008).

1.2.2 Energy

The burning of fossil fuels is the major source of NO_x gases ($NO+NO_2$) to the atmosphere, which have a very short lifetime and are deposited into the ocean's surface almost immediately (Capone et al., 2008). The deposition of these gases is a major source of nitrogen pollution to the marine waters, especially in highly populated coastal regions where fossil fueled based transport is dense (Park et al., 2019). Globally, anthropogenic sources account for approximately 70% of NO_x deposition (Capone et al., 2008). Additionally, motorized navigation is also a relevant source of organic pollution to the marine ecosystems (Valdor et al., 2019).

On the other hand, the use of biofuels as energy source also has a great impact on the N cycle. The production of biofuels increases the demand for nitrogen fertilizers (Erisman et al., 2008) and deforestation (Boucher et al., 2011), with the consequent increase of N runoff to coastal waters (Rabalais et al., 2009). Nowadays, biofuel production only accounts for 1.5% of the global energy demand, but the expected increase in biofuels would increase the impact of this source of energy in N pollution (Erisman et al., 2008).

1.2.3 Urban development

It is estimated that around 40% of the global population lives within 100km of the coastline (Valdor et al., 2019). Due to the rapid urbanization of coastal regions, the increasing sewage discharges have greatly contributed to the N enrichment of marine waters (Nie et al., 2018). Many coastal cities, especially in developing countries, lack a proper wastewater treatment and directly discharge into natural water systems (Djihouessi et al., 2019; Jin et al., 2018). As a consequence, the water quality of coastal regions with intense anthropogenic activity is often very deteriorated (Flo et al., 2019).

Additionally, the increasing deforestation due to urban expansion also contributes to N pollution of the coastal ecosystems. For example, mangroves recycle nutrients within the ecosystem and act as nutrient filters (Holguin et al., 2001), but urban development expands over mangroves destroying them (Adame et al., 2018). Similarly, other coastal habitats with a great implication in the biogeochemistry such as salt marshes or estuaries are destroyed as a consequence of urban expansion (Rivera-Guzmán et al., 2014).

Costal infrastructures may also contribute to the alteration of N processes. Harbors, docks or breakwaters alter the hydromorphological characteristics of the coast (Reyjol et al., 2014), which hinder the dispersion of water pollutants and destroy habitats (Gottardo et al., 2011). Similarly, the construction of dams for water use can greatly limit the river flow and consequently the N export to coastal waters (Capone et al., 2008).

1.2.4 Climate change

Climate change, through the modification of temperature, wind patterns, sea level rise or pH, affects nutrient processes in coastal waters (Statham, 2012) by increasing acidification, deoxygenation and other physicochemical conditions (Kim, 2016).

The increasing surface temperatures result in water stratification, which may have consequences for phytoplankton composition and thus for the N cycle. Diatoms, which prefer stratified waters, may become more abundant, and the lower N:P ratio of diatoms compared to other phytoplankton species may drive a shift in the nutrient ratio of marine waters (Arrigo, 2005). Additionally, the stratification of the water column derived from global warming limits the supply of nutrients from the bottom layers, reducing the bioavailable nitrogen (Voss et al., 2013).

Ocean acidification may also result in a shift in marine N cycling (Voss et al., 2013), as many processes such as nitrogen fixation or nitrification are highly dependent on the pH (Kim, 2016). For example, nitrification may be reduced under lower pH conditions, reducing the supply of nitrate to the ecosystem (Voss et al., 2013). On the other hand, the NH_3/NH_4^+ equilibrium highly depends on the pH, and thus ocean acidification may derive in higher NH_4^+ concentrations. Being NH_4^+ one of the essential nutrients in marine waters, the alteration of this equilibrium may drive a significant change in primary production, and reduce NH_3 emissions from the ocean to the atmosphere (Capone et al., 2008). On the other hand, increasing pCO2 may increase marine denitrification, reducing the available nitrogen in water (Kim, 2016).

Furthermore, climate change is predicted to expand the oxygen minimum zones, exacerbate eutrophication and consequently altering the N cycle (Voss et al., 2013). The oxygen depletion of the oceans as a consequence of climate change will likely increase denitrification and anammox (Kim, 2016), resulting in a lower marine productivity (Capone et al., 2008). This would provoke a higher release of CO_2 from the atmosphere, which in turn would accelerate the effects of climate change (Capone et al., 2008).

Another mechanism by which climate change affects the N cycle is through meteorological changes such as wind pattern or precipitation, which alter the inputs of nitrogen from freshwater resources to the coastal areas. As such, the increase in extreme events enhances nitrogen runoff and modifies the interannual variability (Sinha et al., 2019). As a consequence of the changes in freshwater inputs, the shifts in salinity may induce changes in the coastal biogeochemistry (Pesce et al., 2018).

Finally, sea level rise may change the geomorphology of the coast, enhancing the erosion and modifying the biogeochemistry of the sediments (Statham, 2012). Mangroves and other wetlands are expected to be significantly affected by the sea level rise induced coastal squeeze (Martínez et al., 2014), together with the derived human pressure to regain the space lost to the sea (Rabalais et al., 2009).

Currently, the effect of climate change on the N cycle may be masked by nitrogen pollution or natural variability (Rabalais et al., 2009). Nonetheless, the combined effects of agriculture, urbanization and climate change may have unprecedented consequences in a near future (Pesce et al., 2018). Further research is needed to gain a better understanding of the effects of climate change on the N cycle.

1.3 Impacts of the alteration of the N processes in coastal waters

As nitrogen is a major nutrient in living organisms, the alteration of its biogeochemical processes leads to cascading effects in the productivity and biodiversity of ecosystems (Fowler et al., 2013), as well as to a variety of human health problems (Grattan et al., 2016).

1.3.1 Eutrophication and biodiversity loss

In recent decades population growth and related nutrient sources such as agriculture, wastewater treatment plants (WWTP), urban runoff, and consumption of fossil fuels, have increased nutrient inputs causing eutrophication, which has become one of the most significant problems in many estuaries and coastal zones (Bricker et al., 2003). Nixon (1995) defined eutrophication as “an increase in the rate of supply of organic matter to an ecosystem”, which is mainly caused by nutrient enrichment. Primary production is enhanced by nutrient pollution, predominantly nitrogen and phosphorous (Vollenweider et al., 1996). The most relevant impacts of eutrophication include depletion of oxygen, increased frequency of harmful algal blooms, increased turbidity, deterioration of coastal food webs and reduction of biodiversity (Scavia, Bricker, 2006).

When phytoplankton grows excessively due to nutrient pollution and blocks sunlight, the decomposition of dead biomass can cause a severe depletion of oxygen known as hypoxia (Du et al., 2018). Massive fish kills have often been associated to hypoxic events (Bianchi et al., 2010), and entire dead zones have been created due to nutrient discharges in coastal areas (Yáñez-Arancibia, Day, 2004). Hypoxia can damage a whole ecosystem by affecting benthic communities, changing the biogeochemical cycles (Breitburg et al., 2018) and altering the food webs (Du et al., 2018). Often these zones are created in semi-enclosed areas where water exchange is limited, such as the Gulf of Mexico (Rees, 2012).

Eutrophication can ultimately force a shift in local fish and vegetation communities, with a proliferation of certain macroalgae and phytoplankton species (Voss et al., 2013). This shift can eventually lead to harmful algal blooms (HAB), or increase the frequency, amplitude or toxicity of the naturally occurring blooms (Ferreira et al., 2011). The dangerous nature of HABs depends on the type of algal species: some can generate very harmful toxins even at low concentrations, while other species cause harm when the biomass is so high that it destroys habitat through light shadowing and hypoxia (Anderson et al., 2002). These blooms sometimes result in water discoloration, and consequently HABs are generically referred to as "red tides" (Kudela et al., 2017).

Additionally, the pollution of coastal systems with nutrients such as nitrogen may facilitate the invasion by exotic species (Geedicke et al., 2018), which may be exacerbated by the increasing temperatures due to climate change (Statham, 2012). For example, water hyacinth (Eichhornia crassipes), which is the most widespread invasive aquatic species worldwide, occupies large extensions of freshwater ecosystems and deltas (Toft et al., 2003). Invasive species can cause big losses of biodiversity (Erisman et al., 2008) and alter the biogeochemistry of ecosystems which are often no longer able of recycling nutrients (Sherman, 2017).

Therefrom, nitrogen pollution is considered the leading cause of biodiversity loss in marine environments (Galloway, 2003), with devastating impacts on coastal ecosystems. Coral reefs are very sensitive to eutrophication because it disrupts their natural oligotrophy (Baker et al., 2013). Seagrass meadows can change their morphology when exposed to nitrogen enrichment, and approximately 60% of the lost seagrass worldwide has been attributed to N pollution (Capone et al., 2008). Coastal wetlands such as salt marshes or mangroves are also affected by N pollution, which modifies processes such as denitrification or nitrogen fixation within the ecosystems (Gonçalves Reis et al., 2017). And yet, the conservation of these coastal ecosystems is essential for climate change mitigation as they entail large carbon stocks (blue carbon) (Adame et al., 2018).

1.3.2 Climate change

Climate change is both a pressure to the N processes and an impact derived from the alteration of the N cycle, i.e. it is both influenced by climate change and affects it (Galloway et al., 2008). That is, the marine N cycle could be a significant feedback factor for climate change (Capone et al., 2008) as life on Earth links the associated element cycles (Gruber, Galloway, 2008). The importance of the interactions between the carbon and the nitrogen cycle in the Earth's climate is of growing interest for many scientists (Gruber, Galloway, 2008). For example, N deposition enhances the primary production which leads to the uptake of CO_2 from the atmosphere (Gruber, Galloway, 2008). The Earth's climate is very sensitive to nutrient upwelling, nutrient recycling and the subsequent phytoplankton growth with carbon uptake (Capone et al., 2008).

The formation of N_20, a powerful greenhouse gas, is tightly coupled to the magnitudes of the nitrification and denitrification processes (Gruber, Galloway, 2008). The oceans contribute to approximately 30% of global N_20 production, which is an intermediary compound of both nitrification and denitrification (Voss et al., 2013). The rate of N_20 production highly depends on the oxygen availability (Voss et al., 2013). Thus, the deoxygenation of the ocean derived from global warming may induce a higher release of N_2O, aggravating climate change (Rees, 2012). Coastal ecosystems such as estuaries, intertidal areas or mangroves have been identified as intense N_2O formation sites (Capone et al., 2008). Additionally, the coastal upwelling releases N_2O to the atmosphere where the formation of this gas is favored due to the anoxic conditions. Coastal eutrophication also results in lower oxygen environments, deriving in higher N_2O formations (Capone et al., 2008).

1.3.3 Human health

Many people around the world lack a proper sewage management and access to treated water for cleaning and consumption (Coutinho et al., 2019). As such, numerous human health problems are related to nitrogen pollution both by direct intake and by the effects of nitrogen enrichment in aquatic ecosystems (Camargo, Alonso, 2006).

One of the most widespread illnesses caused directly by nitrogen pollution is methemoglobinemia (Camargo, Alonso, 2006), also known as the blue-baby syndrome, which is caused by the intake of nitrate mainly in young infants (Torkamaneh et al., 2019). Drinking nitrite and nitrate rich waters have also been related to the development of digestive track cancer and other health problems such as birth defects or respiratory track infections (Camargo, Alonso, 2006).

Nitrogen pollution also causes indirect health problems through the enhancement of bacteria and other microorganisms' growth. Waterborne diseases have often been correlated to the presence of nitrogen and other nutrient pollution, which enable the proliferation of opportunistic aquatic pathogens (Coutinho et al., 2019). Many widespread infectious diseases such as cholera or malaria are related to poor water quality (Breton-Deval et al., 2019; Galloway et al., 2008). Moreover, algal toxins which are enhanced by HABs can cause a series of symptoms such as diarrhea, nausea or vomiting (Camargo, Alonso, 2006). These toxins, which accumulate in fish and seafood and subsequently ingested by humans, cause a series of biointoxications such as paralytic shellfish poisoning, amnesic shellfish poisoning, neurotoxic shellfish poisoning, diarrhetic shellfish poisoning or ciguatera poisoning (Grattan et al., 2016).

1.4 The Mediterranean Sea

1.4.1 Overall description

The Mediterranean Sea (MS) (Figure 1.3) is a semi-enclosed sea which is connected to the Atlantic Ocean through a narrow strait which is only 13 km wide and 350 m deep (Pinet, 1996): the Strait of Gibraltar. It is also connected to the Black Sea and to the Red Sea through the artificial Suez Canal. The MS is surrounded by Europe in the north and west, by Africa in the south and by Asia in the east. It covers approximately 2.5 million km^2, and it contains around 3.7 million km^3 of water. Its average depth is about 1,500 m, with a maximum depth of 5,121 m in the Hellenic Trench (Rodríguez Martínez, 1982). The strait of Sicily divides the MS in two basins: the Western and the Eastern basins (Romero Gil, 2003).

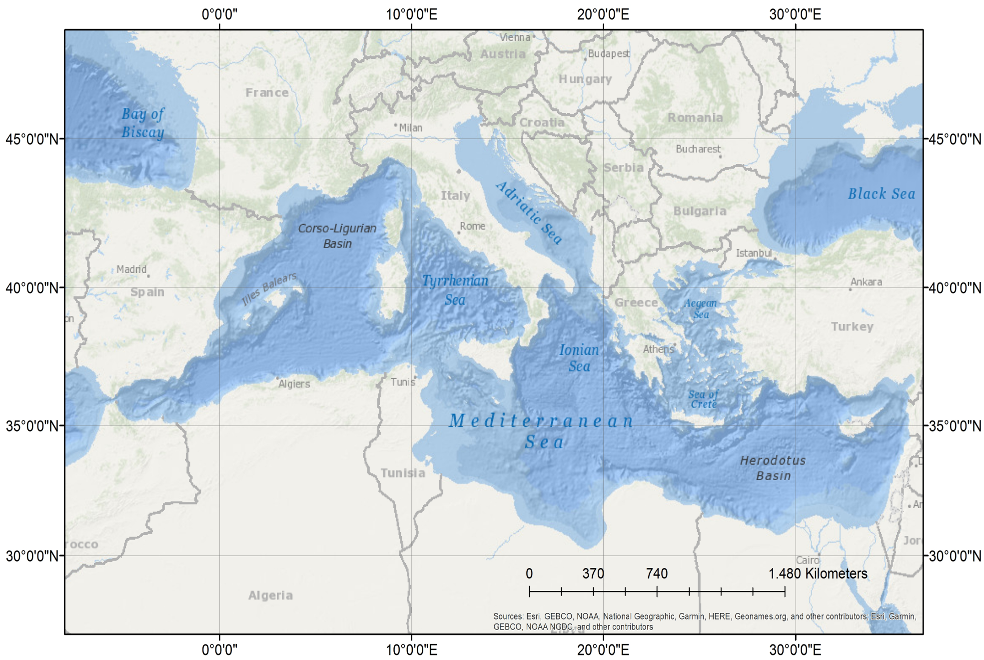

Figure 1.3: The Mediterranean Sea.

As a result of its enclosure, the Mediterranean sea has a microtidal range of approximately 20-40 cm (Flo et al., 2011). The evaporation exceeds the water inputs through precipitation and runoff, creating high salinities (37.9 ‰ mean) (Romero

Gil, 2003) and high densities (Béthoux, Copin-Montégut, 1986). As a consequence, low-density Atlantic waters enter the MS through the strait of Gibraltar's surface. The temperature usually stays above 12.5°C all year round and at all depths, which allows vertical mixing (Rodríguez Martínez, 1982). The deep convection events which occur in winter, brings nutrients to the surface (García-Martínez et al., 2019) and gives rise to intense spring blooms (Severin et al., 2014).

Due to the water deficit, the Mediterranean Sea is oligotrophic, and nutrients deficiency increases from West to East (Romero Gil, 2003). Phosphorus rather than nitrogen limits primary production (Krom et al., 2010), as the P/N ratio is generally higher than the Redfield ratio (Vollenweider et al., 1996). However, the nutrient limitation changes from region to region (Powley et al., 2016) and nutrient co-limitation is also under study (Sebastián, Gasol, 2013). The atmospheric deposition in the MS is strong, delivering more than half of the nitrogen (Guerzoni et al., 1999). Saharan dust deposition is believed to play a significant role in regulating nitrogen fixation (Ridame et al., 2011). Additionally, the Atlantic waters arriving from the strait of Gibraltar are also a relevant source of nitrogen (Powley et al., 2017).

1.4.2 Nitrogen pollution in the Mediterranean Sea

In the Mediterranean Sea, there are around 601 cities with populations greater than 10,000 inhabitants, and more than 600 WWTPs along the coastal cities (Stamou, Kamizoulis, 2008). However, many cities still lack a proper wastewater treatment, and most of the WWTPs do not undergo a tertiary treatment to eliminate nutrients (Powley et al., 2016). As a consequence, nitrogen pollution from urban wastewater is a major source of pollution to the MS.

The Northwestern Mediterranean Sea is surrounded by three highly industrialized countries (Massoud et al., 2003), which are also among the most touristic countries in the world: Spain, France and Italy. In contrast, the north of Africa delimits the southern Mediterranean Sea, with a lower industrialization, but with high urbanization rates and deficient wastewater management (Massoud et al., 2003). The difference in economic situations entails a disparity in the sources of nitrogen pollution, as well as in its management.

On the other hand, agriculture is also an important source of nitrogen pollution to the Mediterranean Sea. Some agriculture-intensive areas such as the Ebro river delta are a major source of excessive nitrogen (Herrero et al., 2018). In the Nile river, the industries of sugarcane and starch significantly contribute to nitrogen loads (Ali et al., 2011). In the last decades, the intensification of fertilizer use in some areas such as Egypt or Turkey has increased the eutrophication in certain areas (Malagó et al., 2019).

Decreases in pH and increases in dissolved organic carbon have also been documented (Aparicio et al., 2016; Merlivat et al., 2018), which affect the dynamics of nitrogen by several processes described earlier. Additionally, climate change is expected to decrease continental inputs (Chirivella Osma et al., 2015), altering the nitrogen sources to coastal waters. An increase in sea temperature has already been observed in the Mediterranean sea (Lejeusne et al., 2010).

1.4.3 Legal framework and management

The Mediterranean Action Plan (MAP) was approved by 16 countries and the European community in 1975, which became the first regional seas programme under the UNEP. Its main objectives were the assessment and management of marine pollution, as well as the development of new laws to protect the Mediterranean (Massoud et al., 2003). The Barcelona convention was signed in 1976 to cooperate among the Mediterranean countries and allow a sustainable development (Massoud et al., 2003). The Mediterranean Pollution Assessment and Control Programme (MED POL) became the first operational programme of the MAP as its land-based pollution assessment and control component. Today, the MAP is more active than ever, with 22 contracting parties: 21 countries plus the European Union (European

Commission, 2019).

Over the last decades, the European Union has adopted 6 important directives which protect the marine environments (Flo Arcas, 2017): the Bathing Water Directive (76/160/EEC) (European Communities Council, 1976), the Urban Waste Water Treatment Directive (91/271/EEC) (European Communities Council, 1991a), the Directive concerning the protection of waters against pollution caused by nitrates from agricultural sources (91/676/EEC) (European Communities Council, 1991b), the Directive concerning integrated pollution prevention and control (96/61/EC) (European Commission, 1996), the Water Framework Directive (2000/60/EC) (European Commission, 2000) and the Marine Strategy Framework Directive (2008/56/EC) (European Commission, 2008). Amongst these directives, the Water Framework Directive is of special interest for nearshore coastal waters, and is often seen as the most substantial and ambitious European environmental legislation to date (Voulvoulis et al., 2017).

At a national level, Spain has adopted several laws to protect marine waters, being the Water Law the most relevant of them, approved in 1985 and updated in many occasions (Gobierno de España, 2001). The Coastal Law came into force in 1969, and was modified in 1988 to regulate the protection, use and maintenance of the maritime-terrestrial public domain, and especially of the seashore. However, this law was substituted in 2013 by a new law which softened the levels of protection of the seafront in favor of occupation and economic activities, reducing the protection easement from 100 to 20 meters (Gobierno de España, 2013). In 2010 a new law came into force to incorporate the European Marine Strategy Framework Directive: the law of protection of the marine environment (Gobierno de España, 2010).

The Water Framework Directive

The "Directive 2000/60/EC of the European Parliament and of the Council establishing a framework for the Community action in the field of water policy", commonly known as the Water Framework Directive (WFD) was published on the 22nd of December 2000. Some amendments have been introduced since then. The purpose of the WFD is to establish a framework for the protection of inland surface waters (rivers and lakes), transitional waters, coastal waters and groundwater (European Commission, 2000). The Directive requires Member States to establish river basin districts (RBDs) and for each of these, a river basin management plan which shall include five main activities: characterization of the RBDs, pressures and impact evaluation, monitoring, establishment of environmental objectives and design and implementation of the programme of measures.

With regard to the setting of environmental objectives, the Article 4 of the Directive establishes that Member States shall protect, enhance and restore all water bodies with the aim of achieving good water status. In order to determine the status of each water body the WFD defines a criterion for its evaluation. For surface water, the status is defined as "the status of a body of surface water determined by the poorer of its ecological status and its chemical state".

The ecological status is defined as "an expression of the quality of the structure and functioning of aquatic ecosystems associated with surface waters". It can be classified as high, good, moderate, poor or bad status. Several quality elements have been established in this Directive for each water body type in order to assess the ecological status. These elements can be divided in three categories: biological quality elements, physico-chemical quality elements and hydromorphological quality elements. For surface water categories, the ecological status classification for a body of water is represented by the lower of the status achieved for any biological and physico-chemical quality elements. In Table 1.1, all the proposed elements by the WFD for coastal waters are collected.

On the other side, the chemical status is classified as "good" or "failing to achieve good". A good chemical status is achieved by a water body which is in compliance with all limit values and environmental quality standards of all relevant legislations mentioned in the WFD.

Biological elements
Composition, abundance and biomass of phytoplankton Composition and abundance of other aquatic flora Composition and abundance of benthic invertebrate fauna
Hydromorphological elements
Depth variation Structure and substrate of the coastal bed Structure of the intertidal zone Direction of dominant currents Wave exposure
Chemical and physico-chemical elements
Transparency Thermal conditions Oxygenation conditions Salinity Nutrient conditions

Table 1.1: Water quality elements to determine the ecological status of coastal waters under the Water Framework Directive. Source: European Commission (2000)

In order to classify the ecological status, the WFD defines the terms ‘high status’, ‘good status’ or ‘moderate status’ for each quality element. The definitions for nutrient conditions are as follows:

- High status : Nutrient concentrations remain within the range normally associated with undisturbed conditions.
- Good status : Nutrient concentrations do not exceed the levels established so as to ensure the functioning of the ecosystem and the achievement of the values specified for the biological quality elements.
- Moderate status : Conditions are consistent with the achievement of the values specified for the biological quality elements.

1.4.4 The Jucar River Basin District

The Jucar River Basin District (JRBD) (Figure 1.4) is located in the East of Spain, and discharges into the Northwestern Mediterranean Sea. The extension of the

JRBD covers 42,735 km^2 (44,871 km^2 including coastal waters) and lies within five Spanish autonomous communities: Aragon (12.58%), Castilla-La Mancha (37.65%), Catalonia (0.21%), Valencian Community (49.42%) and Murcia (0.15%). The JRBD includes 574 km of coastline which fully belong to the Valencian Community (Jucar Hydrographic Confederation, 2014).

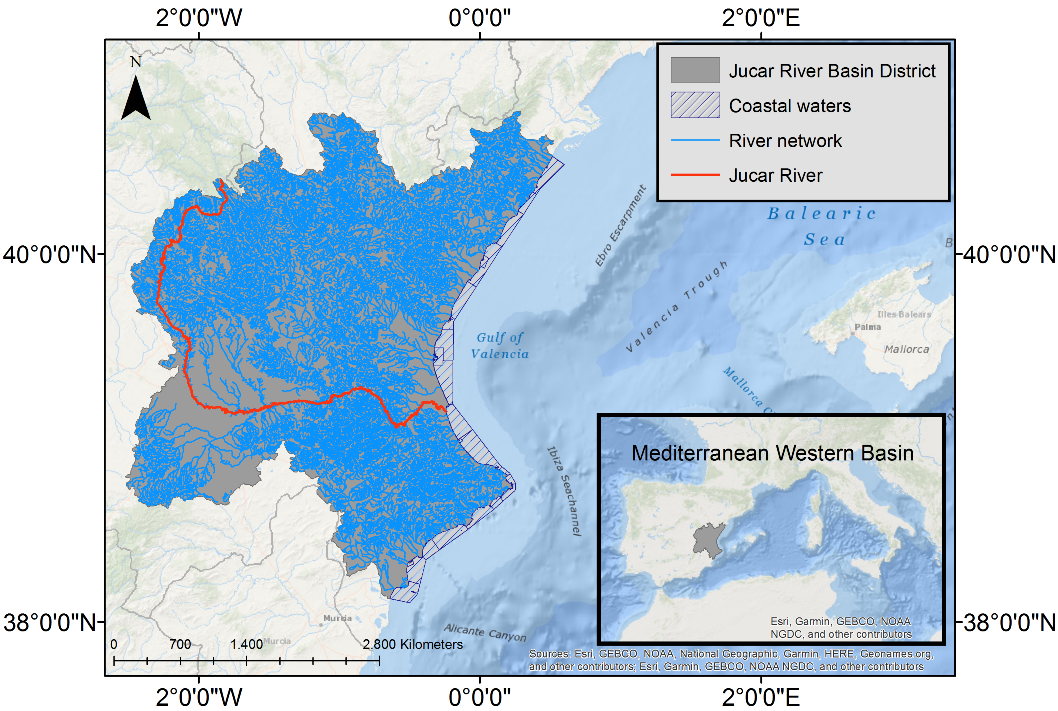

Figure 1.4: The Jucar River Basin District

Geomorphology

The JRBD is a mountainous inland region with a coastal area consisting of plains. The system of mountain ranges of greatest importance is the Iberian System, where the highest point above sea level of the basin (Peñarroya, 2.024m) is located. The Iberian System acts as a barrier to marine fronts, forcing the moisture-laden clouds to rise to higher atmospheric layers, favouring precipitation events in these mountain areas. Turia and Jucar rivers, the main rivers of the basin, originate in the Montes

Universales, a mountain range located in the south-western end of the Iberian System. Likewise, the source of the Mijar river is located in Sierra de Gúdar, south-eastern part of the Iberian System. These three rivers together provide about one third of the surface runoff flowing over the basin. The channels that constitute the main river network have a typical Mediterranean regime, characterized by drier periods in summer and an increase in river flows in autumn (Jucar Hydrographic Confederation, 2010, 2014).

The coastal area of the JRBD is a Neogene alluvial plain, where the nutrient-rich soil is responsible for most of the agricultural production of the irrigated land. The formation of lagoons and marshes are considerably vast and numerous in the JRBD, and are generally defined as extensive floodplains fed mainly by groundwater. The most relevant of these wetlands is the so called L'Albufera de Valencia, which consists of approximately 21,120 hectares including not only the lake but also the surrounding areas composed of large rice tracts and a dune line that protects it from the Mediterranean Sea (Jucar Hydrographic Confederation, 2014).

The predominant rocks are calcarenite and marl, although there are some proportions of limestone and alluvial material too. The latter is found primarily in the final stretches of the main rivers, and is constituted by solid river inputs that after reaching the coast are quickly dispersed by ocean currents. Terrestrial ecosystems bring sedimentary materials to the nearshore marine environments (Jucar Hydrographic Confederation, 2014), while most of the surface of the river basin is covered by very permeable materials that allow infiltration from surface water to groundwater (Jucar Hydrographic Confederation, 2010).

Climate

The climate in the JRBD is considered to be a typical Mediterranean climate, with warm summers and mild winters. Average annual temperatures range from 14ºC to 16.5ºC, with the highest temperatures recorded during the dry season (July and

August). The average annual precipitation is about 500 mm, but there is a large spatial variation from 300 mm in the southern regions to more than 750 mm in other regions. Moreover, during October and November rainfall events of high intensity and short duration may occur, a weather phenomenon locally known as "gota fría" (cold drop) (Jucar Hydrographic Confederation, 2014).

Coastal waters

All coastal waters in the JRBD belong to the Mediterranean ecoregion, with average salinities fluctuating between 30 and 40 kg/m^3. Most of Jucar's coastal waters are shallow (<30m), to a less extent intermediate (30-50m), and sometimes deeper than 50m but never reach 100m (Jucar Hydrographic Confederation, 2004).

Water bodies need to be differentiated according to types for the implementation of the WFD. The Med-GIG intercalibration group (European Commission, 2013) has defined five types of coastal waters for the Mediterranean Sea (European Commission, 2013):

- Type I : highly influenced by freshwater input, salinity <34.5 kg/m^3
- Type II-A : moderately influenced by freshwater inputs (continent influence), salinity between 34.5 and 37.5 kg/m^3
- Type III-W : continental coast, not influenced by freshwater input (Western Basin), salinity >37.5 kg/m^3
- Type III-E : not influenced by freshwater input (Western Basin), salinity >37.5 kg/m^3
- Island-W : island coast (Western Basin), all ranges of salinity

In the JRBD we find two of these water types: type II-A North from Cabo de San Antonio, and type III-W South from Cabo de San Antonio (Jucar Hydrographic Confederation, 2014).

In addition to the types defined by the Med-GIG, the Jucar river basin management plan defines further ecotypes, taking into account water depth (shallow or deep) and substratum (rocky or sandy). Consequently, five ecotypes have been defined for natural coastal waters, and one additional ecotype corresponds to heavily modified coastal waters (Table 1.2). As defined in the Jucar river basin management plan, 22 water bodies have been identified as coastal water bodies, among which 6 have been defined as heavily modified due to the presence of a harbour (Figure 1.5).

Type	Ecotype	Description	Water bodies
II-A	01	Mediterranean coastal waters moderately influenced by freshwater inputs, sandy shallow	C001,C003,C004 C005,C007,C008 C009,C010
II-A	02	Mediterranean coastal waters moderately influenced by freshwater inputs, rocky shallow	C002
III-W	05	Mediterranean coastal waters not influenced by freshwater inputs, sandy shallow	C016
III-W	06	Mediterranean coastal waters not influenced by freshwater inputs, mixed shallow	C015,C017
III-W	08	Mediterranean coastal waters not influenced by freshwater inputs, rocky deep	C011,C012 C013,C014

Table 1.2: Types and ecotypes of coastal waters in the Jucar River Basin District. Source: (Jucar Hydrographic Confederation, 2014)

Anthropogenic pressures

The permanent population within the JRBD is about 5,178,000 inhabitants (year 2012), with a density of 121 people/km^2 (Jucar Hydrographic Confederation, 2014), and with approximately 80% of the population living in the coastline (Jucar Hydrographic Confederation, 2010). The total water demand of the JRBD in 2012 was 3,232.92 hm^3, being agriculture and livestock the main water demands, constituting almost 80% of the total water use. The estimated pollution from point sources are originated from urban and agricultural activities, as well as from other economic activities such as mining, while diffuse pollution are considered to come mainly from

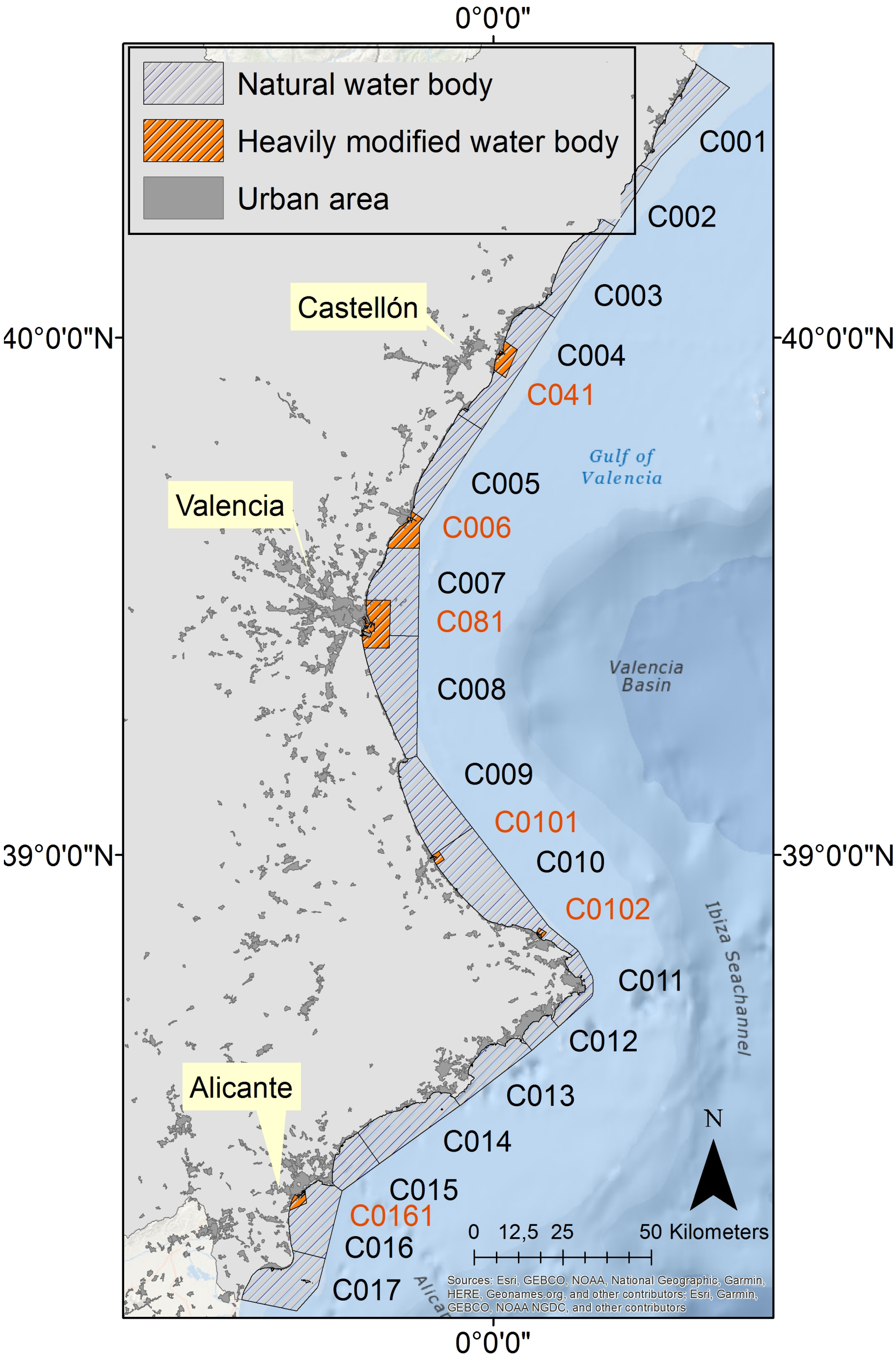

Figure 1.5: Coastal water bodies of the Jucar River Basin District

agriculture and livestock. The Spanish Ministry of the Environment established reference conditions for nutrient concentrations for each water body type based on expert judgement (Table 1.3).

Ecotype	Ammonium (mgN/L)	Nitrite (mgN/L)	Nitrate (mgN/L)
01	0.0644	0.0129	0.4900
02	0.0644	0.0129	0.4900
05	0.0644	0.0129	0.1022
06	0.0644	0.0129	0.1022
08	NA	NA	NA

Table 1.3: Nutrient reference conditions for coastal water bodies of the Jucar River Basin District. NA: Not Available. Source: Spanish Ministry of Environment (2015)

As part of the fullfilment of the WFD, the Valencial government registers all industrial discharges (Table 1.4), as well as urban wastewater which are all discharged through submarine outfalls (Table 1.5) to the coastal waters of the JRBD.

Company	Water Body	V (m^3/yr)	Total N (mg/L)
B.P. oil	C041	1,828,754	51.55
Iberdrola S.A.	C041	69,183	20.22
UBE Chemical Europa	C041	2,421,228	35.53
Marina Mediterranea S.L.	C005	5,040,920	0.5
Fertiberia S.L.	C006	24,559	719
Arcelormital S.L.	C006	3,165,62	30.26
Gas Natural S.A.	C006	9,859,154	1.11
Fertiberia S.L.-refrigeration	C006	46,559,237	0.044
Alevines del Mediterraneo	C006	19789	0.5
Urbamar	C081	53,259	4.9
Regrescos Iberia S.L.	C010	229,175	22.4

Table 1.4: Industrial discharges into the coastal waters of the Jucar river basin district, volumes and nitrogen concentrations. Source: Valencian government.

WWTP	Water body	Volume (m^3/yr)	Total N (mg/L)
Vinaròs	C001	18,471,49	17.56
Benicarló	C001	3,831,444	48.20
Peñíscola	C001	3,657,385	25.09
Alcalá de Xivert	C002	258,500	42.69
Torreblanca	C003	656,153	12.20
Oropesa	C003	3,059,547	5.63
Benicàssim	C004	1,896,719	17.77
Castellón	C0041	13,184,825	49.09
Burriana	C004	4,298,361	18.93
Canet	C005	1,246,475	9.41
l'Horta Nord	C007	3,958,224	45.79
Vera	C0081	69,617,761	27.93
Pinedo	C0081	40,397,176	22.46
Cullera	C009	460,138	3.40
Gandia	C0101	11,916,007	31.73
Oliva	C010	1,153,865	11.68
Denia	C010	6,007,226	8.76
Xàbia	C011	1,510,369	10.51
Teulada	C012	382,680	50.65
Calpe	C013	1,991,351	8.54
Benidorm	C016	4,585,562	29.01
Alicante	C0161	10,875,207	40.64

Table 1.5: Wastewater treatment plants discharging into the coastal waters of the Jucar river basin district, volumes and total nitrogen concentrations. Source: Valencian government.

1.5 The Gulf of Mexico

1.5.1 Overall description

The Gulf of Mexico (GoM) is a marginal sea of the Atlantic Ocean delimited by the United States (US) in the North, Mexico in the South and Cuba in the East (Figure 1.6). The extension of the shoreline is of approximately 6,077 km, and encloses an area of about 1.5 million km^2 (Mendelssohn et al., 2017), contains 2.5 million km^3 of water (UNIDO, 2011) and has an average depth of 1,615m (Mendelssohn et al., 2017). The Caribbean waters enter the GoM through the Yucatan channel and leave through the strait of Florida, constituting the Loop Current (Delgado et al., 2019).

In the Northern GoM, the average sea-surface summer temperature is around 29°C, while winter temperatures range from 14 to 24°C (Mendelssohn et al., 2017). Due to its enclosure, the GoM has small tidal ranges (UNIDO, 2011).

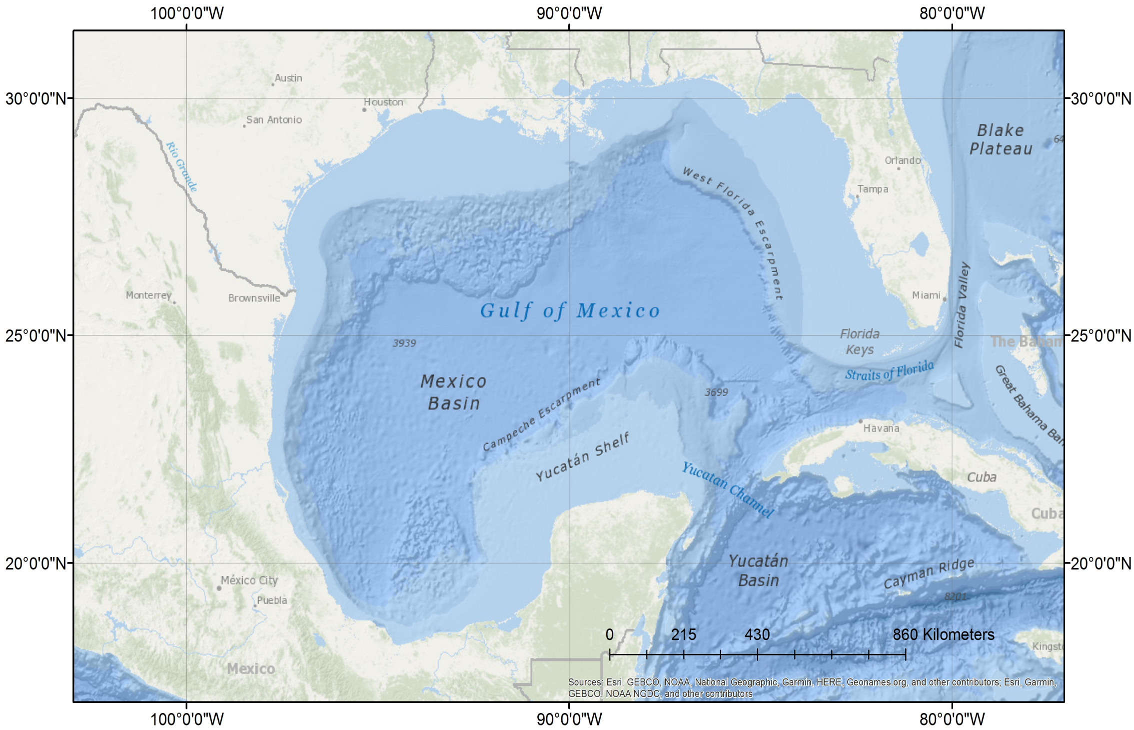

Figure 1.6: The Gulf of Mexico

The GoM's climatology ranges from semi-tropical to tropical (Yáñez-Arancibia, Day, 2004). As a consequence, it is an important global reservoir of biodiversity, with high biomass of fish, sea birds and marine mammals as well as diverse coastal ecosystems such as coral reefs or mangroves (Mendelssohn et al., 2017). Conditions range from eutrophic in coastal waters to oligotrophic in the deeper ocean (UNIDO, 2011). One of the major sources of nutrients to the euphotic zone is the upwelling along the edge of the Loop Current and its associated rings and eddies (Delgado et al., 2019), which increase the annual primary production by about 2 to 3 fold (UNIDO, 2011). Large rivers such as the Mississippi in the north and the Usumacinta-Grijalva in the south, deliver high quantities of nutrients to coastal waters. Nitrogen is believed to limit primary production in the GoM (Turner, Rabalais, 2013).

1.5.2 Nitrogen pollution in the Gulf of Mexico

Sand dunes, estuaries, marshes, sea grasses, coral reefs, mangroves and other coastal habitats are being destroyed by urban growth (Martínez et al., 2014). Wetlands have been cleared for agriculture or urban development, and the local habitats are detroyed by changes in salinity derived from water intrusion (Global Environmental Facility, 2014). This loss of wetlands also increases erosion by waves and tidal currents and is exacerbated by sea level rise (Martínez et al., 2014). Human alterations at large and small scales have led to a system on the verge of collapse.

The GoM is exploited for many economic activities such as fishing, oil drilling or tourism. As a consequence, the whole ecosystem is at risk due to high levels of pollution, habitat destruction and nutrient enrichment (Global Environmental Facility, 2014). The main sources of pollution are the agro-industry, cattle transformation, oil extraction and textile industries (Global Environmental Facility, 2014). Oil production is one of the most important economic activities in the GoM, both in the U.S. and Mexico. In April 2010, an explosion on the Deepwater Horizon oil drilling platform released almost 4.9 million barrels of oil into the GoM, and the presence of oil was documented in more than 1,530km of shoreline (NOAA, 2011).

The region of the Mississippi River outflow has the highest measured rates of primary production. Each summer, widespread areas on the northern continental shelf are affected by severe and persistent hypoxia, kown as a dead zone, which often exceeds 20,000 km^2 in mid-summer (Del Giudice et al., 2019). Agricultural runoff has been identified as the main driver of nutrient pollution, which enhances high phytoplankton concentrations in coastal waters, hypoxia, acidification and harmful algal blooms (Van Meter et al., 2017). In a near future, climate change is expected to exacerbate these impacts (Rabalais et al., 2009). In recent years, Mexican scientists have detected a similar oxygen-depletion zone in the Southern GoM (Global

Environmental Facility, 2014).

Large quantities of urban wastewater are discharged daily to the coastal waters of the GoM. While the U.S. treats 100% of the wastewater discharged into the GoM, Mexico only treats around half of the wastewater (Global Environmental Facility, 2014). These discharges promote an increase in nitrogen concentrations, deriving in eutrophication and ecosystem deterioration (Rivera-Guzmán et al., 2014).

1.5.3 Legal framework and management

In the Northern GoM, several departments and agencies of the U.S. federal government regulate pollution of natural waters. The U.S. Environmental Protection Agency (EPA) has a special program to protect the GoM, established in 1988, by which the Action Plan for reducing, mitigating and controlling hypoxia in the Northern GoM was approved (Heileman, Rabalais, 2009). Additionally, the EPA's Environmental Monitoring and Assessment Program monitors and assesses the status and trends of national ecological resources for nearshore and estuarine waters, while the National Estuary Program monitors and improves the quality of estuaries (UNIDO, 2011). On the other hand, the National Ocean and Atmospheric Administration (NOAA), through the National Marine Fisheries Service, surveys fishery resources and water quality in the GoM. NOAA's National Status and Trends Program monitors contaminants and other physicochemical properties in estuarine and coastal waters of the U.S. (UNIDO, 2011). Additionally, the Clean Water Act which was first enacted in 1948 and amended since then, regulates the discharges of pollutants into the waters and establishes quality standards (U.S. Government, 2002).

In Mexico, the National Law of water regulates the exploitation, distribution and control of water as well as water quantity and quality to achieve a sustainable development (Congreso de los Estados Unidos Mexicanos, 1992). The Official Mexican Standard NOM-001-Semarnat-1996 establishes the contaminants' limits in wastewater discharges into the environment. However, nitrogen discharges to natural water bodies are not well controlled, and no data exists on direct inputs from urban or industrial sources. On the other hand, the Mexican National Commission of Water (CONAGUA) through its water quality monitoring network analyzes several water quality parameters in many monitoring stations along natural waters, including coastal waters, such as biological oxygen demand (BOD), chemical oxygen demand (COD), dissolve oxygen or nutrient concentrations (CONAGUA, 2018a). Other laws such as the National policy of seas and coasts of Mexico and the Mexican law NMX-AA-120-SCFI-2016 protect the coastal ecosystems from pollution and degradation.

Several international programs regulate the collaboration for the protection of the Gulf of Mexico: the Gulf of Mexico Alliance, the Gulf of Mexico Coastal Ocean Observing System, the Gulf of Mexico University Research Collaborative, and, especially, the Gulf of Mexico Large Marine Ecosystem (GoM LME) project (Álvarez Torres et al., 2017). This project started in 2009 as a long-term partnership between the U.S. and Mexico to protect and restore the Gulf of Mexico with an integrated approach. Trough the Transboundary Diagnosis Analysis (TDA) and the subsequent Strategic Action Plan (SAP) the LME approach seeks to accomplish regional integrated management and enables a paradigm shift to an ecosystem-based approach (UNIDO, 2011). Cuba did not have much interaction in the last years but is expected to increase the collaboration in the coming years (Álvarez Torres et al., 2017).

Both the U.S. and Mexico depend economically on the GoM. However, a deficient management such as overfishing, overcapitalization of environmental resources or recreational harvesting has led to the deterioration of the GoM. Additionally, a poor knowledge exchange between these two countries leads to uniformed decision-making (Global Environmental Facility, 2014).

1.5.4 The Central Gulf Hydrological Region

The Central Gulf Hydrological Region (CGHR) (Figure 1.7) includes territories of four states: Veracruz (54.7%), Oaxaca (30.8%), Puebla (13.4%) and Hidalgo (1.1%) (IMTA, 2013). It covers 102, 354 km^2 (CONAGUA, 2015a) of land and 538km of coastline which fully belongs to the state of Veracruz.

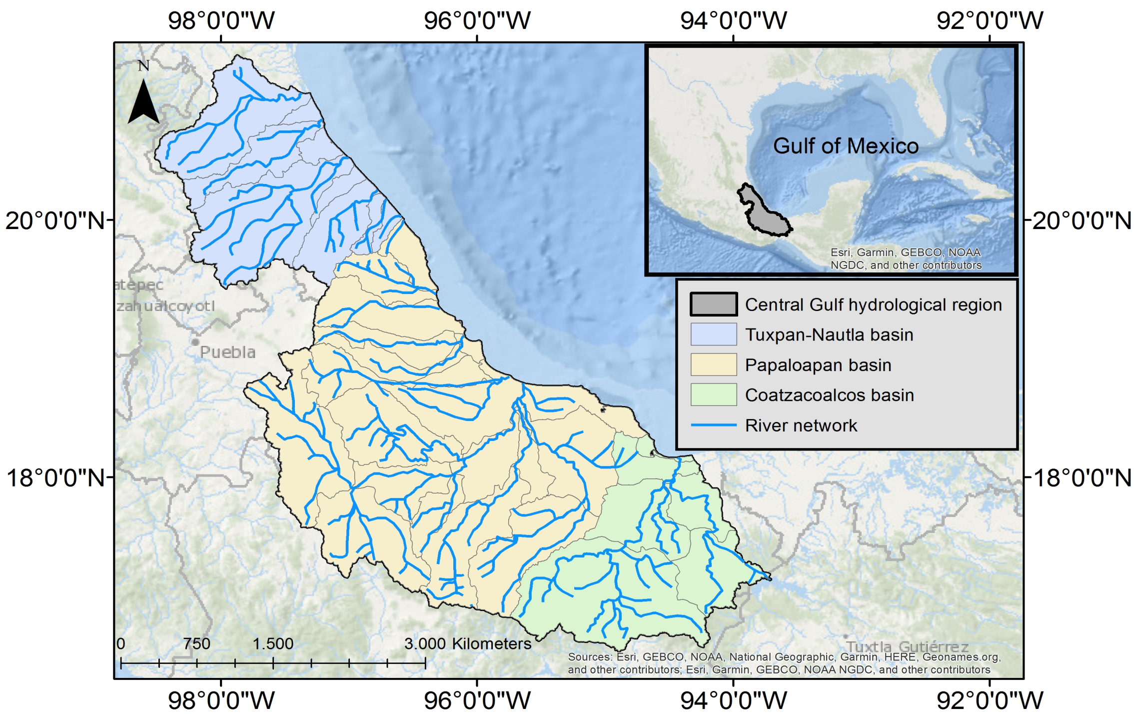

Figure 1.7: The Central Gulf Hydrological Region

Geomorphology

The CGHR consists of a mountainous inland region with a plain coastal area known as the Gulf coastal plain. The mountain range of greatest importance is the Sierra Madre Oriental, which has a rugged topography with frequent valleys, canyons and ravines (IMTA, 2013). Pico de Orizaba, also known as Citlaltepetl in nahuatl, is the highest peak of the CGHR, which rises 5,636 m above sea level. This active volcano is also the highest mountain in Mexico and the third in North America. Its peak is covered in snow all year round, and is home to the largest glacier in Mexico (Viola et al., 2019).

The Veracruz moist forests ecoregion extends over the northern coast of the CGHR, and encompasses lowlands of the Sierra Madre Oriental. It is composed of sedimentary rocks from the Cretaceous period and soils rich in organic matter (Mendelssohn et al., 2017). Numerous rivers drain geologic deposits to coastal salt-water lagoons and Gulf beaches (Mendelssohn et al., 2017), where coastal sand dunes are common (Moreno-Casasola, Espejel, 1986). On the other hand, the Veracruz dry forests ecoregion is located in central Veracruz, surrounded by tropical forests. In this ecoregion which is considerably humid, the soil is calcareous derived from sedimentary rocks (Mendelssohn et al., 2017). The Tuxtla rainforest is located in the south of the CGHR, characterized by volcanic coastal mountains and an important biodiversity. Unfortunately, land clearing for agriculture and livestock ranging has led to the destruction of a significant extension of the rainforest (Yáñez-Arancibia, Day, 2004).

The delimitation of the CGHR has political and administrative purposes, but it tends to follow the hidrological limits. Three sub-hidrological regions make up the CGHR: Tuxpan-Nautla, Papaloapan and Coatzacoalcos (IMTA, 2013).

The region of the Tuxpan-Nautla rivers, in addition to the secondary channels and lagoon-estuarine systems associated with this region, is characterized by presenting the main geomorphological expressions of the coast, such as the dunes, islands, coral reefs or lagoon-estuarine systems. It is the hydrological region with the highest extension of mangroves, i.e. 215.44 km^2 of mangrove area. The annual river discharge is about 14,193 million m^3 (Pereyra Díaz et al., 2010).

The river system of Papaloapan is composed of the Papaloapan river basin and the Actopan, La Antigua and Jamapa rivers as secondary basins. The annual discharge is 44,829 millon m^3 of water and the mangrove extension is 169.47 km^2. Its main estuarine ecosystem is the Alvarado lagoon, which corresponds to the larger coastal flood surface (Pereyra Díaz et al., 2010).

The river system of Coatzacoalcos has an annual discharge of 32,941 millon m^3 and a mangrove extension of 46.59 km^2 (Pereyra Díaz et al., 2010).

Climate

The low elevation and the wet winds from the Gulf of Mexico, together with the location within the intertropical zone, result in almost 65% of the CGHR having a warm weather, with mean annual temperatures of 24-26°C. This weather is observed in the Veracruzan coastal plain, as well as in the northern region (IMTA, 2013). In the mountain range of Sierra Madre Oriental, the climate varies from semi-arid to temperate, while in the peaks of Pico de Orizaba and Cofre de Perote (4,200 m) the climate becomes cold (IMTA, 2013). The mean annual precipitation is 1,590 mm, with a spatial range of 407 mm to 4,380 mm (IMTA, 2013).

Anthropogenic pressures

The population living within the region is of approximately 10.5 million people (CONAGUA, 2018b), of which 57% live in urban areas and 43% in rural areas (IMTA, 2013). The population density is 96 inhabitants per km^2, with 10 cities of more than 100,000 inhabitants (IMTA, 2013).

84.3% of the Veracruzan urban area has a sewarage service (2015) (CONAGUA, 2015b), but Domínguez Serrano (2010) alerts of the considerably lower coverage in rural areas (about 58.6% in the whole country). 51% of the Veracruzan population has access to treatment of wastewater, of which 36% undergoes a biological treatment with biological filters and 47% with activated sludge (CONAGUA, 2015b). As a consequence, there are 325 point of discharges in Veracruz which do not undergo any treatment.

In the Central Gulf hydrological region, there are 151 WWTPs with a mean flow of 5.11 m^3/s (CONAGUA, 2015b). Some WWTPs directly discharge to coastal water bodies (Table 1.6) amongst which the North Beach plant of Veracruz stands out for its capacity. The wastewater is discharged directly to the sea with no submarine outfall, which increases the pollution of the nearby coastal waters and beaches. In addition to these WWTPs, many others discharge into rivers which end up in the sea. Unfortunately, there is no record of the amount of nitrogen discharged to coastal waters.

WWTP	**City**	**Volume (m^3/s)**
U.H. Costa de Oro	Boca del Río	4,815,547
Tuxpan	Tuxpan	5,518,800
Torres Arrecifes	Veracruz	157,680
North Beach	Veracruz	50,457,600

Table 1.6: Watewater treatment plants discharging into the coastal waters of the Central Gulf Hydrological Region. Source: (CONAGUA, 2015b)

Additionally, agriculture and livestock are an important source of nitrogen pollution in the area. The use of fertilizers is not well regulated in Veracruz (SAGARPA, 2009), which is one of the states which uses more fertilizer per cultivated area (SAGARPA, 2009). The government stimulated the use of agrochemicals through the Agriculture Development Program in its agroincentives section. However, farmers lack information regarding the use and application of fertilizers (Anguiano-Cuevas et al., 2015), and consequently around 20-40% of N is lost as ammonium through continental runoff (Anguiano-Cuevas et al., 2015).

CHAPTER 2

The research project

Overall description of the research hypothesis, objectives and structure.

2.1 Problem statement

Nitrogen is one of the most important elements for life on Earth. The biogeochemical nitrogen cycle regulates many key ecological processes such as primary production (Gruber, Galloway, 2008). In the ocean, nitrogen pollution is one of the leading causes of ecosystem degradation (Sinha et al., 2019), and the marine nitrogen processes are altered by anthopogenic activities through many processes such as wastewater discharges (McLaughlin et al., 2017), climate change (Kim, 2016) or through the destruction of marine ecosystem (Baker et al., 2013), as discribed in the introduction chapter. However, there is still a lack of research on how the anthropogenic pressures alter the nitrogen cycle. Some researchers investigated the alteration of processes such as nitrification or denitrification (Voss et al., 2013), or the deterioration of coastal ecosystems such as coral reefs due to nitrogen pollution (Baker et al., 2013; Capone et al., 2008). But the overall understanding of the alteration of the N cycle in coastal waters and its consequences is still very limited. The processes by which human activities modify the N cycle have to be studied in different geographical locations in order to propose prevention and recovery measures, as the consequences may be disastrous for both the environment and humans (see section 1.3). In coastal waters the anthropogenic pressures are especially relevant due to the high population living along the coast and due to the influence of continental water inputs in the coastal biogeochemistry.

As such, in this thesis the processes and activities by which humankind modifies the N cycle in coastal waters are evaluated through the analysis of two study areas with different characteristics: the Mediterranean Sea and the Gulf of Mexico. In the Mediterranean Sea, nitrogen pollution is a growing environmental problem mainly derived from the urbanization along the coast (Stamou, Kamizoulis, 2008). Although many laws regulate nitrogen emissions to coastal waters as developed in section 1.4.3, the alteration of the nitrogen cycle is not yet well understood. On the contrary, in the Southern Gulf of Mexico nitrogen pollution is less regulated and the disposal of wastewater is not well controlled (see section 1.5.3). Additionally, the location of the CGHR in a tropical location entails a significant diversity of coastal ecosystems in comparison to the Mediterran Sea. Therefore, the use of the mentioned case studies allows a diversification of the studies of nitrogen pollution and processes.

2.2 Aims of the research project

The main objective of this doctoral thesis is to evaluate the pressures and impacts of anthropogenic activities on the nitrogen processes in coastal waters of the Northwestern Mediterranean Sea and the Southern Gulf of Mexico to estimate the potential consequences for coastal ecosystems. The main objective is divided in four particular objectives:

1. Estimate how coastal anthropogenic activities modify nitrogen dynamics in coastal waters of the Northwestern Mediterranean Sea and the Southern Gulf of Mexico in order to estimate the impacts to coastal ecosystems and provide a basis for coastal management

2. Evaluate how meteorological variables affect dissolved inorganic nitrogen concentrations in coastal waters of the Northwestern Mediterranean Sea and processes such as nitrification in order to estimate the potential impacts of climate change

3. Estimate the differences in nitrogen pollution between the two study areas based on geomorphological, ecological and socio-economical characteristics

4. Develop new tools to evaluate the alteration of the N cycle in coastal waters

2.3 Research hypothesis

- Anthropogenic activities alter the nitrogen cycle in coastal waters by modifying nitrogen species concentrations and key processes such as nitrification.
- Meteorological variables play a key role in nitrogen species concentrations and processes in coastal waters, which entails a significant impact of climate change on the N cycle.
- Nitrogen processes are modified by human activities in both the Mediterranean Sea and the Gulf of Mexico but geomorphological, ecological and socio-economical characteristics play a significant role on the pressures and impacts of nitrogen pollution.
- New tools can be developed to evaluate the alteration of the N cycle in coastal waters by using mechanistic models, artificial neural networks and grey systems theory.

2.4 Thesis structure

This thesis is presented with the structure of a collection of articles, i.e. as a thesis of published works. A total of four research articles were published in journals indexed in both the SCImago Journal Rank (SCI) and the Journal Citations Report (JCR). The first and the second article correspond to research carried out in the Mediterranean Sea in Spain while the third and the fourth article correspond to research from the Gulf of Mexico in Mexico. The research hypothesis are tested thoughout the articles and the research questions are answered in the final discussion by interpreting the results of the four articles altogether.

The first article is an evaluation of how anthropogenic pressures alter the process of nitrification in coastal waters of the Jucar river basin district, in Spain. This article was written in collaboration between the doctoral candidate, the two thesis directors and two researchers of the Water and Environment Engineering Institute (IIAMA) of the Polytechnic University of Valencia: Remedios Martínez-Guijarro and María Pachés. The PhD candidate is the leading author of the publication and developed the conceptualization and the methodological framework, performed the data curation and analysis and wrote the manuscript.

Then, a second article evaluates the impact of climate change on the trends of dissolved inorganic nitrogen concentrations in a coastal region of the JRBD. The manuscript was prepared in collaboration between the doctoral candidate, the two thesis directors and a professor of the Polytechnic University of Valencia: Rafael García Bartual. The PhD candidate is the leading author of the publication, contributed to the conceptualization, the methodology, the data curation and analysis and wrote about two thirds of the original draft.

The third article presents a new methodology based on grey clustering which allows the establishment of nitrogen management strategies in areas where only a limited amount of data regarding coastal water pollution is available. This method was applied to the Southern Gulf of Mexico, where very limited data about nitrogen pollution was available. This article was written in collaboration between the doctoral candidate, the two thesis directors and a post-doctoral researcher of the École de Technologie Supérieure in Montreal: Sara Patricia Ibarra-Zavaleta. The PhD candidate is the leading author of the publication, developed the conceptualization and the methodology, performed the data anlysis and curation and wrote the article.

The fourth and last article is an evaluation of nitrogen pollution in the area identified in the third article as the most polluted by nitrogen concentrations. This corresponds to a mangrove area of the Southern Gulf of Mexico where the pollution has had several environmental consequences such as the proliferation of the invasive water hyacinths. The publication was developed and written by the PhD candidate, in collaboration with the two thesis directors who supervised and guided the research.

Finally, a general discussion is carried out which discusses the overall results of the four articles as part of the same research project which is the doctoral thesis. The research question is answered, and the hypothesis and objectives are discussed based on the obtained results. Also, general conclusions are made which sumarize the results of the four articles as part of the same research.

2.5 Significance of the research

This research thesis establishes new perspectives on the mechanisms by which humans modify nitrogen processes in the coastal waters of the Mediterranean Sea and the Gulf of Mexico. Through the evaluation of samples collected in two inshore coastal regions (<200m), an estimation of the impacts of both nitrogen pollution and climate change is carried out. The results and discussion presented herein entail new inshights into the anthropogenic alteration of the N cycle in coastal waters and the potential consequences. As nitrogen is one of the main elements driving primary production in coastal ecosystems, the understanding of its processes and the modifications caused by human activities allows a better understanding of the prevention and recovery measures to be addopted. Moreover, the tools developed throughout the research for the evaluation of nitrogen alteration also constitute an important contribution which could be applied to other study areas.

2.6 Methodological framework

For each of the four research articles a different methodology was used to deal with the requirements of the different objectives. The tools developed throughout the articles are also an important contribution of this PhD thesis.

The first publication uses a simple biogeochemical model to identify the anthropogenic impact on nitrification dynamics. Based on the principle of conservation of mass nitrite dynamics are modeled through a mass balance in zero dimensions.

The second article uses models based on artifitial neural networks and climate change projections from regional models in order to estimate the future trends of dissolved inorganic nitrogen concentrations in coastal waters of the Jucar River Basin District.

The third article develops a new methodology based on grey clustering and entropy weighting to derive useful information for nitrogen pollution management under limited data availability. The grey systems theory is used to propose cientifically sound management practices for coastal areas where only a small amount of data exists.

The fourth and last publication uses statistical technics such as cluster analysis and the Mann-Kendall test to carry out a spatiotemporal analysis of nitrogen pollution in a mangrove area.

Each of the methodologies are developed throughout the publications.

CHAPTER 3

Anthropogenic impact on nitrification dynamics in coastal waters of the Mediterranean Sea

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Reference: Temino-Boes et al. (2019a)

3.1 Abstract

The anthropogenic alteration of the nitrogen cycle results in the modification of the whole food web. And yet, the impact caused on nitrogen dynamics in marine systems is still very uncertain. We propose a workflow to evaluate changes to coastal nitrification by modelling nitrite dynamics, the intermediary compound. Nitrite concentrations were estimated with a simple steady state nitrification model, which was calibrated in 9 NW Mediterranean coastal sites with different anthropogenic pressures, located within 250 km. The results obtained indicate that nitrite peaks are observed in winter and explained by nitrification response to temperature, but these dynamics are altered in impacted coastal waters. We found the second step of nitrification to be more sensitive to temperature, which entails a significant impact of climate change on the decoupling of the two steps of nitrification. The results could be extrapolated to numerous coastal regions of the Mediterranean Sea with similar characteristics.

3.2 Introduction

Rockström et al. (2009) established the alteration of the nitrogen (N) cycle as one of the three planetary processes, together with climate change and biodiversity loss, sufficiently altered by human activity as to potentially have disastrous consequences for humans. Some authors are concerned about nitrogen being "the next carbon" (Battye et al., 2017). Due to their vulnerability to anthropogenically driven change, coastal zones have been highly impacted (Arhonditsis et al., 2000; De Vittor et al., 2016; Smith et al., 2014). Population growth and related nutrient sources such as agriculture, wastewater, urban runoff, and fossil fuels have increased nutrient inputs to coastal waters to many times their natural levels (Bricker et al., 2008). As such, many researchers have evidenced the impact that human activities have caused to food webs or biogeochemical processes in many coastal systems (Borja et al., 2004; Lundberg et al., 2005; Wang et al., 1999). In the Mediterranean Sea, direct wastewater discharges account for a large amount of the total nitrogen input (Powley et al., 2016; Stamou, Kamizoulis, 2008). Nearshore coastal waters (0-200 m) are particularly vulnerable and need a special attention, as the nutrient gradient from land to ocean is considerably large in the Mediterranean Sea (Flo et al., 2011).

Nitrification plays a crucial role in marine primary production (Yool et al., 2007) and in the N cycle of coastal zones (Damashek et al., 2016; McLaughlin et al., 2017). This process alone does not change the total amount of nitrogen in an ecosystem, but it affects its speciation and fate: nitrate (the product of nitrification) serves as substrate for denitrification, which removes N from the system via N_2 gas (Carini et al., 2010). Nitrification is generally described as a two-step process occurring under aerobic conditions: oxidation of ammonium to nitrite and oxidation of nitrite to nitrate (Kim, 2016). It links reduced and oxidized forms of nitrogen. Although ammonium oxidation is considered the limiting step, both steps are expected to be tightly coupled. However, evidence of decoupling in coastal waters was observed especially at high temperatures (Beman et al., 2013; Heiss, Fulweiler, 2016), which leads to the accumulation of nitrite. As an intermediary compound in many key biological processes, nitrite dynamics have historically been used as an indicator of the balance between oxidative and reductive pathways in marine systems (Lomas, Lipschultz, 2006). Nitrite production processes in aerobic waters include the oxidation of ammonia and assimilatory nitrate reduction by phytoplankton and heterotrophic bacteria, while removal pathways for nitrite include oxidation by nitrite-oxidizing bacteria and phytoplankton uptake (Schaefer, Hollibaugh, 2017).

Increasing evidence indicates that many environmental factors such as pH, temperature or oxygen concentration affect nitrification processes (Damashek et al., 2016; Schaefer, Hollibaugh, 2017). However, when it comes to how humans alter inorganic nitrogen transformations in marine environments research is still very scarce. Kim (2016) summarized how climate change will alter marine N cycle and indicated the need for further research on marine inorganic N transformations, while

McLaughlin et al. (2017) and Bartl et al. (2018) studied the alteration of nitrification caused by wastewater discharges and pointed out the need for further research on anthropogenic nutrient effect on coastal biogeochemistry. Ocean acidification results in reduced nitrification rates (Beman et al., 2010; Huesemann et al., 2002; Kitidis et al., 2011) while other anthropogenic pressures such as N deposition (Kim, 2016) or wastewater effluents might increase nitrification (McLaughlin et al., 2017). Clearly, the overall anthropogenic effect on nitrification in coastal systems needs to be evaluated further. In the Mediterranean Sea, the urbanization on the littoral zone has severely impacted the natural balance of ecosystems (Lejeusne et al., 2010). Nitrification dynamics are altered in those areas with high anthropogenic pressure, leading to a change in nitrogen cycling along the year (Kapetanaki et al., 2015). The modification of such an important process in the N cycle may have consequences on phytoplankton abundance and diversity, with cascading effects on other organisms. The importance of nitrification in the N biogeochemistry in coastal waters has already been proved by many authors (Damashek et al., 2016; Heiss, Fulweiler, 2016; Huesemann et al., 2002), but the mechanisms by which anthropogenic activity alters nitrification in coastal waters need to be studied in more detail.

The aim of this study was to propose a simple workflow for the evaluation of nitrification alteration in coastal waters due to anthropogenic activity. Nitrite, as the intermediary compound in the two steps of nitrification, was used to study nitrification. We modelled nitrite dynamics in several coastal sites located within approximately 250 km of coast. All modelled water bodies have similar characteristics but different anthropogenic pressures, so that nitrification parameters could be related to anthropogenic pressure. This methodology is applicable to other coastal areas of the Mediterranean Sea, where nitrification is the main driver of nitrite dynamics (Bianchi et al., 1994).

3.3 Materials and Methods

3.3.1 Study area

The Jucar River Basin District (JRBD) lies in the Mediterranean coast of Spain, covering 42,735 km^2 with 574 km of coastline. The management plan defines 16 natural coastal water bodies. In this study we focused on 9 of them, which belong to the typology II-A (moderately influenced by freshwater inputs with salinity between 34.5 and 37.5 g.kg^{-1}). These water bodies (presented in Figure 1.4) have similar geomorphology, littoral transport, dominant winds, rainfall, area of fluvial basins, continental inputs and wet zones. C002 is the reference site for typology II-A with no relevant anthropogenic influence, as determined by Romero et al. (2013) and Pachés et al. (2012) who evaluated pressures and impacts according to annex V of the Water Framework Directive (WFD). Some coastal waters in the JRBD are considered under the WFD as heavily modified due to the presence of a harbor (Figure 3.1); these water bodies were not included in our study.

Hermosilla Gómez (2009) studied the influence of the sampling locations in the evaluation of the anthropogenic pressures and the ecological status of the coasts of Valencia. By means of statistical analysis, she determined that sampling sites should be located inshore (over the coast) and at the surface so that samples are taken from the area affected by anthropogenic eutrophication. Besides, the data and methods developed in Spain for the intercalibration exercise of the Mediterranean intercalibration group (MedGIG) within the WFD are most based on inshore sampling stations (MedGIG, 2009). Thus, in order to compare the results obtained in this study with previous ecological evaluations in the water bodies considered, inshore sampling was more convenient. 46 monitoring sites were distributed all along the coast, with 4 to 7 stations in each water body. Each month from August 2008 until January 2011, water samples were taken from beyond the wave breakpoint at a 10 cm depth. Temperature was measured in situ with a multiparametric probe YSI (6600 V2).

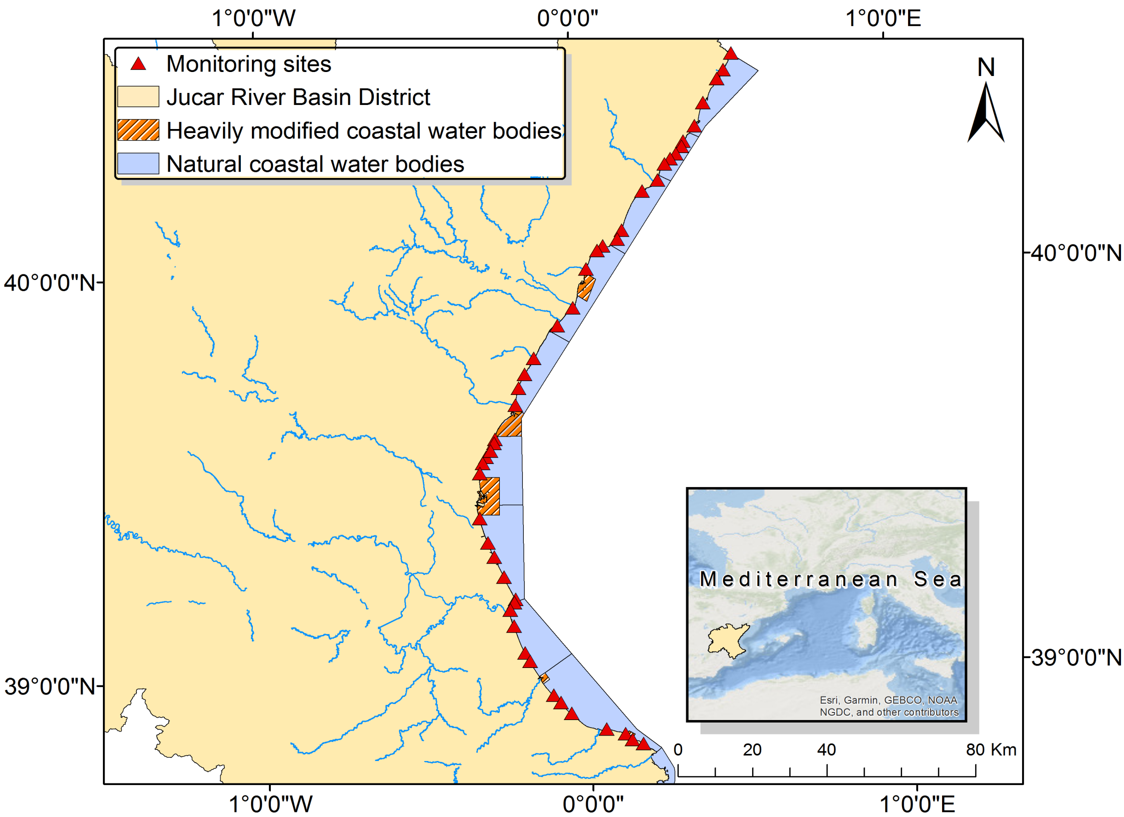

Figure 3.1: Jucar River Basin District: natural coastal water bodies of typology II-A, heavily modified coastal water bodies (which as a result of physical alterations by human activity is substantially changed in character) and monitoring sites.

Water samples were collected in plastic bottles, refrigerated, and carried to the laboratory within 12 hours. A Portasal 8410A salinometer was calibrated to determine salinity (I.A.P.S.O. Standard Seawater, Ocean Scientific International Ltd., K15 = 0.99986, S = 34.995‰). Samples were divided into several sets following the conservation procedures suggested by APHA (2005) and filtered through 0.45 m cellulose acetate membrane filters (Millipore HAWP). These membranes are stored at -20°C in order to break the cells for chlorophyll-a analysis.

For the determination of chlorophyll-a, the trichromatic method was used, based on visible spectroscopy APHA (2005). The filters are introduced in 6 ml of 90% acetone in water with 1% calcium carbonate. The optical density of the extract was determined at different wavelengths (630, 647 and 664 nm) to determine the pigment content, and at 750 nm to determine the optical density not due to chlorophyll-a. The equations proposed by Jeffrey and Humprey (1975) were used for concentration calculations. The detection limit was 0.2 $mgC.m^{-3}$ of chlorophyll-a.

Nutrients (ammonium, nitrite and nitrate) were analyzed with an Alliance Instruments Integral Futura air-segmented continuous-flow autoanalyzer, following the procedure described by Treguer, Le Corre (1975) and taking into account the remarks made by Kirkwood et al. (1991) and Parsons et al. (1984). The equipment optimization is carried out following Coakley (1981) theories. Ammonium and nitrite were analyzed with the filtered samples, right after filtration, while the samples kept for nitrate determination were frozen for a later analysis. Ammonium was measured based on Berthelot's reaction. Under alkaline conditions, ammonium reacts with the hypochlorite forming a monochloramine. This compound, in the presence of phenol and an excess of hypochlorite, forms indophenol blue. The nitroprusside ion catalyzes the reaction and trisodium citrate eliminates the interference of Ca and Mg (Solòrzano, 1969). Nitrite concentrations were determined with Shinn (1941) water analysis method, adapted for seawater by Bendschneider, Robinson (1952). This method is based on the reaction of nitrite ion with sulfanilamide in acidic conditions, producing a diazo compound that forms a pink complex with N-naphthylethylene diamine. For the determination of nitrate concentrations, this compound is reduced to nitrite by means of a Cu/Cd reducing column in basic conditions (pH = 8.5), following the method described by (Grasshoff, 1976). Subsequently, nitrite is analyzed by the procedure described above. High purity Merck reagents for analysis and ultra-pure water (Milli-Q 185) were used. The detection limits were $1.4x10^{-3}$ $mgN.L^{-1}$ for ammonium and nitrate and $1.4x10^{-4}$ $mgN.L^{-1}$ for nitrite.

3.3.2 Workflow

The proposed workflow is schematized in Figure 3.2 and explained in detail in next sections.

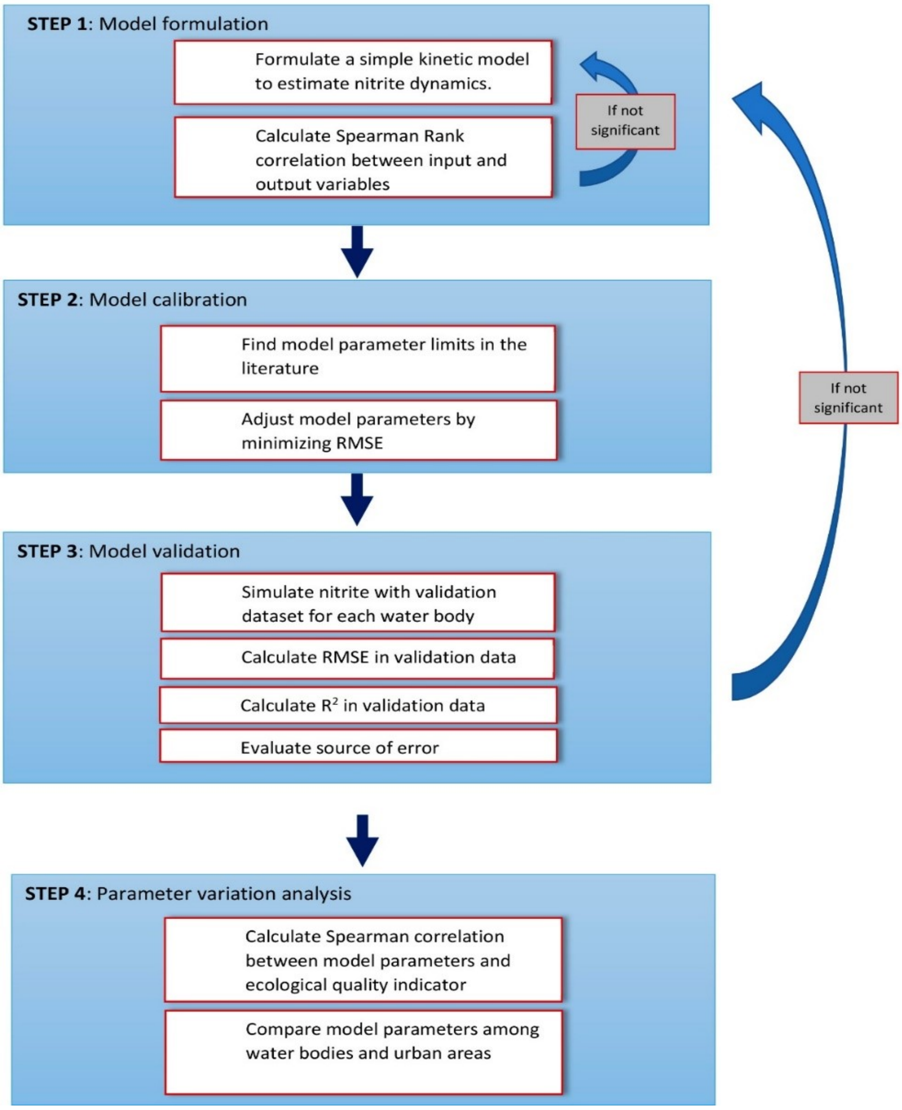

Figure 3.2: Descriptive diagram of the research workflow.

3.3.3 Model formulation

The equation solved is based on the principle of the conservation of mass. The main processes driving nitrite dynamics were studied from the literature and used for the development of the model, neglecting the less relevant processes. We applied a mass balance in zero dimensions in each water body which was considered as a control volume. As samples were taken at the surface, we considered appropriate to neglect the effect of the sediment. Simple and well-known principles can be used to build simple models which can give an overall understanding of nitrogen processes. When a basic understanding of the system is aimed and the requirement to the precision of estimated values is low, simple models perform better (Hojberg et al., 2007). Complex models require large amounts of data and such a model would not add value to our research purpose.

Nitrite production pathways in coastal waters include ammonia oxidation and assimilatory nitrate reduction by phytoplankton and heterotrophic bacteria, while removal pathways for nitrite include nitrite oxidation and phytoplankton uptake (Schaefer, Hollibaugh, 2017). Ammonium is the preferred form of nitrogen for phytoplankton uptake (Chau, Jin, 1998; Zouiten et al., 2013), so we considered direct nitrite uptake to be negligible. Additionally, the study area is characterized by low phytoplankton concentrations in natural conditions (Pachés et al., 2012). Thus, nitrite release by phytoplankton was also neglected. An analysis of the relationship between the model error and phytoplankton concentrations was carried out to confirm this assumption (see section 3.3.4). Bianchi et al. (1994) also determined that nitrite concentrations in the NW Mediterranean Sea are regulated by the two steps of nitrification. Therefore, we considered only nitrification processes to estimate nitrite: formed with ammonium oxidation (nitrification first step) and eliminated by nitrite oxidation (nitrification second step). Studies carried out in other coastal areas also pointed out the significant role of nitrification (Damashek et al., 2016; Schaefer, Hollibaugh, 2017).

At low nitrogen concentrations as those found in natural systems, the process of nitrification is generally represented by a first order kinetic reaction (Bowie et al., 1985). Previous studies typically considered only the temperature effect on nitrification. Some authors also introduced the effect of dissolved oxygen as a limiting factor (Chau, Jin, 1998; Umgiesser et al., 2003; Zouiten et al., 2013). Nonetheless, the samples used in this study, which were taken at the sea surface, had all high oxygen concentrations (averaged 8.3 ± 1.4 mgO.L^{-1} measured during campaigns). Consequently, we did not add oxygen limitation to our model. pH, which also affects nitrification rates (Park et al., 2007), was measured during the campaigns and variations were not relevant (averaged 8.14 ± 0.13).

Flo et al. (2011) showed that continental influence is the main driver of nutrient variability within 200 m of coast in the NW Mediterranean Sea. The water bodies considered in this study have a length of >13 km along the coast, and samples were taken at less than 50 m from the coastline. As such, the continental influence on nutrient concentrations is much larger than the effect of the dispersion along the coast. Additionally, as the two steps of nitrification are tightly coupled (Schaefer, Hollibaugh, 2017), nitrite is oxidized to nitrate almost as fast as it is created (see Table 3.1), whereas longitudinal mixing along >13 km is expected to be a much slower process (Stamou, Kamizoulis, 2008). Therefore, we decided not to consider dispersion with adjacent water bodies to simplify our model.

The main nitrogen sources to the JRBD coastal waters are agriculture and urban population (Romero et al., 2013), which means that most of the nitrogen inputs are in the form of ammonium or nitrate. Hence, we considered no relevant direct nitrite inputs. An analysis of the relationship between the model error and salinity was carried out to confirm this assumption (see section 3.3.4).
Equation 3.3.1 represents nitrite mass balance under these assumptions.

$$\frac{\partial[NO_2^-]}{\partial t} = k_1\theta_1^{T-20}[NH_4^+] - k_2\theta_2^{T-20}[NO_2^-] \quad (3.3.1)$$

Where, $[NO_2]$ is nitrite concentration ($mgN.L^{-1}$), $[NH_4^+]$ is ammonium concentration ($mgN.L^{-1}$), t is time (day), k_1 is ammonium oxidation rate at 20°C (day^{-1}), θ_1 is temperature coefficient for ammonium oxidation, k_2 is nitrite oxidation rate at 20°C (day^{-1}), θ_2 is temperature coefficient for nitrite oxidation, T is temperature (°C).

The steady state approach is very frequently used in water quality modelling (Chapra, 1997; Wang et al., 2013). This approach enables the calculation of the nitrite concentration each month, if the conditions found at the time of the sampling were maintained. Under this assumption the accumulation term was set to zero.

Nitrite concentrations can be estimated with the following equation, derived from Equation 3.3.1

$$[NO_2^-] = (\frac{k_1}{k_2})(\frac{\theta_1}{\theta_2})^{T-20}[NH_4^+] \tag{3.3.2}$$

k_1 and k_2 depend mathematically on each other (see Equation 3.3.2), making the separate calibration of both parameters unfeasible. The same applied to θ_1 and θ_2. We defined K and Θ as new parameters equivalent to the ratios $\frac{k_1}{k_2}$ and $\frac{\theta_1}{\theta_2}$ respectively:

$$[NO_2^-] = K\Theta^{T-20}[NH_4^+] \tag{3.3.3}$$

Thus, K represents the ratio of ammonium oxidation to nitrite oxidation, while Θ represents the ratio of ammonium to nitrite oxidation sensitivity to temperature.

Output sensitivity to input variables can be estimates with Spearman rank correlation coefficient in nonlinear but monotonic relationships (Pianosi et al., 2016). As such, the Spearman correlation coefficient was calculated between selected input (temperature and ammonium) and output variables to determine the relative importance in nitrite estimation. The calculation of this correlation confirms whether the selected input variables are relevant for the estimation of nitrite concentrations, or else the simplified model needs to be re-evaluated.

3.3.4 Model calibration and validation

We carried out a literature review to set parameter limits. The values found are presented in Table 3.1.

Parameter	Range	Units
k_1	0.05-0.5	d^{-1}
k_2	0.5-10	d^{-1}
θ_1	1.02-1.12	-
θ_2	1.02-1.12	-

Table 3.1: Bibliographical parameter values. References: (Bowie et al., 1985; Chau, Jin, 1998; Myszograj, 2015; Zouiten et al., 2013)

Mean monthly values for all variables were calculated for each water body from

August 2008 to January 2011. The dataset was divided in two sub-datasets; one was used as calibration data and the second as validation data. Odd monthly observations (1,3,4. . . ,29) of input and output variables were used for calibration whereas even observations (2,4,6,. . . ,30) were left for validation (see Figure 3.2). The parameters K and Θ were optimized to reproduce nitrite observed concentrations by minimizing the rooted mean squared error (RMSE) in calibration data. Then, the model was run with the validation dataset and nitrite estimations were compared to observations. The RMSE and the coefficient of determination (R^2) were calculated to estimate the goodness of fit.

Two of the neglected processes during the model formulation may be the main source of error to our model: phytoplankton release and continental inputs. To evaluate the source of error in the model, we calculated Spearman correlation between monthly error and phytoplankton and between monthly error and salinity in each water body.

3.3.5 Parameter variation analysis

Once the model was validated, the relationship between model parameter differences among water bodies and two physicochemical variables was evaluated to determine the source of spatial changes in nitrification dynamics. pH and dissolved oxygen were very similar in all water bodies as mentioned above and consequently not included in this evaluation. The two physical variables analyzed were temperature and salinity. The Spearman correlation coefficient between these two variables and calibrated model parameters was calculated to determine whether they may influence the studied nitrification parameter values.

Phytoplankton biomass is established as an indicator of the ecological status of coastal waters under the WFD. In the JRBD, Pachés et al. (2012) identified chlorophyll-a 50^{th} percentile to be the most appropriate statistical parameter to measure anthropogenic pressure, and Romero et al. (2013) related phytoplankton to anthropogenic pressures such as population density, agriculture and industry. As such, we used chlorophyll-a 50^{th} percentile as an indicator of the alteration provoked by human pressures. We calculated the Spearman correlation coefficient between model parameters and chlorophyll-a 50^{th} percentile to determine whether anthropogenic pressures may have altered nitrification parameters.

3.4 Results

3.4.1 Variable values

Ammonium, nitrite and nitrate concentrations in each water body are presented in Figure 3.3, as well as temperature, salinity and chlorophyll-a.

The highest N concentrations were found in C007, the water body located north

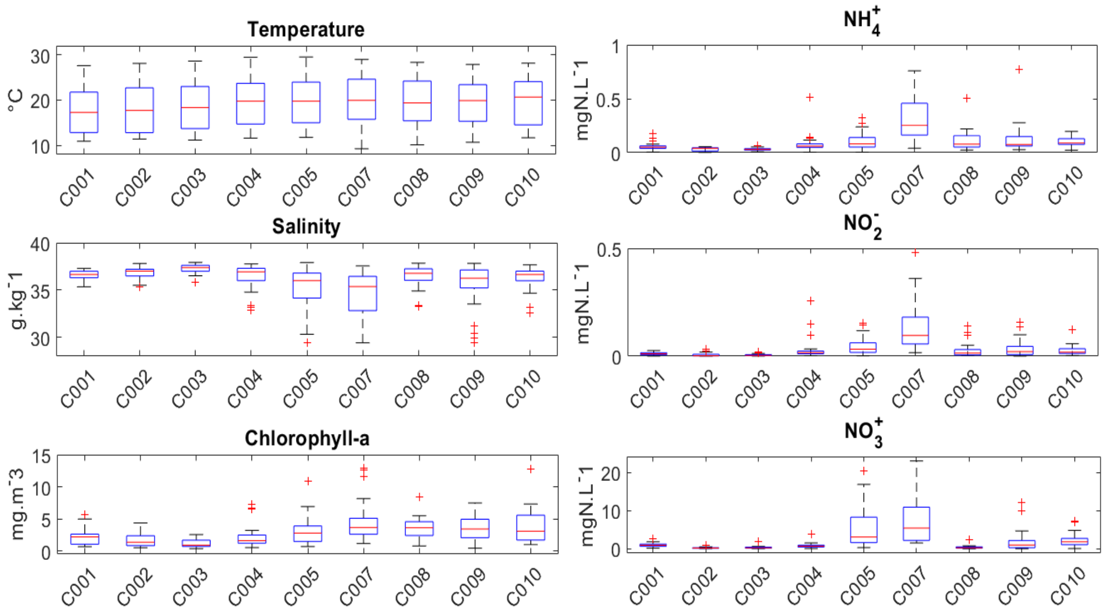

Figure 3.3: Boxplot of ammonium, nitrite and nitrate concentrations of all water bodies from August 2008 to January 2011. Each data point corresponds to the mean concentration of all monitoring sites of a water body for a given time.

of Valencia city. Chlorophyll-a was also high in C007; the most polluted site of the JRBD (Pachés et al., 2012; Temino-Boes et al., 2018). C002, the reference water body, had low N concentrations, together with C001 and C003. The lowest salinities were found in C005 and C007, with some low salinity events in C009. The latest water body corresponds to the discharge of the Jucar river. Temperature is slightly lower in sites C001 to C003.

3.4.2 Model results

Spearman correlation between model forcings (water temperature and ammonium) and output variable (nitrite concentration) was calculated to determine which variable had the highest influence on nitrite concentrations in each water body. We found a significant rank correlation between nitrite and temperature in all water bodies except C005 and C007 (Table 3.2) which correspond to the sites with highest continental influence (see salinity in Figure 3.3).

Water Body	T	NH_4^+
C001	-0.38*	0.49*
C002	-0.67*	0.28
C003	-0.55*	0.30
C004	-0.61*	0.44
C005	-0.36	0.56*
C007	0.08	0.79*
C008	-0.60*	0.85*
C009	-0.44*	0.57*
C010	-0.37*	0.52*

*Significant correlations at the 95% confidence level

Table 3.2: Spearman rank correlation between output variable (nitrite) and input variables (temperature and ammonium).

On the other hand, ammonium was significantly correlated to nitrite in all water bodies except C002 to C004. These sites correspond to the lowest observed inorganic nitrogen concentrations and chlorophyll-a (Figure 3.3).

We calibrated and validated the model for each water body, and the obtained results are presented in Figure 3.4. The parameters K and Θ obtained for each water body are shown in Table 3.3. We calculated the RMSE and R^2 in validation data

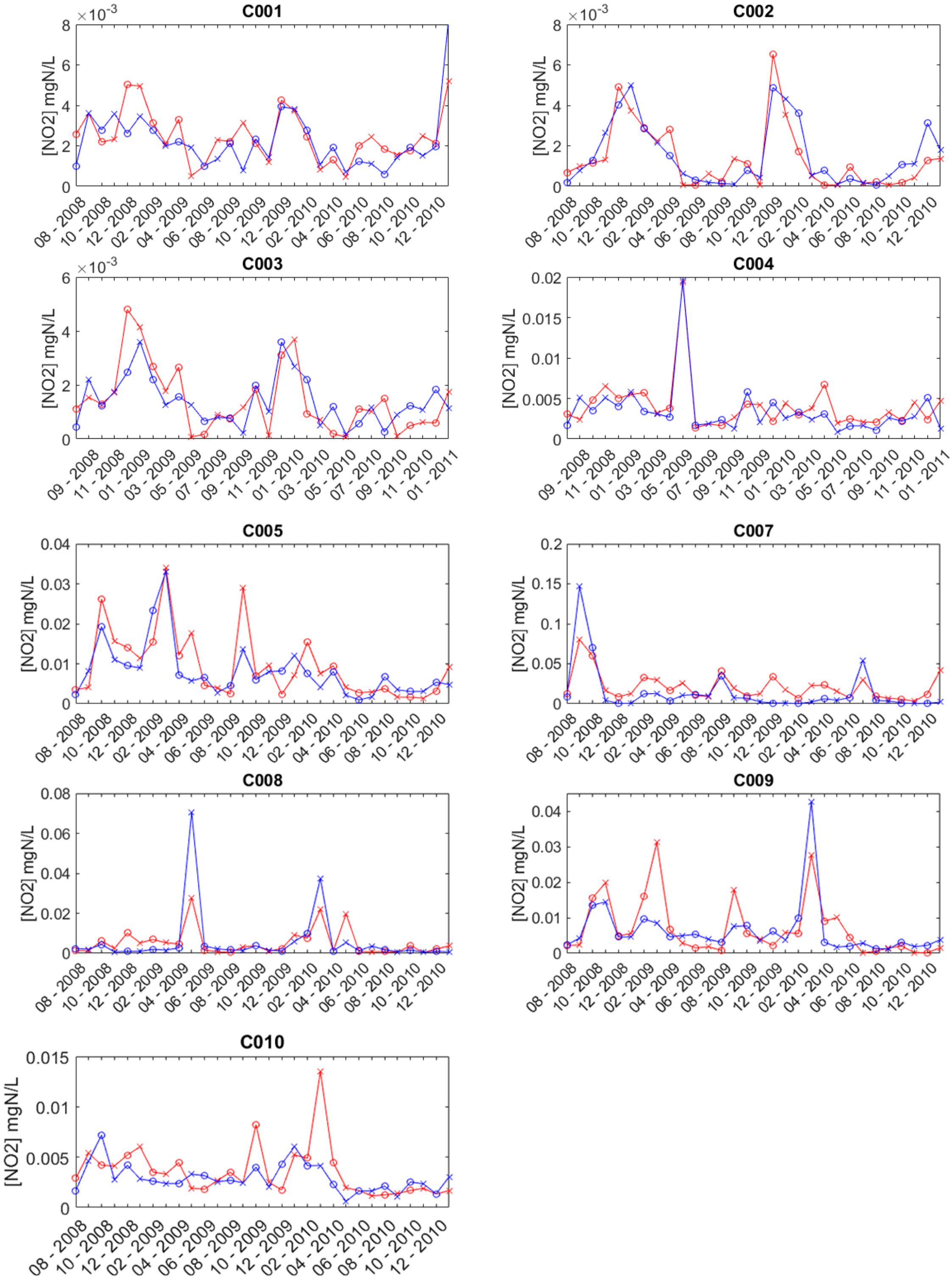

Figure 3.4: Mean nitrite measured (red line) and estimated (blue line) concentrations in all water bodies from August 2008 to January 2011.

(Table 3.3). Ammonium oxidation rate is often estimated as an order of magnitude lower than nitrite oxidation for surface water quality modelling as shown in Table 3.1. This observation agrees with our findings which established a K mean value of 0.17 (Table 3.3).

Water Body	K	Θ	RMSE(mg.L^{-1})	R^2
C001	0.15	0.94	1.33E-03	0.55*
C002	0.08	0.80	7.10E-04	0.84*
C003	0.13	0.91	6.75E-04	0.71*
C004	0.20	0.98	1.49E-03	0.95*
C005	0.33	0.92	5.97E-03	0.70*
C007	0.09	1.27	2.46E-02	0.74*
C008	0.11	1.10	1.30E-02	0.72*
C009	0.25	0.97	8.37E-03	0.46*
C010	0.19	0.97	2.61E-03	0.31*

*Significant correlations at the 95% confidence level

Table 3.3: Calibrated parameters (K and Θ) for each water body, root mean squared error (RMSE) and coefficient of determination (R^2) between measured and estimated nitrite concentration in validation data.

In most water bodies Θ was below 1, which indicates that nitrite oxidation is more sensitive to temperature changes than ammonium. Under this circumstance, nitrite peaks are observed in low temperature periods (December and January). The sites with the lowest anthropogenic pressures (C002 and C003) show clear nitrite peaks in the mentioned period. Only two water bodies (C007 and C008) presented a Θ higher than 1. No significant correlation was found in any water body between monthly error and chlorophyll-a (as a measure of phytoplankton), while the correlation with salinity was significant in water bodies C005 and C010 (Table 3.4). When salinity was low, the model error was higher due to continental nitrite inputs which were not considered in the model.

3.4.3 Analysis of spatial parameter variations

Spearman rank correlations between salinity, temperature and chlorophyll-a with model parameters and RMSE are calculated in Table 3.5. Both Θ and the RMSE

Water Body	S	Chl-a
C001	-0.27	-0.06
C002	-0.26	-0.11
C003	0.15	0.01
C004	0.34	0.29
C005	0.52*	-0.16
C007	0.34	0.26
C008	0.03	-0.09
C009	0.48*	-0.22
C010	0.33*	-0.05

*Significant correlations at the 95% confidence level

Table 3.4: Spearman rank correlation between error with chlorophyll-a (Chl-a) and salinity (S)

have a high rank correlation with chlorophyll-a 50^{th} percentile, an indicator of the ecological status of coastal waters. Additionally, salinity is related to the RMSE. Figure 3.5 shows how the parameter Θ, which represents the difference in temperature influence between ammonium and nitrite oxidation, is influenced by anthropogenic activity. Closer to big urban areas, like the city of Valencia in C007, Θ increases, while it decreases in C002 or C003 where the population is smaller. On the contrary, K does not have an anthropogenic influence (Table 3.5).

Parameter	S	T	P50 chlorophyll-a
K	-0.41	0.45	0.02
Θ	-0.42	0.50	0.80*
RMSE	-0.73*	0.42	0.97*

*Significant correlations at the 95% confidence level

Table 3.5: Spearman Rank Correlation of model parameters and root mean squared error (RMSE) with mean salinity, mean temperature and chlorophyll-a 50^{th} percentile.)

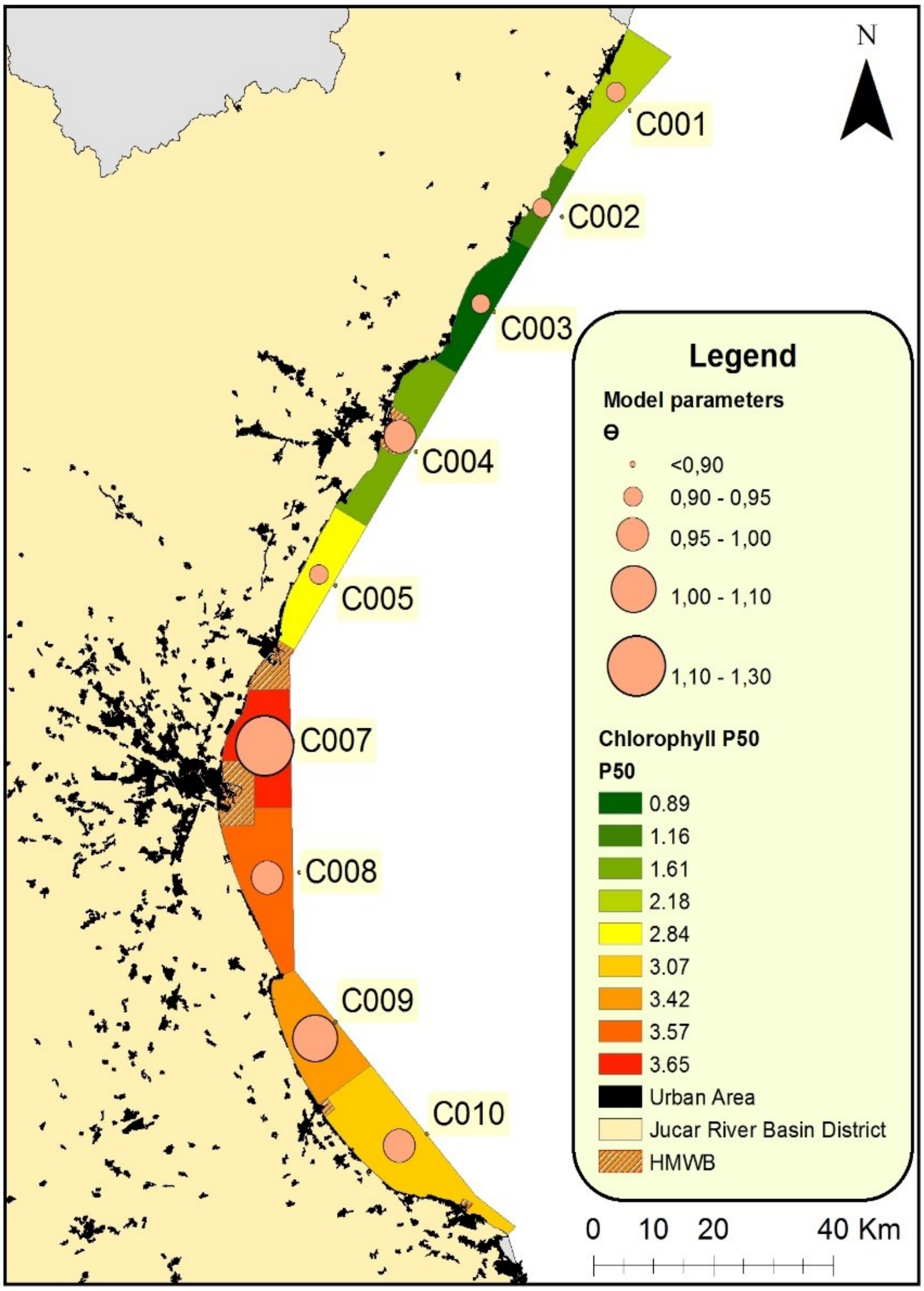

Figure 3.5: Model parameter Θ for each water body, 50^{th} percentile of chlorophyll-a, population and Heavily modified water bodies (HMWB) due to the presence of a harbour.

3.5 Discussion

The natural annual cycle of nitrite showed peaks in cold months (December and January), as found in the reference water body C002 (Figure 3.4). However, this cycle was highly perturbed in anthropogenically altered coastal zones, with peaks occurring both in cold and warm seasons driven by ammonium concentrations. Our results demonstrate that the two steps of nitrification are decoupled in coastal waters, agreeing with late findings (Heiss, Fulweiler, 2016; Schaefer, Hollibaugh, 2017). Different speeds in the two steps of nitrification were also observed in the Jucar estuary (Romero et al., 2007). In our model, peaks occur due to the different response to temperature in ammonium and nitrite oxidation (parameter Θ). Many previous studies found high nitrite concentrations at warmer seasons (Bristow et al., 2015; Heiss, Fulweiler, 2016; Schaefer, Hollibaugh, 2017) while others (such as this study) observed nitrite peaks at low temperatures (Pitcher et al., 2011).

The changes observed in nitrite dynamics among water bodies indicate a shift in nitrification temperature dependence parameter Θ due to anthropogenic activity (Figure 3.5). Nitrification requires the mediation of a vast diversity of microorganisms, which makes it an essential process for marine life. Pachés et al. (2012) proved how anthropogenic activity is changing microorganism composition in coastal waters of the JRBD, which may explain the spatial differences found in ammonium and nitrite oxidation temperature parameters. Although no previous study considered this dependence in coastal waters, studies carried out in wastewater determined the dependence of nitrification temperature coefficient on microorganism composition and abundance (Myszograj, 2015). In addition, wastewater effluents alter the biogeochemical cycling and phytoplankton composition (Howard et al., 2017) which may have caused shifts in nitrification temperature dependence. Future research is required to describe the processes driving nitrification dependency on temperature. Previous studies identified a dependence of nitrification rates on salinity (Bernhard et al., 2005; Heiss, Fulweiler, 2016), and low salinity events with elevated concentrations of certain ammonium oxidizing archaea (Schaefer, Hollibaugh, 2017).

Bernhard et al. (2005) indicated that the abundance and diversity of ammonium oxidizing bacteria is highly controlled by salinity, and Heiss, Fulweiler (2016) found lower nitrite oxidation rates with higher salinity events. Bianchi et al. (1999) linked high ammonium oxidizing rates with low salinity events in the NW Mediterranean Sea.

We found temperature to be an important driver of ammonium and nitrite oxidation decoupling under natural conditions, which entails climate change could have a great impact in this process. In the reference water body C002, which represents unaltered nutrient concentrations, the value of Θ was lower than 1. This result indicates that under pristine conditions the second step of nitrification (nitrite oxidation) is more sensitive to temperature than the first step. Climate change will therefore have a greater impact in this second step. In addition, some studies forecast an important precipitation loss in the Jucar area (Chirivella et al., 2016; Miró et al., 2018) which would considerably reduce the riverine inputs of ammonium and other forms of nitrogen. The decrease in ammonium concentrations would have a direct effect on the rate of nitrification. Therefore, it may be expected to have lower nitrite concentrations due to reduced nitrification rates and a shift in nitrite peaks due to higher temperatures. Further research is needed to evaluate how the combined effect of nitrogen pollution and climate change will modify the nitrification process in coastal waters.

The model performed well in general. However, there was a wide variation among sites in the accuracy of the model. The coefficient of determination R^2 is lower in C001, C009 and C010 (Table 3.3). As the number of stressors increases, the functioning of the ecosystem is altered, and the estimation of nutrient concentrations is hindered (O'Meara et al., 2017). High nitrite events no longer occur due to natural conditions but rather to an unusual increase in human inputs. Continental inputs are the main source of error to sites C005 and C009 as shown by the Spearman correlations between error and salinity (see Table 3.4). Those water bodies have higher continental influence as indicated by the low salinities. The Jucar river discharges in C009, which is most probably the source of nitrite during the peaks not reproduced by the model. High nitrite concentrations in C010 also correspond to low salinity event indicating an external source of nitrite not simulated in our model. Although nitrite concentrations in C001 did not have a significant correlation with salinity, this water body is located close to the Ebro delta, which may influence nitrification dynamics in this water body. On the other hand, phytoplankton does not have a significant correlation with the error (Table 3.4) which indicates that neglecting phytoplankton uptake and release is not an important source of error to the model.

The proposed workflow is applicable to other coastal areas with samples taken at the surface to avoid the effect of dissolved oxygen limitation. pH variations along the year in the Mediterranean Sea are usually less than $\pm$ 0.1 pH units (Flecha et al., 2015), and therefore pH is not expected to be one of the main drivers of nitrification. The effect of phytoplankton and external inputs are the most important processes to be considered before applying the model to other coastal areas. In the Mediterranean Sea, marine waters are often oligotrophic (Vollenweider et al., 1996) and phytoplankton release of nitrite is presumably negligible in most areas. The nitrification kinetic model proposed could be extended to add other processes in the application to other study sites. However, the steps proposed in the workflow of Figure 3.2 can be followed for the study of any areas if the model is adapted. Future studies are needed to evaluate the mechanisms by which nitrification dynamics are altered by human activity and which are its most relevant consequences.

3.6 Conclusion

Our results show how nitrification dynamics are perturbed in highly populated coastal zones. Under natural conditions nitrite peaks are observed in winter due to low temperatures, but this tendency is completely altered in anthropogenically impacted water bodies. The change observed in the sensitivity to temperature of the two steps of nitrification was highly correlated to chlorophyll-a 50^{th} percentile, a measure of the ecological status (Spearman correlation r=0.80). Temperature was the main driver of monthly variation in natural conditions, which indicates a potential effect of climate change on nitrification dynamics. Nitrification is a fundamental process of nitrogen biogeochemistry. As a key nutrient, the alteration of the nitrogen cycle may result in the change of the whole food web in marine ecosystems. Further research concerning the human driven changes of the nitrogen cycle in marine environments is essential to enable experts to propose recovery measures and avoid reaching a point of no return.

CHAPTER 4

Future trends of dissolved inorganic nitrogen concentrations in Northwestern Mediterranean coastal waters under climate change

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4.1 Abtract

This research analyzes the effect of meteorological variables on dissolved inorganic nitrogen (DIN) species in coastal inshore waters of a Northwestern Mediterranean region under climate change. We built simple mathematical schemes based on artificial neural networks (ANN), trained with field data. Then, we used regional climatic projections for the Spanish Mediterranean coast to provide inputs to the trained ANNs, and thus, allowing the estimation of future DIN trends throughout the 21st century. The results obtained indicate that nitrite and nitrate concentrations are expected to decrease mainly due to rising temperatures and decreasing continental inputs. Major changes are projected for the winter season. Ammonium concentrations are not expected to undergo a significant annual trend but may either increase or decrease during some months. These results entail a preliminary simplified approach to estimate the impact of meteorological changes on DIN concentrations in coastal waters under climate change.

4.2 Introduction

Climate change is expected to exacerbate the imbalance of the nitrogen cycle (Gruber, Galloway, 2008), which could already be even greater than expected (Paulmier, Ruiz-Pino, 2009). Coastal areas are known to be particularly vulnerable. In fact, some authors envisage that the future management of nutrient export might have a dramatic impact on coastal water quality (Sinha et al., 2019). Other researchers underline that anthropogenic pressures such as population increase and agricultural practices, plus the cumulative effect of climate change, will probably aggravate nutrient cycling alteration in coastal waters (Rabalais et al., 2009; Sinha et al., 2019). Several investigations outline that nutrient processes will be modified as a response to changes in temperature (Wagena, Easton, 2018), wind patterns (Deng et al., 2018), hydrology, sea level rise (Statham, 2012) and precipitation (Störmer, 2011).

Global warming can also contribute to hypoxia in coastal areas by reducing the vertical exchange, making the system more sensitive to nutrient loads (Du et al., 2018). As a consequence of the changes induced, a shift in the relationship between nutrients and phytoplankton should be expected, which might require a re-evaluation of nutrient criteria for ecological status assessment (Liu et al., 2018). Complex interactions among environmental and climate drivers regulate phytoplankton in coastal zones (Pesce et al., 2018), which entails a significant impact of climate change on primary production. The combined effect of higher temperatures and changes in nutrient availability can have drastic consequences for phytoplankton production in coastal waters (Lee et al., 2019), which will add up to the impact of increasing anthropogenic nutrient loadings (Huo et al., 2019). Additionally, the macrobenthos community may also be affected by sea level rise, leading to an increase in nitrogen flux to the water column (Brito et al., 2012).

Dissolved inorganic nitrogen (DIN), i.e. ammonium, nitrite and nitrate, are the most reactive forms of nitrogen in marine waters and play an important role in primary production (Camargo, Alonso, 2006). Nitrate is the most stable form of inorganic nitrogen in oxygenated environments and is generally the dominating form of DIN in estuaries and the surrounding coastal waters (Statham, 2012). Ammonium is also a relevant N species which is often associated to urban influence (Flo et al., 2011). Finally, even though nitrite is the less abundant of the three forms of DIN due to its instability, it is often used as an indicator of the balance between oxidative and reductive reactions (Temino-Boes et al., 2019a). As a consequence of climate change, the variations in rainfall patterns may lead to the reduction of DIN inputs to coastal waters through river discharges (Pesce et al., 2018), while processes such as ammonification, nitrification and denitrification could be altered by rising temperatures or ocean acidification (Temino-Boes et al., 2019a; Wannicke et al., 2018).

The Mediterranean coast has been identified as one of the most responsive regions to climate change, driven by a significant decrease in the expected mean precipitation (Herrmann et al., 2014). According to some authors, a reduction in the system's biomass can be expected in the Mediterranean Sea during the 21st century (Lazzari et al., 2014), as well as seagrass degradation (Ontoria et al., 2019), surface water warming, salinity increase (Vargas-Yáñez et al., 2017) and a decrease in nutrient availability (Herrmann et al., 2014). On the other hand, renewable water resources are also expected to decrease (García-Ruiz et al., 2011), due to higher rates of sea surface evaporation and reduced rainfall (Romanou et al., 2010), while water demand continues to rise (García-Ruiz et al., 2011; Wang, Polcher, 2019). Under future climate scenarios in the Northwestern Mediterranean Sea, changes in deep water convection mechanisms in winter will likely diminish the importance of nutrient upwelling, whilst horizontal currents will become a more relevant fertilization mechanism (Macias et al., 2018). These alterations may lead to significant changes in both nutrient distribution and phytoplankton community structures (Severin et al., 2014), which in turn could possibly shift towards small-size groups (Herrmann et al., 2014).

Flo et al. (2011) defined coastal inshore waters (CIW) of the Mediterranean Sea as the coastal waters laying between the shore and 200 m into the sea. This reduced region is a unique habitat for many species, and a major socio-economic interest, with tourism activities increasingly threatening the ecosystems (Colella et al., 2016). The Mediterranean CIW are particularly vulnerable to anthropogenic influences, and its characteristics differ considerably from other coastal regions located further into the sea ($> 200m$). Significantly higher DIN concentrations were reported in CIW, where continental influence is the major driver of nitrogen concentrations (Flo et al., 2011), mainly derived from river discharges. The Ebro river delta, the most important delta in the Iberian peninsula, has a mean surface elevation of 0.87 m over the average sea water level, which makes it very sensitive to potential sea level rise, critically threatening nutrient removal dynamics (Genua-Olmedo et al., 2016). Both climate change and agricultural practices have significant impacts on nitrate concentrations in the Ebro basin, while phosphate concentrations are mainly driven by agricultural and industrial practices (Aguilera et al., 2015). In the case of the Jucar River Basin District (Southeast of Spain), temperatures are expected to increase up to 4.86°C in summer by 2040 (Chirivella et al., 2016) and consequently alter nitrogen transformation processes (Temino-Boes et al., 2019a).

The aforementioned impacts and the systems implicated are extremely difficult to model successfully due to their inherent complexity and the great number of variables involved. In this context, artificial neural networks (ANN) provide a very attractive modelling framework, which has become increasingly popular, particularly in the evaluation of climate change impacts (Altunkaynak, 2007; Liu, Lin, 2010). The human brain inspired the mechanisms used for ANNs development. They have been extensively used in many fields, including water quality evaluation (He et al., 2011). One of the main advantages of ANN models in comparison to deterministic models is that an extensive knowledge of the physicochemical processes is not required (He et al., 2011). Besides, ANN models can deal with nonlinear relationships among variables (Liu, Lin, 2010), improving the accuracy of long-term forecasts (Doğan et al., 2016). The effect of climate change on water resources has been estimated with ANNs in urban areas (Al-Zahrani, Abo-Monasar, 2015), aquifers (Coppola Jr. et al., 2005), deltas (Byakatonda et al., 2016), rivers (Piotrowski et al., 2015), lakes (Altunkaynak, 2007; Doğan et al., 2016) or marine environments (Coutinho et al., 2019). Results show that ANN models often outperform conventional methods (Al-Zahrani, Abo-Monasar, 2015). Nutrient mechanisms, biogeochemical cycling (Bittig et al., 2018) and primary production (Mattei et al., 2018) in the ocean under climate change scenarios have also been evaluated with ANNs .

Nonetheless, only few studies have focused on the forecasting of global warming effects on nutrient cycling in coastal regions (Basu et al., 2010; Wang, Polcher, 2019). In this research, we developed simple ANN modelling schemes as a first approach to evaluate regional climate change impacts on DIN concentrations trends in CIW through meteorological variables. More specifically, we propose a non-linear three-layered feedforward artificial neural network structure, containing a single output node. We trained and tested three different ANN models with such topology with field data, in order to estimate ammonium, nitrite and nitrate concentrations. Using these trained ANNs expected changes in DIN species concentrations are then estimated, considering two meteorological projections under regional climate change scenarios corresponding to the representative concentrations pathways (RCP) 4.5 and 8.5 respectively (Moss et al., 2010). Due to the necessary simplifications of the physical processes, the results obtained are of qualitative interest rather than quantitative. Our study site is an inshore Mediterranean coastal area of the South East of Spain, exposed to very limited anthropogenic pressures.

4.3 Materials and Methods

4.3.1 Study area

The Jucar River Basin District is located in the Spanish Mediterranean coast. In this study we focus in the water body C002 (Figure 4.1) which is the pristine reference site for the moderately influenced by continental inputs region. As very limited anthropogenic alteration of water quality exists in this area (Romero et al., 2013), it becomes easier to study the effect of physical and meteorological variables on nitrogen concentrations. Five monitoring sites were located within C002, which are presented in Figure 4.1. Ebro river delta is located approximately 60 km North from the study site and represents the highest continental water input with a mean annual flow of 286 $m^3.s^{-1}$ for the period 2000-2018. Additionally, the aquifer of El Maestrazgo discharges directly to our study site through several submarine springs with a mean approximate flow of 1.5 $m^3.s^{-1}$ (Garcia-Solsona et al., 2010).

In this study, we focus on coastal inshore waters (0 - 200 m), in which continental influence is the main driver of nutrient concentrations (Flo et al., 2011). The samples collected for the development of this work were taken at $<$ 50 m from the shore, where the depth is $<$ 1.5 m. As a consequence, the water column is completely

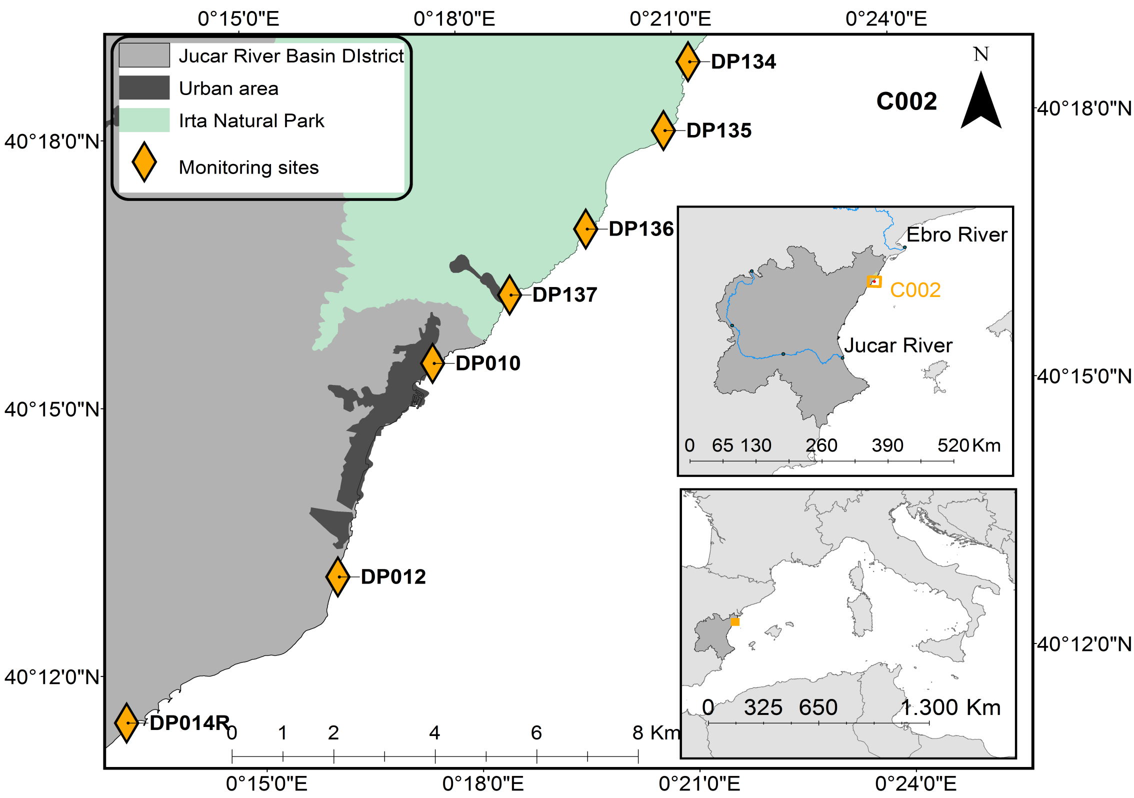


Figure 4.1: Study site corresponding to the water body C002 identified as reference site of the Jucar River Basin District. Five monitoring sites are shown.

mixed, and no stratification exists. Additionally, samples were taken at the surface, which implies that the effect of the sediment can be neglected. The small tidal range in the Mediterranean Sea prevent the dispersion of nutrients into the sea (Flo et al., 2011).

Water samples were collected from each monitoring site once per month from February 2006 to January 2011. Samples were taken in plastic bottles at the surface and from beyond the wave breakpoint, refrigerated and carried to the laboratory. The temperature and pH were measured in situ with a YSI 6600 Multi Parameter V2 Sonde. Salinity was measured at the laboratory with a Portasal 8410A salinometer. The procedures to measure ammonium, nitrite and nitrate are explained with detail in Temino-Boes et al. (2019a). Air temperature, wind speed and rainfall data were obtained from the Ministry of Agriculture, Fisheries and Food, and Ebro river discharges were obtained from the Ebro Water Authority.

4.3.2 Data pre-analysis

Considering that continental influence is the main driver of nutrient concentrations (Flo et al., 2011) in CIW of the Northwestern Mediterranean, several physical and meteorological variables were selected as potential input variables to model nutrient concentrations. These variables were: wind speed, rainfall, salinity, Ebro river flow, pH and water temperature. The output sensitivity to input variables relationships can be estimated based on the Spearman rank correlation if a nonlinear but monotonic relationship is assumed (Pianosi et al., 2016). In order to determine to which variables nitrogen concentrations are more sensitive, we calculated the Spearman rank correlation coefficients. The results of this analysis were used to select the most appropriate input variables to the model.

Rainfall can significantly affect nitrogen in CIW trough different processes: by diluting nutrient concentrations, through river runoff or through submarine groundwater discharge (SGD). Nitrogen discharges through SGD have been reported to be significant in the study area (Garcia-Solsona et al., 2010), particularly in the form of nitrate (Ballesteros et al., 2007). The aquifer of El Maestrazgo, which discharges through coastal springs in Irta National Park, is mainly recharged through rainfall infiltration (Ballesteros et al., 2007). The time lag between SGD flux response to freshwater infiltrated has been reported to be approximately 3 months (Garcia-Solsona et al., 2010). In order to determine the time lag between rainfall and nitrate concentrations in our model, we calculated the cross-correlation with R version 3.5.1.

4.3.3 Artificial neural networks

Artificial neural networks (ANN) are data-driven models that have shown to be very successful modelling tools in a diversity of research areas (Abrahart et al., 2004;

Alanis et al., 2019; Govindaraju, 2000). In particular, they have proved to be very efficient in the prediction of relevant variables in complex systems characterized by nonlinear dependencies of data, as it is the case of the ones analyzed herein. Several ANN schemes were trained in this research, in order to extract the most relevant interactions between the measured variables and synthesize them through simple network topologies. These ANN schemes are built with the final aim of simulating long-term future expectable trends in the system under different climatic scenarios, as other authors have proposed (Abdullahi, Elkiran, 2017; Elgaali, Garcia, 2007). These modelling steps can also be helpful to gain a better understanding of the studied system behavior and its internal relationships between the involved physical variables mentioned before. The type of ANNs employed herein is the well-known feed forward multilayer perceptron of three layers with supervised learning, trained with the classical error-backpropagation learning algorithm (Gardner, Dorling, 1998; Rumelhart et al., 1986).

The structure of the networks is made up of three layers: an input layer comprising a group of explanatory variables, a hidden layer with nodes including non-linear activation functions, and an output layer corresponding to a selected target variable to be predicted. The training process of the networks allows to configure the network internal weights in order to minimize the error function, in this case, the average squared error with respect to the measure (known values) of the target variable. The activation function used for the hidden nodes was the popular logistic function (Kohonen, 1988):

$$\varphi(x) = \frac{1}{1 + e^{-x}} \tag{4.3.1}$$

Where x is the input value to the particular node, resulting from operations in previous layers and connections to the node. $\varphi(x)$ is the value produced by the activation function, i.e., output of the particular node under consideration.

The choice of the number of hidden nodes (n_h) affects the training process and the effectiveness and final performance of the network. Complex relationships between inputs and outputs are difficult to be captured with too few hidden nodes, while too many hidden nodes may result in network over-training and a loss of generalization capacity of the network. Due to the sample size available for this study, the option for a parsimonious model is generally recommended. According to it, we applied the criteria (Lachtermacher, Fuller, 1994), adopting the minimum n_h value matching this criteria:

$$\frac{1.1N}{10} \leq n_h \left(I+1\right) < \frac{3N}{10} \tag{4.3.2}$$

where N is the sample size, and I is the number of input variables.

The data used for network training is the sample corresponding to the period from February 2006 to January 2010, while the period from February 2010 to January 2011 is reserved for validation. This partition is consistent with the criteria suggested by (Haykin, 1999):

$$r_{val} = 1 - \frac{\sqrt{2W-1} \; - 1}{2\left(W-1\right)} \tag{4.3.3}$$

where W is the number of weights in the neural network, and r_{VAL} is the proportion of the total data used for training.

As it is the case with other black-box models, the overall performance is highly influenced by the data preprocessing (Nawi et al., 2013). In particular, the computational efficiency of the networks is enhanced if both input and output variables are scaled. Consequently, all variables involved in the ANN modelling were previously pre-processed through equation 4.3.4:

$$x' = \left(\frac{x - x_{MIN}}{x_{MAX} - x_{MIN}}\right)^{\gamma} \tag{4.3.4}$$

where x represents the original variable, x_{MIN} is the minimum value, x_{MAX} is the maximum value of the sample, x' is the transformed variable, and γ is an exponent introduced in order to reduce the final skewness. γ values are conveniently chosen for each of the variables considered in the ANN modelling process, ranging from 0.3 to 1.0.

The back-propagation algorithm was used to train all the networks. This sequential iterative method adjusts the network weights in small steps, following the direction of negative gradient of the error function. The learning rate was manually modified to smaller values as the training process advanced, to avoid undesirable oscillatory behavior of the training error function. During the learning process, the order of presentation of patterns was randomized through the shuffling of the cases, which is usually advantageous to avoid local minima. While other more powerful and quicker algorithms are commonly used (Burney et al., 2007), the reduced size of the networks involved herein allowed an efficient use of the simpler error-backpropagation algorithm until the error function reached a specified convergence with satisfactory quickness.

Training and validation processes of the different ANNs proposed were performed using the software STATISTICA.

4.3.4 Climate change scenarios

The National Plan for Adaptation to Climate Change (PNACC), through the Scenarios-PNACC initiative, collects regional climate information for Spain, both of current climate and of future scenarios for the next decades. The projections of meteorological variables are based on the Fifth Assessment Report (AR5) of the Intergovernmental Panel on Climate Change (IPCC). The initiative integrates the results of international dynamic and statistic regionalization projects such as Euro-CORDEX and VALUE, with national projections developed by the National Meteorological Agency (AEMET) and by the Meteorology Group of Santander (CSIC - University of Cantabria). We downloaded projections of daily meteorological variables for future emission scenarios from the Platform of Exchange and Consultation of Information on Adaptation to Climate Change in Spain (AdapteCCA.es), under RCP 4.5 and RCP 8.5. Mean monthly estimations for air temperature, humidity and rainfall were calculated from 2011 to 2100 for both RCPs.

Due to the lack of water temperature and salinity projections under climate change in the study area a simplified approach to estimate these variables is necessary. Linear stepwise regression models were used to estimate salinity and water temperature from meteorological variables, i.e. air temperature, rainfall and humidity. For the estimation of salinity also Ebro river flow was used. All variables were previously normalized through a unity-based normalization. The first 4 years of measurements were used for model calibration and the last year for validation.

The Spanish center for studies and experimentation of public works (CEDEX) assessed the impact of climate change on water resources in a natural regime in the Spanish basins throughout the 21st century. The model developed is the Integrated Precipitation Simulation model (SIMPA), a distributed simulation model of the hydrological cycle that establishes water balances for the different processes. It estimates the contribution from meteorological data and the physical characteristics of the territory. The model is fed with regionalized projections of climate change procured by AEMET and provides the expected values of the main hydrological variables. The results are available online through a downloadable computer application (CAMREC), a plugin for QGIS 2.18. The changes expected in the Ebro river flow at its mouth throughout the 21st century under RCP 4.5 and RCP 8.5 were obtained from CAMREC.

Monthly DIN concentrations from 2011 to 2100 were estimated by means of the developed ANN model. For each month, Mann-Kendall trend test was applied to determine whether the trends observed are statistically significant. This test is a non-parametric monotonic trend analysis which identifies the increasing or decreasing patterns in time series data (Chaudhuri, Dutta, 2014; Colella et al., 2016). The magnitude of the trend was evaluated with Sen's slope (Sen, 1968), a non-parametric method which does not require assumptions on the normal distribution of the data (Kitsiou, Karydis, 2011). The annual trend is evaluated with the season Mann-Kendall test and the seasonal Sen's slope. These tests are performed with the package "trend" in R version 3.5.1.

4.4 Results

4.4.1 Monitoring data

The data obtained from the monitoring campaigns are presented in Figure 4.2. Water temperature and pH are similar between monitoring sites. Salinity however is lower in DP010 which can be attributed to SGD inputs. DIN concentrations are higher in DP010, nitrate concentrations particularly. This monitoring site is located close to an urban area as opposed to the other sites which are within Irta National Park. Additionally, the SGD in this area entails an input of DIN especially in the form of nitrate (Ballesteros et al., 2007).

As indicated in section 4.3.2, the cross-correlation between nitrate and rainfall was evaluated. The result of the analysis is presented in Figure 4.3. The correlation is maximum with a time-lag of 4 months between rainfall and nitrate concentrations. This finding is in close agreement with the time lag in the aquifer's discharge time in Garcia-Solsona et al. (2010).

The Spearman correlations between physicochemical variables and DIN concentrations is shown in Table 4.4.1. Based on these correlations the input variables selected for DIN species estimation were water temperature, salinity and rainfall (with a 4-month time lag). Ebro river flow, the pH and the wind speed were discarded for not having any significant correlation.

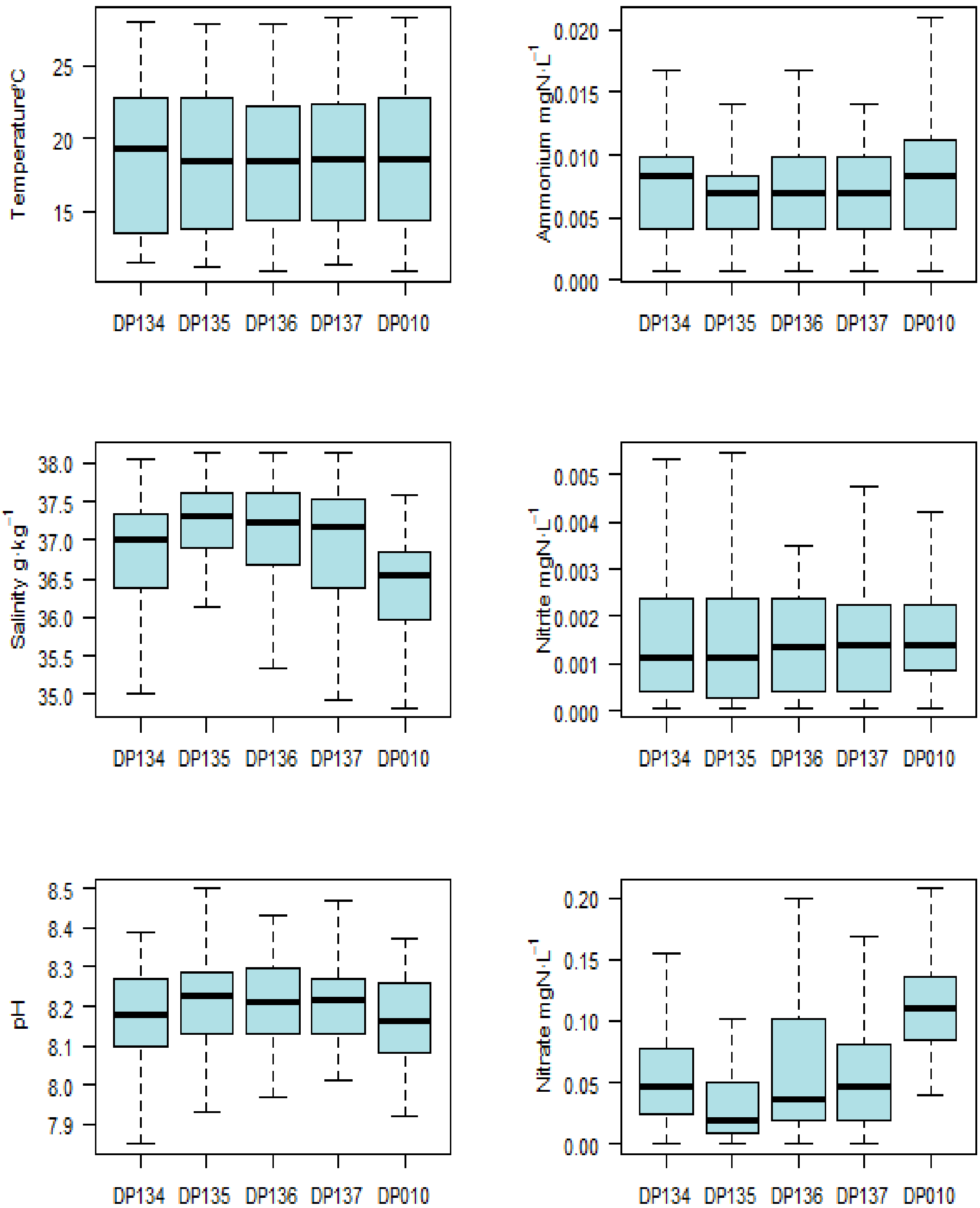


Figure 4.2: Boxplot of water temperature, salinity and pH (left) and dissolved inorganic nitrogen species concentrations (right) obtained during monthly monitoring campaigns from February 2006 to January 2011, in the 5 monitoring sites. The median is represented by a black horizontal line, outliers are not represented.

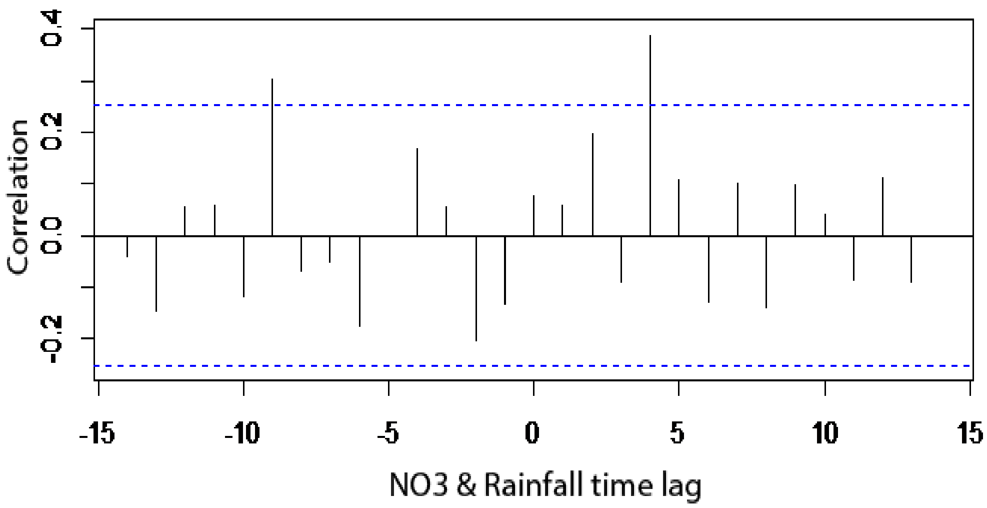


Figure 4.3: Cross-correlation between nitrate concentration and rainfall. Horizontal axis shows the time lag in nitrate concentrations while vertical axis shows the correlation between nitrate and rainfall.

	NH_4^+	NO_2^-	NO_3^-	R-4	Q	WT	pH	S	W
NH_4^+	-	-0.05	0.23	0.19	0.09	0.25*	0.10	-0.39*	-0.07
NO_2^-		-	0.43*	0.19	0.06	-0.54*	-0.05	-0.11	0.03
NO_3^-			-	0.46*	0.23	-0.33*	0.10	-0.64*	-0.16
R-4				-	0.32*	-0.02	0.16	-0.37*	-0.06
Q					-	-0.35*	-0.04	-0.46*	-0.04
WT						-	0.29*	0.12	-0.02
pH							-	-0.08	-0.14
S								-	0.20

*Significant correlations at 0.05 significance level

Table 4.1: Spearman correlations between studied variables.NH_4^+, NO_2^- and NO_3^- in $mgN.L^{-1}$, R-4: rainfall in $mm.day^{-1}$ with a 4-month time lag, Q: Ebro river flow in $m^3.s^{-1}$, WT: water temperature in °C, S: salinity in $g.kg^{-1}$, W: wind speed in $m.s^{-1}$.) The asterisk indicates a statistically significant correlation at a 0.05 significant level.

4.4.2 ANN model

A simple artificial neural network architecture is proposed to predict values of each of the DIN species, i.e., NH_4^+, NO_2^- and NO_3^-. One network is built and trained for each of these variables, although the three networks developed have the same 3-layer topology.

The variables used as predictors, that is, the input variables of the networks, are the same for each of the three neural networks. The selected predictors are those physical parameters that showed higher correlation: salinity, temperature and rainfall. Consequently, the number of nodes in the input layer is three, and the number of nodes in the output layer is one.

The number of hidden nodes was calculated with equation 4.3.2, resulting in n_h=2, which is also consistent with recommendation (Wanas et al., 1998). This network size proved to be optimal, as other networks with n_h=1, 3 and 4 were later tested, yielding to worse performance indexes. Consequently, the architecture of the proposed ANN consists on a 3-layer feedforward neural network with 3 input nodes, two hidden nodes and one output node (either NH_4^+, NO_2^- or NO_3^-), as indicated in Figure 4.4.

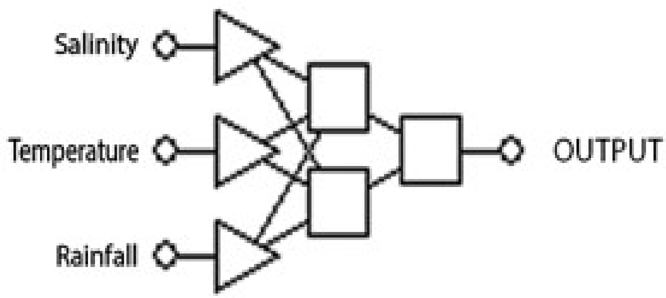


Figure 4.4: Feedforward neural network topology

The obtained rooted mean squared errors (RMSE) for training and validation data are presented in Table 4.2. While Figure 4.5 shows the model outputs for ammonium, nitrite and nitrate and the R^2 for each model.

RMSE	NH_4^+	NO_2^-	NO_3^-
Training	4.10E-03	1.48E-03	2.63E-02
Validation	3.15E-03	8.15E-04	1.99E-02

Table 4.2: Rooted mean squared error (RMSE) in $mgN.L^{-1}$ for training and validation data

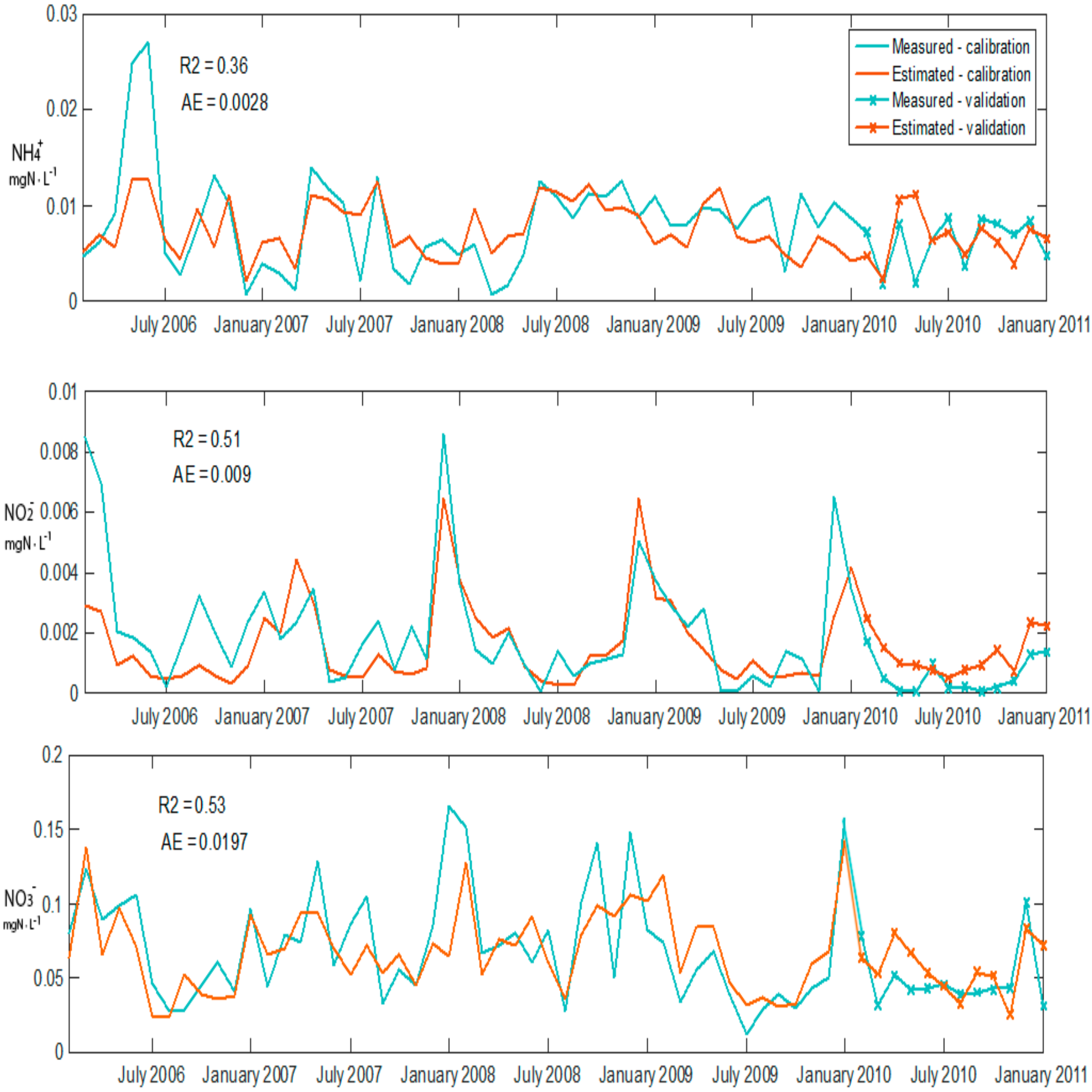


Figure 4.5: NH_4^+, NO_2^- and NO_3^- models based on artificial neural networks. Rainfall with a 4-month time lag, water temperature and salinity are the input variables. The coefficient of determination R^2 and the absolute error (AE) in $mgN.L^{-1}$ is shown.

4.4.3 Water temperature and salinity models

Linear regression model parameters to estimate water temperature and salinity are presented in Table 4.3. Water temperature is estimated from air temperature solely, while salinity is estimated with rainfall (with a 4-month time lag), humidity and Ebro river flow. Both models are found to be statistically significant as determined by the R^2, adjusted-R^2 and p-value shown in Table 4.4. Durbin-Watson statistic tests the residuals to determine if there is any significant correlation based on the order in which they occur in the data. There is no serial autocorrelation in the residual at a 95 % level of significance as indicated in Table 4.3.

As indicated in section 4.3.4, the first 48 measurements corresponding to the first 4 years were used to build the model and the last 12 values were used for validation. Both calibration and validation data are shown in Figure 4.6. The coefficient of determination R^2 was very similar in calibration and validation for both models.

Model	Parameter	Estimate	Standard Error	T statistic	p-value
1. Water Temperature	Constant	0.1032	0.0242	4.2700	0.0001
	T_{air}	0.8944	0.0424	21.0767	0.0000
2. Salinity	Constant	0.1032	0.0242	4.2700	0.0001
	R-4	-0.1927	0.0947	-2.0353	0.0479
	H	-0.2734	0.0996	-2.7454	0.0087
	Q	-0.5436	0.1055	-5.1549	0.0000

Table 4.3: Stepwise linear regression models of water temperature (1) and salinity (2). T_{air}: air temperature, R-4: 4-month lag rainfall, H: humidity and Q: Ebro flow.

Parameter	Model 1: Water Temperature	Model 2: Salinity
R^2	90.62	50.99
R^2 adjusted	90.41	47.65
Standard error	0.0937	0.1589
Durbin-Watson statistic	1.9702	1.5951
Durbin-Watson p-value	0.4079	0.0722
ANOVA F-Ratio	444.23	15.26
ANOVA p-value	0.0000	0.0000

Table 4.4: : Model R^2, standard error, Durbin-Watson statistics and ANOVA

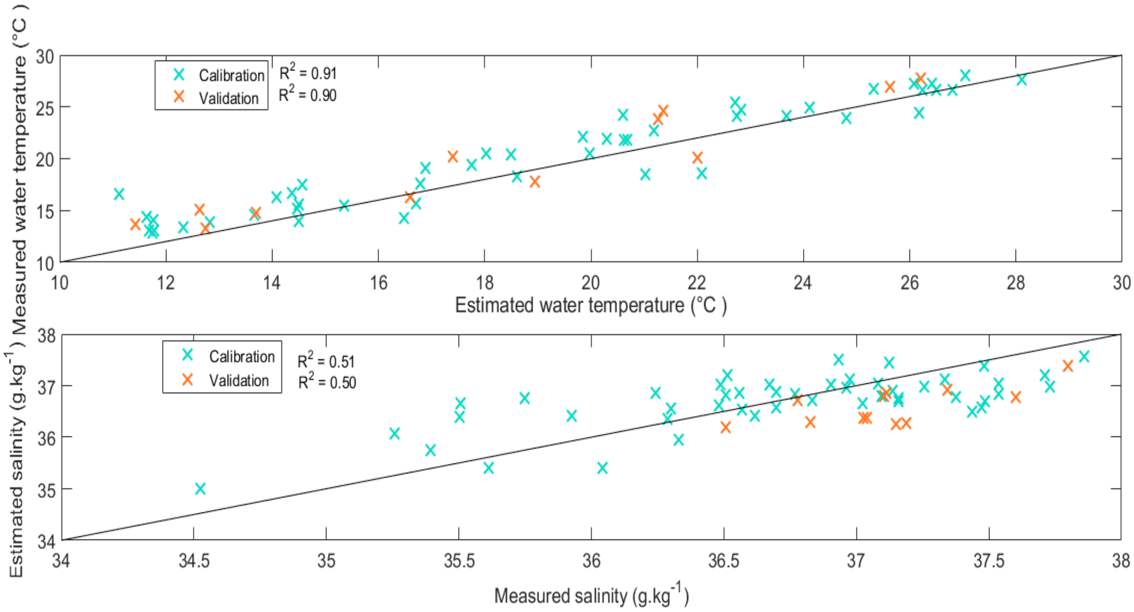


Figure 4.6: Linear models for the estimation of water temperature (left) and salinity (right). The coefficient of determination R^2 and the absolute error (AE) are shown for both calibration and validation data

4.4.4 The effect of climate change on DIN concentrations

Estimations of air temperature, humidity and rainfall from 2011 to 2100 under climate change scenarios were downloaded from AdapteCCA.es website and changes in Ebro river flow were obtained from CAMREC as mentioned in section 4.3.4. The changes projected for theses variables under climate change each month for the period 2070-2100 relative to 1971-2000 are presented in Figure 4.7.

Salinity and water temperatures for both RCP 4.5 and RCP 8.5 emission scenarios were calculated with the linear models developed in the previous section. By means of the ANN models, DIN concentration trends between 2011 and 2100 were estimated. Results are represented in Figure 4.8.

The Sen's slope for each month was calculated to measure the magnitude of the increasing or decreasing trend for DIN species over the period 2011 to 2100. Additionally, Mann-Kendall test was applied to evaluate whether the observed trend is statistically significant. The results are shown in Table 4.5. Nitrite and nitrate concentrations are expected to decrease both under RCP 4.5 and RCP 8.5 on an

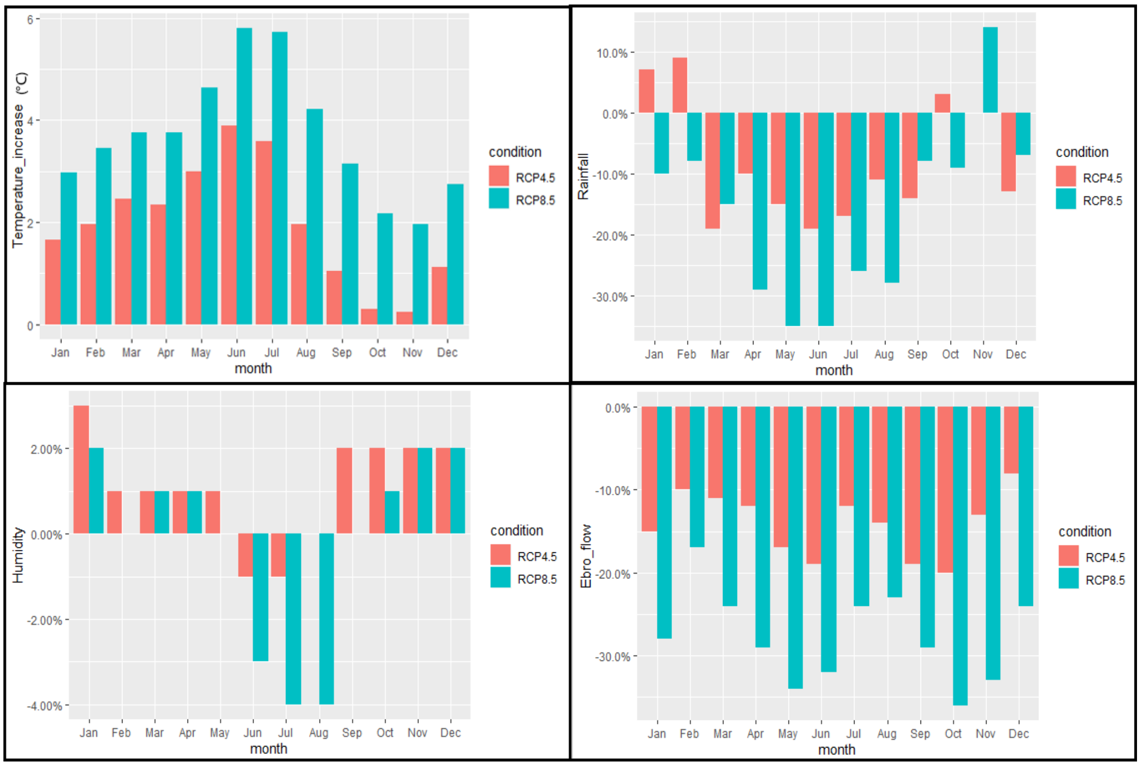


Figure 4.7: Changes in air temperature, rainfall, humidity and Ebro river flow for the period 2070-2100 compared to 1971-2000 (1961-2000 for Ebro river flow).

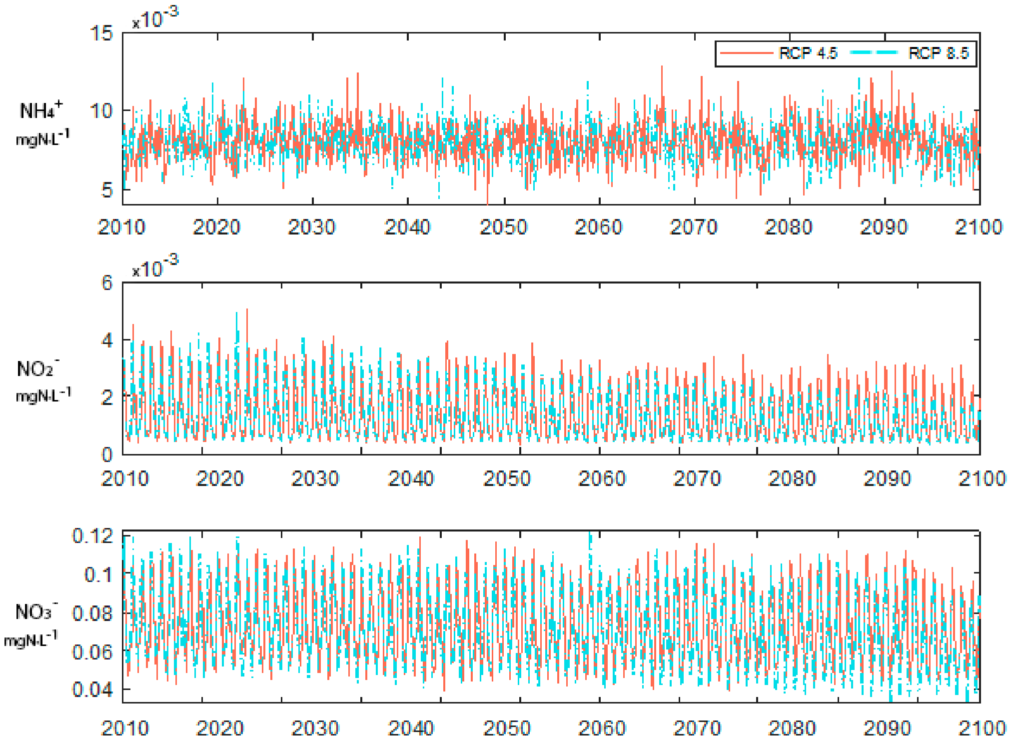
annual basis, with greater decrease found for RCP 8.5. Nitrite peaks, which are observed under low temperature conditions, are expected to decline. On the other hand, ammonium is expected to increase mainly between January and March and decrease from September to December, but the global trend was not statistically significant.

Month	NH4 4.5	NO2 4.5	NO3 4.5	NH4 8.5	NO2 8.5	NO3 8.5
January	7.14E-06**	-1.18E-05**	-4.65E-05*	7.89E-06**	-2.16E-05**	-1.94E-04**
February	2.94E-06	-5.06E-06**	-4.06E-05	2.00E-05**	-1.33E-05**	-1.91E-04**
March	7.32E-06*	-3.44E-06**	-1.53E-05	9.09E-06**	-5.88E-06**	-1.66E-04**
April	-4.76E-06	-3.13E-06**	-6.40E-05*	-2.99E-06	-4.76E-06**	-1.19E-04**
May	4.35E-06	0.00E+00	-4.17E-05	4.35E-06	-3.33E-06**	-1.32E-04**
June	4.35E-06	0.00E+00	-4.17E-05	4.35E-06	-3.33E-06**	-1.32E-04**
July	2.56E-06	-9.04E-07**	-5.37E-05**	2.18E-06	-1.80E-06**	-1.75E-04**
August	4.76E-08	-8.88E-07**	-6.86E-05**	1.19E-05**	-2.48E-06**	-1.83E-04**
September	2.41E-06	-1.46E-06**	-5.29E-05**	-1.46E-06**	-3.23E-06**	-1.90E-04**
October	-8.54E-06*	-2.21E-06**	-7.43E-05**	-8.96E-06**	-4.64E-06**	-1.85E-04**
November	-9.87E-06*	-4.13E-06**	-8.59E-06**	-1.80E-05**	-8.59E-06**	-1.66E-04**
December	-7.28E-06	-1.08E-05**	-9.36E-05**	-1.21E-05**	-2.43E-05**	-1.84E-04**
Anual	2.34E-07	-2.34E-06**	-5.84E-05**	2.35E-06	-5.22E-06**	-1.64E-04**

*Significant correlations at the 0.05 significance level

**Significant correlations at the 0.01 significance level

Table 4.5: Sen's slope for monthly changes in nitrate, nitrite or ammonium concentrations between 2011 and 2100 projections for each month under RCP 4.5 and RCP 8.5. The annual trend is evaluated with the seasonal Sen's slope. Red represents decreasing trends while blue represents increasing trends.



centering

Figure 4.8: Projections of ammonium, nitrite and nitrate concentrations from 2011 to 2100 by means of the ANN models under RCP 4.5 and RCP 8.5 scenarios.

4.5 Discussion

Artificial neural networks have proved to be a useful tool to evaluate the effects of climate change on DIN species. The proposed models showed the ability to estimate the impact of future meteorological conditions on the trends of DIN concentrations in CIW. Nonetheless, the results should be interpreted cautiously due to the assumptions made throughout the evaluation. Nitrite and nitrate models reached R^2 values over 0.50, which can be acceptable, considering the high variability generally found in coastal waters. Due to the high uncertainty in ammonium concentrations in Northwestern Mediterranean coastal waters (Paches et al., 2019), the model performance was lower for this nutrient (Figure 4.5). Also, the additional uncertainty introduced by the linear models developed for water temperature and salinity estimations should be pointed out. Water temperature model reached $R^2 = 0.90$; but salinity model had $R^2 = 0.50$, implying a degree of uncertainty introduced to ANN model inputs for future projections. The observed errors in ANN outputs can be attributed to both natural and anthropogenic sources. Anthropogenic nitrogen inputs, even if considered to be very limited in our study area (Romero et al., 2013), may account for some of the uncertainties. For instance, nitrogen inputs through Ebro river or submarine groundwater discharges are not constant along the year. On the other hand, the discharges of the aquifer El Maestrazgo are related to other parameters on top of precipitation. Nonetheless, the main contribution of this work lies in the evaluation of the overall expected tendency of nitrogen concentrations under climate change scenarios. In this sense, and according to the modelling results obtained, nitrite and nitrate concentrations are expected to drop under both RCP 4.5 and RCP 8.5 climate change scenarios, with greater decreases under RCP 8.5. Nitrite peaks generally occur due to low temperatures which decouple both steps of nitrification (Temino-Boes et al., 2019a). In accordance to this, future projections show a reduction of peaks during December and January, mainly due to the expected increase in minimum temperatures. Overall, the decaying trend of nitrite levels under climate change scenarios is basically driven by future rising temperatures. Nitrate is also expected to decrease, driven by both higher temperatures and decreasing rainfall. It is interesting to note that maximum monthly cumulative rainfall occurs in September, resulting in higher aquifer recharge during this month. This yields to groundwater discharge peaks during successive months, with an average time delay of 4 months, i.e., January. A decrease of future expected rainfall, more particularly during this rainiest month, will result in significant groundwater discharges reduction, which in turn will affect nitrate levels. This is consistent with simulation results obtained under RCP 8.5, where the most significant decreases in future nitrate concentration are expected during January.

The expected trends derived from the presented simulations herein, are consistent with known processes governing the dynamics of the nitrogen cycle. As pointed out by previous researchers, higher nitrification and denitrification rates are actually driven by higher temperatures, and thus, are expected to decrease future nitrogen availability (Wagena, Easton, 2018). Other authors already indicated that changes in temperature and precipitation could decrease nitrogen yields in coastal waters (Alam et al., 2017). Some studies point out a significant imbalance of the ocean's nitrogen budget, with greater losses than inputs (Voss et al., 2013). Bi et al. (2018) also found a negative correlation between nitrogen concentrations and temperature. Precipitation was also correlated to nitrogen concentration in previous studies, indicating that climate change might reduce nitrogen loads (Bi et al., 2018). Concerning ammonium concentrations, our results indicate that significant changes are not expected on an annual basis. While ammonification and other related processes are intensified due to higher temperatures, other factors are counteracting such effect, such as lower future precipitation and lower river discharges. Not being simultaneous drivers, though, smaller changes and trend fluctuations are expected for individual months.

The modelling framework presented herein necessary implies an important oversimplification of the complex systems under investigation. It neglects certain underlying physicochemical processes involved, and therefore, many uncertainty sources need to be accounted for. Although most relevant climatic drivers were considered in the analysis, other pressures such as changes in anthropogenic nutrient loads were not taken into consideration. For instance, 65% of the Ebro delta is occupied by rice fields (Genua-Olmedo et al., 2016), which implies that nutrient management in agriculture is a key factor for future export of DIN (Jennerjahn, 2012). The future fertilization policy applied in the Ebro catchment is uncertain, ranging from a 10% increase to a 15% decrease (Herrero et al., 2018). Obviously, the sort and amount of fertilizer will change due to changes in rainfall and air temperatures, which would influence coastal nutrient loads (Statham, 2012). Socioeconomic decisions about land use and management will have determining consequences for hydrological processes (Zarzuelo et al., 2019) and thus, on coastal nutrient enrichment (Sinha et al., 2019). Clearly, an interdisciplinary collaboration is necessary between natural and social sciences (Jennerjahn, 2012). Another aspect to be outlined is the highly regulated Ebro river, affecting its average discharges to the Mediterranean. About 96% of the catchment is regulated by dams (Jiménez et al., 2017), causing significant reductions of river flow over the past decades (Fatorić, Chelleri, 2012). In the future, higher water regulation due to increasing water demand (Wang, Polcher, 2019) and more intense human activity is generally expected in the Mediterranean region (Herrero et al., 2018). Depletion of river flows in the delta areas may enhance saline intrusion in the lower reaches of rivers and into the groundwater reserves (García-Ruiz et al., 2011). Under such conditions, the vulnerability of the Ebro valley will likely increase (Barrera-Escoda et al., 2014), influencing the nitrogen export to coastal waters. Natural and human-induced hydrodynamic alterations (Zarzuelo et al., 2019) may also have a significant impact on nutrient discharges. Furthermore, the potential changes in phytoplankton community and their ability to assimilate nitrogen induced by higher temperatures was not considered in this study (Kumar et al., 2018). In spite of these limitations, the study area selected corresponds to an area of low anthropogenic inputs (Romero et al., 2013) which indicates that climate change may have a greater impact than changes derived from direct human inputs.

On a global scale, the alteration of nitrogen transformations leads to many complex cascading effects (Gruber, Galloway, 2008). For example, the enhancement of nitrification and denitrification processes may lead to further emissions of greenhouse gases such as nitrous oxide (Jennerjahn, 2012). The nitrogen cycle is closely related to other biogeochemical cycles such as carbon or phosphorus (Gruber, Galloway, 2008), which implies that a change in nitrogen dynamics would cause important alterations to these elements through stoichiometric biological requirements (Voss et al., 2013). As a consequence, changes in DIN speciation and cycling along the year would have important impacts on phytoplankton production (Lee et al., 2019). Nutrient limitation conditions could be modified as a consequence of climate change impacts (Paerl, 2018). Additionally, a decreased nutrient availability may provoke a change in phytoplankton communities (Herrmann et al., 2014), leading to changes in the food chain. Altered species distribution and bloom timing can affect the food web structure, affecting higher trophic levels (Störmer, 2011). Ecosystem services provided by coastal systems may consequently be affected by the impacts of climate change (Baron et al., 2013; Pesce et al., 2018). For instance, shifts in nitrogen transformation processes may lead to changes in the potential for carbon sequestration or may cause a loss of biodiversity (Baron et al., 2013).

Overall, the results obtained in this study indicate that climate change is expected to decrease DIN concentrations in Mediterranean CIW due to increasing temperatures and lower continental inputs. The results obtained are of practical interest for management purposes, but the limitations of a simplified analysis should be recognized. Future studies should focus in the development of more sophisticated models with a combined evaluation of climate change and changes in anthropogenic nutrient loads. Additionally, the consequences for primary production and higher trophic levels should be evaluated, as well as the expected disruption of the whole coastal ecosystem.

4.6 Conclusion

The modelling approach proposed herein, together with the results derived from the performed simulations, represent a first approach to evaluate the potential climate change impact on dissolved inorganic nitrogen concentrations in coastal inshore waters (< 200 m). More specifically, we focused on the effect of the main meteorological variables on DIN species in the CIW of a Northwestern Mediterranean region with low anthropogenic inputs. As such, quantitative conclusions are necessarily limited, as many uncertainty sources need to be accounted for, as explained previously.

In order to evaluate the impact of climate change on DIN concentrations, we used artificial neural network models trained with real field data collected monthly during a period of 5 years. The most relevant climatic variables were considered as drivers. Results indicate that nitrite and nitrate concentrations are expected to decrease under climate change scenarios RCP 4.5 and RCP 8.5. Cold months such as December, January and February are expected to undergo the major concentration changes due to rising temperature and decreasing continental inputs. Ammonium did not show a significant annual tendency but may increase from January to March and decrease from September to December. The alteration of the nitrogen cycle in coastal waters may have serious consequences for upper trophic levels, disrupting the whole food web. Future research should focus on the evaluation of the combined effects of climate change and other human induced changes such as river flow regulations or nitrogen pollution. The evaluation of future nitrogen dynamics in coastal waters with more complex approaches is essential in order to develop preventive action plans.

CHAPTER 5

Using grey clustering to evaluate nitrogen pollution in estuaries with limited data

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5.1 Abstract

Many techniques exist for the evaluation of nutrient pollution, but most of them require large amounts of data and are difficult to implement in countries where accurate water quality information is not available. New methods to manage subjectivity, inaccuracy or variability are required in such environments so that water managers can invest the scarce economic resources available to restore the most vulnerable areas. We propose a new methodology based on grey clustering which classifies monitoring sites according to their need for nitrogen pollution management when only small amounts of data are available. Grey clustering focuses on the extraction of information with small samples, allowing management decision making with limited data. We applied the entropy-weight method, based on the concept of information entropy, to determine the clustering weight of each criterion used for classification. In order to reference the pollution level to the anthropogenic pressure, we developed two grey indexes: the Grey Nitrogen Management Priority index (GNMP index) to evaluate the relative need for nitrogen pollution management based on a spatiotemporal analysis of total nitrogen concentrations, and the Grey Land Use Pollution index (GLUP index), which evaluates the anthropogenic pressures of nitrogen pollution based on land use. Both indexes were then confronted to validate the classification. We applied the developed methodology to eight estuaries of the Southern Gulf of Mexico associated to beaches, mangroves and other coastal ecosystems which may be threatened by the presence of nitrogen pollution. The application of the new method has proved to be a powerful tool for decision making when data availability and reliability are limited. This method could also be applied to assess other pollutants.

5.2 Introduction

Many methods have been developed to identify nutrient pollution (Andersen et al., 2011; Ferreira et al., 2011; Garmendia et al., 2012; Lundberg et al., 2005; Primpas et al., 2010). However, most of these methods were developed in countries where large water quality datasets are available and nutrient emissions are regulated. Consequently, they consider many variables and tend to require large amounts of data. These tools become difficult to implement for those countries where environmental monitoring and policy is less developed. The progress towards the implementation of nutrient pollution management tools entails a challenge for these countries and requires a gradual implementation (Garmendia et al., 2012). It has been recognized that results of environmental management should not be generalized worldwide as economic development plays an important role in sustainable practices (Sánchez-Hernández et al., 2017). The development of tools to be implemented in areas of limited data is necessary and has proven to contribute to bringing useful nutrient management information and prioritize problems for attention (Do-Thu et al., 2011; Firmansyah et al., 2017; Montangero, Belevi, 2007, 2008). New methods are necessary for a rapid overall evaluation of coastal water quality with the scarce and sometimes unreliable data available (Shaban et al., 2010; Xianyu et al., 2017), while governments switch to more restrictive environmental policies.

Multivariate statistical techniques such as cluster analysis are widely used for the spatiotemporal variation analysis of water quality (Hajigholizadeh, Melesse, 2017; Kitsiou, Karydis, 2011; Shaban et al., 2010; Vadde et al., 2018). But in developing countries decision making often relies on limited data (Schärer et al., 2006), and traditional methods cannot deal with the uncertainty from data collection, storage, processing and interpretation (Lermontov et al., 2009). Conventional water quality indexes are weak in dealing with inaccuracies or vagueness (Azarnivand, 2017), and thus, new methods to asses uncertainty are required. Fuzzy logic has proven to be a useful and robust method under these circumstances (Schärer et al., 2006), which enables the processing of imprecise information (Adriaenssens et al., 2004). However, most fuzzy indexes require many parameters and are not reliable when information of a single pollutant is available or when samples are too small. In opposition to fuzzy logic, grey systems can deal with small samples (Delgado, Romero, 2016) and focus on objects with clear extension and unclear intension (Liu, Lin, 2010), as further explained by Delgado, Romero (2016).

The grey systems theory was developed by Deng (1985) to deal with situations where the available information is poor or the samples used are small (Liu, Lin, 2010). This theory works with uncertain systems in which only partial or low quality data are available (Gong, Forrest, 2014), allowing the decision maker to excavate and extract useful information and to reach an accurate conclusion. A few authors have investigated the implementation of grey theory in water quality analysis (Zhang et al., 2019; Wen, Wei, 2006; Zhu, Liu, 2009), which is a useful technique when the system is only partially known. Grey clustering is one of the most useful contents of the grey systems theory, which allows the classification of objects into definable classes (Delgado, Romero, 2016). The grey clustering method based on whitenization weight functions is mainly used to verify whether objects belong to predetermined classes so that objects of each class can be treated differently (Liu, Lin, 2010). As such, several criteria can be combined for decision-making by assigning a weight to each criterion which can be determined by different weighting methods.

The entropy weighting method is an objective multiple criteria decision approach based on the concept of information entropy developed by Shannon (1948). The information entropy of a criterion is a measurement of its disorder degree and the useful information it can provide (Vatansever, Akgűl, 2018). As such, the higher the entropy of a criterion is, the lower the information it can provide and the lower the clustering weight should be, and vice versa (Sepehri et al., 2019). Delgado, Romero (2016) proposed the incorporation of the entropy weighting method to determine the clustering weights in grey clustering analysis for environmental conflict analysis. Since then, other researchers have evaluated the suitability of integrating grey clustering and the entropy weighting method in other applications such as power systems security risk assessment (Peng et al., 2017), green transportation planning (Ma et al., 2017) or power quality assessment (Sacasqui et al., 2018). The entropy weighting method has also been used for the development water quality indexes in combination with other tools which deal with uncertainty such as fuzzy systems theory (Chen et al., 2019).

For the first time, this paper proposes a methodology to evaluate a pollutant with limited data which uses grey clustering based on whitenization weight functions and the entropy weighting method. The aim is to classify estuaries based on their need for nitrogen pollution management with the limited and inaccurate data available as a first step for its remediation. The assignment of high priority areas allows the water managers to invest the limited economic resources to those areas. Firstly, we developed a pollution management priority index based on grey clustering: the Grey Nitrogen Management Priority index (GNMP index). This index was applied to the evaluation of nitrogen pollution based on spatiotemporal variations of a single pollutant: total nitrogen. Then, we developed a second index with grey clustering which evaluated the nitrogen pollution pressures based on land use: Grey Land Use Pressure index (GLUP index). The results of both indexes were compared to determine the accuracy of the methodology. This method was applied to eight estuaries with mangroves and other wetlands of the Southern Gulf of Mexico where nitrogen pollution is a threat to the ecosystems but where very little information is available.

5.3 Materials and Methods

Water pollution management decisions often needs to be taken out of limited data, i.e. samples which are too small for statistical analysis or where only information from one pollutant is available. With the aim of classifying nitrogen pollution and its management requirements in several estuaries for which only limited information is available, we developed two indexes based on grey clustering:

- Grey Nitrogen Management Priority index: GNMP index
- Grey Land Use Pressures index: GLUP index

Since water pollution should be evaluated in relation to the anthropogenic pressures (Ninčević-Gladan et al., 2015), both indexes were confronted in order to determine the relationship between nitrogen pollution and land use pressures. As such, nitrogen pollution management priorities can be established, and remediation plans can be proposed based on the GLUP index. The method developed is schematized in Figure 5.1 and explained with detail in the next sections.

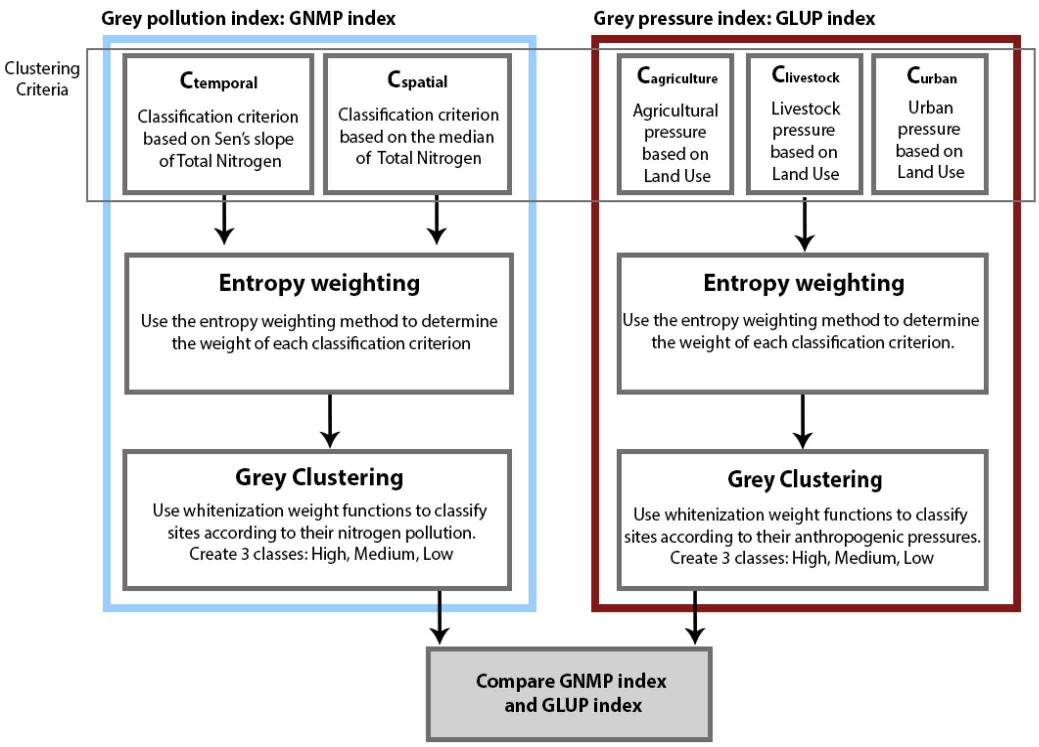

Figure 5.1: Schema of the methodology developed to evaluate nitrogen pollution with limited data. GNMP: Grey Nitrogen Management Priority Index. GLUP: Grey LandUse Pressure

5.3.1 Study area

The Mexican legislation does not consider nutrient pollution in natural water bodies and the accurate monitoring of nitrogen in coastal systems is not regulated. As a consequence, the lack of data prevents stakeholders from implementing the existing assessment methods and proposing recovery measures. Phytoplankton growth is generally nitrogen limited in the Gulf of Mexico (Turner, Rabalais, 2013) and the control of nitrogen pollution is a must for environmental protection.

The Mexican state of Veracruz is located in the Southwestern Gulf of Mexico and covers 745 km of coastline. Approximately 27% of the state population lives within 20 km of the coast (Macauley et al., 2007). The estuaries in Veracruz have been affected by nutrient enrichment for decades (Macauley et al., 2007; Temino-Boes et al., 2019b), but agriculture, urbanization and other economic activities such as tourism along the coast are still a grown source of water pollution (Adame et al., 2018; Rivera-Guzmán et al., 2014). The Mexican legislation does not regulate nitrogen emissions to natural water bodies, and no data exist on direct inputs from urban or industrial sources. Nonetheless, nitrogen pollution has dramatic consequences for mangroves in estuaries, and it allows the massive intrusion of water hyacinths into beaches and mangroves (Temino-Boes et al., 2019b). Clearly, management decisions need to be taken as soon as possible to set remediation plans and avoid further deterioration.

We evaluated 8 monitoring sites located within estuaries with mangroves of the Central Gulf hydrological region of the state of Veracruz in Mexico (Figure 5.2). The local government provided the nitrogen concentrations used in this study, who measured nitrogen concentrations in several monitoring sites located along the coast. Total nitrogen was measured according to the Mexican standards NMX-AA-026-SCFI-2010 and NMX-AA-079-SCFI-2001. The data used for this study includes four annual measurements from 2013 to 2016: two measures correspond to the dry season (16 October to 15 May) and two correspond to the wet season (16 May to

15 October). However, the campaigns were not always equally spaced, and some uncertainties exist related to the exact date of the sampling. To deal with the inaccuracies and the uncertainty in the methods used during the campaigns (locations of the monitoring site, time of sample collection, etc.), we considered grey systems theory to be a reliable tool. The land use associated to mangroves from 2010 and 2015 was downloaded from the National Commission for the Knowledge and Use of Biodiversity website (CONABIO, 2016). The main objective was to prioritize nitrogen pollution management within the estuaries due to the consequences it may have for the surrounding ecosystems such as mangroves.

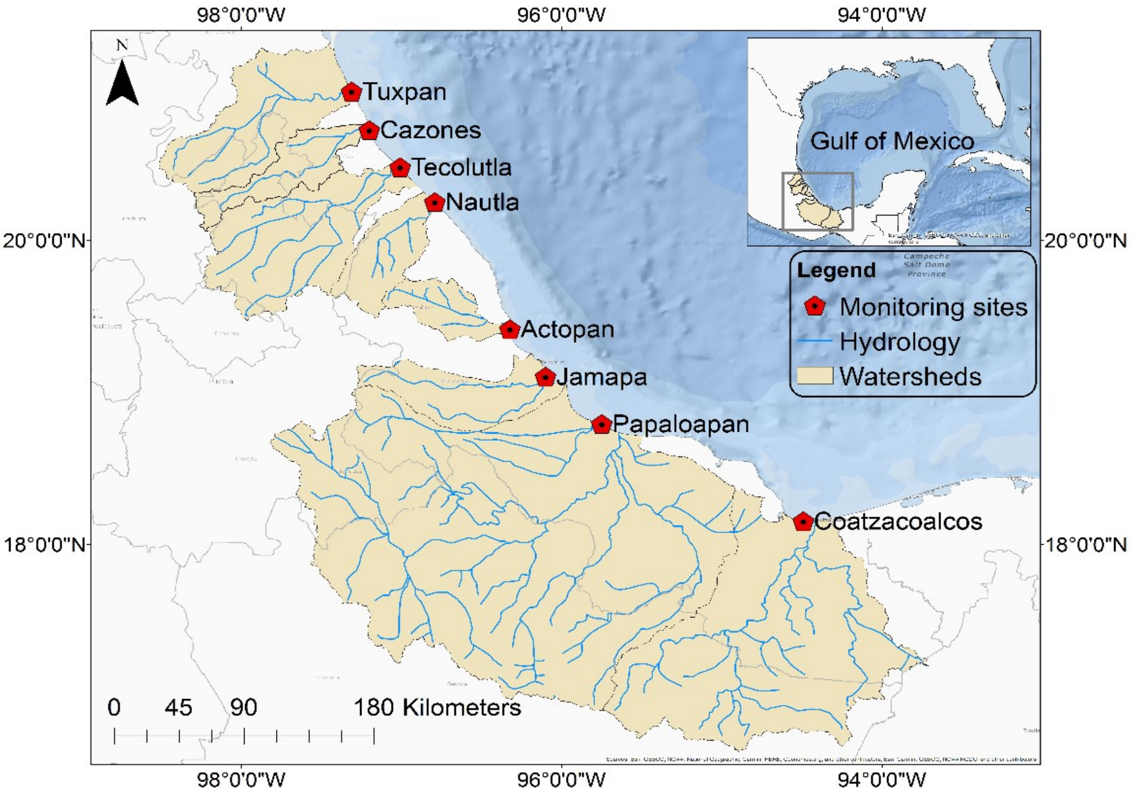

Figure 5.2: Study area with the eight monitoring sites and the corresponding watersheds

5.3.2 Spatiotemporal criteria for Grey Nitrogen Management Priority (GNMP) index

Water pollution evaluation has always relied on spatiotemporal analysis (Ali et al., 2016; Hajigholizadeh, Melesse, 2017; Temino-Boes et al., 2019b). As such, a good water pollution evaluation should consider both spatial and temporal variations of water quality, which should be reflected when developing a classification method (Li et al., 2016). The detection of upward temporal trends in environmental parameters is necessary to not only rank concentrations but also identify those areas with increasing pollution (Chaudhuri, Dutta, 2014), especially in developing countries where water quality problems are often rapidly increasing (Li et al., 2016). The evaluation of differences in spatial mean concentrations of pollutants gives an idea of which site is more polluted now but does not provide information on the future trends. Additionally, an increasing trend clearly indicates a growing source of pollution. Considering the above-mentioned, and with the aim of developing a method which evaluates a single pollutant based on its spatiotemporal variations, we selected two criteria as inputs for the GNMP index: spatial nitrogen differences among sites and temporal trends in each site.

Temporal criterion

The first parameter evaluates the temporal trend of total nitrogen concentrations in each monitoring site. The usual method to determine the trend is based on least squares regression. However, this method requires a linear trend, assumptions on the normal distribution of the data and is very sensitive to outliers. Hence, we used a non-parametric estimation of the trend called Sen's slope (Sen, 1968). Non-parametric methods do not require assumptions on the normal distribution of the data and are not distorted by outliers or missing data (Kitsiou, Karydis, 2011). These methods show useful results for the evaluation of incomplete environmental monitoring data (Scannapieco et al., 2012). Sen's slope has been used in many applications for water quality analysis to detect trends in pollutants (Koh et al., 2017; Machiwal et al., 2019; Tabari et al., 2011) as it represents an absolute measure of change (Miró et al., 2018). As such, we used the Sen's slope to derive an indicator which represents the temporal trend in nitrogen concentrations. We calculated the Seasonal Sen's slope for total N concentrations in each monitoring site with the package "trend" in R version 3.5.1. The Seasonal Sen's slope takes into account the seasonality of the data. In our case study, the seasonality was four, as four samples were collected each year. The scores are first computed for each season separately and finally the corrected Z-statistics for the entire series is calculated (Pohlert, 2020). In order to generate a normalized criterion ranging from zero to one which would allow us to compare pollution trends in each site, we used the following equation:

$$C_{temporal_i} = \frac{s_i - s_{min}}{s_{max} - s_{min}} \tag{5.3.1}$$

Where, $C_{temporal_i}$ is the temporal variation criterion in site i, s_i is Sen's slope in i, s_{min} is the minimum Sen's slope between all sites and s_{max} is the maximum Sen's slope between all sites.

Spatial criterion

To evaluate the spatial differences of nitrogen concentrations among the monitoring sites we used the median of total N of each site. The median is a robust measure of central tendency, which is not skewed by outliers. As the sampling size is not large and data reliability is not clear, the median was selected as a better measure than the mean. We determined a normalized criterion with values going from 0 to 1 which allows the comparison of nitrogen concentrations among sites:

$$C_{spatial_i} = \frac{M_i - M_{min}}{M_{max} - M_{min}} \tag{5.3.2}$$

where, $C_{spatial_i}$ is the spatial variation criterion in site i, M_i is the median of total nitrogen in site i, M_{min} is the minimum median value between all study sites and M_{max} is the maximum median value between all sites.

5.3.3 Pressure criteria for the Grey Land Use Pressure (GLUP) index

For the development of the GLUP index, we defined the criteria by evaluating the anthropogenic pressures on N pollution based on land use. We downloaded maps of land use from the National Commission for the Knowledge and Use of Biodiversity website (CONABIO, 2016), which used SPOT images to create them. The images which more closely correspond to nitrogen data were images from 2010 and 2015. Although this timeframe does not correspond fully with nitrogen monitoring years (2013-2016), it represents the trend of land use changes. Nonetheless, the inaccuracy in the dates of land use maps is addressed by grey clustering which can deal with incomplete information. After carefully reviewing the scientific literature we identified three main sources of nitrogen pollution associated to land use in the study area: agriculture, livestock and urban expansion along the coast. We defined one criterion for each source.

Agriculture

Veracruz is the second state in Mexico with the highest amount of land used for agriculture. The agriculture production is mainly composed of cereals (40.1% of the cultivated land), industrial crops (31.5%) and fruit trees (21.6%) (SAGARPA, 2009). The application of fertilizers to increase agricultural productivity is encouraged by governmental policies, while farmers are not provided with appropriate training (Anguiano-Cuevas et al., 2015). Consequently, natural water bodies are being increasingly impacted by diffuse nutrient pollution generated from such practices. Besides, the conversion of forest and grassland to crop agriculture also may contribute significantly to nitrogen loading to coastal systems (López-Portillo et al., 2017). As such, the first pressure criterion $C_{agriculture}$ used as input for the GLUP index calculation was the percentage of the watershed used for agriculture.

Livestock

The livestock subsector in Mexico is very diverse and widespread throughout the territory. Livestock farming in Veracruz consists of both farms that are managed with modern and competitive systems and others which use the most traditional practices. It is also characterized by its extensive management and seasonal production. Most cattle feed is based on grazing, with pastures managed in a free grazing system. Livestock occupies about 51% of the total area of the state with 3.7 million hectares. The bovine cattle stands out for its importance in production, which is used both for meat and milk production (SAGARPA, 2009). As a consequence, land clearing for cattle ranching is also a predominant source of pollution throughout the studied watersheds (González-Marín et al., 2017; López-Portillo et al., 2017; Rivera-Guzmán et al., 2014; Rodríguez-Romero et al., 2018; Vázquez-González et al., 2015). Therefore, the second pressure criterion used for the calculation of the GLUP index is the percentage of the watershed used for livestock production, $C_{livestock}$.

Urban

Most of the urban areas in Veracruz are located along the coast and consequently urban development expands over beaches, dunes and mangroves, parallel to the coastline (Martínez et al., 2014). In fact, many researchers identified the rapid urbanization over beaches and mangroves throughout the coast as one of the main source of water pollution to our study sites (Marín-Muñiz et al., 2016; Martinez et al., 2017; Martínez et al., 2014; Mendoza-González et al., 2012; Rodríguez-Romero et al., 2018). The accelerated urban development does not allow the implementation of the required wastewater treatment facilities (Rodríguez-Romero et al., 2018) or the adequate coastal ecosystem management (Martínez et al., 2014). Moreover, direct urban pollution affects the lower course of the watersheds, adding to the fact that self-purification is not as efficient as in the upper course (Rodríguez-Romero et al., 2018). As such, for the urban pressure criterion we considered more adequate to focus on the urban development along the coast. The aim of this criterion was to represent exclusively the urban expansion over the coastal ecosystems such as beaches, dunes or mangroves. This expansion occurs generally at less than 1km from the coast, especially in touristic areas (Mendoza-González et al., 2012). As such, the selection of a buffer of 1km around the sampling points was considered adequate. Therefore, we calculated the urban expansion within 1km of the sampling points observed between 2010 and 2015, which was the third input criterion C_{Urban} for the GLUP index.

5.3.4 Grey clustering

In grey systems theory, a system with totally unknown information is called a black system, while a system with fully known information is a white system. In between we find grey systems which have partially known information (Tseng, 2009), with small samples and poor information (Liu, Lin, 2010). Similarly, a grey number is a number whose value lies within an interval, but whose exact value is unknown. In this context, whitenization weight functions are used to determine the preference a grey number has over the interval of values it might take by describing what is known (Liu, Lin, 2010). Grey clustering is a method developed to classify observation objects into classes using either grey incidence or whitenization weight functions (Liu, Lin, 2010). The second method is mainly used to check whether objects belong to predefined classes (Liu, Lin, 2010).

The point of a grey class with a maximum degree of greyness is known as the center λ (Liu, Lin, 2010). The center-point triangular whitenization weight function relies on the center of the interval, where the cognitive certainty of the object belonging to a defined class is higher and therefore is often considered more reliable and scientific (Delgado, Romero, 2016). For grey clustering in s classes, the left and right endpoints are extended horizontally from λ_1 to zero and from λ_s to the highest possible value of the criterion (Ye et al., 2018). As such, an object whose criterion is lower than λ_1 totally belongs to the first grey class, while an object whose criterion is greater than λ_s totally belongs to the highest class. Center-point triangular whitenization weight functions were used in other environmental applications, demonstrating the usefulness of this method to solve such problems (Delgado et al., 2018; Delgado, Romero, 2016). The steps followed for the grey clustering are described below (Liu, Lin, 2010):

Step 1. Define n criteria (j=1,2,...n), m objects (i=1,2,...m) to be classified in s classes (k=1,2,...s), and the observed data values $x_{i,j}$

Step 2. Divide the values field of each criterion into s equal grey intervals ([a_0, a_1], [a_1, a_2], ... [a_{s-1}, a_s]) and define the center-points λ_k of each interval (λ_1, λ_2, ... λ_s)

Step 3. Determine the whitenization wheight function $f_j^k\,(x_{i,j})$ for each k^{th} class of each j^{th} criterion with the next equations:

For k=1

$$f_j^1 = \begin{cases} 1 & x < \lambda_1 \\ \frac{\lambda_2 - x}{\lambda_2 - \lambda_1} & x \in [\lambda_1, \lambda_2] \\ 0 & x > \lambda_2 \end{cases} \tag{5.3.3}$$

For $1 < k < s$

$$f_j^k = \begin{cases} 0 & x \notin [\lambda_{k-1}, \lambda_{k+1}] \\ \frac{x - \lambda_{k-1}}{\lambda_k - \lambda_{k-1}} & x \in [\lambda_{k-1}, \lambda_k] \\ \frac{\lambda_{k+1} - x}{\lambda_{k+1} - \lambda_k} & x \in [\lambda_k, \lambda_{k+1}] \end{cases} \tag{5.3.4}$$

For k=s

$$f_j^1 = \begin{cases} 0 & x < \lambda_{s-1} \\ \frac{x-\lambda_{s-1}}{\lambda_s-\lambda_{s-1}} & x \in [\lambda_{s-1}, \lambda_s] \\ 1 & x > \lambda_s \end{cases} \tag{5.3.5}$$

Step 3. Select a clustering weight η_j for each criterion j

Step 4. Calculate the clustering coefficients for each criterion j and each class k as:

$$\sigma_i^k = \sum_{j=1}^{m} \eta_j \bullet f_j^k (x_{ij}) \; i = 1, 2, ...m \quad j = 1, 2, ...n \quad k = 1, 2, ...s \tag{5.3.6}$$

Step 5. If $=1 \leq k^{MAX} \leq s \left\{\sigma_i^k\right\} = \sigma_i^{k^*}$ then object i belongs to grey class k^*

For each criterion, we defined three classes corresponding to "High", "Medium" and "Low" priorities, and thus, the whitenization weight functions are as represented in Figure 5.3. The clustering objects correspond to the monitoring sites. The clustering criteria used were the spatial and temporal criteria defined in section 5.3.2 for the GNMP index and the agriculture, livestock and urban criteria defined in section 5.6 for the GLUP index (Table 5.1). The clustering weights are defined based on the entropy weighting method explained in 5.3.5.

Index	Criteria	Description
GNMP	$C_{temporal}$	Normalized index based on the Sen' slope (equ. 5.3.1)
	$C_{spatial}$	Normalized index based on the median of total nitrogen (equ. 5.3.2)
GLUP	$C_{agriculture}$	Percentage of the watershed used for agriculture
	$C_{livestock}$	Percentage of the watershed used for livestock production
	C_{urban}	Increase in urban area within 1km of the sampling site from 2010 to 2015 (ha)

Table 5.1: Description of the criteria used for Grey Nitrogen Management Priority (GNMP) and Grey Land Use Pressure (GLUP) indexes

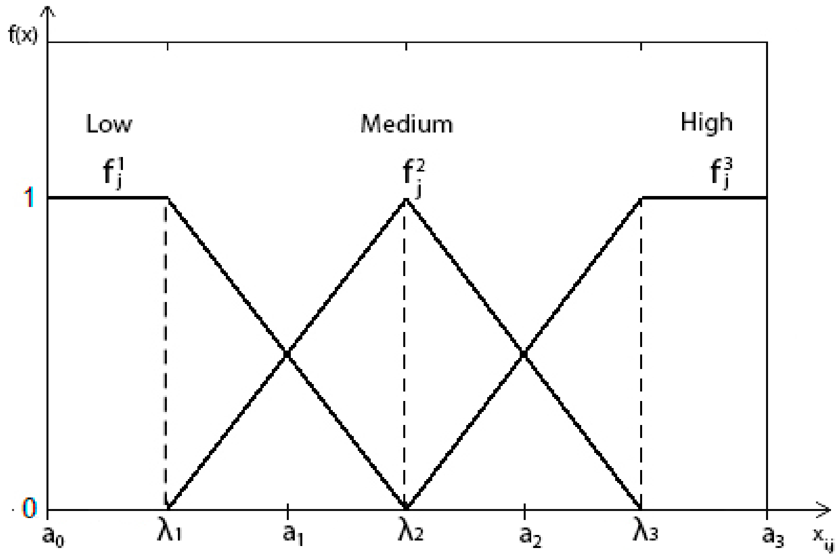

Figure 5.3: Center-point whitenization weight functions used for each criterion and with three grey classes (high, medium and low)

5.3.5 Entropy weighting method

The clustering weights are calculated with the Shannon entropy, which measures the uncertainty in the information provided by each criterion (Delgado, Romero, 2016):

Step 1. Normalize each criterion:

$$P_{ij} = \frac{x_{ij}}{\sum_{i=1}^{m} x_{ij}} \tag{5.3.7}$$

Step 2. Calculate the entropy Hj of each criterion:

$$H_j = -\frac{1}{ln(m)} \sum_{i=1}^{m} p_{ij} ln\ (p_{ij}) \tag{5.3.8}$$

Step 3. Calculate the degree of divergence div_j of the average intrinsic information provided by each criterion:

$$div_j = 1 - H_j \tag{5.3.9}$$

Step 4. Calculate the clustering weight η_j of each criterion:

$$\eta_j = \frac{div_j}{\sum_{j=1}^{n} div_j} \tag{5.3.10}$$

5.4 Results

5.4.1 Total nitrogen concentrations

Total nitrogen concentrations in each sampling site are presented in Figure 5.4. The median was greater in the Northern regions with a maximum value in Nautla. The lowest total nitrogen concentrations were found in Papaloapan and Coatzacoalcos. In Figure 5.5, the time variations of total nitrogen between 2013 and 2016 are represented with four measurements per year. An upward tendency was observed in Tuxpan, Tecolutla and Nautla.

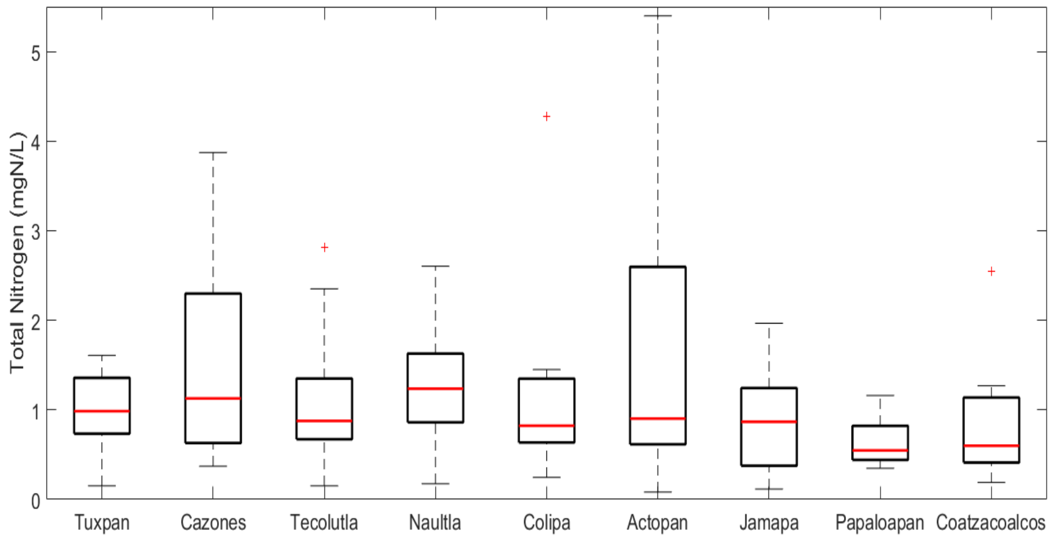

Figure 5.4: Boxplot of total nitrogen concentrations in all monitoring sites, between 2013 and 2016 with four values per year

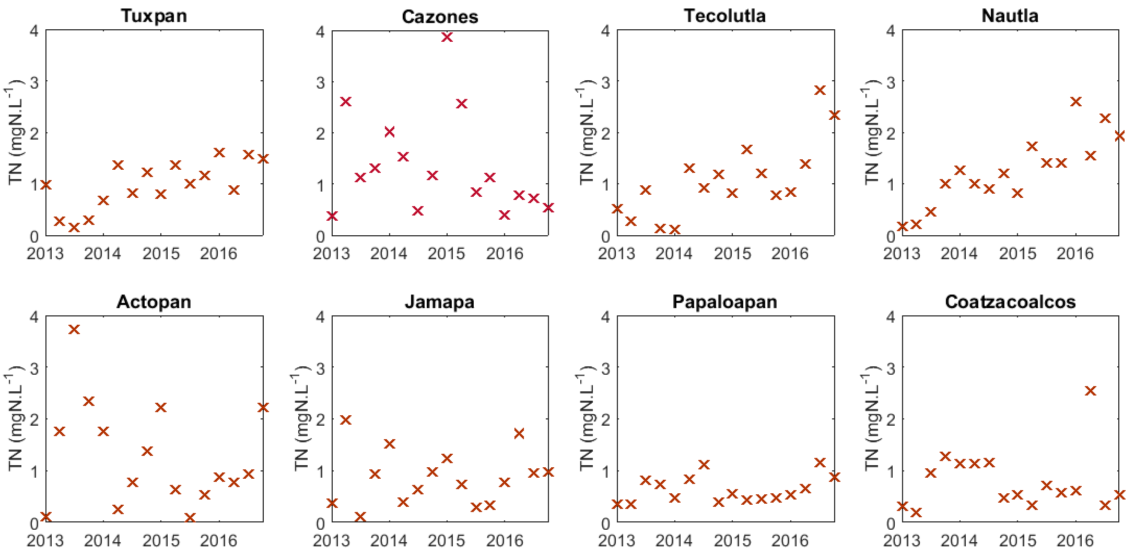

Figure 5.5: Total nitrogen concentrations in all monitoring sites, between 2013 and 2016 with four values per year

5.4.2 Grey Nitrogen Management Priority (GNMP) index

Sen's slope and the median of total nitrogen are shown in Table 5.2, together with temporal and spatial criteria and their clustering weights. The spatial criterion, which compares the current total nitrogen concentrations in each site, had a higher clustering weight (0.60) derived from the entropy-weighting method, compared to the temporal indicator which measures the trend in total nitrogen concentrations in each site (0.40).

Three grey classes were obtained corresponding to low, medium and high N pollution management priority. The clustering coefficients for each class and each criterion, together with the global clustering coefficients and the derived GNMP index are shown in Table 5.3. Two sites, Tuxpan and Nautla, were classified with a high nitrogen management priority, while two sites, Papaloapan and Coatzacoalcos, were classified with low priority. The other sites had a medium priority.

Site	Sen´s slope ($mgN.L^{-1}$)	Median TN ($mgN.L^{-1}$)	$C_{temporal}$	$C_{spatial}$
Tuxpan	0.34	0.99	0.78	0.64
Cazones	-0.13	0.90	0.07	0.51
Tecolutla	0.36	0.89	0.81	0.49
Nautla	0.49	1.24	1.00	1.00
Actopan	-0.18	0.90	0.00	0.51
Jamapa	0.07	0.86	0.37	0.45
Papaloapan	0.06	0.55	0.36	0.00
Coatzacoalcos	0.00	0.60	0.27	0.07
Clustering weight	-	-	0.40	0.60

Table 5.2: Sen's slope, Median total nitrogen (TN), Ctemporal, Cspatial and clustering weights

Site	$C_{temporal}$			$C_{spatial}$			**Global**			GNMP
	L	M	H	L	M	H	L	M	H	
Tuxpan	0.00	0.17	0.83	0.00	0.59	0.41	0.00	0.42	0.58	High
Cazones	1.00	0.00	0.00	0.00	0.99	0.02	0.40	0.59	0.01	Medium
Tecolutla	0.00	0.08	0.92	0.02	0.98	0.00	0.01	0.62	0.37	Medium
Nautla	0.00	0.00	1.00	0.00	0.00	1.00	0.00	0.00	1.00	High
Actopan	1.00	0.00	0.00	0.00	0.99	0.02	0.40	0.59	0.01	Medium
Jamapa	0.38	0.62	0.00	0.15	0.85	0.00	0.24	0.76	0.00	Medium
Papal.	0.43	0.58	0.00	1.00	0.00	0.00	0.77	0.23	0.00	Low
Coatza.	0.69	0.31	0.00	1.00	0.00	0.00	0.88	0.12	0.00	Low

Table 5.3: Clustering coefficients for each criterion, the global clustering coefficients and the derived Grey Nitrogen Management Priority (GNMP) index. L:low, M:Medium, H:high

5.4.3 Grey Land Use Pressure (GLUP) index

We evaluated the extent of the agricultural area within each watershed, together with the livestock area (Figure 5.6). Additionally, we calculated the increase in urban areas around the study sites. As an example, the three sites with a greater increase in the urban areas are shown in Figure 5.7.

The three criteria for land use evaluation and their clustering weights are presented in Table 5.4, while the clustering coefficients and the derived GLUP index are presented in Table 5.5. The classification agrees with the results obtained with the GNMP index (see Table 5.3). The urban criterion had the highest clustering

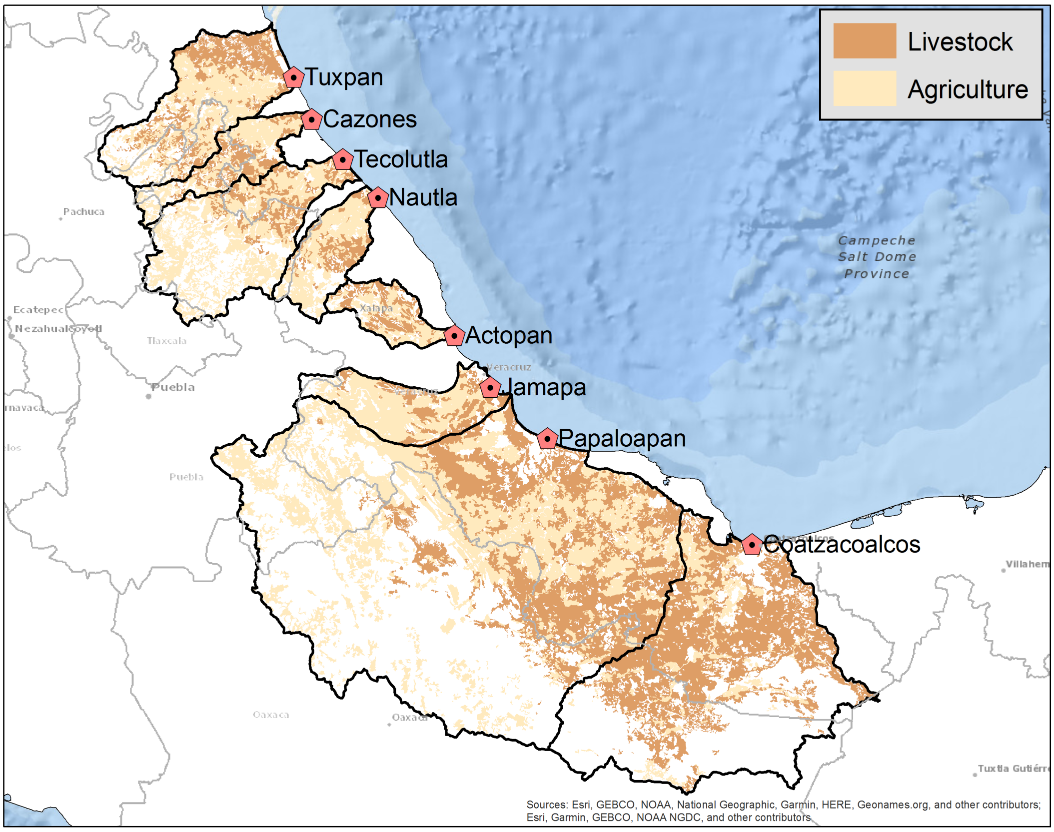

Figure 5.6: Agricultural and livestock production areas within the studied watersheds

weight (0.67), while the agricultural criterion weight (0.22) and the livestock weight (0.11) were lower.

Site	$C_{agriculture}$	$C_{livestock}$	C_{urban}
Tuxpan	43	29	14.9
Cazones	51	28	6.5
Tecolutla	49	13	9.6
Nautla	56	22	18.7
Actopan	45	32	6.8
Jamapa	57	25	6.9
Papaloapan	30	21	4.4
Coatzacoalcos	9	40	0.0
Clustering weight	0.22	0.11	0.67

Table 5.4: $C_{agriculture}$, $C_{livestock}$, C_{urban} and their clustering weights for all monitoring sites

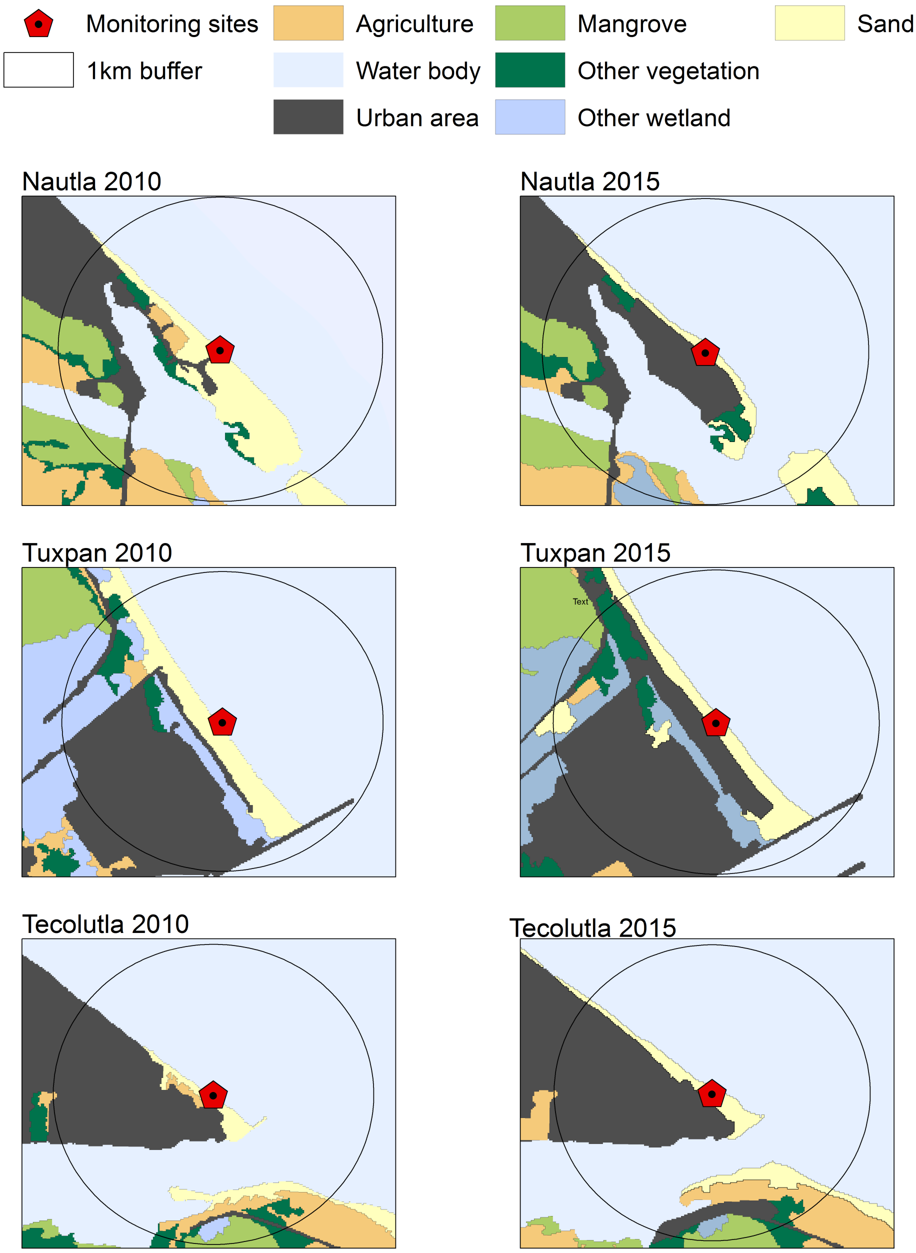

Figure 5.7: Urban area development between 2010 and 2015 in a 1km buffer around the study sites Nautla, Tuxpan and Tecolutla

Site	$C_{agriculture}$			$C_{livestock}$			C_{urban}			**Global**			GLUP
	L	M	H	L	M	H	L	M	H	L	M	H	
Tuxpan	0.00	0.40	0.60	0.00	0.67	0.33	0.00	0.11	0.89	0.00	0.24	0.76	High
Cazones	0.00	0.00	1.00	0.00	0.79	0.21	0.46	0.54	0.00	0.31	0.45	0.24	Medium
Tecolutla	0.00	0.00	1.00	1.00	0.00	0.00	0.00	0.97	0.03	0.11	0.65	0.24	Medium
Nautla	0.00	0.00	1.00	0.46	0.54	0.00	0.00	0.00	1.00	0.05	0.06	0.89	High
Actopan	0.00	0.26	0.74	0.00	0.36	0.64	0.41	0.59	0.00	0.27	0.49	0.23	Medium
Jamapa	0.00	0.00	1.00	0.16	0.84	0.00	0.39	0.61	0.00	0.28	0.51	0.21	Medium
Papaloapan	0.18	0.82	0.00	0.61	0.39	0.00	0.79	0.21	0.00	0.64	0.36	0.00	Low
Coatzacoalcos	1.00	0.00	0.00	0.00	0.00	1.00	1.00	0.00	0.00	0.89	0.00	0.11	Low

Table 5.5: Clustering coefficients for each class (low, medium and high) and each criterion and the Grey Land Use Pressure (GLUP) index for all monitoring sites. L:low, M:Medium, H:high

5.5 Discussion

The GNMP index, based on the global clustering coefficients presented in Table 5.3, was high for Tuxpan and Nautla. In terms of the temporal criteria both sites were classified as high while the spatial criterion indicated high priority for Nautla and medium priority for Tuxpan. Similarly, Tecolutla was high according to the temporal criterion indicating rapidly increasing nitrogen concentrations but was classified medium based on the spatial criterion; its overall classification was medium. The remaining monitoring sites could be evaluated similarly, indicating that the integration of both temporal and spatial differences among sites derives in a more accurate evaluation of the nitrogen management requirements. The inclusion of temporal trends into the index developed is a new proposal which was not used in most of the water quality assessment indexes developed to date (Da Costa Lobato et al., 2015; Gharibi et al., 2012; Islam et al., 2013; Ocampo-Duque et al., 2007; Shooshtarian et al., 2018). Yet, the detection of temporal trends is especially important in areas where water pollution increases rapidly due to the lack of water pollution management (Li et al., 2016), which are the areas aimed by the newly developed method.

Environmental managers could determine the restoration practices required based on whether the nitrogen pollution is increasing over time or on whether the current concentrations are high.

The comparison of the classification of the GNMP index with the GLUP index is necessary in order to validate the nitrogen pollution evaluation. The linkage between pollution levels and pressures allows the evaluation of the anthropogenic influence on nutrient concentrations. It also allows to check whether the selected land use pressures have a real impact on nutrient pollution and to guide management plans (Romero et al., 2013). All monitoring sites were placed in the same class by the GNMP and the GLUP indexes, indicating that land use pressures were detected accurately. The results indicate that Nautla and Tuxpan estuaries have the highest urgency for N pollution management which agrees with previous studies which indicated the existence of N pollution in these estuaries (González-Marín et al., 2017; Marín-Muñiz et al., 2016; Rivera-Guzmán et al., 2014; Rodríguez-Romero et al., 2018; Temino-Boes et al., 2019b). Studies in Nautla river indicated that human settlements are a major source of N pollution to the river at its lower course (Rodríguez-Romero et al., 2018). Casitas, the town located at Nautla estuary, has undergone severe changes in physicochemical characteristics of water in the last years (Rivera-Guzmán et al., 2014), and has lost most of its mangroves losing its filtering capacity (Marín-Muñiz et al., 2016; Rivera-Guzmán et al., 2014).

The entropy weighting method allowed the detection of the most divergent criteria for nitrogen management. As such, in the studied area the spatial criterion had a higher clustering weight (0.60) than the temporal criterion (0.40), indicating that the divergence in the values of the median of total nitrogen are higher than the divergence in the Sen's slope. The entropy weighting method allows a more flexible determination of the importance of each criterion depending on the characteristics of the area under study by evaluating the useful information provided by each criterion. On the other hand, the clustering weights assigned to the GLUP index indicate which land use criterion has a higher divergence and thus which land use activity may have a higher influence in nitrogen pollution. The highest clustering weight for the GLUP index was assigned to the urban criterion, indicating that the urban development along the coast should be the first pollution source to be addressed for nitrogen management. Tecolutla and Nautla are located within a popular touristic area named Costa Esmeralda, where tourism expansion has led to urban development over beaches and mangroves (Martínez et al., 2014). Tecolutla river basin experienced an increase of 67% of the urban area between 1994 and 2010 (Osuna-Osuna et al., 2015) and in Tuxpan the human population almost doubled in 20 years (Rivera-Guzmán et al., 2014). At large, urban expansion in Veracruz has taken place over mangroves, grasslands, beaches and croplands (Martínez et al., 2014), and tourism has increased along the coast (Mendoza-González et al., 2012), reducing the coastal resilience of Veracruz while population grows (Martinez et al., 2017).

While conventional clustering methods assign a fixed class to each object, grey clustering does not provide a deterministic solution, but rather allows the partial assignment of an object to a class by means of grey numbers. For example, both Cazones and Tecolutla were classified in the medium class. However, the GNMP index of Cazones is somewhere between low (0.40 clustering coefficient) and medium (0.59 clustering coefficient), while Tecolutla's GNMP is localized between medium and high (Table 5.3). The same applies for the GLUP index (Table 5.5). This flexibility in the classification allows the pollution managers to make decisions which are aligned with the ecosystems' requirements, the site restoration strategies or the economic resources available, allowing a scientific understanding of nitrogen pollution when only small sampled are available. The exploration of the information provided by the available data enables a comprehensive evaluation of nitrogen pollution.

The limitations of the developed methodology should be clear before its application. This approach evaluates one single pollutant while no additional data is available, but the development of more frequent and exhaustive campaigns is necessary for the management of the coastal water quality. When economic resources are limited, governments and scientists could start by managing nutrient pollution in the areas indicated by the method developed. But once more data become available, the use of integrative methods to evaluate the overall water quality would be a necessary step forward. Additionally, it is important to point out that as no pristine site exists, it is not possible to indicate whether all monitored sites are polluted. Although the priority should be put in those areas with a greater pollution, the sites with a lower priority should not be completely left aside. On the other hand, it is also important to consider that the studied estuaries belong to watersheds of different sizes. As such, the cleaning capacity of rivers via dilution differs among sites. The risk of water pollution in Coatzacoalcos and Papaloapan is therefore reduced due to their dilution capacity, compared to Actopan river for example. The aim of our approach is to evaluate the pollution within the estuary to estimate the potential consequences of nitrogen pollution to the surrounding ecosystems such as beaches or mangroves. For example, the consequences of nitrogen pollution in Nautla estuary include the degradation of touristic beaches with consequences for the local economy, as well as the deterioration of mangroves (Temino-Boes et al., 2019b). But the impact of high nitrogen concentrations in Papaloapan river in the eutrophication of the Gulf of Mexico as a whole would be much worse than N pollution in Actopan river. The large marine ecosystem perspective is not addressed by this study.

Nitrogen pollution in estuaries, mangroves and coastal waters has severe environmental consequences. In Veracruz, 75% of the estuaries rated poor for water quality a decade ago (Macauley et al., 2007), and the urbanization along the coast has since then increased nutrient pollution (Temino-Boes et al., 2019b). Massive mats of water hyacinths, driven by nutrient pollution, were observed in Nautla and Tecolutla estuaries, extending over mangroves, altering their nutrient cycles and blocking sunlight (Temino-Boes et al., 2019b). Nitrogen pollution also has big economic impacts, as many of the small villages located in the coastal regions of Veracruz depend on tourism and fishing, activities which are directly affected by nitrogen pollution (González-Marín et al., 2017). Ultimately, water pollution also affects wildlife populations (González-Marín et al., 2017) and eutrophic conditions in coastal systems along the Gulf of Mexico may drive harmful algal blooms (Ulloa et al., 2017). Despite the consequences mentioned, the lack of effective water monitoring and evaluation programs prevents stakeholders from developing management plans. The methodology developed herein allows the detection of high N concentrations in estuaries as well as those estuaries with increasing trends and links the pollution to land uses. As such, based on our results, Nautla and Tuxpan estuaries have a high priority for N pollution management which should be approached mainly through the sustainable management of urban development. Both Tuxpan and Nautla are touristic destinations, which has enhanced urban growth. Tecolutla which is also a touristic destination was classified as medium priority, but the high temporal criterion indicates that N pollution increased over time and could reach higher N concentrations in a near future. Therefore, the sustainable management of tourism growth could lead to a reduction of the coastal pollution which in turn would allow a conservation of the natural heritage.

In regions where the monitoring of coastal waters is not regulated, simple methods which allow the evaluation of water pollution with limited data are very useful. It is necessary to recognize the scarcity factor to allow the distribution of the available resources efficiently (Sánchez-Hernández et al., 2017). As such, grey clustering allows the detection of areas with a high urgency for N management and allows the planning of the available economic and human resources. When data sources are limited and inaccurate, the grey evaluation developed can help with the establishment priority areas to allow decision makers to identify potential threats and propose recovery measures. This method could be used to evaluate other pollutants, and could be applied in other countries with limited data such as most Latin American countries which present similar limitations with water pollution assessment and management (Gómez et al., 2012; Kathuria, 2006). Future research should focus on how to efficiently combine the existing tools to deal with uncertainty, such as fuzzy logic, grey systems or rough sets theory, whose employment can deal with real-world problems especially in countries with limited economic resources.

5.6 Conslusion

Many countries lack proper coastal water monitoring programs and consequently the data available for pollution assessment is limited. As such, the application of grey clustering together with entropy weighting significantly contributes to the accurate prioritization of N pollution management. The integration of spatial and temporal variations in a unique index, i.e. the GNMP index, evaluated both current and future trends of N pollution. On the other hand, the analysis of land use changes through the GLUP index and the application of the entropy weighting method identified the main sources of N pollution based on land use. For the study area we found urban development around the sampling site to be the main driver of N pollution. This allows the establishment of N pollution management strategies, such as the control of the urban expansion over beaches and mangroves, allowing a sustainable development while conserving the natural heritage. When economic resources are limited, the establishment of priority areas is necessary in order to allow a scientifically sound assignment of the scarce economic resources.

It is nonetheless crucial to understand and consider the limitations of the methodology. Grey clustering provides useful information derived from small and inaccurate samples, which can be extremely useful when the situation from which we departed is a completely lack of pollution evaluation. From this perspective, the information provided by the grey clustering analysis is with no doubt an important step forward. However, this is not an ideal situation which provides a thorough and unique diagnosis of the pollution levels, its pressures and impacts. The implementation of more stringent coastal monitoring programs and the development of strict environmental policies to protect water resources is necessary for the correct management of coastal pollution. But this situation is far from realistic in many developing countries. Meanwhile, research should focus on how to deal with the lack of data by combining and implementing tools such as fuzzy logic, grey systems or rough sets theory.

CHAPTER 6

A spatiotemporal analysis of nitrogen pollution in a coastal region with mangroves of the Southern Gulf of Mexico

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6.1 Abstract

Nitrogen pollution is a growing problem in many rivers and estuaries of the Southern Gulf of Mexico. In Costa Esmeralda, a tourist destination in Veracruz, the increasing nitrogen pollution is causing severe environmental damage. However, very few studies addressed nitrogen pollution and its consequences for beaches and mangroves. In this study, a spatiotemporal evaluation of nitrogen concentrations was performed along two rivers discharging into Costa Esmeralda and the associated mangrove and coastal areas. The data used was obtained from the local government, which measured ammonium, nitrate and organic nitrogen concentrations between 2013 and 2016 with four annual measurements. Clustering analysis was used to detect the nitrogen concentration differences between riverine and coastal sites. Additionally, Mann-Kendall test was used to detect the trends throughout the study period. The Mann-Whitney W-test determined the difference in the median concentrations between the dry and the wet season. The results indicate that organic nitrogen concentrations are increasing in river mouths and coastal waters. Nitrogen pollution caused an intrusion of water hyacinths in touristic beaches and completely covered mangroves. The decomposition of these plants in saline waters was identified as the main potential source of increasing organic concentrations, driven by nitrogen pollution from wastewater, deforestation and fertilizers, and causing many environmental and socio-economic damage to the area. The results shed light on the prevailing water pollution problems in the Southern Gulf of Mexico.

6.2 Introduction

The Gulf of Mexico is a semi-enclosed coastal sea with moderately high productivity that supports great biological diversity. It provides many goods and services such as oil and gas production, fisheries, habitat for endangered species, tourism and support for state economies (Muñoz-Sevilla, Le Bail, 2017). The Gulf of Mexico is a shared ecosystem in which environmental solutions are a common responsibility among governments, primarily the United States and Mexico (Yañez-Arancibia et al., 2013). In the Northern Gulf of Mexico, nitrogen (N) riverine discharges from Mississippi and Atchafalaya rivers have caused high phytoplankton concentrations in coastal waters, hypoxia (Bianchi et al., 2010), acidification (Laurent et al., 2017), toxic algal blooms (Bargu et al., 2016), and have generated one of the largest marine hypoxic zones known as a dead zone (He, Xu, 2015). Agricultural runoff has been identified as the main driver of eutrophication (Alexander et al., 2008). While nutrient pollution and its consequences in the northern Gulf is a long-standing problem and has been largely addressed by scientists and the U.S. government, the southern Gulf corresponding to the Mexican coast is still a growing ecological and human health issue with limited attention. The Southern Gulf of Mexico has a much higher poverty rate and increasing populations are degrading coastal ecosystems and the services they provide to society (Álvarez Torres et al., 2017).

The Mexican state of Veracruz has a significant share of the Southern Gulf of Mexico's coastal waters. The alteration of the coast in Veracruz started many years ago, and today human activity is still a growing pressure to the coast (Martinez et al., 2017). Veracruz estuaries have long been affected by nutrient over-enrichment, which has caused poor water quality (Macauley et al., 2007). Eutrophic conditions in coastal lagoons have prevailed for at least 30 years, with significant anthropogenic impact all along the coast as they receive excess nutrients (Rivera-Guzmán et al., 2014). Over 10 years ago already scientists determined that deforestation and agricultural runoff were significantly contributing to the degradation of coastal waters in Veracruz due to nutrient loads (Macauley et al., 2007). And yet, there is still an intensification of agriculture, urbanization and other economic activities along the coast (Rivera-Guzmán et al., 2014). The application of fertilizers to increase agricultural productivity has been encouraged by governmental policies, while farmers are not provided with appropriate training (Anguiano-Cuevas et al., 2015). Consequently, natural water bodies are being increasingly impacted by diffuse nutrient pollution generated from such practices. Additionally, sewage discharges which most of the time lack a proper treatment process, also represent a significant input of nutrients to coastal waters (Okolodkov et al., 2016). As a consequence, harmful algal blooms are an issue of concern in the Mexican coast of the Gulf of Mexico (Ulloa et al., 2017), and the prevalence of cholera has been related to poor water quality (Mokondoko et al., 2016).

Mexico is the fourth mangrove-richest country in the world (Giri et al., 2011), one of the most productive ecosystems on Earth that grow in coastal areas. Mangroves provide food and shelter for many marine species and birds, and act as natural barriers against hurricanes, tsunamis and sea level rise (Holguin et al., 2006). Moreover, mangroves are a large carbon stock known as blue carbon (Thorhaug et al., 2019), and the deforestation of these ecosystems entails large greenhouse gas emissions (Kauffman et al., 2016). Despite all of the above-mentioned, 35% of mangroves were lost worldwide between 1980 and 2000 (Giri et al., 2011) and still continue to decrease (Feller et al., 2017). If the current deforestation rate does not change all mangroves could be gone by next century (Duke et al., 2007). The high primary production in mangroves is generally attributed to leaf degradation processes (Torres et al., 2018), which recycle nutrients within the ecosystem (Holguin et al., 2006). Mangroves play a significant role in N dynamics, which indicates that anthropogenic nutrient enrichment may cause extensive impact in the N cycling (Gonçalves Reis et al., 2017). With urban development, mangroves receive more nutrients, which could lead to an accelerated change (Geedicke et al., 2018). For instance, N enrichment alters biological processes such as nitrogen fixation or denitrification and modifies the competitive ability among species. As a consequence of anthropogenic N, mangroves may increase N_2O fluxes to the atmosphere, also contributing to global warming (Gonçalves Reis et al., 2017). The alteration of mangrove functioning as a consequence of N enrichment may reduce the goods and services they provide, such as coastal fisheries or improvement of water quality (Holguin et al., 2006). In Mexico, tourism, agricultural and urban development along the coast cause serious mangrove degradation (Adame et al., 2018), affecting the resilience of coastal lagoons (López-Portillo et al., 2017). Additionally, high N concentrations in mangroves enables the growth of exotic species (Geedicke et al., 2018).

Water hyacinth (Eichhornia crassipes) is considered to be one of the most invasive aquatic species on Earth (Villamagna, Murphy, 2010). This floating plant prevails in tropical and subtropical areas where nutrient pollution exists due to agricultural runoff, deforestation or untreated wastewater discharges (Villamagna, Murphy, 2010). Nutrient availability and temperature regulates its growth (Oliveira-Junior et al., 2018; Ruiz Téllez et al., 2008). As such, water hyacinth blooms in summer as a result of high temperatures and sustained by the nutrient pollution. The presence of water hyacinth in the ecosystem may have both beneficial and detrimental effects. On one side, this plant is often used for phytoremediation, as it absorbs pollutants such as nutrients or heavy metals (Tabla-Hernandez et al., 2019). Nonetheless, when the extent of the invasion is too large the threads to the ecosystem can be very significant. Decaying plants may reduce the available oxygen and unbalance the nutrient cycling (Fox et al., 2008). This free-floating plant was introduced in Veracruz's rivers many years ago. Due to the rapid urbanization of the coast over beaches and mangroves (Martínez et al., 2014) and to the lack of wastewater treatment, nutrient pollution is a growing problem in many estuaries of Veracruz (Rivera-Guzmán et al., 2014), which may lead to the unlimited growth of water hyacinths.

Despite the growing environmental damage in the Southern Gulf of Mexico, few studies (Macauley et al., 2007; Rivera-Guzmán et al., 2014; Ulloa et al., 2017) have addressed nitrogen pollution and its consequences. In this paper, we evaluate the spatial and temporal variations of ammonium, nitrate and organic nitrogen concentrations along two rivers and their coastal areas associated to mangroves where water hyacinth invasion is prevalent. The main objective was to determine whether nitrogen pollution or changes in N speciation may have occurred along the river and the coast and determine the possible sources and consequences for beaches and mangroves. Our results can be extrapolated to other regions of the Southern Gulf of Mexico with similar characteristics.

6.3 Materials and Methods

6.3.1 Study Area

This research focused on two rivers of the state of Veracruz discharging to the Gulf of Mexico. The river mouths are located within Costa Esmeralda, a tourist destination with low and medium density tourism (Pérez-Maqueo et al., 2017). Most of the communities in the studied areas are marginalized, with a high percentage of the population living in poverty (González-Marín et al., 2017). The inhabitants are mainly engaged in fishing, agriculture or tourism.

The coastal area is covered by wetlands, including mangroves. A large area of mangroves has been lost in the last decades, mainly due to agriculture and cattle ranching (Marín-Muñiz et al., 2016) or to disturbance from hurricanes (González-Marín et al., 2017). Urban wastewater does not undergo any treatment before the discharge into natural systems and industrial waste such as fruit juice companies discharge their waste into the rivers (González-Marín et al., 2017). In order to study the source of nitrogen to mangrove areas and to the coast through Tecolutla and Nautla rivers, we selected 6 and 4 monitoring sites along each river respectively. An additional site was located in each river mouth. One coastal site was placed 1 km from Tecolutla river mouth and three sites 1 km, 4 km and 7 km from Nautla river mouth respectively. The study area is presented in Figure 6.1 and the monitoring sites in Table 6.1, together with the distance to the coast and the mean salinity, which was calculated with four measurements from 2016.

The data used was obtained from the local government, which measures nitrogen concentrations in these monitoring sites. Ammonium and organic nitrogen were measured according to the Mexican standard NMX-AA-026-SCFI-2010 and nitrate

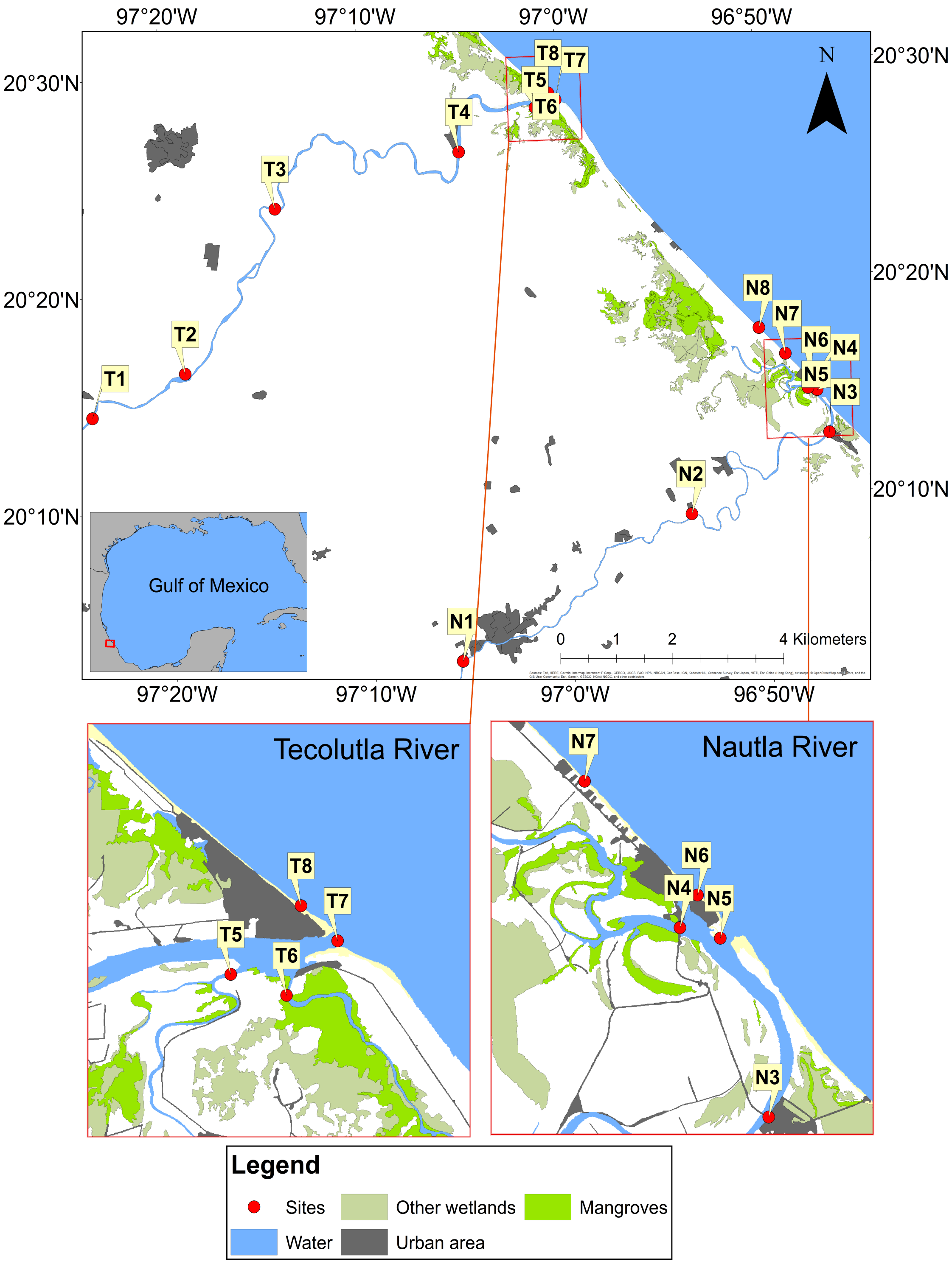


Figure 6.1: Study area with monitoring sites

based on NMX-AA-079-SCFI-2001. The data used for this study includes four annual measurements from 2013 to 2016. Each year two measurements were made during the dry season and two during the wet season.

Code	Name	Location	Distance to sea km	salinity $g.L^{-1}$
T1	Espinal bridge	Tecolutla river	65	0.13
T2	Paso Valencia	Tecolutla river	55	0.12
T3	Remolino bridge	Tecolutla river	35	0.14
T4	Tecolutla bridge	Tecolutla river	10	0.31
T5	Cruz de los esteros	Tecolutla river	2	1.56
T6	Los Naranjos	Tecolutla river	1	6.35
T7	Tecolutla estuary	Tecolutla esturay	0.2	15.97
T8	Tecolutla beach	Coast	0	36.61
N1	Martinez de la Torre	Nautla river	55	0.12
N2	El Pital	Nautla river	30	0.12
N3	Nautla bridge	Nautla river	4	0.30
N4	Casitas bridge	Nautla river	1	6.16
N5	Nautla estuary	Nautla estuary	0.5	8.81
N6	Casitas beach	Coast	0	31.29
N7	El Palmar	Coast	0	37.01
N8	Monte Gordo	Coast	0	37.31

Table 6.1: Codes and locations of the monitoring sites used in this study and provided by the local government. Mean salinity was calculated with 4 measurements during 2016 provided by the local government.

6.3.2 Data analysis

The spatiotemporal analysis of water quality parameters allows the assessment of possible sources and consequences of water pollution (Ali et al., 2016). Therefore, we performed several spatial and temporal statistical analysis to our data.

Spatial analysis

Firstly, spatial variations in nitrogen species concentrations were identified. As water quality data do not usually meet the requirements for the use of parametric statistics (Kitsiou, Karydis, 2011) non-parametric methods were selected. Cluster analysis (CA) is a non-parametric multivariate statistical method which groups objects in clusters based on similarities among objects of the same group and differences within groups. The clusters obtained are consequently groups of observations with similar characteristics. In this study CA was used to classify monitoring sites (objects) into groups of different nitrogen concentration level (clusters). Ward method was used as clustering strategy as it has been defined as the most appropriate method to evaluate eutrophication (Kitsiou, Karydis, 2011; Primpas et al., 2010). The squared Euclidean distance was selected as the distance measure to increase the importance of large distances among monitoring sites (Hajigholizadeh, Melesse, 2017). Three variables were used for classification: ammonium, nitrate and organic N concentrations. Outliers are not discarded as they carry information related to ecosystem's stress (Kitsiou, Karydis, 2011). We considered that using the median of each monitoring site was more robust due to the presence of outliers. Each variable was standardized prior to CA implementation. Two groups (clusters) were defined which correspond to coastal and riverine samples.

Temporal analysis

Mann-Kendall test was used to detect temporal trends in nitrogen species concentrations and to identify whether the observed trends are statistically significant. This test is a non-parametric monotonic trend analysis which identifies the increasing or decreasing patterns in time series data (Chaudhuri, Dutta, 2014). Non-parametric methods do not require assumptions on the normal distribution of the data and are not distorted by outliers or missing data (Kitsiou, Karydis, 2011). The test was applied to ammonium, nitrate and organic N concentrations from 2013 to 2016. Mann-Whitney (Wilcoxon) W-test was used to compare the medians of each nitrogen species in the dry and wet seasons. Additionally, for those sites with a statistically significant trend the temporal variation for each season was analyzed.

6.4 Results

6.4.1 Spatial variations

Ammonium, nitrate, organic N and total N concentrations in each monitoring site are presented in Figure 6.2.

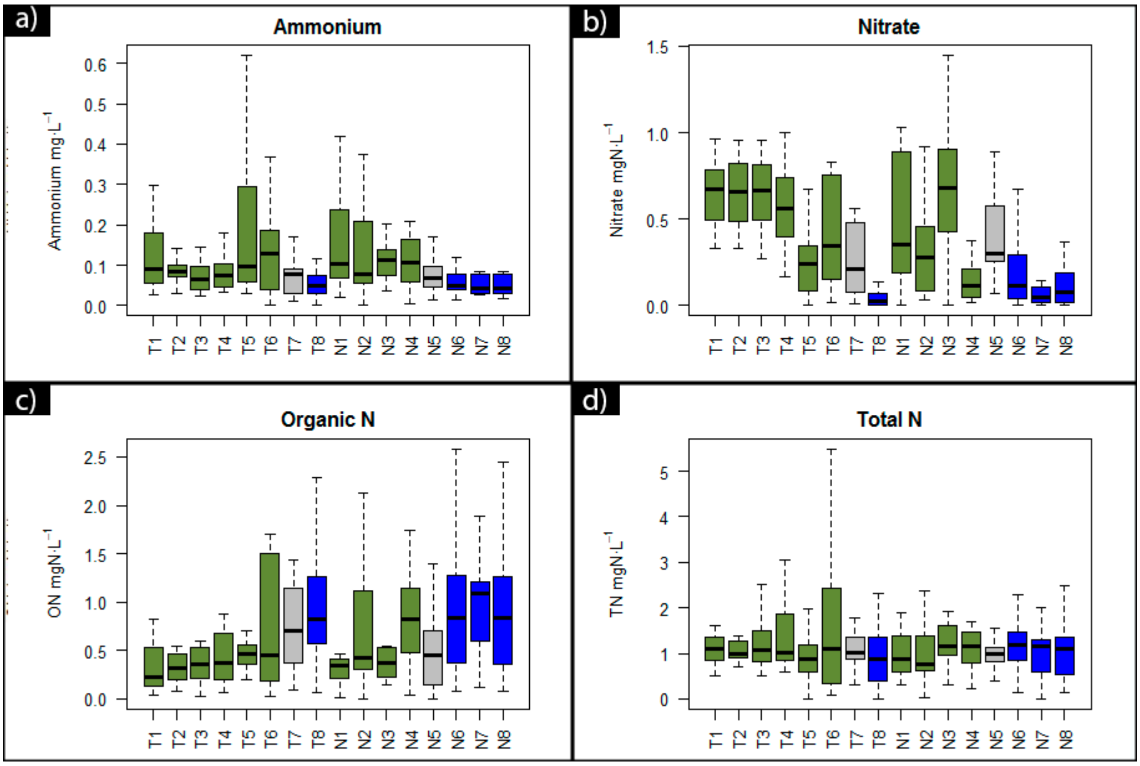


Figure 6.2: Boxplot of ammonium, nitrate, organic N and total N in all monitoring sites, with four annual measurements from 2013 to 2016. Outliers are not represented. Green is used for riverine sites, grey for estuaries and blue for coasts.

Both ammonium and nitrate concentrations were lower in coastal areas than in river sites due to the dilution of riverine nutrients with marine water. However, organic nitrogen was higher in coastal sites of both Tecolutla and Nautla watersheds. Total nitrogen did not present any difference between riverine and coastal sites.

Cluster analysis identified two groups which correspond to rivers (including estuaries) and coastal sites respectively (Figure 6.3). River sites had higher ammonium and nitrate concentrations, while organic nitrogen was higher in coastal sites. These differences can be observed in Figure 6.4.

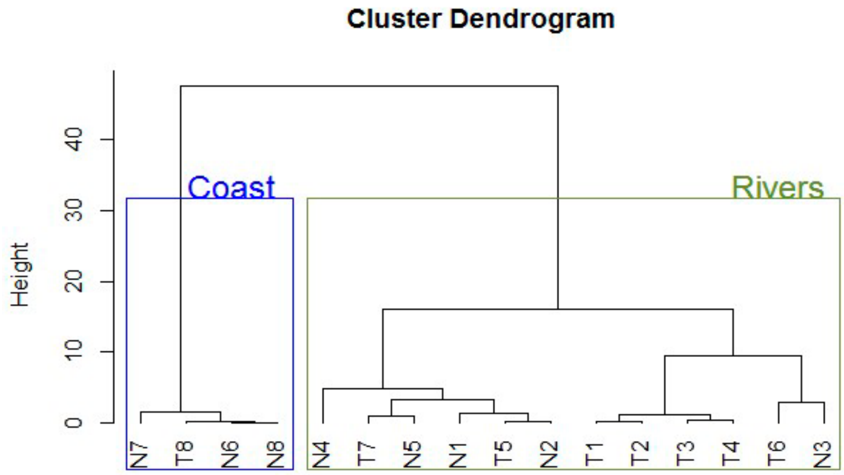


Figure 6.3: Cluster Dendogram using squared Euclidian distance and Ward's method. Classification variables are ammonium, nitrate and organic nitrogen concentrations.

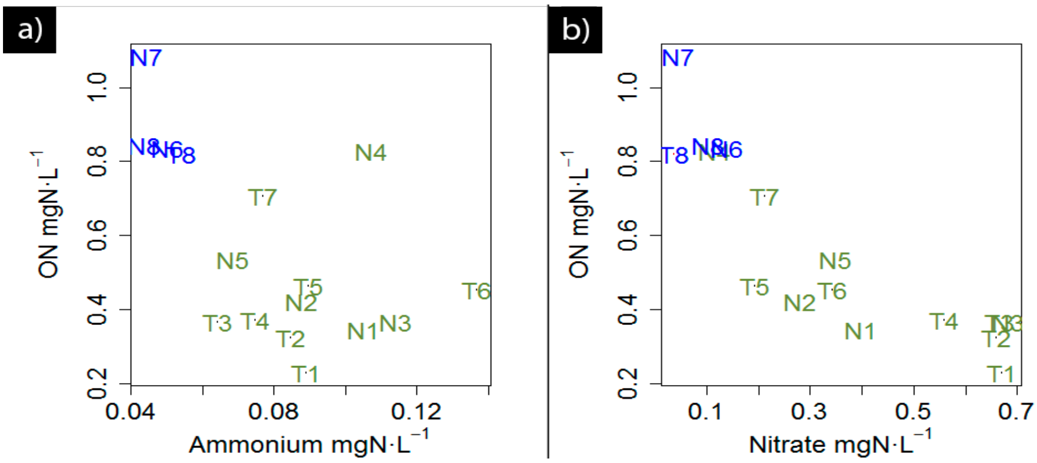


Figure 6.4: Scatterplot of organic N versus ammonium (left) and organic N versus nitrate (right). The cluster Coast is plotted in blue and Rivers cluster in green.

6.4.2 Temporal variations

Mann Kendall test was applied to each N compound in each monitoring site. Kendall tau's coefficient is shown in Figure 6.5, and significant upward or downward trends are located above or below the red lines respectively. Ammonium had a significant

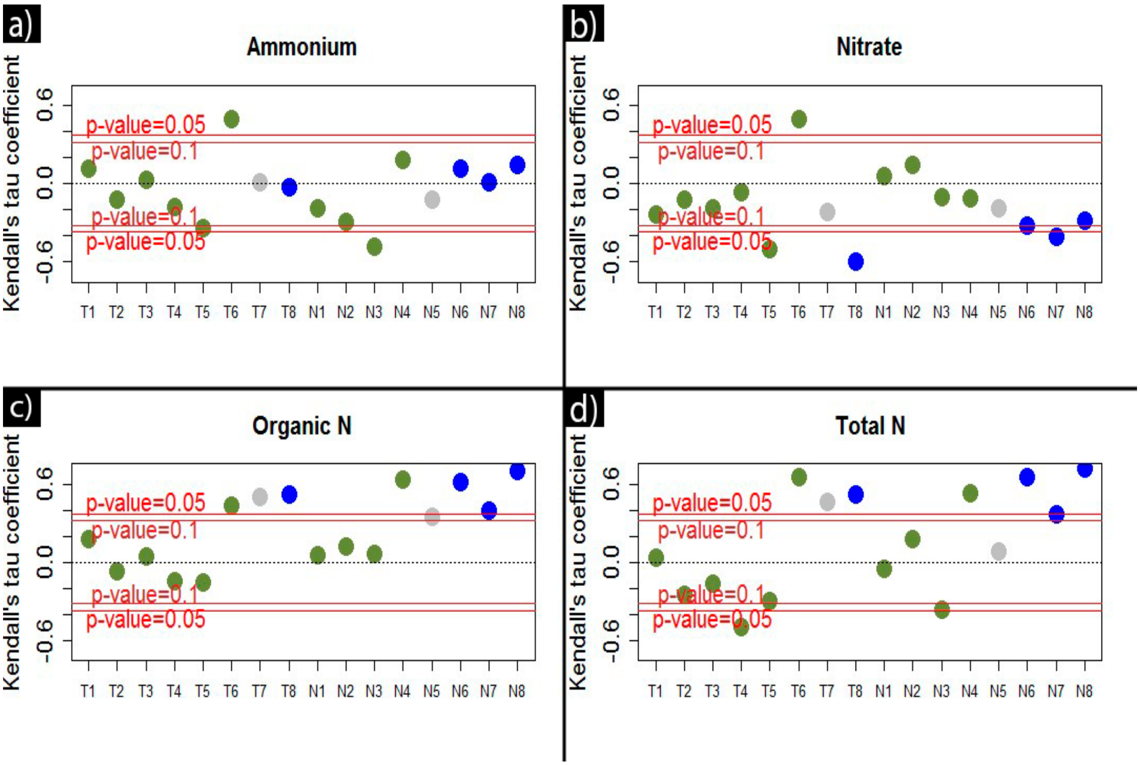


Figure 6.5: Kendall's tau coefficient for ammonium, nitrate, organic N and total N in rivers (green), estuarine (grey) and coasts (blue). 90% and 95% confidence levels are located above (increasing trend) or below (decreasing trend) red lines.

upward tendency in T6 and a downward tendency in N3. T6 corresponds to a mangrove-covered area close to Tecolutla river mouth. Nitrate also showcased an upward trend in T6, while it decreased in coastal sites. On the other hand, organic N has a general upward tendency in coastal waters and close to both Tecolutla and Nautla river mouths. The tendency observed for total nitrogen was similar to that of organic nitrogen.

Differences in ammonium, nitrate and organic nitrogen among the wet and dry season were analyzed with Wilcoxon W-test and results are presented in Table 6.2. Nitrate and organic nitrogen did not have a significant difference in any of the monitored sites. On the other side, ammonium had a significant difference between the dry and the wet season only in T3, N4 and N8 at a 0.05 significance level. The dry season presented higher concentrations in T3, while N4 and N8 had higher concentrations in the wet season.

Site	W-NH_4^+	p-value	W-NO_3^-	p-value	W-ON	p-value
T1	33	n.s.	40	n.s.	35	n.s.
T2	35	n.s.	28	n.s.	37	n.s.
T3	55	0.01	22	n.s.	36	n.s.
T4	25	n.s.	17	n.s.	33	n.s.
T5	26	n.s.	26	n.s.	32.5	n.s.
T6	16	n.s.	28	n.s.	34	n.s.
T7	33	n.s.	21	n.s.	36	n.s.
T8	21	n.s.	42	n.s.	31	n.s.
N1	40	n.s.	23.5	n.s.	39.5	n.s.
N2	34	n.s.	24	n.s.	29	n.s.
N3	43.5	n.s.	22	n.s.	45	n.s.
N4	9	0.01	40	n.s.	35	n.s.
N5	27	n.s.	35	n.s.	28	n.s.
N6	17	n.s.	19	n.s.	38	n.s.
N7	14	n.s.	32	n.s.	33	n.s.
N8	11	0.03	16	n.s.	34	n.s.

Table 6.2: Wilcoxon W test results testing the differences in ammonium (NH_4^+), nitrate (NO_3^-) and organic nitrogen (ON) between the dry and the wet season. p-values are shown only for significant differences (p-value < 0.05) and reported as n.s. (not significant) when p-value > 0.05.

Additionally, the increases in organic nitrogen concentrations in coastal sites and the lower course of Nautla and Tecolutla river were analyzed seasonally in Figure 6.6. T6 has an extreme value in the dry season which may be due to an unusual input of nitrogen, while N7 did not have an increasing trend in the dry season. Nonetheless, in most sites increasing trend appears in both the dry and the wet season.

6.5 Discussion

Our main findings together with the potential causes and consequences of nitrogen pollution are summarized in Figure 6.7.

The limit to consider poor conditions for inorganic nitrogen concentrations in Veracruz estuaries was established at 0.1 mg.L^{-1} by (Macauley et al., 2007). Our study sites were all above the established limit which indicates poor water conditions in both Tecolutla and Nautla estuaries. The spatial analysis showed that both

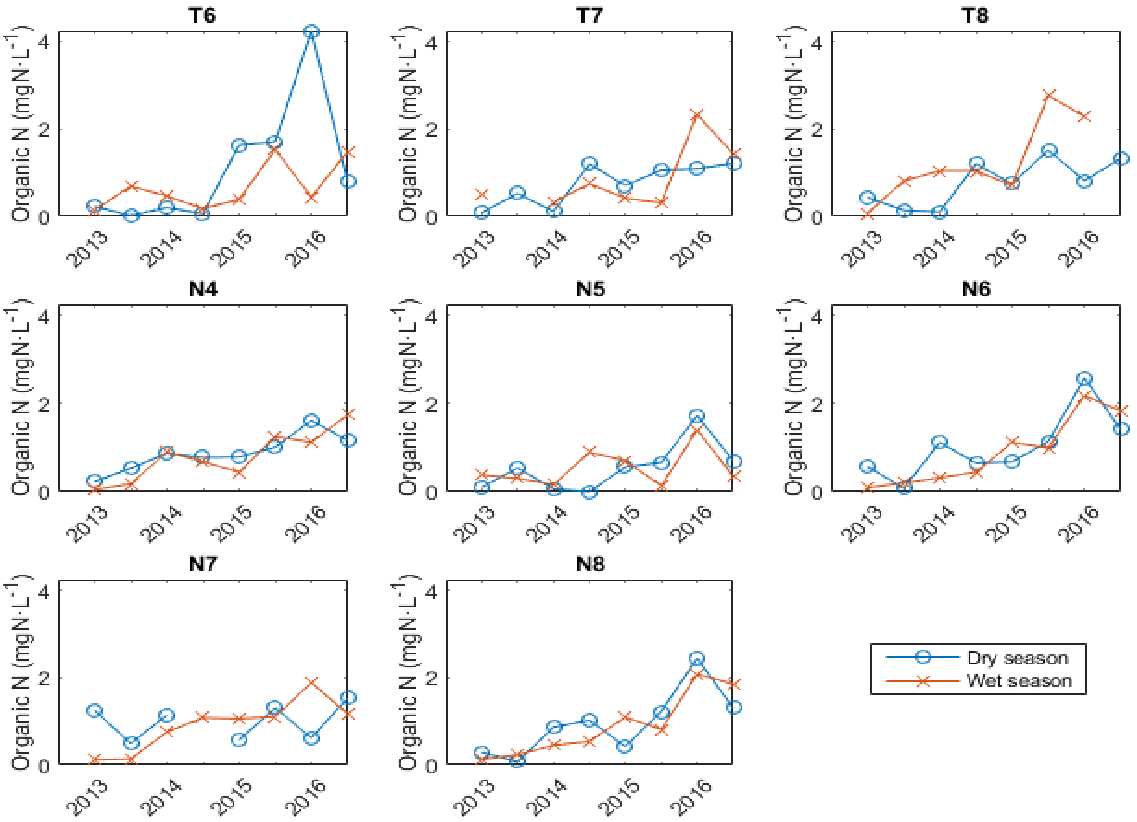
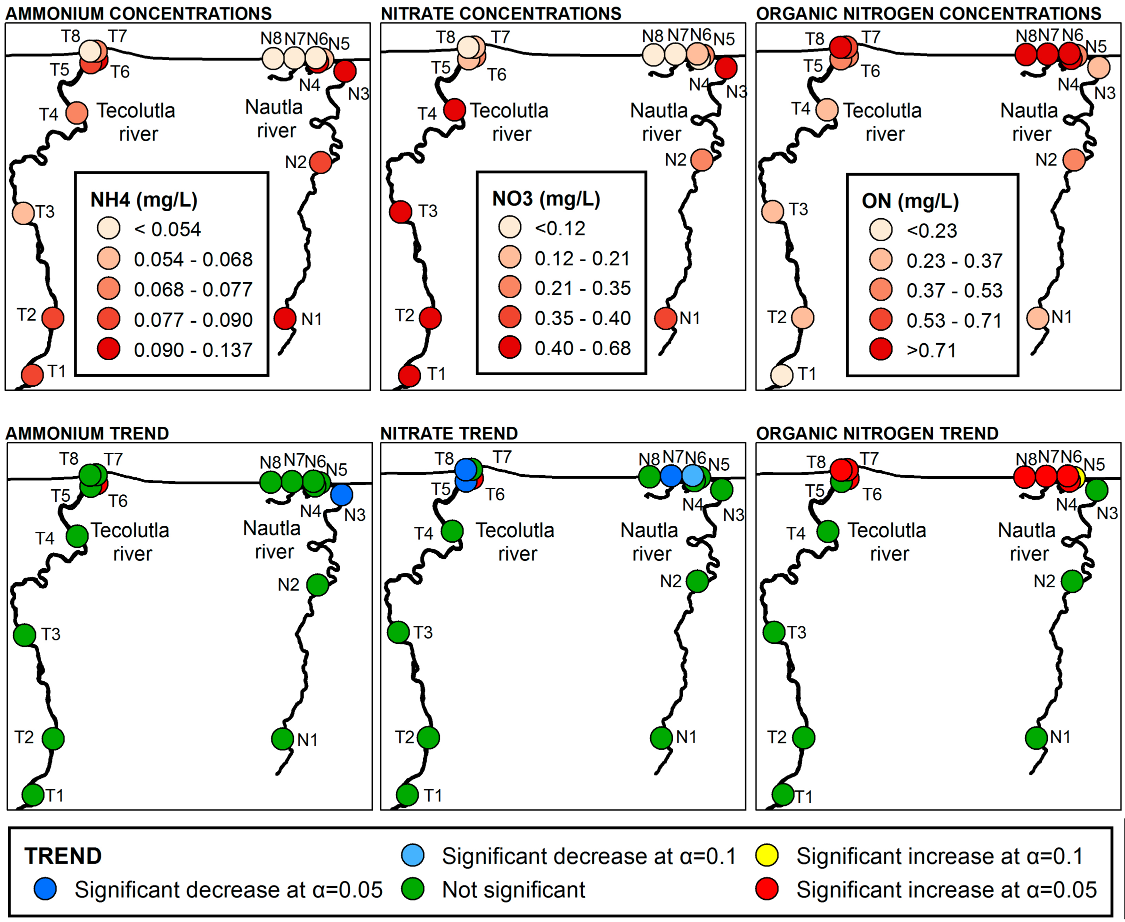


Figure 6.6: Organic nitrogen concentrations between 2013 and 2016 in the dry (blue) and wet (red) season; 2 values are shown per season.

ammonium and nitrate are diluted when reaching coastal areas, as indicated by the lower concentrations in coastal waters than in both rivers. However, organic nitrogen is higher in coastal sites than in riverine sites. On the other hand, temporal analysis indicated a clear increase in organic nitrogen concentrations during the studied period in coastal waters and a decrease in nitrate concentrations. The lack of trends along both rivers indicates that the nitrogen source does not come from the upper course but is rather localized in the river mouth and the surrounding coastal areas. Total nitrogen also showed an upward tendency which implies an external source of nitrogen to the system (Figure 6.5). Ammonium concentrations increased only in T6, which is located within a mangrove area. In this particular site, nitrate and organic nitrogen are also increasing. This may indicate the deterioration of mangroves, which are subject to pollution and deforestation. N3 is located within an urban area, which explains the high ammonium and nitrate concentrations which are derived from urban pollution. Nonetheless, a decreasing trend of ammonium concentrations in this site indicates that the pollution may have been reduced during the study period. The results of seasonal variations in nitrogen pollution indicates that the pollution is similar along the year. In general, no differences were observed between the dry and the wet season (Table 6.2), which is in agreement with previous studies in Veracruz coastal systems (Rivera-Guzmán et al., 2014). Nautla estuary has receives a high amount of freshwater runoff all year round, and fluctuations in nutrient concentrations are rather linked to changes in organic matter decomposition (Rivera-Guzmán et al., 2014).

The coastal resilience of Veracruz has been reduced by population growth and the increasing need for goods and services (Martinez et al., 2017). The urbanization of the coast and the lack of wastewater treatment (Ulloa et al., 2017) are driving the increase in N concentrations in river mouths and coastal waters (Figure 6.5). A study in Nautla river indicated that the lower course of the river is the most affected by water pollution, human settlements being the major source of N pollution (Rodríguez-Romero et al., 2018). Eutrophic conditions were detected in Casitas (Nautla estuary) (Ulloa et al., 2017) and eutrophication in Veracruz's coastal waters have been pointed out by many studies (Okolodkov et al., 2016; Rivera-Guzmán et al., 2014; Ulloa et al., 2017). Additionally, the deforestation and overexploitation of natural resources in Tecolutla are seen as a major problem causing ecosystems degradation (González-Marín et al., 2017). In the whole coastal region known as Costa Esmeralda beaches and mangroves decreased while urban coverage increased (Martínez et al., 2014). The fertilizers used in agriculture may also have a significant impact in N enrichment of coastal systems: an estimated 20-40% of N fertilizer is lost as ammonium in coastal systems through continental runoff (Anguiano-Cuevas et al., 2015). Veracruz is one of the states in Mexico which uses more fertilizer per cultivated area (SAGARPA, 2016). The water hyacinth invasion is a sign of the urgent need for nutrient pollution management in the area, which can be exacerbated



MAIN FINDINGS

- Ammonium and nitrate are lower in coastal waters than along the river while organic nitrogen is higher
- Nitrate concentrations decreased in coastal waters during the study period while organic concentrations increased in all coastal sites

POTENTIAL CAUSES

- Ammonium and nitrate are dilluted when reaching coastal waters
- Organic nitrogen is higher in coastal waters due to the decomposition of water hyacinths and other organic matter, and decreasing nitrate concentrations may be linked to higher uptake of hyacinths
- Increasing nitrogen pollution along the coast is attributed to a lack of wastewater treatment, deforestation and unefficient fertilizer use

CONSEQUENCES

- Poor water quality along the coast due to increasing organic nitrogen concentrations
- Eutrophic conditions
- Water hyacinth intrusion in beaches and mangroves

Figure 6.7: Summary of main findings and potential causes and consequences of nitrogen pollution. Nitrogen concentrations were calculated as the median of four annual measurements from 2013 to 2016; temporal trends were evaluated with Mann-Kendall test for the same study period.

by the increasing water temperatures due to climate change. Massive mats of water hyacinths were recently observed in Nautla and Tecolutla rivers as can be observed in

Figure 8. The extension of the invasion has reached a point in which ecological and socio-economic impacts may be critical. Water hyacinths absorb nutrients, leading to a reduction in ammonium or nitrate concentrations (Villamagna, Murphy, 2010), as observed in our study area. Nitrogen pollution (as ammonium or as nitrate) can be absorbed by water hyacinths (Fox et al., 2008) which prevents the detection of increasing concentrations in the water column. Salinity limits the plant's survival (Villamagna, Murphy, 2010), which leads to the accumulation of dead hyacinths in the river mouths and the surrounding beaches (Figure 6.8 (d) and (f)). AS such, increasing organic nutrient concentrations in the water column (Figure 6.5) may be attributed to the decomposition of water hyacinth (Villamagna, Murphy, 2010). We found increasing organic nitrogen trends in T6 to T8 and N4 to N8, which corresponds with sites which have a salinity above 6 $g.L^{-1}$. According to the latest studies, water hyacinths are only able to survive at salinities lower than 5 $g.L^{-1}$ (Guezo et al., 2017).

Mangroves have also been invaded by water hyacinth (Figure 6.8 (e)), which may lead to the disruption of the ecosystem. The floating plants cover the whole water surface, which may prevent the oxygen from dissolving into the water body or disturb the primary production by blocking sunlight (Villamagna, Murphy, 2010). Oxygen levels can reach dangerous concentrations for fish under the matt of hyacinth, especially if a large amount of plants decompose at the same time consuming most of the system's oxygen (Villamagna, Murphy, 2010). The nutrient cycle is also affected by the absorption of inorganic forms and the release of organic compounds through plant decomposition. The detritus generated in mangrove areas is the basis of a food web which supports a large variety of species (Holguin et al., 2001). When the N cycle in mangroves is altered, the impact affects the whole ecosystem including zooplankton, macroinvertebrates or fish (Toft et al., 2003). Water pollution and wetland degradation ultimately cause decreasing wildlife populations (González-Marín et al., 2017).

In addition to the damage caused to mangrove ecosystems, water hyacinths can also affect the economy of the coastal villages. On one hand, if the hyacinth invasion is large (as seen in the photos of Figure 6.8) fishermen could be affected by a reduced quantity of fish or by a shift in fish communities (Villamagna, Murphy, 2010). Mangroves provide shelter and food for fish and seafood, and fisherman develop most of their activity in the surrounding areas (Marín-Muñiz et al., 2016). On the other hand, the study area is located within a touristic destination known as Costa Esmeralda, and sun tourism yields important economic revenues (Pérez-Maqueo et al., 2017). The tourism industry can be greatly affected by the incursion of decaying water hyacinths into the beaches. Many local businesses clean up the decomposing plants, but this practice becomes inefficient if the invasion is too large. Mangroves are also used as a tourist attraction and local people offer boat tours (Marín-Muñiz et al., 2016), which become unfeasible when these ecosystems are completely covered by the exotic floating plants.

Water hyacinth is very difficult to eradicate (Villamagna, Murphy, 2010). However, there are many management decisions that could be considered to reduce nitrogen pollution and improve water quality. Firstly, wastewater treatment plants should be implemented in the whole area, especially in touristic areas where peak tourism seasons can bring up to 79 tourists per hectare (Pérez-Maqueo et al., 2017). Moreover, the use of fertilizers has an urgent need for regulation in the Southern Gulf of Mexico. Nutrient management technics need to consider the right source, rate, time and place for fertilizer application (Ulrich-Schad et al., 2017). The use of the optimum rate would result in less fertilizer applied for an equivalent yield, which implies reduced production costs. In fact, higher N fertilizer application rates do not imply a higher nutrient use efficiency (Thorburn et al., 2017). Nutrient management plans provide a written guide to help farmers efficiently utilize fertilizers and simultaneously protect water resources (Ulrich-Schad et al., 2017). Besides, the conversion of mangroves, forests and grasslands also may contribute significantly to nitrogen loading to coastal systems (Van Meter et al., 2017). Mexico has exhibited one of the highest rates of deforestation in Latin America in recent years

(Mokondoko et al., 2016). The potential practices for lowering N loadings involve both the implementation of conservation policies and a change in human behavior. Motivating behavioral change requires both available technology and understanding the incentives and disincentives (Robertson, Vitousek, 2009).

Recovery projects need to take into consideration the engagement of the local population. Nautla inhabitants see mangroves as food supply, material for construction and tourist attraction; while they perceive wetland loss as a threat, they do not generally understand what is causing it (Marín-Muñiz et al., 2016). The use of wetlands by local communities in Veracruz is also decreasing wildlife populations due to water pollution, hunting or deforestation (González-Marín et al., 2017). In order to improve their socioeconomic conditions while preserving mangroves and beaches, new sustainable economic opportunities need to be generated. Medium density tourism in the area can be compatible with coastal ecosystems' protection (Pérez-Maqueo et al., 2017), but social involvement and environmental education are key to achieving a sustainable development (Zaldívar-Jiménez et al., 2017). At a large scale, mangrove conservation and restoration is a major priority in the Gulf of Mexico Large Marine Ecosystem (LME) (Zaldívar-Jiménez et al., 2017). Several international collaborations have already been started between the United States and Mexico (Álvarez Torres et al., 2017). Common strategies are required as problems originating in one country may impact the whole LME (Álvarez Torres et al., 2017). Joint efforts to preserve the Gulf of Mexico's natural resources would allow a dramatic improvement in both ecosystems health and human development (Hudson, 2017), as well as a great climate change mitigation effort through blue carbon storage (Thorhaug et al., 2019; Vázquez-González et al., 2015), even with small mangroves (Adame et al., 2018).

Figure 6.8: Photos of Tecolutla and Nautla rivers at their lower course: (a) Mangrove in Tecolutla with touristic boat (14/07/2019) (b) Tecolutla river mouth with fisherman and some water hyacinths (14/07/2019) (c) Nautla bridge with water hyacinths in the riverside (14/07/2019) (d) Casitas estuary (Nautla) with dead hyacinths when they reach saline waters (16/07/2019 (e) Mangrove in Nautla river invaded by water hyacinth (16/07/2019) (f) Casitas beach at Nautla river mouth covered by decomposing water hyacinths (16/07/2019).

6.6 Conclusions

Our results indicate that organic nitrogen concentrations are increasing in coastal waters of Costa Esmeralda. The main potential cause is the decomposition of water hyacinths, an invasive aquatic species which grows disproportionately driven by nitrogen pollution from deforestation, untreated wastewater and fertilizers. Water hyacinths die when reaching saline coastal waters, leading to an incursion of touristic beaches and an increase in organic concentrations. Additionally, mangroves in the area are also affected by nitrogen pollution and by the invasion of water hyacinth. The nutrient enrichment of such important ecosystems may lead to the disruption of the whole food web, altering fish communities and wildlife, and causing many environmental and socio-economical problems. The results of this study could be extrapolated to other regions of the Southern Gulf of Mexico with similar characteristics. Recovery measures should include the establishment of sewage treatment plants, a management plan for the use of fertilizers and policies regulating the deforestation of coastal mangroves and other ecosystems. Additionally, the involvement of the local population is required for the achievement of a sustainable development which allows the maintenance of ecotourism activities while conserving natural resources.

CHAPTER 7

Final Discussion

Interpretation of the results and contextualization.

7.1 Anthropogenic land uses which modify nitrogen dynamics in coastal waters

7.1.1 Urban development

Urban development has been identified as an important source of nitrogen perturbation in coastal waters in both the Mediterranean Sea (section 3) and the Gulf of Mexico (sections 5 and 6).

In the Northwestern Mediterranean Sea, we observed how the anthropogenic pressure modifies the response of nitrification to temperature. The urban expansion along the coast has driven shifts in phytoplankton communities (Pachés et al., 2012), which in turn modify the main processes of the nitrogen cycle carried out by microorganisms such as nitrification. These results could be applied to other processes such as denitrification, which also depend on microorganisms.

On the other hand, in the Gulf of Mexico we observed that urban expansion along the coast which occurs mainly for tourism activities, was the first driver of nitrogen pollution in estuaries (section 5). The results from the fourth publication (section 6) indicate how urban expansion and the derived nitrogen pollution also alters nitrogen dynamics through the proliferation of invasive species such as water hyacinths. These plants decompose in beaches impacting the local economy which depends on tourism.

Globally, the urban development along the coast has been identified as a leading cause of nitrogen alteration by modifying both nitrogen concentrations and transformations (Stamou, Kamizoulis, 2008; Geedicke et al., 2018; Holguin et al., 2006). The biogeochemical cycles of nutrients such as nitrogen have long been altered in densely populates areas (Struyf et al., 2004), and coastal waters are particularly vulnerable to anthropogenic pressures due to the large populations living close to the coastline. Urban expansion often takes place without a proper sustainable management which deteriorates coastal ecosystems and water quality, altering the processes of important biogeochemical cycles such as the nitrogen cycle (Stamou, Kamizoulis, 2008).

7.1.2 Agriculture and livestock

The influence of agriculture and livestock on nitrogen pollution of coastal waters was evaluated in the Gulf of Mexico through the study carried out in the third publication (section 5). The results indicate that both agriculture (η=0.22) and livestock (η=0.11) have an influence on nitrogen concentrations in estuaries, although the influence of the urban expansion (η=0.67) is considerably higher.

These results are particular to the study area, and may not apply to other regions where the influence of agriculture or livestock may be higher. For instance, Van Meter et al. (2017) indicated that nitrogen pollution from fertilizers in the Mississippi river mouth in the Northern GoM is the main cause of the coastal hypoxia and the derived dead zone. Similarly, the Ebro delta in the Northwestern Mediterranean has significant nitrogen pollution derived from the use of fertilizers for agriculture (Herrero et al., 2018). Worldwide, nitrogen-use efficiency in agriculture is generally very low (Erisman et al., 2008), which leads to the nitrogen enrichment of coastal ecosystems (Rockström et al., 2009). Livestock production has also largely increased resulting in the unbalance of the nitrogen cylce (Battye et al., 2017).

7.2 The alteration of the nitrogen processes in coastal waters by climate change

7.2.1 Temperature

The effect of temperature on nitrogen processes was evaluated in the Mediterranean Sea through the first (section 3) and second (section 4) articles.

Firstly, temperature was identified as an important driver of nitrification in coastal waters (section 3), which entails a significant impact of climate change on this nitrogen transformation process. The second step of nitrification (nitrite to nitrate) was found to be more sensitive to temperature than the first step (ammonium to nitrite) under natural conditions. As such, the increasing temperatures derived from climate change may modify the decoupling of the two steps of nitrification. With increasing temperatures, the tranformation of nitrite into nitrate would increase faster than the tranformation of ammonium into nitrite, resulting in a reduction of nitrite concentrations, which agrees with the results found in the second publication (section 4).

A reduction of both nitrite and nitrate concentrations was predicted by the model developed in the second article (section 4). Temperature was negatively correlated to both nitrite (r= -0.54) and nitrate (r= -0.36), which entails a reduction of these compounds under climate change. These decreasing trends driven by the rising temperatures will be particularly noticeable in winter, which is when nitrite peaks are observed due to low temperatures (sections 3 and 4). This reduction was observed under both RCP 4.5 and RCP 8.5 scenarios, although for the RCP 8.5 the decreasing trends were significant for all the individual months. On the other hand, the correlation of ammonium concentrations with temperature was positive (r=0.25), although this correlation was not statistically significant ($\alpha > 0.05$). The annual trend of ammonium was not statistically significant, neither for RCP 4.5 nor for RCP 8.5, although increasing or decreasing trends were observed for some individual months.

Finally, urban settlements modified the response of the nitrification process to temperature (section 3), which indicates that the combined effect of nitrogen pollution and climate change will significantly impact nitrification. An intercollaboration of disciplines will be required to understand the interactions between human societies and the nitrogen cycle (Jennerjahn, 2012).

7.2.2 Rainfall and river runoff

The response of dissolved inorganic nitrogen (DIN) concentrations to the alteration of precipitation patterns was evaluated through the model developed in the second publication for the JRBD (section 4). Rainfall is expected to undergo important changes in the JRBD under both RCP 4.5 and 8.5, with mean annual reductions of around 10% and 20% respectively (IPCC, 2014). Similarly, the Ebro river flow would experience a mean annual reduction of 14% under RCP 4.5 and of 28% under RCP 8.5 (section 4). This lower precipitation rates in the JRBD will result in lower inputs of DIN to coastal waters. In the study area, nitrate is the most affected DIN compound by the reduction of freshwater inputs driven by lower groundwater discharges. The reduced freshwater inputs through the Ebro river flow will also impact DIN concentrations, which have a significant positive correlation with salinity (section 4).

The positive correlation between precipitation and total nitrogen loads was also observed in previous studies (Bi et al., 2018). Kumar et al. (2018) indicated that changes in salinity due to the alteration of precipitation patterns may affect the N uptake of phytoplankton, modifying the N cycle in coastal waters. However, the local response of nitrogen dynamics to changes in precipitation patterns depends on the trends under the different climatic scenarios for each region. For example, in other areas of the Mediterranean Sea the water flow is expected to increase in winter and decrease in summer (Pesce et al., 2018). In our study area, the mean rainfall rate for 2070-2100 relative to 1971-2000 is expected to increase only in January and February under RCP 4.5 (between 5% and 10%) and in November under RCP 8.5 (almost 15%) (section 4). For the rest of the months a significant reduction of rainfall is expected.

7.2.3 Overall impact of climate change

The overall impact of climate change on the N cycle is the result of the combined effects of temperature rise, changes in precipitation, sea level rise, acidification and other indirect factors such as the modification of plankton communitites (Herrmann et al., 2014). In the JRBD the trends in DIN concentrations were analyzed, detecting an overall decreasing trend of nitrite and nitrate (section 4), and changes in nitrification dynamics (section 3). These changes are the consequence of temperature rise and changes in rainfall and river runoff. However, the effect of sea level rise and acidification were not taken into account, but they are also expected to have an impact on N dynamics. For example, ocean acidification might have a significant influence on decreasing nitrification rates (Kim, 2016), and sea level rise may also have important consequences for phytoplankton uptake, especially in shallow waters (Pesce et al., 2018). Additionally, the future biogeochemistry of nitrogen in coastal waters depends both on climate change and the nitrogen pollution fluxes from riverines exports (Richon et al., 2019). The use of fertilizers is expected to increase in the next decades (Bosch et al., 2018), as well as the flow regulation due to the reduction of flow in certain rivers (Pesce et al., 2018).

In order to evaluate the overall impact of climate change in the whole Mediterranean Sea (not only coastal waters), other factors such as the changes in nitrogen inputs from the strait of Gibraltar need to be accounted for (Richon et al., 2019). However, the major changes are expected to occur close to river mouths, where the anthropogenic influence is higher (Lazzari et al., 2014). In other regions such as the United States, the changes observed in precipitation and temperature will likely reduce nitrogen yields to most coastal areas (Alam et al., 2017). In China, temperature was also negatively correlated to total nitrogen while precipitation was proportional to nitrogen loads (Bi et al., 2018). Moreover, a reduction of nitrogen discharges due to climate change are expecte in the Mekong river in Asia (Whitehead et al., 2019). Globally, climate change is expected to induce major changes on the nitrogen dynamics in coastal waters.

7.3 Aspects of the N cycle altered by anthropogenic pressures

7.3.1 Modification of the biogeochemical processes

We evaluated how urban pressures alter nitrification dynamics and the possible similarities that could be applied to other processes such as denitrification (section 3). Because the oxidized and reduced forms of nitrogen are linked through nitrification (Herbert, 1999), the alteration of nitrification will have significant cascading effects for other processes of the N cycle. Nitrification provides the nitrate used as substrate for denitrification, which in turn eliminates nitrogen from the system. Therefore, the alteration of nitrification will also impact the nitrogen loss to the atmosphere through denitrification. Alam et al. (2017) predicted an increase in denitrification rates derived from rising temperatures, which would reduce nitrate concentrations in coastal waters, such as predicted by the results found in the second article (section 4). High temperatures may also enhance nitrogen uptake for primary production or ammonium release from the sediment (Pesce et al., 2018). Additionally, increasing coastal hypoxia derived from warmer waters are expected to alter the nitrogen processes which depend on dissolved oxygen (Du et al., 2018). As such, both nitrification and denitrification could be affected by oxygen depletion (Voss et al., 2013).

Similarly, the proliferation of the invasive species as a consequence of N pollution modifies the N dynamics, as observed in the GoM through the fourth publication (section 6). The growth of hyacinths can cause a reduction of nitrogen compounds such as nitrate and ammonium driven by the uptake for the plant's growth (Villamagna, Murphy, 2010). Then, these plants die when they reach the sea because they do not survive in saline waters. This decomposition drives an increase in organic nitrogen concentrations along the estuaries and the surrounding coastal waters. Consequently, the alteration of the nitrogen species drives a shift in the biogeochemistry of the coast.

7.3.2 Changes in seasonal variations

The nitrite concentrations evaluated in the Mediterranean coastal area showed peaks in winter under natural conditions, but these peaks were altered in the most populated coastal areas (section 3). Cold periods result in the decoupling of the two steps of nitrification due to the different response to temperature of the two steps. In the polluted areas, the alteration of the biogeochemistry derives in a modification of this process, and peaks no longer occur as a response to changes in temperature but rather depend on the changes in ammonium concentrations. As such, the anthropogenic pollution modifies the intra-annual dynamics of nitrification.

On the other hand, the changes provoked by climate change on DIN concentrations in the JRBD vary from month to month (section 4). Nitrite concentrations are expected to undergo higher decreasing trends in January and December under both RCP 4.5 and RCP 8.5 due to the increase of the minimum annual temperatures. The rate of nitrate decrease was highest in December under RCP 4.5, and in January and February under RCP 8.5. These changes are partly due to the rising temperatures, although the decrease in rainfall and the derived lower groundwater and river discharges are the major driver of the trends observed in nitrate concentrations. Finally, ammonium is expected to increase in January under RCP 4.5, while for RCP 8.5 decreases are observed from January to March and decreases from September to December.

In the GoM, seasonal differences were evaluated in the fourth publication (section 6), although no statistically significant differences were observed. Both the wet and the dry season presented increasing trends of organic nitrogen concentrations in coastal waters. Other researchers indicated that the inputs of nitrogen from freshwater were similar all year round (Rivera-Guzmán et al., 2014). Nonetheless, a more specific analysis of the seasonal differences may expose the seasonal variations in pollution.

Other researchers also concluded that the anthropogenic impacts to the nitrogen dynamics varies depending on the season. For instance, the changes in precipitation patterns are expected to modify the seasonal export of nitrogen concentrations to coastal regions (Whitehead et al., 2019). Čerkasova et al. (2018) found different nutrient load changes for each season under climate change, and Voss et al. (2013) indicated how seasonal coastal upwelling or winter mixing may be destroyed by climate change. We conclude that the anthropogenic pressures alter the seasonal N dynamics.

7.3.3 Destruction of coastal ecosystems

The anthropogenic pressures such as the urban development along the coast result in the destruction of the coastal ecosystems. In the GoM, we evaluated how the urbanization over beaches and mangroves destroys the ecosystems and increases the nitrogen pollution to coastal waters (section 5). We also studied the potential influence of mangrove destruction in the alteration of the N dynamics. Mangroves recycle nutrients, and consequently their destruction can increase the N inputs to coastal waters (Gonçalves Reis et al., 2017). Additionally, the detritus generated in mangroves is the basis of a whole food web, which can be completely modified if mangroves are destroyed (Holguin et al., 2001).

Overall, coastal ecosystems play a significant role in the global N cycle, as developed in the introduction (section 1.1.3). The destruction of these ecosystems entails an important alteration of the N cycle, which has global consequences. For example, the destruction of mangroves may increase the release of N_2O (Gonçalves Reis et al., 2017) and enchance global warming. Therefore, the conservation of coastal ecosystems such as wetlands, coral reefs or dunes is essential to minimize the alteration of the N cycle in coastal waters.

7.4 Differences between the two case studies

7.4.1 Geomorphological and ecological differences

Both the Gulf of Mexico and the Mediterranean Sea are semi-enclosed seas, which entails they have a series of common characteristics. Both have micro-tidal ranges, and the enclosure generates particular mixing conditions. Land surrounds both seas, making the anthropogenic pressures especially relevant. Nonetheless, important differences exist as well. The Mediterranean Sea is considered oligotrophic, with low naturally occuring nutrient concentrations, and phosphorus is considered the limiting nutrient (Krom et al., 2010). On the other hand, the Gulf of Mexico has higher nutrient concentrations and nitrogen is said to limit primary production (Turner, Rabalais, 2013).

We studied a particular area of each sea located within the nearshore coastal waters. Inorganic nitrogen concentrations were higher in the studied region of the GoM (section 6) than in the Mediterranean Sea (section 4), but the reference conditions to evaluate pollution cannot be the same independently of the region under evaluation. The low nitrogen inputs in the pristine site C002 of the JRBD allowed us to develop a model which forecasts inorganic nitrogen cocentrations under the different climate change scenarios. Similarly, the pristine conditions allowed the estimation of nitrite dynamics under natural conditions. The study of these phenomenons becomes infeasible in the CGHR of the GoM because of the inexistence of unpolluted areas.

The climatic differences amongst the two sites studied also entail the existence of diverse ecosystems. For example, in the Gulf of Mexico due to its location in tropical latitudes, we were able to evaluate the pollution in mangroves. The deforestation of mangroves and other ecosystems along the coast of the GoM play an important role in the unbalance of the N cycle as discussed in the previous section. The different biodiversity existing in the Mediterranean Sea and in the Gulf of Mexico derive in different consequences of nitrogen pollution. For example, the water hyacinth invasion found in Veracruz indicates particular nitrogen pollution conditions which were not found in the Mediterranean studied area.

7.4.2 Socio-economic differences

In Spain, the regulation of nitrogen pollution is controlled by several laws including european directives, which strictly control the nitrogen inputs to coastal waters. Each direct input from WWTPs or from the industry is registered by the local government (section 1.4.4). Additionally, the regular monitoring campaigns allowed the obtention of a large database which can be used for many data analysis. Unfortunately, in the last years the monitoring campaigns have been less frequent which has hindered the evaluation of N pollution and processes in the coastal waters of the JRBD. Nonetheless, for this study we counted on a large database to carry out the research.

On the other hand, Mexico does not have a strict control of the nitrogen emissions to coastal waters and wastewater is often discharged without treatment. Additionally, the monitoring of coastal waters is very limited and irregular. As such, the limited data available does not allow the application of statistical techniques or mechanistic models. Furhtermore, the economic resources available to restore the ecosystems are limited and thus the most affected sites need to be assessed in the first place.

The differences mentioned were decisive in the election of the different techniques used in each publication. In the Mediterranean Sea, we developed models to assess on one side nitrification and climate change on the other. The first model was a mechanistic model (section 3) while we used artificial neural networks to evaluate climate change (section 4). These techniques require quality information to be applied. As such, the use of these models was not possible in the GoM where the available information was limited. Grey systems are a specific technique developed to derive useful information when only limited data is avalaible. Therefore, we developed a method to evaluate N pollution with limited data based on Grey clustering, which allowed us to reach scientifically sound conclusions (section 5). Then, we performed a statistical evaluation of a more reduced area where more information was available (section 6).

We conclude that the techniques used and therefore the results obtained depend drastically on the socio-economic characteristics of the area under study. It is not possible to apply the same techniques worldwide as the economic development plays a decisive role. Additionally, the restoration measures would as well depend on the economic resources and on the societies living within the coastal area. Other researchers also pointed out the need for specific sustainable practices depending on national differences (Sánchez-Hernández et al., 2017) or the resources availability (Do-Thu et al., 2011; Firmansyah et al., 2017).

7.5 New tools to evaluate the anthropogenic alteration of the N cycle in coastal waters

7.5.1 Biogeochemical model

A simple biogeochemical model was developed in the first publication (section 3) to evaluate the anthropogenic impact on the process of nitrification. Through the modelling of the intermediary compound, nitrite, the differences in nitrification parameters among the sites with different anthropogenic pressures was evaluated. The results obtained indicate that the application of simplified mechanistic models is a useful method to compare the processes of the N cycle in coastal waters under different human pressures. When more information becomes available, the application of more complex models could be a step forwards.

Mechanistic biogeochemical models have long been used to study the nitrogen processes in water (Bowie et al., 1985). However, our study represents the first attempt to use a simplified biogeochemical model with the aim of evaluating the anthropogenic pressures to a N process in marine waters. The same approach could be used to study the human impact on other N processes and allow a comprehensive estimation of the overall impact to the N cycle in coastal waters.

7.5.2 Artificial neural networks

Artificial neural networks have proved to be a useful tool to model complex interations (section 4). In this context, we were able to model dissolved inorganic nitrogen concentrations based on physical variables under pristine conditions. Then, we estimated the future trends of DIN concentrations under the different climate change scenarios. Although simplifications needed to be made, ANNs allowed a preliminary forecast of the future trends of DIN concentrations in the pristine inshore coastal waters of the NW Mediterranean Sea.

Other researchers also evaluated the use of ANNs in the evaluation of the impact of climate change on nutrients in marine waters (Wang, Polcher, 2019; Bittig et al., 2018). Nonetheless, this is the first time that ANNs are used to evaluate the future trends of nitrogen concentrations in coastal waters. Although the data availability limited the study to a simplified approach which considered only qualitative conclusions rather than quantitative, further research could be carried out to develop more complex ANN models with the ability to forecast the quantitative trends of nitrogen species concentrations in coastal waters under climate change.

7.5.3 Grey systems theory

Grey systems theory was used to derive a nitrogen evaluation method when only small and uncertain samples are available (section 5). The method was applied to the coastal waters of the GoM, where the index which prioritizes N pollution management (GNMP index) matched with the index developed to evaluate the pressures related to land use (GLUP index). This study represents the first attempt to incorporate grey systems theory to the evaluation of N pollution in coastal waters, which could be very useful for countries which do not have a historical database of water quality parameters. We also incorporated the concept of Shannon entropy to identify the anthropogenic activities which have a greater impact on the N pollution. The method developed could be also applied to evaluate other water pollutants.

7.6 Tying results to the big picture

This research entails new insights into the anthropogenic alteration of nitrogen in coastal waters. For the first time, an evaluation of how anthropogenic pressures modify the decoupling of the two steps of nitrification and a preliminary estimation of the climate change impact on DIN concentrations in nearshore coastal waters of the NW Mediterranean Sea was carried out. In the GoM, a new method based on Grey systems was developed to derive useful information on nitrogen pollution, which allowed us to conclude that urban expansion along the coast is the main driver of nitrogen pollution in Veracruz estuaries. Finally, an evaluation of nitrogen pollution in a mangrove area was carried out and the impact for the expansion of the invasive water hyacinth was discussed.

The results of this thesis contribute to the evaluation of the anthropogenic alteration of the N processes in coastal waters. The modification of nitrification as well as the changes in DIN concentrations in coastal waters derive in an unbalance of the whole N cycle, which may carry important consequences for the ecosystems. Similarly, the destruction of mangroves and other wetlands, as well as the proliferation of invasive species as a consequence of N pollution results in a significant loss of biodiversity.

On a global scale, we can conclude that anthropogenic pressures modify the biogeochemistry of nitrogen in coastal waters as endorsed by previous studies in diverse ecosystems around the world (Beman et al., 2010; Kim, 2016). The consequences of this alteration inlcude the deterioration of marine ecosystems, human health problems and the exhacerbation of climate change, as developed in section 1.3. Ultimately, the alteration of the N cycle provokes cascading effects which derive in the unbalance of other cycles such as the carbon cycle, with dramatic consequences for life on Earth (Gruber, Galloway, 2008).

7.7 Limitations of the research

For this research, only two study areas were used, and therefore the extrapolation of the results to other regions needs to be done with caution. As the coastal ecosytems are very diverse and the socio-economic circumstances play a key role, the conclusions reached in this study cannot be extrapolated worldwide. Nonetheless, these results can be used as a starting point for the evaluation, interpretation and comparison of research carried out in different geographical locations and contexts.

Due to the limitation of data and the restriccion of the research to the study areas, only certain aspects of the alteration of the N cycle in coastal waters was evaluated. For instance, the process of nitrification was evaluated while many other processes are also modified my human activity. Similarly, the trends of DIN concentrations were forecasted while organic nitrogen was not taken into consideration. In the GoM, a mangrove area was studied while many other coastal ecosystems take part in the N cycle.

Additionally, simplifications were necessarily made throughout the research. Both the biogeochemical model and the artifitial neural networks model were simplified to study the effect of the urban settlements and climate change respectively. In the third article, the Grey systems theory was used to derive useful information, but additional data would be needed to reach robust conclusions. Therefore, the results found in this research need to be corroborated with further studies and replication of the research in other regions with different characteristics.

7.8 Future research

Future research should focus on the evaluation of the alteration of the processes of the N cycle in coastal waters altogether. Additionally, further research should evaluate the combined effects of the changes in anthropogenic nitrogen inputs and climate change. While more data become available, the development of more complex models would allow an exhaustive evaluation of the mechanisms by which humans modify N dynamics in marine waters. Furthermore, the interconnection of the nitrogen cycle with other important elements such as carbon or phosphorus should be evaluated in order to determine the full impact on the Earth's ecosystems and on climate change. Finally, the consequences of the alteration of the nitrogen cycle on biodiversity, human health and climate change should be evaluated.

7.9 Final conclusions

Throughout the research an evaluation of the pressures and impacts of anthropogenic activities on nitrogen dynamics in coastal waters of the Northwestern Mediterranean Sea and the Southern Gulf of Mexico was carried out. The main conclusions shed light on the research questions and objectives raised. Both nitrogen pollution and climate change modify the nitrogen species concentrations and the nitrogen processes. Important differences were found between the two study areas selected based on both the geomorphological and ecological characteristics and on the socio-economic conditions. Additionally, useful tools were developed based on simple mechanistic modelling, artificial neural networks and grey systems theory. The main conclusions reached are enumerated hereafter:

1. Urban development along the coast is the main cause of the alteration of the N processes in the nearshore coastal waters of the two study areas.

2. Climate change can modify nitrogen processes in coastal waters by modifying both the biogeochemistry and the continental nitrogen inputs. In the stud-

ied area of the NW Mediterranean Sea DIN concentrations are expected to decrease under both RCP 4.5 and RCP 8.5.

3. Anthropogenic pressures alter nitrification in coastal waters of the Mediterranean Sea, a key N process, which can have cascading consequences for the whole N cycle.
4. The interannual cyles of nitrogen are modified by human activities, both through nitrogen pollution and climate change.
5. The destruction of coastal ecosystems such as mangroves modify the N concentrations in coastal waters.
6. Geomorphological and ecological differences amongst the study sites result in different results and conclusions concerning the impact of anthropogenic pressures on the N dynamics.
7. Socio-economic development plays a significant role in the pressures and impacts of nitrogen pollution, as well as in the methods that need to be applied to study the alteration of nitrogen processes.
8. Simplified mechanistic biogeochemical models are useful for an overall evaluation of the impact of anthropogenic pressures on nitrogen processes.
9. Artifitial neural networks can be used to forecast the trends of nitrogen compounds under climate change scenarios.
10. Grey systems theory is a useful technique for the evaluation of nitrogen pollution under limited data availability.

Bibliography

APHA . Standard Methods for the Examination of Water and Wastewater. Washington D.C.: American Public Health Association, American Water Works Association, Water Environment Federation, 2005. 21th.

Abdullahi Jazuli, Elkiran Gozen. Prediction of the future impact of climate change on reference evapotranspiration in Cyprus using artificial neural network // Procedia Comput. Sci. 2017. 120. 276–283.

Abrahart R.J., Kneale P.E., See L.M. Neural networks for hydrological modelling. 2004. 316.

Adame M. F., Najera E., Lovelock C. E., Brown C. J. Avoided emissions and conservation of scrub mangroves: potential for a Blue Carbon project in the Gulf of California, Mexico // Biol. Lett. 2018. 14.

Adriaenssens Veronique, Baets Bernard De, Goethals Peter L.M., Pauw Niels De. Fuzzy rule-based models for decision support in ecosystem management // Sci. Total Environ. 2004. 319, 1-3. 1–12.

Aguilera R, Marcé R, Sabater S. Detection and attribution of global change effects on river nutrient dynamics in a large Mediterranean basin // Biogeosciences. 2015. 12. 4085–4098.

Al-Zahrani Muhammad A., Abo-Monasar Amin. Urban residential water demand prediction based on artificial neural networks and time series models // Water Resour. Manag. 2015. 29, 10. 3651–3662.

Alam Md Jahangir, Goodall Jonathan L., Bowes Benjamin D., Girvetz Evan H. The Impact of Projected Climate Change Scenarios on Nitrogen Yield at a Regional Scale for the Contiguous United States // JAWRA J. Am. Water Resour. Assoc. 2017. 53, 4. 854–870.

Alanis A., Arana-Daniel N., Lopez-Franco C. Artificial neural networks for engineering applications. 2019. 176.

Alexander Richard B., Smith Richard A., Schwarz Gregory E., Boyer Elizabeth W., Nolan Jacqueline V., Brakebill Jhn W. Differences in Phosphorus and Nitrogen Delivery to The Gulf of Mexico from the Mississippi River Basin // Environ. Sci. Technol. 2008. 42, 3. 822–830.

Ali Sayeda M., Sabae Shawky Z., Fayez Mohammed, Monib Mohammed, Hegazi Nabil A. The influence of agro-industrial effluents on River Nile pollution // J. Adv. Res. 2011. 2, 1. 85–95.

Ali Tarig A., Mortula Maruf, Atabay Serter, Navadeh Ehsan. A GIS-based spatiotemporal study of the variability of water quality in the Dubai creek, UAE // Water Qual. Res. J. Canada. 2016. 51, 3. 219–232.

Altunkaynak Abdüsselam. Forecasting surface water level fluctuations of lake van by artificial neural networks // Water Resour. Manag. 2007. 21, 2. 399–408.

Álvarez Torres Porfirio, Rabalais Nancy N., Piña Gutiérrez José Manuel, Padrón López Rosa Martha. Research and community of practice of the Gulf of Mexico large marine ecosystem // Environ. Dev. 2017. 22. 166–174.

Andersen Jesper H., Axe Philip, Backer Hermanni, Carstensen Jacob, Claussen Ulrich, Fleming-Lehtinen Vivi, Järvinen Marko, Kaartokallio Hermanni, Knuut-tila Seppo, Korpinen Samuli, Kubiliute Aiste, Laamanen Maria, Lysiak-Pastuszak Elzbieta, Martin Georg, Murray Ciarán, Møhlenberg Flemming, Nausch Günther, Norkko Alf, Villnäs Anna. Getting the measure of eutrophication in the Baltic Sea: Towards improved assessment principles and methods // Biogeochemistry. 2011. 106, 2. 137–156.

Anderson Donald M, Glibert Patricia M, Burkholder Joann M. Harmful Algal Blooms and Eutrophication: Nutrient Sources, Composition, and Consequences. 25, 4b. 2002. 704–726.

Anguiano-Cuevas J. Refugio, Olivos-Ortiz Aramis, Cervantes Omar, Azuz-Adeath Isaac, Ramírez-Álvarez Nancy, Rivera-Rodríguez María C. Evaluation of trophic state in the Palo Verde estuary (Colima, México), action to regulating agricultural activities // Rev. Gestão Costeira Integr. 2015. 15, 4. 507–522.

Aparicio Fran L., Nieto-Cid Mar, Borrull Encarna, Calvo Eva, Pelejero Carles, Sala Maria Montserrat, Pinhassi Jarone, Gasol Josep M., Marrasé Cèlia. Eutrophication and acidification: Do they induce changes in the dissolved organic matter dynamics in the coastal Mediterranean Sea? // Sci. Total Environ. 2016. 563-564. 179–189.

Arhonditsis G., Tsirtsis G., Angelidis M.O., Karydis M. Quantification of the effects of nonpoint nutrient sources to coastal marine eutrophication: applications to a semi-enclosed gulf in the Mediterranean Sea // Ecol. Modell. 2000. 129, 2. 209–227.

Arrigo Kevin R. Marine microorganisms and global nutrient cycles // Nature. 2005. 437, 7057. 349–355.

Azarnivand Ali. Comment on “Assessing water quality of five typical reservoirs in lower reaches of Yellow River, China: using a water quality index method” by

Wei Hou, Shaohua Sun, Mingquan Wang, Xiang Li, Nuo Zhang, Xiaodong Xin, Li Sun, Wei Li, and Ruibao Jia // Ecol. Indic. 2017. 75. 8–9.

Baker D. M., Rodríguez-Martínez R. E., Fogel M. L. Tourism's nitrogen footprint on a Mesoamerican coral reef // Coral Reefs. 2013. 32. 691–699.

Ballesteros BJ, Marina M, Mejías M, Domínguez JA. Caracterización hidroquímica del acuífero carbonatado profundo de El Maestrazgo (Castellón).[Hydrochemical characterisation of the deep, carbonated El Maestrazgo aquifer (Castellón)] // Coast. aquifers challenges Solut. 2007. 1. 549–564.

Bargu Sibel, Baustian Melissa M., Rabalais Nancy N., Del Rio Ross, Von Korff Benjamin, Turner R. Eugene. Influence of the Mississippi River on Pseudo-nitzschia spp. Abundance and Toxicity in Louisiana Coastal Waters // Estuaries and Coasts. 2016. 39, 5. 1345–1356.

Baron J. S., Hall E. K., Nolan B. T., Finlay J. C., Bernhardt E. S., Harrison J. A., Chan F., Boyer E. W. The interactive effects of excess reactive nitrogen and climate change on aquatic ecosystems and water resources of the United States // Biogeochemistry. 2013. 114, 1-3. 71–92.

Barrera-Escoda A., Gonçalves M., Guerreiro D., Cunillera J., Baldasano J. M. Projections of temperature and precipitation extremes in the North Western Mediterranean Basin by dynamical downscaling of climate scenarios at high resolution (1971–2050) // Clim. Change. 2014. 122, 4. 567–582.

Bartl Ines, Liskow Iris, Schulz Kirstin, Umlauf Lars, Voss Maren. River plume and bottom boundary layer – Hotspots for nitrification in a coastal bay? // Estuar. Coast. Shelf Sci. 2018. 208. 70–82.

Basu Nandita B., Destouni Georgia, Jawitz James W., Thompson Sally E., Loukinova Natalia V., Darracq Amélie, Zanardo Stefano, Yaeger Mary, Sivapalan Murugesu, Rinaldo Andrea, Rao P. Suresh C. Nutrient loads exported from managed catchments reveal emergent biogeochemical stationarity // Geophys. Res. Lett. dec 2010. 37, 23. n/a–n/a.

Battye William, Aneja Viney P., Schlesinger William H. Is nitrogen the next carbon? // Earth's Futur. 2017. 5, 9. 894–904.

Beman J Michael, Chow Cheryl Emiliane, King Andrew L, Feng Yuanyuan, Fuhrman Jed A., Andersson Andreas, Bates Nicholas R., Popp Brian N., Hutchins David A. Global declines in oceanic nitrification rates as a consequence of ocean acidification // Proc. Natl. Acad. Sci. 2010. 108, 1. 208–213.

Beman J. Michael, Leilei Shih Joy, Popp Brian N. Nitrite oxidation in the upper water column and oxygen minimum zone of the eastern tropical North Pacific Ocean // ISME J. 2013. 7, 11. 2192–2205.

Bendschneider K., Robinson R.J. A new spectrophotometric determination of nitrite in sea water // J. Mar. Res. 1952. 2. 87–96.

Bernhard Anne E., Donn Thomas, Giblin Anne E., Stahl David A. Loss of diversity of ammonia-oxidizing bacteria correlates with increasing salinity in an estuary system // Environ. Microbiol. sep 2005. 7, 9. 1289–1297.

Béthoux J. Pierre, Copin-Montégut Gérard. Biological fixation of atmospheric nitrogen in the Mediterranean Sea // Limnol. Oceanogr. 1986. 31, 6. 1353–1358.

Bi Wuxia, Weng Baisha, Yuan Zhe, Ye Mao, Zhang Cheng, Zhao Yu, Yan Dengming, Xu Ting. Evolution Characteristics of Surface Water Quality Due to Climate Change and LUCC under Scenario Simulations: A Case Study in the Luanhe River Basin // Int. J. Environ. Res. Public Health. 2018. 15, 1724.

Bianchi M., Feliatra , Lefevre D. Regulation of nitrification in the land-ocean contact area of the Rhône River plume (NW Mediterranean) // Aquat. Microb. Ecol. 1999. 18. 301–312.

Bianchi M., Morin P., Le Corre P. Nitrification rates, nitrite and nitrate distribution in the Almeria-Oran frontal systems (eastern Alboran Sea) // J. Mar. Syst. 1994. 5, 3-5. 327–342.

Bianchi T.S., Di Marco S.F., Cowan Jr. J.H., Hetland R.D., Chapman P., Day J.W., Allison M.A. The science of hypoxia in the Northern Gulf of Mexico: A review // Sci. Total Environ. 2010. 408, 7. 1471–1484.

Bittig Henry C., Steinhoff Tobias, Claustre Hervé, Fiedler Björn, Williams Nancy L., Sauzède Raphaëlle, Körtzinger Arne, Gattuso Jean-Pierre. An Alternative to Static Climatologies: Robust Estimation of Open Ocean CO2 Variables and Nutrient Concentrations From T, S, and O2 Data Using Bayesian Neural Networks // Front. Mar. Sci. 2018. 5. 328.

Borja Ángel, Franco Javier, Valencia Victoriano, Bald Juan, Muxika Iñigo, Belzunce María Jesús, Solaun Oihana. Implementation of the European water framework directive from the Basque country (northern Spain): a methodological approach // Mar. Pollut. Bull. 2004. 48. 209–218.

Bosch Darrell J., Wagena Moges B., Ross Andrew C., Collick Amy S., Easton Zachary M. Meeting Water Quality Goals under Climate Change in Chesapeake Bay Watershed, USA // JAWRA J. Am. Water Resour. Assoc. 2018. 54, 6. 1239–1257.

Boucher Doug, Elias Pipa, Lininger Katherine, May-Tobin Calen, Roquemore Sarah, Saxon Earl. The Root of the Problem: What's Driving Tropical Deforestation Today? 2011. 113.

Bowie George L., Mills William B., Porcella Donald B., Campbell Carrie L., Pagenkopf James R., Rupp Gretchen L., Johnson Kay M., Chan Peter W.H., Gherini Steven A. Rates, Constants, and Kinetics Formulations in Surface Water Quality Modeling (Second Edition). 1985. 455.

Breitburg Denise, Levin Lisa A., Oschlies Andreas, Grégoire Marilaure, Chavez Francisco P., Conley Daniel J., Garçon Véronique, Gilbert Denis, Gutiérrez Dimitri, Isensee Kirsten, Jacinto Gil S., Limburg Karin E., Montes Ivonne, Naqvi S. W.A., Pitcher Grant C., Rabalais Nancy N., Roman Michael R., Rose Kenneth A., Seibel Brad A., Telszewski Maciej, Yasuhara Moriaki, Zhang Jing. Declining oxygen in the global ocean and coastal waters // Science (80-.). 2018. 359, 46.

Breton-Deval Luz, Sanchez-Flores Alejandro, Juárez Katy, Vera-Estrella Rosario. Integrative study of microbial community dynamics and water quality along The Apatlaco River // Environ. Pollut. 2019. 255.

Bricker S. B., Ferreira J. G., Simas T. An integrated methodology for assessment of estuarine trophic status // Ecol. Modell. 2003. 169. 39–60.

Bricker S.B., Longstaff B., Dennison W., Jones A., Boicourt K., Wicks C., Woerner J. Effects of nutrient enrichment in the nation's estuaries: A decade of change // Harmful Algae. 2008. 8, 1. 21–32.

Bristow Laura A, Sarode Neha, Cartee John, Caro-Quintero Alejandro, Thamdrup Bo, Stewart Frank J. Biogeochemical and metagenomic analysis of nitrite accumulation in the Gulf of Mexico hypoxic zone // Limnol. Oceanogr. 2015. 60, 5. 1733–1750.

Brito Ana C., Newton Alice, Tett Paul, Fernandes Teresa F. How will shallow coastal lagoons respond to climate change? A modelling investigation // Estuar. Coast. Shelf Sci. 2012. 112. 98–104.

Burney S.M.A., Jilani T.A., Ardil C. A comparison of first and second order training algorithms for artificial neural networks // Int. J. Comput. Inf. Eng. 2007. 1, 1. 145–151.

Byakatonda J., Parida B. P., Kenabatho P. K., Moalafhi D. B. Modeling dryness severity using artificial neural network at the Okavango Delta, Botswana // Glob. Nest J. 2016. 18, 3. 463–481.

CONABIO . http://www.conabio.gob.mx/informacion/gis/. 2016.

CONAGUA . Atlas del Agua en México. 2015a. 135.

CONAGUA . Inventatio Nacional de Plantas Municipales de Potabilización y de Tratamiento de Aguas Residuales en Operación. 2015b.

CONAGUA . Calidad del agua en México. 2018a.

CONAGUA . Estadística del agua en México. 2018b.

Camargo Julio A., Alonso Álvaro. Ecological and toxicological effects of inorganic nitrogen pollution in aquatic ecosystems: A global assessment // Environ. Int. 2006. 32, 6. 831–849.

Capone Douglas G., Bronk Deborah A., Mulholland Margaret R., Carpenter Edward J. Nitrogen in the marine environment. 2008. 2nd Editio. 1729.

Carini Stephen A., McCarthy Mark J., Gardner Wayne S. An isotope dilution method to measure nitrification rates in the northern Gulf of Mexico and other eutrophic waters // Cont. Shelf Res. 2010. 30. 1795–1801.

Čerkasova Natalja, Umgiesser Georg, Ertürk Ali. Development of a hydrology and water quality model for a large transboundary river watershed to investigate the impacts of climate change – A SWAT application // Ecol. Eng. 2018. 124. 99–115.

Chapra Steven C. Surface Water Quality Modelling. New York, 1997.

Chau K. W., Jin Haisheng. Eutrophication Model for a Coastal Bay in Hong Kong // J. Environ. Eng. 1998. 124, 7. 628–638.

Chaudhuri Sutapa, Dutta Debashree. Mann-Kendall trend of pollutants, temperature and humidity over an urban station of India with forecast verification using different ARIMA models // Environ. Monit. Assess. 2014. 186, 8. 4719–4742.

Chen Zhonghan, Huang Ping, Zhang Zhou. Interaction between carbon dioxide emissions and eutrophication in a drinking water reservoir: A three-dimensional ecological modeling approach // Sci. Total Environ. 2019. 663. 369–379.

Chirivella Osma V, Capilla Romá J E, Pérez Martín M A. Modelling regional impacts of climate change on water resources: the Júcar basin, Spain // Hydrol. Sci. J. 2015. 60, 1. 30–49.

Chirivella Vicente, Capilla José E., Pérez-Martín Miguel A. Dynamical versus statistical downscaling for the generation of regional climate change scenarios at a Western Mediterranean basin: The Júcar River District // J. Water Clim. Chang. 2016. 7, 2. 379–392.

Coakley W.A. Handbook of automated analysis. Continuous flow techniques. New York: Marcel Dekker, 1981.

Colella Simone, Falcini Federico, Rinaldi Eleonora, Sammartino Michela, Santoleri Rosalia. Mediterranean ocean colour chlorophyll trends // PLoS One. 2016. 11, 6. 1–17.

Congreso de los Estados Unidos Mexicanos . Ley de Aguas Nacionales. 1992. 110.

Coppola Jr. Emery A., Rana Anthony J., Poulton Mary M., Szidarovszky Ferenc, Uhl Vincent W. A neural network model for predicting aquifer water level elevations // Ground Water. 2005. 43, 2. 231–241.

Coutinho F. H., Thompson C. C., Cabral A. S., Paranhos R., Dutilh B. E., Thompson F. L. Modelling the influence of environmental parameters over marine planktonic microbial communities using artificial neural networks // Sci. Total Environ. 2019. 677. 205–214.

Da Costa Lobato Tarcísio, Hauser-Davis Rachel Ann, Oliveira Terezinha Ferreira de, Maciel Marinalva Cardoso, Tavares Maria Regina Madruga, Silveira Antônio Morais da, Saraiva Augusto Cesar Fonseca. Categorization of the trophic status of a hydroelectric power plant reservoir in the Brazilian Amazon by statistical analyses and fuzzy approaches // Sci. Total Environ. 2015. 506-507. 613–620.

Damashek Julian, Casciotti Karen L., Francis Christopher A. Variable Nitrification Rates Across Environmental Gradients in Turbid, Nutrient-Rich Estuary Waters of San Francisco Bay // Estuaries and Coasts. 2016. 39, 4. 1050–1071.

De Vittor Cinzia, Relitti Federica, Kralj Martina, Covelli Stefano, Emili Andrea. Oxygen, carbon, and nutrient exchanges at the sediment-water interface in the Mar Piccolo of Taranto (Ionian Sea, southern Italy) // Environ. Sci. Pollut. Res. 2016. 23, 13. 12566–12581.

Del Giudice Dario, Matli V. R.R., Obenour Daniel R. Bayesian mechanistic modeling characterizes Gulf of Mexico hypoxia: 1968–2016 and future scenarios // Ecol. Appl. 2019. 30, 2.

Delgado Alexi, Montellanos Pamela, Llave Janfranco. Air quality level assessment in Lima city using the grey clustering method // IEEE Int. Conf. Autom. / 23rd Congr. Chilean-Association-of-Automatic-Control. 2018.

Delgado Alexi, Romero I. Environmental conflict analysis using an integrated grey clustering and entropy-weight method: A case study of a mining project in Peru // Environ. Model. Softw. 2016. 77. 108–121.

Delgado Juan Antonio, Sudre Joël, Tanahara Sorayda, Montes Ivonne, Martín Hernández-Ayón José, Zirino Alberto. Effect of Caribbean Water incursion into the Gulf of Mexico derived from absolute dynamic topography, satellite data, and remotely sensed chlorophyll a // Ocean Sci. 2019. 15. 1561–1578.

Deng Jianming, Paerl Hans W., Qin Boqiang, Zhang Yunlin, Zhu Guangwei, Jeppesen Erik, Cai Yongjiu, Xu Hai. Climatically-modulated decline in wind speed may strongly affect eutrophication in shallow lakes // Sci. Total Environ. 2018. 645. 1361–1370.

Deng Julong. Generation functions of grey systems // Fuzzy Math. 1985. 5. 11–22.

Djihouessi Metogbe Belfrid, Djihouessi Mahougnon Bernauld, Aina Martin P. A review of habitat and biodiversity research in Lake Nokoué Benin Republic: Current state of knowledge and prospects for further research. 2019. 131–145.

Do-Thu Nga, Morel Antoine, Nguyen-Viet Hung, Pham-Duc Phuc, Nishida Kei, Kootattep Thammarat. Assessing nutrient fluxes in a Vietnamese rural area despite limited and highly uncertain data // Resour. Conserv. Recycl. 2011. 55, 9-10. 849–856.

Doğan Emrah, Kocamaz Uğur Erkin, Utkucu Murat, Yıldırım Eray. Modelling daily water level fluctuations of Lake Van (Eastern Turkey) using Artificial Neural Networks // Fundam. Appl. Limnol. / Arch. für Hydrobiol. 2016. 187, 3. 177–189.

Domínguez Serrano Judith. El acceso al agua y saneamiento: un problema de capacidad institucional local // Prim. Congr. la Red Investig. Soc. Sobre Agua. 2010. XIX. 311–350.

Du Jiabi, Shen Jian, Park Kyeong, Wang Ya Ping, Yu Xin. Worsened physical condition due to climate change contributes to the increasing hypoxia in Chesapeake Bay // Sci. Total Environ. 2018. 630. 707–717.

Duke N. C., Meynecke J.-O., Dittmann S., Ellison A. M., Anger K., Berger U., Cannicci S., Diele K., Ewel K. C., Field C. D., Koedam N., Lee S. Y., Marchand C., Nordhaus I., Dahdouh-Guebas F. A World Without Mangroves? // Science (80-.). 2007. 317, 5834. 41b–42b.

Elgaali E., Garcia L.A. Using Neural Networks to Model the Impacts of Climate Change on Water Supplies // J. Water Resour. Plan. Manag. 2007. 133, 3.

Erisman Jan Willem, Sutton Mark A., Galloway James, Klimont Zbigniew, Winiwarter Wilfried. How a century of ammonia synthesis changed the world // Nat. Geosci. 2008. 1, 10. 636–639.

European Commission . Council Directive 96/61/EC of 24 September 1996 concerning integrated pollution prevention and control. 1996.

European Commission . Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000 establishing a framework for Community action in the field of water policy. 2000. 1–33.

European Commission . Directive 2008/56/EC of the European Parliament and of the Council, of 17 June 2008, establising a framework for community action in the field of marine environmental policy (Marine Strategy Framework Directive). 2008.

European Commission . Commission Decission of 20 September 2013 establishing, pursuant to Directive 2000/60/EC of the European Parliament and of the Council, the values of the Member State monitoring system classifications as a result of the intercalibration exercise and repea. 2013.

European Commission . https://ec.europa.eu/environment/marine/. 2019.

European Communities Council . Council Directive 76/160/EEC of 8 December 1975 concerning the quality of bathing water. 1976.

European Communities Council . Council Directive 91/271/EEC of 21 May 1991 concerning urban waste-water treatment. 1991a.

European Communities Council . Council Directive 91/676/EEC of 12 December 1991 concerning the protection of waters against pollution caused by nitrates from agricultural sources. 1991b.

Fatorić Sandra, Chelleri Lorenzo. Vulnerability to the effects of climate change and adaptation: The case of the Spanish Ebro Delta // Ocean Coast. Manag. 2012. 60. 1–10.

Feller Ilka C., Friess Daniel A., Krauss Ken W., Lewis Roy R. The state of the world's mangroves in the 21st century under climate change // Hydrobiologia. 2017. 803, 1. 1–12.

Ferreira João G., Andersen Jesper H., Borja Angel, Bricker Suzanne B., Camp Jordi, Cardoso da Silva Margarida, Garcés Esther, Heiskanen Anna Stiina, Humborg Christoph, Ignatiades Lydia, Lancelot Christiane, Menesguen Alain, Tett Paul, Hoepffner Nicolas, Claussen Ulrich. Overview of eutrophication indicators to assess environmental status within the European Marine Strategy Framework Directive // Estuar. Coast. Shelf Sci. 2011. 93, 2. 117–131.

Firmansyah I., Spiller M., Ruijter F.J. de, Carsjens G.J., Zeeman G. Assessment of nitrogen and phosphorus flows in agricultural and urban systems in a small island under limited data availability // Sci. Total Environ. 2017. 574. 1521–1532.

Flecha Susana, Pérez Fiz F., García-Lafuente Jesús, Sammartino Simone, Ríos Aida. F., Huertas I. Emma. Trends of pH decrease in the Mediterranean Sea through high frequency observational data: indication of ocean acidification in the basin // J. Chem. Inf. Model. 2015. 53, 9. 1689–1699.

Flo Arcas Eva. Opening the black box of coastal inshore waters in the NW Mediterranean Sea : environmental quality tools and assessment. 2017. 370.

Flo Eva, Garcés Esther, Camp Jordi. Land Uses Simplified Index (LUSI): Determining land pressures and their link with coastal eutrophication // Front. Mar. Sci. 2019. 6, FEB.

Flo Eva, Garcés Esther, Manzanera Marta, Camp Jordi. Coastal inshore waters in the NW Mediterranean: Physicochemical and biological characterization and management implications // Estuar. Coast. Shelf Sci. 2011. 93, 4. 279–289.

Fowler David, Coyle Mhairi, Skiba Ute, Sutton Mark A., Cape J. Neil, Reis Stefan, Sheppard Lucy J., Jenkins Alan, Grizzetti Bruna, Galloway James N., Vitousek Peter, Leach Allison, Bouwman Alexander F., Butterbach-Bahl Klaus, Dentener Frank, Stevenson David, Amann Marcus, Voss Maren. The global nitrogen cycle in the twenty-first century // Philos. Trans. R. Soc. B Biol. Sci. 2013. 368, 1621.

Fox L. J., Struik P. C., Appleton B. L., Rule J. H. Nitrogen phytoremediation by water hyacinth (Eichhornia crassipes (Mart.) Solms) // Water. Air. Soil Pollut. 2008. 194, 1-4. 199–207.

Fuchs Richard, Alexander Peter, Brown Calum, Cossar Frances, Henry Roslyn C., Rounsevell Mark. Why the US–China trade war spells disaster for the Amazon. 2019. 451–454.

Galloway J. N. The Global Nitrogen Cycle // Treatise on Geochemistry. 8-9. 2003. 557–583.

Galloway J. N., Dentener F. J., Capone D. G., Boyer E. W., Howarth R. W., Seitzinger S. P., Asner G. P., Cleveland C. C., Green P. A., Holland E. A., Karl D. M., Michaels A. F., Porter J. H., Townsend A. R., Vörösmarty C. J. Nitrogen cycles: Past, present, and future // Biogeochemistry. sep 2004. 70, 2. 153–226.

Galloway James N., Townsend Alan R., Erisman Jan Willem, Bekunda Mateete, Cai Zucong, Freney John R., Martinelli Luiz A., Seitzinger Sybil P., Sutton Mark A. Transformation of the nitrogen cycle: Recent trends, questions, and potential solutions. 2008. 889–892.

García-Martínez María del Carmen, Vargas-Yáñez Manuel, Moya Francina, Santiago Rocío, Muñoz María, Reul Andreas, Ramírez Teodoro, Balbín Rosa. Average nutrient and chlorophyll distributions in the western Mediterranean: RADMED project // Oceanologia. 2019. 61, 1. 143–169.

García-Ruiz José M., López-Moreno Ignacio I., Vicente-Serrano Sergio M., Lasanta-Martínez Teodoro, Beguería Santiago. Mediterranean water resources in a global change scenario // Earth-Science Rev. 2011. 105, 3-4. 121–139.

Garcia-Solsona E., Garcia-Orellana J., Masqué P., Rodellas V., Mejías M., Ballesteros B., Domínguez J. A. Groundwater and nutrient discharge through karstic coastal springs (Castelló, Spain) // Biogeosciences. 2010. 7, 9. 2625–2638.

Gardner G.W., Dorling S.R. Artificial neural networks (the multilayer perceptron)—a review of applications in the atmospheric sciences // Atmos. Environ. 1998. 32. 2627–2636.

Garmendia Maialen, Bricker Suzanne, Revilla Marta, Borja Ángel, Franco Javier, Bald Juan, Valencia Victoriano. Eutrophication Assessment in Basque Estuaries: Comparing a North American and a European Method // Estuaries and Coasts. 2012. 35. 991–1006.

Geedicke Ina, Oldeland Jens, Leishman Michelle R. Urban stormwater run-off promotes compression of saltmarshes by freshwater plants and mangrove forests // Sci. Total Environ. 2018. 637-638. 137–144.

Genua-Olmedo Ana, Alcaraz Carles, Caiola Nuno, Ibáñez Carles. Sea level rise impacts on rice production: The Ebro Delta as an example // Sci. Total Environ. 2016. 571. 1200–1210.

Gharibi Hamed, Mahvi Amir Hossein, Nabizadeh Ramin, Arabalibeik Hossein, Yunesian Masud, Sowlat Mohammad Hossein. A novel approach in water quality assessment based on fuzzy logic // J. Environ. Manage. 2012. 112. 87–95.

Giri C., Ochieng E., Tieszen L. L., Zhu Z., Singh A., Loveland T., Masek J., Duke N. Status and distribution of mangrove forests of the world using earth observation satellite data // Glob. Ecol. Biogeogr. 2011. 20, 1. 154–159.

Global Environmental Facility . Implementation of the Strategic Action Program of the Gulf of Mexico Large Marine Ecosystem. 2014.

Gobierno de España . Real Decreto Legislativo 1/2001, de 20 de julio, por el que se aprueba el Texto Refundido de la Ley de Aguas (con las modificaciones de la Ley 62/2003, de 30 de diciembre, de medidas fiscales, administrativas y del orden social). 2001.

Gobierno de España . Ley 41/2010, de 29 de diciembre, de Protección del Medio Marino. 2010.

Gobierno de España . Ley 2/2013, de 29 de mayo, de protección y uso sostenible del litoral y de modificación de la Ley 22/1988, de 28 de julio, de Costas (BOE núm. 129, de 30 de mayo de 2013). 2013. 74–76.

Gómez N., Licursi M., Bauer D.E., Ambrosio E.S., Rodrigues Capítulo A. Assessment of Biotic Integrity of the Coastal Freshwater Tidal Zone of a Temperate Estuary of South America through Multiple Indicators // Estuaries and Coasts. 2012. 35. 1328–1339.

Gonçalves Reis Carla Roberta, Bielefeld Nardoto Gabriela, Silva Oliveira Rafael. Global overview on nitrogen dynamics in mangroves and consequences of increasing nitrogen availability for these systems // Plant Soil. 2017. 410, 1-2. 1–19.

Gong Zaiwu, Forrest Jeffrey Yi Lin. Special issue on meteorological disaster risk analysis and assessment: On basis of grey systems theory // Nat. Hazards. mar 2014. 71, 2. 995–1000.

González-Marín Rosa María, Moreno-Casasola Patricia, Castro-Luna Alejandro Antonio, Castillo Alicia. Regaining the traditional use of wildlife in wetlands on the coastal plain of Veracruz, Mexico: ensuring food security in the face of global climate change // Reg. Environ. Chang. 2017. 17, 5. 1343–1354.

Gottardo S., Semenzin E., Giove S., Zabeo A., Critto A., Zwart D. de, Ginebreda A., Marcomini A. Integrated risk assessment for WFD ecological status classification applied to Llobregat river basin (Spain). Part I—Fuzzy approach to aggregate biological indicators // Sci. Total Environ. 2011. 409, 22. 4701–4712.

Govindaraju R.S. Artificial neural networks in hydrology. 2000.

Grasshoff K. Methods of seawater analysis. New York: Verlag Chemie: Weinstein, 1976.

Grattan Lynn M., Holobaugh Sailor, Morris J. Glenn. Harmful algal blooms and public health // Harmful Algae. 2016. 57. 2–8.

Gruber Nicolas, Galloway James N. An Earth-system perspective of the global nitrogen cycle // Nature. 2008. 451, 7176. 293–296.

Guerzoni Stefano, Chester Roy, Dulac Francois, Herut Barak, Loye-Pilot Marie Dominique, Measures Chris, Migon Christophe, Molinaroli Emanuela, Moulin Cyril, Rossini Paolo, Saydam Cemal, Soudine Alexandre, Ziveri Patricia. The role of atmospheric deposition in the biochemistry of the Mediterranean Sea // Prog. Oceanogr. 1999. 44. 147–190.

Guezo Nadege Chimene, Fiogbe Emile Didier, Azon Mahunan Tobias Césaire, Kouamelan Paul Essetchi, Ouattara Allassane. Evaluation of sodium chloride (NaCl) effects on water hyacinth // EWASH TI J. 2017. 1, 4. 34–40.

Hajigholizadeh Mohammad, Melesse Assefa M. Assortment and spatiotemporal analysis of surface water quality using cluster and discriminant analyses // Catena. 2017. 151. 247–258.

Haykin S. Neural networks, a comprehensive foundation. 1999.

He Jianxun, Valeo Caterina, Chu Angus, Neumann Norman F. Stormwater quantity and quality response to climate change using artificial neural networks // Hydrol. Process. 2011. 25, 8. 1298–1312.

He Songjie, Xu Y. Jun. Three Decadal Inputs of Nitrogen and Phosphorus from Four Major Coastal Rivers to the Summer Hypoxic Zone of the Northern Gulf of Mexico // Water Air Soil Pollut. 2015. 226:311.

Heileman S., Rabalais N. Gulf of Mexico: LME 5 // UNEP large Mar. Ecosyst. Rep. A Perspect. Chang. Cond. LMEs world's Reg. seas. 2009. 182. 637–688.

Heiss Elise M., Fulweiler Robinson W. Coastal water column ammonium and nitrite oxidation are decoupled in summer // Estuar. Coast. Shelf Sci. 2016. 178. 110–119.

Herbert R.A. Nitrogen cycling in coastal marine ecosystems // FEMS Microbiol. Rev. 1999. 23, 5. 563–590.

Hermosilla Gómez Zuriñe. Desarrollo metodológico para la correcta evaluación del estado ecológico de las aguas costeras de la Comunidad Valenciana, en el ámbito de la Directiva Marco del Agua, utilizando la clorofila a como parámetro indicador de la calidad. 2009. 132.

Herrero Albert, Gutiérrez-Cánovas Cayetano, Vigiak Olga, Lutz Stefanie, Kumar Rohini, Gampe David, Huber-García Verena, Ludwig Ralf, Batalla Ramon, Sabater Sergi. Multiple stressor effects on biological quality elements in the Ebro River: Present diagnosis and predicted responses // Sci. Total Environ. 2018. 630. 1608–1618.

Herrmann Marine, Estournel Claude, Adloff Fanny, Diaz Fédéric. Impact of climate change on the northwestern Mediterranean Sea pelagic planktonic ecosystem and associated carbon cycle // J. Geophys. Res. Ocean. 2014. 119. 5815–5836.

Hojberg Anker Lajer, Refsgaard Jens Christian, Van Geer Frans, Jorgensen Lisbeth Flindt, Zsuffa István. Use of Models to Support the Monitoring Requirements in the Water Framework Directive // Water Resour. Manag. 2007. 21, 10. 1649–1672.

Holguin Gina, Gonzalez-Zamorano Patricia, De-Bashan Luz E., Mendoza Renato, Amador Edgar, Bashan Yoav. Mangrove health in an arid environment encroached by urban development—a case study // Sci. Total Environ. 2006. 363, 1-3. 260–274.

Holguin Gina, Vazquez Patricia, Bashan Yoav. The role of sediment microorganisms in the productivity, conservation, and rehabilitation of mangrove ecosystems: an overview // Biol. Fertil. Soils. 2001. 33. 265–278.

Howard Meredith D.A., Kudela Raphael M., McLaughlin Karen. New insights into impacts of anthropogenic nutrients on urban ecosystem processes on the Southern California coastal shelf: Introduction and synthesis // Estuar. Coast. Shelf Sci. 2017. 186. 163–170.

Hudson Andrew. Restoring and Protecting the world's large marine ecosystems: An engine for job creation and sustainable economic development // Environ. Dev. 2017. 22. 150–155.

Huesemann Michael H., Skillman Ann D., Crecelius Eric A. The inhibition of marine nitrification by ocean disposal of carbon dioxide // Mar. Pollut. Bull. 2002. 44, 2. 142–148.

Huo Shouliang, Zhang Hanxiao, Ma Chunzi, Xi Beidou, Zhang Jingtian, He Zhuoshi, Li Xiaochuang, Wu Fengchang. Algae community response to climate change and nutrient loading recorded by sedimentary phytoplankton pigments in the Changtan Reservoir, China // J. Hydrol. 2019. 571. 311–321.

IMTA . Programa Nacional Contra Contingencias Hidráulicas. 2013.

IPCC . Climate Change 2014: Synthesis Report. Contribution of Working Groups I, II and III to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change [Core Writing Team, R.K. Pachauri and L.A. Meyer (eds.)]. Geneva, Switzerland, 2014. 151.

Islam Nilufar, Sadiq Rehan, Rodriguez Manuel J., Francisque Alex. Evaluation of source water protection strategies: A fuzzy-based model // J. Environ. Manage. 2013. 121. 191–201.

Jennerjahn Tim C. Biogeochemical response of tropical coastal systems to present and past environmental change // Earth-Science Rev. 2012. 114, 1-2. 19–41.

Jiménez José A., Valdemoro Herminia I., Bosom Eva, Sánchez-Arcilla Agustín, Nicholls Robert J. Impacts of sea-level rise-induced erosion on the Catalan coast // Reg. Environ. Chang. 2017. 17, 2. 593–603.

Jin Li, Whitehead Paul G., Rodda Harvey, Macadam Ian, Sarkar Sananda. Simulating climate change and socio-economic change impacts on flows and water quality in the Mahanadi River system, India // Sci. Total Environ. 2018. 637-638. 907–917.

Jucar Hydrographic Confederation . Júcar Pilot River Basin, Provisional Article 5 Report Pursuant to the Water Framework Directive. 2004.

Jucar Hydrographic Confederation . Presentación de la cuenca. 2010.

Jucar Hydrographic Confederation . Plan hidrológico de la Demarcación hidrográfica del Júcar. Ciclo de planificación hidrológica 2015-2021. 2014.

Kapetanaki Natalia, Krasakopoulou Evangelia, Stathopoulou Eleni, Pavlidou Alexandra, Zervoudaki Soultana, Dassenakis Manos, Scoullos Michael. Simulation of Coastal Processes affecting pH with Impacts on Carbon and Nutrient Biogeochemistry. 19, 2. 2015. 290–304.

Kathuria Vinish. Controlling water pollution in developing and transition countries—lessons from three successful cases // J. Environ. Manage. 2006. 78. 405–426.

Kauffman J. Boone, Hernandez Trejo Humberto, del Carmen Jesus Garcia Maria, Heider Chris, Contreras Wilfrido M. Carbon stocks of mangroves and losses arising from their conversion to cattle pastures in the Pantanos de Centla, Mexico // Wetl. Ecol. Manag. 2016. 24, 2. 203–216.

Kim Haryun. Review of Inorganic Nitrogen Transformations and Effect of Global Climate Change on Inorganic Nitrogen Cycling in Ocean Ecosystems // Ocean Sci. J. 2016. 51, 2. 159–167.

Kirkwood D., Aminot A., Pertillä M. Report on the Results of the ICES Fourth Intercomparison Exercise for Nutrients in Sea Water. Cooperative Research Report No. 174. Copenhagen, 1991. 83.

Kitidis Vassilis, Laverock Bonnie, McNeill Louise C., Beesley Amanda, Cummings Denise, Tait Karen, Osborn Mark A., Widdicombe Stephen. Impact of ocean acidification on benthic and water column ammonia oxidation // Geophys. Res. Lett. 2011. 38, 21. 2–6.

Kitsiou Dimitra, Karydis Michael. Coastal marine eutrophication assessment: A review on data analysis // Environ. Int. 2011. 37, 4. 778–801.

Koh Eun-Hee, Lee Seung Hyun, Kaown Dugin, Moon Hee Sun, Lee Eunhee, Lee Kang-Kun, Kang Bong-Rae. Impacts of land use change and groundwater management on long-term nitrate-nitrogen and chloride trends in groundwater of Jeju Island, Korea // Environ. Earth Sci. 2017. 76, 4. 176.

Kohonen Teuvo. An introduction to neural computing // Neural Networks. 1988. 1, 1. 3–16.

Krom M.D., Emeis K-C, Van Cappellen P. Why is the Eastern Mediterranean phosphorus limited? // Prog. Oceanogr. 2010. 85, 3. 236–244.

Kudela R.M., Berdalet Elisa, Enevoldsen Henrik, Pitcher Grant, Raine Robin, Urban Ed. GEOHAB-The Global Ecology and Oceanography of Harmful Algal Blooms Program: Motivation, goals and legacy // Oceanography. 2017. 30, 1. 12–21.

Kumar Sanjeev, Bhavya P. S., Ramesh R., Gupta G. V.M., Chiriboga Fidel, Singh Arvind, Karunasagar Indrani, Rai Ashwin, Rehnstam-Holm Ann Sofi, Edler Lars, Godhe Anna. Nitrogen uptake potential under different temperature-salinity conditions: Implications for nitrogen cycling under climate change scenarios // Mar. Environ. Res. 2018. 141. 196–204.

Lachtermacher G., Fuller J.D. Backpropagation in hydrological time series forecasting. In: Hipel, K.W., McLeod, A.I., Panu, U.S., Singh, V.P. (Eds.), Stochastic and Statistical Methods in Hydrology and Environmental Engineering. Dordrecht: Kluwer Academic, 1994.

Lam Phyllis, Kuypers Marcel M.M. Microbial Nitrogen Cycling Processes in Oxygen Minimum Zones // Ann. Rev. Mar. Sci. 2011. 3, 1. 317–345.

Laurent Arnaud, Fennel Katja, Cai Wei-Jun, Huang Wei-Jen, Barbero Leticia, Wanninkhof Rik. Eutrophication-induced acidification of coastal waters in the northern Gulf of Mexico: Insights into origin and processes from a coupled physical-biogeochemical model // Geophys. Res. Lett. 2017. 44, 2. 946–956.

Lazzari P., Mattia G., Solidoro C., Salon S., Crise A., Zavatarelli M., Oddo P., Vichi M. The impacts of climate change and environmental management policies on the trophic regimes in the Mediterranean Sea: Scenario analyses // J. Mar. Syst. 2014. 135. 137–149.

Lee Kyung Ha, Jeong Hae Jin, Lee Kitack, Franks Peter J.S., Seong Kyeong Ah, Lee Sung Yeon, Lee Moo Joon, Hyeon Jang Se, Potvin Eric, Suk Lim An, Yoon Eun Young, Yoo Yeong Du, Kang Nam Seon, Kim Kwang Young. Effects of warming and eutrophication on coastal phytoplankton production // Harmful Algae. 2019. 81. 106–118.

Lejeusne Christophe, Chevaldonné Pierre, Pergent-Martini Christine, Boudouresque Charles F., Pérez Thierry. Climate change effects on a miniature ocean: the highly diverse, highly impacted Mediterranean Sea // Trends Ecol. Evol. 2010. 25, 4. 250–260.

Lermontov André, Yokoyama Lídia, Lermontov Mihail, Machado Maria Augusta Soares. River quality analysis using fuzzy water quality index: Ribeira do Iguape river watershed, Brazil // Ecol. Indic. 2009. 9, 6. 1188–1197.

Li Ranran, Zou Zhihong, An Yan. Water quality assessment in Qu River based on fuzzy water pollution index method // J. Environ. Sci. 2016. 50. 87–92.

Liu Lina, Ma Chunzi, Huo Shouliang, Xi Beidou, He Zhuoshi, Zhang Hanxiao, Zhang Jingtian, Xia Xinghui. Impacts of climate change and land use on the development of nutrient criteria // J. Hydrol. 2018. 563. 533–542.

Liu Sifeng, Lin Yi. Grey systems: theory and applications. Berlin: Springer, 2010.

Lomas Michael W., Lipschultz Fredric. Forming the primary nitrite maximum: Nitrifiers or phytoplankton? // Limnol. Oceanogr. 2006. 51, 5. 2453–2467.

López-Portillo Jorge, Lara-Domínguez Ana Laura, Vázquez Gabriela, Aké-Castillo José A. Water Quality and Mangrove-Derived Tannins in Four Coastal Lagoons from the Gulf of Mexico with Variable Hydrologic Dynamics // J. Coast. Res. 2017. 77. 28–38.

Lundberg Cecilia, Lönnroth Malin, Von Numers Mikael, Bonsdorff Erik. A multivariate assessment of coastal eutrophication. Examples from the Gulf of Finland, northern Baltic Sea // Mar. Pollut. Bull. 2005. 50. 1185–1196.

Ma Fang, He Jie, Ma Jiping, Xia Shengguo. Evaluation of urban green transportation planning based on central point triangle whiten weight function and entropy-AHP // Transp. Res. Procedia. 25. 2017. 3634–3644.

Macauley J. M., Harwell L. C., Alafita H. V. The ecological condition of Veracruz, Mexico Estuaries // Environ. Monit. Assess. 2007. 133. 177–185.

Machiwal Deepesh, Islam Adlul, Kamble Trupti. Trends and probabilistic stability index for evaluating groundwater quality: The case of quaternary alluvial and quartzite aquifer system of India // J. Environ. Manage. 2019. 237. 457–475.

Macias Diego, Garcia-Gorriz Elisa, Stips Adolf. Deep winter convection and phytoplankton dynamics in the NW Mediterranean Sea under present climate and future (horizon 2030) scenarios // Sci. Rep. 2018. 8, 1. 6626.

Malagó Anna, Bouraoui Fayçal, Grizzetti Bruna, De Roo Ad. Modelling nutrient fluxes into the Mediterranean Sea // J. Hydrol. Reg. Stud. 2019. 22, March. 100592.

Marín-Muñiz José Luis, Hernández Alarcón María E, Silva Rivera Evodia, Moreno-Casasola Patricia. Perceptions about environmental services and loss of forested wetlands in Monte Gordo community, Veracruz // Madera y Bosques. 2016. 22, June. 53–69.

Martinez M.Luisa, Silva Rodolfo, Lithgow Debora, Mendoza Edgar, Flores Pamela, Martínez Rubí, Cruz Cesia. Human Impact on Coastal Resilience along the Coast of Veracruz, Mexico // J. Coast. Res. 2017. 77. 143–153.

Martínez Ma. Luisa, Mendoza-González Gabriela, Silva-Casarín Rodolfo, Mendoza-Baldwin Edgar. Land use changes and sea level rise may induce a "coastal squeeze" on the coasts of Veracruz, Mexico // Glob. Environ. Chang. 2014. 29. 180–188.

Massoud M.A, Scrimshaw M.D, Lester J.N. Qualitative assessment of the effectiveness of the Mediterranean action plan: wastewater management in the Mediterranean region // Ocean Coast. Manag. 2003. 46, 9-10. 875–899.

Mattei F., Franceschini S., Scardi M. A depth-resolved artificial neural network model of marine phytoplankton primary production // Ecol. Modell. 2018. 382. 51–62.

McLaughlin Karen, Nezlin Nikolay P., Howard Meredith D.A., Beck Carly D.A., Kudela Raphael M., Mengel Michael J., Robertson George L. Rapid nitrification of wastewater ammonium near coastal ocean outfalls, Southern California, USA // Estuar. Coast. Shelf Sci. 2017. 186. 263–275.

MedGIG . Water Framework Directive inercalibration technical report. Part 3: Coastal and Transitional waters. 2009. 244.

Mendelssohn Irving A., Byrnes Mark R., Kneib Ronald T., Vittor Barry A. Coastal habitats of the Gulf of Mexico // Habitats Biota Gulf Mex. Before Deep. Horiz. Oil Spill. 1. 2017. 359–640.

Mendoza-González G, Martínez M L, Lithgow D, Pérez-Maqueo O, Simonin P. Land use change and its effects on the value of ecosystem services along the coast of the Gulf of Mexico // Ecol. Econ. 2012. 82. 23–32.

Merlivat Liliane, Boutin Jacqueline, Antoine David, Beaumont Laurence, Golbol Melek, Vellucci Vincenzo. Increase of dissolved inorganic carbon and decrease in pH in near-surface waters in the Mediterranean Sea during the past two decades // Biogeosciences. 2018. 15. 5653–5662.

Miró Juan Javier, Estrela María José, Caselles Vicente, Gómez Igor. Spatial and temporal rainfall changes in the Júcar and Segura basins (1955–2016): Fine-scale trends // Int. J. Climatol. 2018. 38, 13. 4699–4722.

Mokondoko Pierre, Manson Robert H., Pérez-Maqueo Octavio. Assessing the service of water quality regulation by quantifying the effects of land use on water quality and public health in central Veracruz, Mexico // Ecosyst. Serv. 2016. 22. 161–173.

Montangero Agnes, Belevi Hasan. Assessing nutrient flows in septic tanks by eliciting expert judgement: A promising method in the context of developing countries // Water Res. 2007. 41, 5. 1052–1064.

Montangero Agnès, Belevi Hasan. An approach to optimise nutrient management in environmental sanitation systems despite limited data // J. Environ. Manage. sep 2008. 88, 4. 1538–1551.

Moreno-Casasola Patricia, Espejel Ileana. Classification and ordination of coastal sand dune vegetation along the Gulf and Caribbean Sea of Mexico // Vegetatio. 1986. 66, 3. 147–182.

*Moss Richard H., Edmonds Jae A., Hibbard Kathy A., Manning Martin R., Rose Steven K., Van Vuuren Detlef P., Carter Timothy R., Emori Seita, Kainuma

Mikiko, Kram Tom, Meehl Gerald A., Mitchell John F.B., Nakicenovic Nebojsa, Riahi Keywan, Smith Steven J., Stouffer Ronald J., Thomson Allison M., Weyant John P., Wilbanks Thomas J. The next generation of scenarios for climate change research and assessment // Nature. 2010. 463, 7282. 747–756.

Muñoz-Sevilla Norma Patricia, Le Bail Maxime. Latin American and Caribbean regional perspective on Ecosystem Based Management (EBM) of Large Marine Ecosystems goods and services // Environ. Dev. 2017. 22. 9–17.

Myszograj Sylwia. The Impact of Temperature on the Removal of Nitrogen Compounds in Activated Sludge System // Br. J. Appl. Sci. Technol. 2015. 11, 1. 1–13.

NOAA . The Gulf of Mexico at a glance. A second glance. 2011.

Nawi N.M., Atomi W.H., Rehman M.Z. The effect of data pre-processing on optimized training of artificial neural networks // Procedia Technol. 2013. 11. 32–39.

Nie Jing, Feng Huan, Witherell Benjamin B, Alebus Marzooq, Mahajan Manoj D, Zhang Weiguo, Yu Lizhong. Causes, Assessment, and Treatment of Nutrient (N and P) Pollution in Rivers, Estuaries, and Coastal Waters // Curr. Pollut. Reports. 2018. 4. 154–161.

Ninčević-Gladan Živana, Bužančić Mia, Kušpilić Grozdan, Grbec Branka, Matijević Slavica, Skejić Sanda, Marasović Ivona, Morović Mira. The response of phytoplankton community to anthropogenic pressure gradient in the coastal waters of the eastern Adriatic Sea // Ecol. Indic. 2015. 56. 106–115.

Nixon S W. Coastal marine eutrophication: A definition, social causes, and future concerns // Ophelia. 1995. 41. 199–219.

O'Meara Theresa A., Hillman Jenny R., Thrush Simon F. Rising tides, cumulative impacts and cascading changes to estuarine ecosystem functions // Sci. Rep. 2017. 7, 1. 1–7.

Ocampo-Duque William, Schuhmacher Marta, Domingo José L. A neural-fuzzy approach to classify the ecological status in surface waters // Environ. Pollut. 2007. 148, 2. 634–641.

Okolodkov Yuri B., Campos-Bautista Guadalupe, Gárate-Lizárraga Ismael. Circadian rhythm of a red-tide dinoflagellate Peridinium quadridentatum in the port of Veracruz, Gulf of Mexico, its thecal morphology, nomenclature and geographical distribution // Mar. Pollut. Bull. 2016. 108. 289–296.

Oliveira-Junior Ernandes Sobreira, Tang Yingying, Berg Sanne J.P. van den, Cardoso Simone J., Lamers Leon P.M., Kosten Sarian. The impact of water hyacinth (Eichhornia crassipes) on greenhouse gas emission and nutrient mobilization depends on rooting and plant coverage // Aquat. Bot. 2018. 145. 1–9.

Ontoria Yaiza, Gonzalez-Guedes Eva, Sanmartí Neus, Bernardeau-Esteller Jaime, Ruiz Juan M., Romero Javier, Pérez Marta. Interactive effects of global warming and eutrophication on a fast-growing Mediterranean seagrass // Mar. Environ. Res. 2019. 145. 27–38.

Osuna-Osuna Ana Karen, De Jesús Díaz-Torres José, De Anda-Sánchez José, Villegas-García Edgardo, Gallardo-Valdez Juan, Davila-Vazquez Gustavo. Assessment of land use and land cover change in Tecolutla River Basin, Veracruz, Mexico; during the period 1994-2010 // Ambient. Agua - An Interdiscip. J. Appl. Sci. 2015. 10. 350–362.

Pachés M., Romero I., Hermosilla Z., Martinez-Guijarro R. PHYMED: An ecological classification system for the Water Framework Directive based on phytoplankton community composition // Ecol. Indic. 2012. 19. 15–23.

Paches Maria, Aguado Daniel, Martínez-Guijarro Remedios, Romero Inmaculada. Long-term study of seasonal changes in phytoplankton community structure in the western Mediterranean (Valencian Community) // Environ. Sci. Pollut. Res. 2019. 26. 14266–14276.

Pacyna J.M. Atmospheric Deposition // Encycl. Ecol. 2008. 275–285.

Paerl Hans W. Why does N-limitation persist in the world's marine waters? // Mar. Chem. 2018. 206. 1–6.

Park Geun Ha, Lee Seon Eun, Kim Young il, Kim Dongseon, Lee Kitack, Kang Jeongwon, Kim Yeo Hun, Kim Haryun, Park Seunghee, Kim Tae Wook. Atmospheric deposition of anthropogenic inorganic nitrogen in airborne particles and precipitation in the East Sea in the northwestern Pacific Ocean // Sci. Total Environ. 2019. 681. 400–412.

Park Seongjun, Bae Wookeun, Chung Jinwook, Baek Seung Cheon. Empirical model of the pH dependence of the maximum specific nitrification rate // Process Biochem. 2007. 42, 12. 1671–1676.

Parsons T.R., Maita Y., Lalli C.M. A Manual of Chemical and Biological Methods for Seawater Analysis. London: Pergamon Press, 1984. 173.

Paulmier A., Ruiz-Pino D. Oxygen minimum zones (OMZs) in the modern ocean // Prog. Oceanogr. 2009. 80, 3-4. 113–128.

Peng Peng, Sifeng Liu, Chuanmin Mi, Jing Tao. A study on the assessment of power system security risk based on grey clustering and maximum entropy theory // 2016 IEEE Int. Conf. Syst. Man, Cybern. SMC 2016 - Conf. Proc. 2017. 3002–3007.

Pereyra Díaz Domitilo, Perez Sesma José Antonio, Salas Ortega María del Rocío. Atlas del patrimonio natural, histórico y cultural de Veracruz. 2010. 122.

Pérez-Maqueo Octavio, Martínez M. Luisa, Cóscatl Nahuacatl Rosendo. Is the protection of beach and dune vegetation compatible with tourism? // Tour. Manag. 2017. 58. 175–183.

Pesce M., Critto A., Torresan S., Giubilato E., Santini M., Zirino A., Ouyang W., Marcomini A. Modelling climate change impacts on nutrients and primary production in coastal waters // Sci. Total Environ. 2018. 628-629. 919–937.

Pianosi Francesca, Beven Keith, Freer Jim, Hall Jim W., Rougier Jonathan, Stephenson David B., Wagener Thorsten. Sensitivity analysis of environmental models: A systematic review with practical workflow // Environ. Model. Softw. 2016. 79. 214–232.

Pinet Paul R. Invitation to oceanography. 1996. 508.

Piotrowski Adam P., Napiorkowski Maciej J., Napiorkowski Jaroslaw J., Osuch Marzena. Comparing various artificial neural network types for water temperature prediction in rivers // J. Hydrol. 2015. 529, 1. 302–315.

Pitcher Angela, Wuchter Cornelia, Siedenberg Kathi, Schouten Stefan, Damsté Jaap S Sinninghe. Crenarchaeol tracks winter blooms of ammonia-oxidizing Thaumarchaeota in the coastal North Sea // Limnol. Oceanogr. 2011. 56, 6. 2308–2318.

Pohlert Thorsten. Non-Parametric Trend Tests and Change-Point Detection Depends. 2020.

Powley Helen R, Du Hans H, Lima Ana T, Krom Michael D, Cappellen Philippe Van. Direct Discharges of Domestic Wastewater are a Major Source of Phosphorus and Nitrogen to the Mediterranean Sea // Environ. Sci. Technol. 2016. 50. 8722–8730.

Powley Helen R., Krom Michael D., Van Cappellen Philippe. Understanding the unique biogeochemistry of the Mediterranean Sea: Insights from a coupled phosphorus and nitrogen model // Global Biogeochem. Cycles. 2017. 31, 6. 1010–1031.

Prabakaran G., Vaithiyanathan D., Ganesan Madhavi. Fuzzy decision support system for improving the crop productivity and efficient use of fertilizers // Comput. Electron. Agric. 2018. 150. 88–97.

Primpas Ioannis, Tsirtsis George, Karydis Michael, Kokkoris Giorgos D. Principal component analysis: Development of a multivariate index for assessing eutrophication according to the European water framework directive // Ecol. Indic. 2010. 10. 178–183.

Rabalais N. N., Turner R. E., Diaz R. J., Justic D. Global change and eutrophication of coastal waters // ICES J. Mar. Sci. 2009. 66, 7. 1528–1537.

Rees A. P. Pressures on the marine environment and the changing climate of ocean biogeochemistry // Philos. Trans. R. Soc. A Math. Phys. Eng. Sci. 2012. 370, 1980. 5613–5635.

Reyjol Yorick, Argillier Christine, Bonne Wendy, Borja Angel, Buijse Anthonie D., Cardoso Ana Cristina, Daufresne Martin, Kernan Martin, Ferreira Maria Teresa, Poikane Sandra, Prat Narcís, Solheim Anne-Lyche, Stroffek Stéphane, Usseglio-Polatera Philippe, Villeneuve Bertrand, Bund Wouter van de. Assessing the ecological status in the context of the European Water Framework Directive: Where do we go now? // Sci. Total Environ. 2014. 497-498. 332–344.

Richon Camille, Dutay Jean Claude, Bopp Laurent, Le Vu Briac, Orr James C., Somot Samuel, Dulac Francois. Biogeochemical response of the Mediterranean Sea to the transient SRES-A2 climate change scenario // Biogeosciences. 2019. 16, 1. 135–165.

Ridame C, Le Moal M, Guieu C, Ternon E, Biegala I C, L 'helguen S, Pujo-Pay M. Nutrient control of N 2 fixation in the oligotrophic Mediterranean Sea and the impact of Saharan dust events // Biogeosciences. 2011. 8. 2773–2783.

Rivera-Guzmán Nadia E., Moreno-Casasola Patricia, Ibarra-Obando Silvia E., Sosa Vinicio J., Herrera-Silveira Jorge. Long term state of coastal lagoons in Veracruz, Mexico: Effects of land use changes in watersheds on seagrasses habitats // Ocean Coast. Manag. 2014. 87. 30–39.

Robertson G. Philip, Vitousek Peter M. Nitrogen in Agriculture: Balancing the Cost of an Essential Resource // Annu. Rev. Environ. Resour. 2009. 34, 1. 97–125.

Rockström Johan, Steffen Will, Noone Kevin, Persson Åsa, Chapin F. Stuart, Lambin Eric, Lenton Timothy M., Scheffer Marten, Folke Carl, Schellnhuber Hans Joachim, Nykvist Björn, Wit Cynthia A. de, Hughes Terry, Leeuw Sander van der, Rodhe Henning, Sörlin Sverker, Snyder Peter K., Costanza Robert, Svedin Uno, Falkenmark Malin, Karlberg Louise, Corell Robert W., Fabry Victoria J., Hansen James, Walker Brian, Liverman Diana, Richardson Katherine, Crutzen Paul, Foley Jonathan. Planetary boundaries: Exploring the safe operating space for humanity // Ecol. Soc. 2009. 14, 2.

Rodríguez Martínez Jaime. Oceanografía del mar Mediterráneo. Madrid: Ediciones Pirámide, S.A., 1982.

Rodríguez-Romero Alexis, Rico-Sánchez Axel, Mendoza-Martínez Erick, Gómez-Ruiz Andrea, Sedeño-Díaz Jacinto, López-López Eugenia, Rodríguez-Romero Alexis Joseph, Rico-Sánchez Axel Eduardo, Mendoza-Martínez Erick, Gómez-Ruiz Andrea, Sedeño-Díaz Jacinto Elías, López-López Eugenia. Impact of Changes of Land Use on Water Quality, from Tropical Forest to Anthropogenic Occupation: A Multivariate Approach // Water. 2018. 10, 11. 1518.

Romanou A., Tselioudis G., Zerefos C. S., Clayson C. A., Curry J. A., Andersson A. Evaporation-precipitation variability over the mediterranean and the black seas from satellite and reanalysis estimates // J. Clim. 2010. 23, 19. 5268–5287.

Romero Gil Inmaculada. Comportamiento de nutrientes en la pluma del río Ebro. 2003. 583.

Romero I., Moragues M., González del Río J., Hermosilla Z., Sánchez-Arcilla A., Sierra J. P., Mösso C. Nutrient Behavior in the Júcar Estuary and Plume // J. Coast. Res. Spec. Issue. 2007. 47. 48 – 55.

Romero I., Pachés M., Martínez-Guijarro R., Ferrer J. Glophymed: An index to establish the ecological status for the Water Framework Directive based on phytoplankton in coastal waters // Mar. Pollut. Bull. 2013. 75, 1-2. 218–223.

Ruiz Téllez Trinidad, Martín Elsa, López Rodrigo, Granado Gloria Lorenzo, Albano Pérez Eva, Morán López Ricardo, Manuel Juan, Guzmán Sánchez. The Water Hyacinth, Eichhornia crassipes: an invasive plant in the Guadiana River Basin (Spain) // Aquat. Invasions. 2008. 3, 1. 42–53.

Rumelhart David E., Hinton Geoffrey E., Williams Ronal. Learning representations by back-propagating errors // Nature. 1986. 323. 533–536.

SAGARPA . Diagnóstico del Sector Primario en Veracruz. 2009.

SAGARPA . Uso de fertilizantes químicos en la superficie sembrada 2016. 2016.

Sacasqui Marcos, Luyo Jaime, Delgado Alexi. A Unified Index for Power Quality Assessment in Distributed Generation Systems Using Grey Clustering and Entropy Weight // 2018 IEEE ANDESCON, ANDESCON 2018 - Conf. Proc. dec 2018.

Sánchez-Hernández M., Robina-Ramírez Rafael, De Clercq Willem. Water Management Reporting in the Agro-Food Sector in South Africa // Water. 2017. 9, 12. 830.

Scannapieco D., Naddeo V., Zarra T., Belgiorno V. River water quality assessment: A comparison of binary- and fuzzy logic-based approaches // Ecol. Eng. 2012. 47. 132–140.

Scavia Donald, Bricker Suzanne B. Coastal eutrophication assessment in the United States // Biogeochemistry. 2006. 79. 187–208.

Schaefer Sylvia C., Hollibaugh James T. Temperature Decouples Ammonium and Nitrite Oxidation in Coastal Waters // Environ. Sci. Technol. 2017. 51, 6. 3157–3164.

Schärer M., Page T., Beven K. A fuzzy decision tree to predict phosphorus export at the catchment scale // J. Hydrol. 2006. 331, 3-4. 484–494.

Sebastián Marta, Gasol Josep M. Heterogeneity in the nutrient limitation of different bacterioplankton groups in the Eastern Mediterranean Sea // ISME J. 2013. 7, 8. 1665–1668.

Sen Pranab Kumar. Estimates of the Regression Coefficient Based on Kendall's Tau // J. Am. Stat. Assoc. 1968. 63, 324. 1379–1389.

Sepehri Mehdi, Malekinezhad Hossein, Hosseini Seyed Zeynalabedin, Ildoromi Ali Reza. Assessment of flood hazard mapping in urban areas using entropy weighting method: a case study in Hamadan city, Iran // Acta Geophys. 2019. 67, 5. 1435–1449.

Severin Tatiana, Kessouri Faycal, Rembauville Mathieu, Sánchez-Pérez Elvira Denisse, Oriol Louise, Caparros Jocelyne, Pujo-Pay Mireille, Ghiglione Jean-Francois, D'Ortenzio Fabrizio, Taillandier Vincent, Mayot Nicolas, De Madron Xavier Durrieu, Ulses Caroline, Estournel Claude, Conan Pascal. Open-ocean convection process: A driver of the winter nutrient supply and the spring phytoplankton distribution in the Northwestern Mediterranean Sea // J. Geophys. Res. Ocean. 2014. 122. 4587–4601.

Shaban M., Urban B., El Saadi A., Faisal M. Detection and mapping of water pollution variation in the Nile Delta using multivariate clustering and GIS techniques // J. Environ. Manage. 2010. 91. 1785–1793.

Shannon C E. A Mathematical Theory of Communication // Bell Syst. Tech. J. 1948. 27. 623–656.

Sherman Benjamin H. Multiple marine ecological disturbance assessments for latin american and caribbean large marine ecosystems // Environ. Dev. 2017. 22. 129–142.

Shinn M.B. Colorimetric method for the determination of nitrite // Ind. Eng. Chem. Anal. Ed. 1941. 13. 33–35.

Shooshtarian Mohammad Reza, Dehghani Mansooreh, Margherita Ferrante, Gea Oliveri Conti, Mortezazadeh Shima. Land use change and conversion effects on ground water quality trends: An integration of land change modeler in GIS and a new Ground Water Quality Index developed by fuzzy multi-criteria group decision-making models // Food Chem. Toxicol. 2018. 114. 204–214.

Sinha E., Michalak A. M., Calvin K. V., Lawrence P. J. Societal decisions about climate mitigation will have dramatic impacts on eutrophication in the 21st century // Nat. Commun. 2019. 10, 1. 939.

Smith Alastair F., Fryer Rob J., Webster Lynda, Berx Bee, Taylor Alison, Walsham Pamela, Turrell William R. Setting background nutrient levels for coastal waters with oceanic influences // Estuar. Coast. Shelf Sci. 2014. 145. 69–79.

Solòrzano L. Determination of ammonia in natural waters by the phenol hypoclorite method // Limnol. Oceanogr. 1969. 14. 799–801.

Sospedra J, Falco S, Morata T, Gadea I, Rodilla M. Benthic fluxes of oxygen and nutrients in sublittoral fine sands in a north-western Mediterranean coastal area // Cont. Shelf Res. 2015. 97. 32–42.

Spanish Ministry of Environment . Real Decreto por el que se establecen los criterios de seguimiento y evaluación del estado de las aguas superficiales y las normas de calidad ambiental. 2015.

Stamou Anastasios I, Kamizoulis George. Estimation of the effect of the degree of sewage treatment on the status of pollution along the coastline of the Mediterranean Sea using broad scale modelling // J. Environ. Manage. 2008. 90, 2. 931–939.

Statham Peter J. Nutrients in estuaries — An overview and the potential impacts of climate change // Sci. Total Environ. 2012. 434. 213–227.

Störmer Oda. Climate Change Impacts on Coastal Waters of the Baltic Sea // Glob. Chang. Balt. Coast. Zo. 2011. 51–69.

Struyf Eric, Van Damme Stefan, Meire Patrick. Possible effects of climate change on estuarine nutrient fluxes: a case study in the highly nutrified Schelde estuary (Belgium, The Netherlands) // Estuar. Coast. Shelf Sci. aug 2004. 60, 4. 649–661.

Tabari Hossein, Marofi Safar, Ahmadi Mohammad, Tabari H, Marofi · S, Ahmadi M. Long-term variations of water quality parameters in the Maroon River, Iran // Env. Monit Assess. 2011. 177. 273–287.

Tabla-Hernandez J., Rodriguez-Espinosa P. F., Mendoza-Pérez J. A., Sánchez-Ortíz E., Martinez-Tavera E., Hernandez-Ramirez A. G., Tabla-Hernandez J., Rodriguez-Espinosa P. F., Mendoza-Pérez J. A., Sánchez-Ortíz E., Martinez-Tavera E., Hernandez-Ramirez A. G. Assessment of Potential Toxic Metals in a Ramsar Wetland, Central Mexico and its Self-Depuration through Eichhornia crassipes // Water. 2019. 11, 6. 1248.

Temino-Boes Regina, Romero Inmaculada, Martinez-Guijarro Remedios, Pachés María. The importance of considering pollution along the coast from heavily modified water bodies under the water framework directive // WIT Trans. Ecol. Environ. 2018. 228. 307–316.

Temino-Boes Regina, Romero Inmaculada, Pachés María, Martinez-Guijarro Remedios, Romero-Lopez Rabindranarth. Anthropogenic impact on nitrification dynamics in coastal waters of the Mediterranean Sea // Mar. Pollut. Bull. 2019a. 145. 14–22.

Temino-Boes Regina, Romero-López Rabindranarth, Romero Inmaculada. A Spatiotemporal Analysis of Nitrogen Pollution in a Coastal Region with Mangroves of the Southern Gulf of Mexico // Water. 2019b. 11. 2143.

Temino-boes Regina, Romero-lopez Rabindranarth, Ibarra-zavaleta Sara Patricia, Romero Inmaculada. Using grey clustering to evaluate nitrogen pollution in estuaries with limited data // Sci. Total Environ. 2020. 722. 137964.

Thorburn Peter J., Biggs Jody S., Palmer Jeda, Meier Elizabeth A., Verburg Kirsten, Skocaj Danielle M. Prioritizing Crop Management to Increase Nitrogen Use Efficiency in Australian Sugarcane Crops // Front. Plant Sci. sep 2017. 8:1504.

Thorhaug Anitra L., Poulos Helen M., López-Portillo Jorge, Barr Jordan, Lara-Domínguez Ana Laura, Ku Tim C., Berlyn Graeme P. Gulf of Mexico estuarine blue carbon stock, extent and flux: Mangroves, marshes, and seagrasses: A North American hotspot // Sci. Total Environ. 2019. 653. 1253–1261.

Toft Jason D., Simenstad Charles A., Cordell Jeffery R., Grimaldo Lenny F. The effects of introduced water hyacinth on habitat structure, invertebrate assemblages, and fish diets // Estuaries. 2003. 26, 3. 746–758.

Torkamaneh Davoud, Chalifour François P., Beauchamp Chantal J., Agrama Hesham, Boahen Steve, Maaroufi Halim, Rajcan Istvan, Belzile François. Genome-wide association analyses reveal the genetic basis of biomass accumulation under symbiotic nitrogen fixation in African soybean // Theor. Appl. Genet. 2019. 133. 665–676.

Torres Jony R, Infante-Mata Dulce, Sánchez Alberto J, Espinoza-Tenorio Alejandro, Barba Everardo. Degradación de hojarasca y aporte de nutrientes del manglar en la Laguna Mecoacán, Golfo de México // Biol. Trop. 2018. 66, 2. 892–907.

Treguer P., Le Corre P. Manuel d'analyse des sels nutritifs dans l'eau de mer. 1975. 110.

Tseng Ming Lang. A causal and effect decision making model of service quality expectation using grey-fuzzy DEMATEL approach // Expert Syst. Appl. 2009. 36, 4. 7738–7748.

Turner R. Eugene, Rabalais Nancy N. Nitrogen and phosphorus phytoplankton growth limitation in the Northern Gulf of Mexico // Aquat. Microb. Ecol. 2013. 68. 159–169.

UNIDO . Integrated Assessment and Management of the Gulf of Mexico Large Marine Ecosystem. Transboundary Diagnostic Analysis. 2011.

U.S. Government . Federal Water Pollution Control Act. 2002.

Ulloa Marco J., Álvarez-Torres Porfirio, Horak-Romo Karla P., Ortega-Izaguirre Rogelio. Harmful algal blooms and eutrophication along the mexican coast of the Gulf of Mexico large marine ecosystem // Environ. Dev. 2017. 22. 120–128.

Ulrich-Schad J.D., García de Jalón S., Babin N., Pape A., Prokopy L.S. Measuring and understanding agricultural producers' adoption of nutrient best management practices // J. Soil Water Conserv. 2017. 72, 5. 506–518.

Umgiesser Georg, Melaku Canu Donata, Solidoro Cosimo, Ambrose Robert. A finite element ecological model: a first application to the Venice Lagoon // Environ. Model. Softw. 2003. 18, 2. 131–145.

Vadde Kiran Kumar, Wang Jianjun, Cao Long, Yuan Tianma, McCarthy Alan J., Sekar Raju. Assessment of Water Quality and Identification of Pollution Risk Locations in Tiaoxi River (Taihu Watershed), China // Water. 2018. 10, 2. 183.

Valdor Paloma F., Gómez Aina G., Juanes José A., Kerléguer Camille, Steinberg Peter, Tanner Edwina, MacLeod Catriona, Knights Antony M., Seitz Rochelle D., Airoldi Laura, Firth Louise B., Crowe Tasman, Chatzinikolaou Eva, Smith Alison, Arvanitidis Christos, Burt John A., Brooks Paul R., Ponti Massimo, Soares-Gomes Abilio, Ovejero Aida, Méndez Gonzalo. A global atlas of the environmental risk of marinas on water quality // Mar. Pollut. Bull. dec 2019. 149. 110661.

Van Meter K.J., Basu N.B., Van Cappellen P. Two centuries of nitrogen dynamics: Legacy sources and sinks in the Mississippi and Susquehanna River Basins // Global Biogeochem. Cycles. 2017. 31. 2–23.

Vargas-Yáñez M., García-Martínez M. C., Moya F., Balbín R., López-Jurado J. L., Serra M., Zunino P., Pascual J., Salat J. Updating temperature and salinity mean values and trends in the Western Mediterranean: The RADMED project // Prog. Oceanogr. 2017. 157. 27–46.

Vatansever Kemal, Akgűl Yakup. Performance evaluation of websites using entropy and grey relational analysis methods: The case of airline companies // Decis. Sci. Lett. 2018. 7. 119–130.

Vázquez-González César, Moreno-Casasola Patricia, Juárez Abraham, Rivera-Guzmán Nadia, Monroy Roberto, Espejel Ileana. Trade-offs in fishery yield between wetland conservation and land conversion on the Gulf of Mexico // Ocean Coast. Manag. 2015. 114. 194–203.

Villamagna A. M., Murphy B. R. Ecological and socio-economic impacts of invasive water hyacinth (Eichhornia crassipes): a review // Freshw. Biol. 2010. 55, 2. 282–298.

Viola Donna, McKay Christopher P., Navarro-González Rafael. A method for monitoring glacial loss and temperature variation using satellite observations: Case study of Pico de Orizaba and Iztaccíhuatl (Mexico) // Arctic, Antarct. Alp. Res. jan 2019. 51, 1. 379–396.

Vollenweider R.A, Rinaldi A, Viviani R, Todini E. Assessment of the state of eutrophication in the Mediterranean Sea. MAP Technical Reports Series No . 106. 1996.

Voss Maren, Bange Hermann W, Dippner Joachim W, Middelburg Jack J, Montoya Joseph P, Ward Bess. The marine nitrogen cycle: recent discoveries, uncertainties and the potential relevance of climate change. // Philos. Trans. R. Soc. Lond. B. Biol. Sci. 2013. 368, 1621. 20130121.

Voulvoulis Nikolaos, Arpon Karl Dominic, Giakoumis Theodoros. The EU Water Framework Directive: From great expectations to problems with implementation // Sci. Total Environ. 2017. 575. 358–366.

Wagena Moges B., Easton Zachary M. Agricultural conservation practices can help mitigate the impact of climate change // Sci. Total Environ. 2018. 635. 132–143.

Wanas N., Auda G., Kamel M.S., Karray F. On the optimal number of hidden nodes in a neural network // IEEE Can. Conf. Electr. Comput. Eng. Proc. 1998. 918–921.

Wang Fuxing, Polcher Jan. Assessing the freshwater flux from the continents to the Mediterranean Sea // Sci. Rep. 2019. 9, 1. 8024.

Wang P F, Martin J, Morrison G. Water Quality and Eutrophication in Tampa Bay, Florida // Estuar. Coast. Shelf Sci. 1999. 49, 1. 1–20.

Wang Qinggai, Li Shibei, Jia Peng, Qi Changjun, Ding Feng. A review of surface water quality models. // ScientificWorldJournal. 2013. 2013. 231768.

Wannicke Nicola, Frey Claudia, Law Cliff S., Voss Maren. The response of the marine nitrogen cycle to ocean acidification // Glob. Chang. Biol. 2018. 24, 11.

Wen X U, Wei Chen. Application of grey clustering method in eutrophication assessment for lake water // J. Am. Sci. 2006. 2, 4. 53–58.

Whitehead P.G., Jin L., Bussi G., Voepel H.E., Darby S.E., Vasilopoulos G., Manley R., Rodda H., Hutton C., Hackney C., Tri Van Pham Dang, Hung N.N. Water quality modelling of the Mekong River basin: Climate change and socioeconomics drive flow and nutrient flux changes to the Mekong Delta // Sci. Total Environ. 2019. 673. 218–229.

Xianyu Kong, Yanfang Liu, Huimin Jian, Rongguo Su, Qingzhen Yao, Xiaoyong Shi. New Approach for Rapid Assessment of Trophic Status of Yellow Sea and

East China Sea Using Easy-to-Measure Parameters // J. Ocean Univ. China. 2017. 16, 5. 781–792.

Yáñez-Arancibia Alejandro, Day John W. Environmental sub-regions in the Gulf of Mexico coastal zone: The ecosystem approach as an integrated management tool // Ocean Coast. Manag. 47, 11-12 SPEC. ISS. 2004. 727–757.

Yañez-Arancibia Alejandro, Day John W., Reyes Enrique. Understanding the Coastal Ecosystem-Based Management Approach in the Gulf of Mexico // J. Coast. Res. 2013. 63. 244–262.

Ye Jing, Dang Yaoguo, Li Bingjun. Grey-Markov prediction model based on background value optimization and central-point triangular whitenization weight function // Commun. Nonlinear Sci. Numer. Simul. 2018. 54. 320–330.

Yool Andrew, Martin Adrian P., Fernández Camila, Clark Darren R. The significance of nitrification for oceanic new production // Nature. 2007. 447, 7147. 999–1002.

Zaldívar-Jiménez Arturo, Guevara-Porras Paloma Ladrón-de, Pérez-Ceballos Rosela, Díaz-Mondragón Salomón, Rosado-Solórzano Roberto. US-Mexico joint Gulf of Mexico large marine ecosystem based assessment and management: Experience in community involvement and mangrove wetland restoration in Términos lagoon, Mexico // Environ. Dev. 2017. 22. 206–213.

Zarzuelo Carmen, D'Alpaos Andrea, Carniello Luca, López-Ruiz Alejandro, Díez-Minguito Manuel, Ortega-Sánchez Miguel. Natural and Human-Induced Flow and Sediment Transport within Tidal Creek Networks Influenced by Ocean-Bay Tides // Water. 2019. 11, 7. 1493.

Zhang Qi, Yu Ruihong, Jin Ye, Zhang Zhuangzhuang, Liu Xinyu, Xue Hao, Hao Yanling, Wang Lixin, Zhang Qi, Yu Ruihong, Jin Ye, Zhang Zhuangzhuang, Liu Xinyu, Xue Hao, Hao Yanling, Wang Lixin. Temporal and Spatial Variation

Trends in Water Quality Based on the WPI Index in the Shallow Lake of an Arid Area: A Case Study of Lake Ulansuhai, China // Water. 2019. 11, 7. 1410.

Zhu Changjun, Liu Qinghua. Evaluation of water quality using grey clustering // Second Int. Work. Knowl. Discov. Data Min. 2009. 803–805.

Zouiten Hala, Díaz César Álvarez, Gómez Andrés García, Cortezón José Antonio Revilla, Alba Javier García. An advanced tool for eutrophication modeling in coastal lagoons: Application to the Victoria lagoon in the north of Spain // Ecol. Modell. 2013. 265. 99–113.