



# The interplay of freshwater inputs and catchment geology in regulating seawater chemistry in Irish coastal areas

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## ABSTRACT

Open ocean carbonate chemistry is altered by the dissolution of atmospheric CO<sub>2</sub> in seawater. Up to 40% of anthropogenic CO<sub>2</sub> emissions have dissolved in the surface ocean since the pre-industrial era, driving changes in marine carbonate pools and promoting ocean acidification. Under open ocean conditions, Total Alkalinity (TA) generally relates with salinity and temperature due to the conservative nature of its constituents. In coastal areas, however, land-ocean interactions may greatly contribute to making TA far less predictable, since freshwater inputs can affect the chemistry of coastal water masses by increasing TA and Dissolved Inorganic Carbon (DIC) or, alternatively, lowering them through dilution. Here we analysed and compared coastal carbonate chemistry dynamics in selected coastal areas of Ireland, in order to assess whether rivers and their catchment geology can influence coastal water chemistry and to verify the occurrence of local ocean acidification processes. Data on TA, DIC, salinity, temperature, and nutrients (total nitrogen, phosphate, and silicate) collected during several surveys along the Irish coastline by The Marine Institute Foras Na Mara (MIFNM) from 2009 to 2018 were analysed against those available on the main watercourses feeding the selected coastal areas. The relationships among the different variables were scrutinized, also considering the geological characteristics of river catchments. Results showed a clear linkage between coastal water chemistry and local freshwater inputs, whereas changes in the geology of catchment areas exerted only a secondary influence. An in-depth scrutiny of the Galway Bay sector performed by comparing MIFNM data with those collected during an oceanographic cruise carried out in October 2017 further indicated remarkable effects of the interaction between river inputs and submarine groundwater discharges on seasonal variations in the water chemistry of the area. Future studies, integrating chemical data across the land-ocean boundary, may provide additional, useful information on the factors actually affecting the variation in water carbonates in coastal areas. Elucidating how land-ocean interactions influence the coastal carbonate system may ultimately provide a key for a more advanced understanding of the resilience of coastal areas to ocean acidification.

## 1. Introduction

Since the industrial revolution, the progressive increase in atmospheric CO<sub>2</sub> has been absorbed by the ocean (up to 40%: Feely et al., 2004; Khatiwala et al., 2009; Friedlingstein et al., 2020; Cañzos et al., 2022). The rising of CO<sub>2</sub> reflects on oceans buffer capacity (Billé et al., 2013), which has experienced in the past decades a considerable reduction (Doney et al., 2009; Ridge and McKinley, 2021; Devries, 2022). This phenomenon, known as ocean acidification, leads to changes in the carbonate chemistry of surface waters, ultimately altering primary production rates and calcification rates in benthic organisms (Kleypas and Langdon, 2006; Doney et al., 2009; Davis et al., 2021).

Most of the attention has generally focused on open ocean environments where empirical relations between temperature, salinity and oxygen have been generally used to reconstruct the carbonate system (Alin et al., 2012; Carter et al., 2018; Bushinsky et al., 2019). Empirical models provide robust predictions over decadal scales; however, for predictions over longer time scales it has been repeatedly emphasized the necessity of a readjustment taking explicitly into account human CO<sub>2</sub> emissions (Alin et al., 2012; Shen et al., 2019). It is worth noting that under open ocean conditions salinity and Total Alkalinity (TA) are highly correlated, since the main freshwater sources are limited to rainfall and ice melting and negligible contributions are provided by continental freshwater inputs (Key et al., 2006; Wu et al., 2019). In

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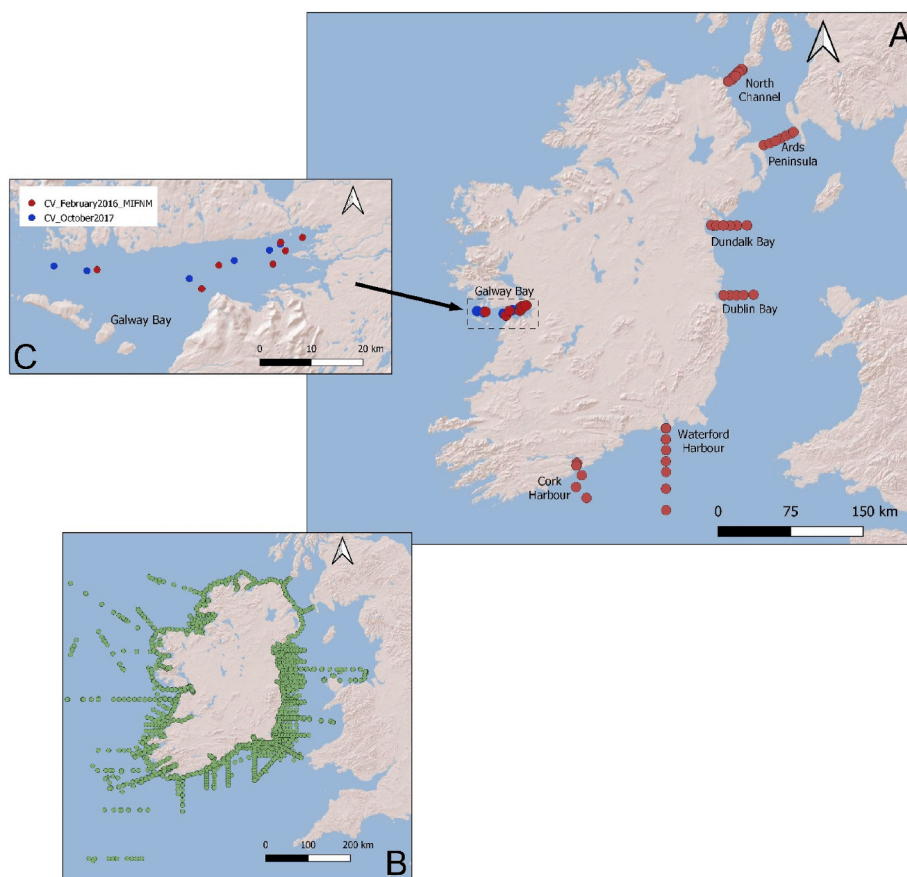
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**Fig. 1.** (A) Sampling stations of The Marine Institute Foras Na Mara (MIFNM) oceanographic cruise performed in October 2017 (blue) and those selected from the MIFNM database (in red) (B) locations included in the MIFNM full database; (C) detail of the sampling stations in Galway Bay considered for the seasonal comparison (see text for further details). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

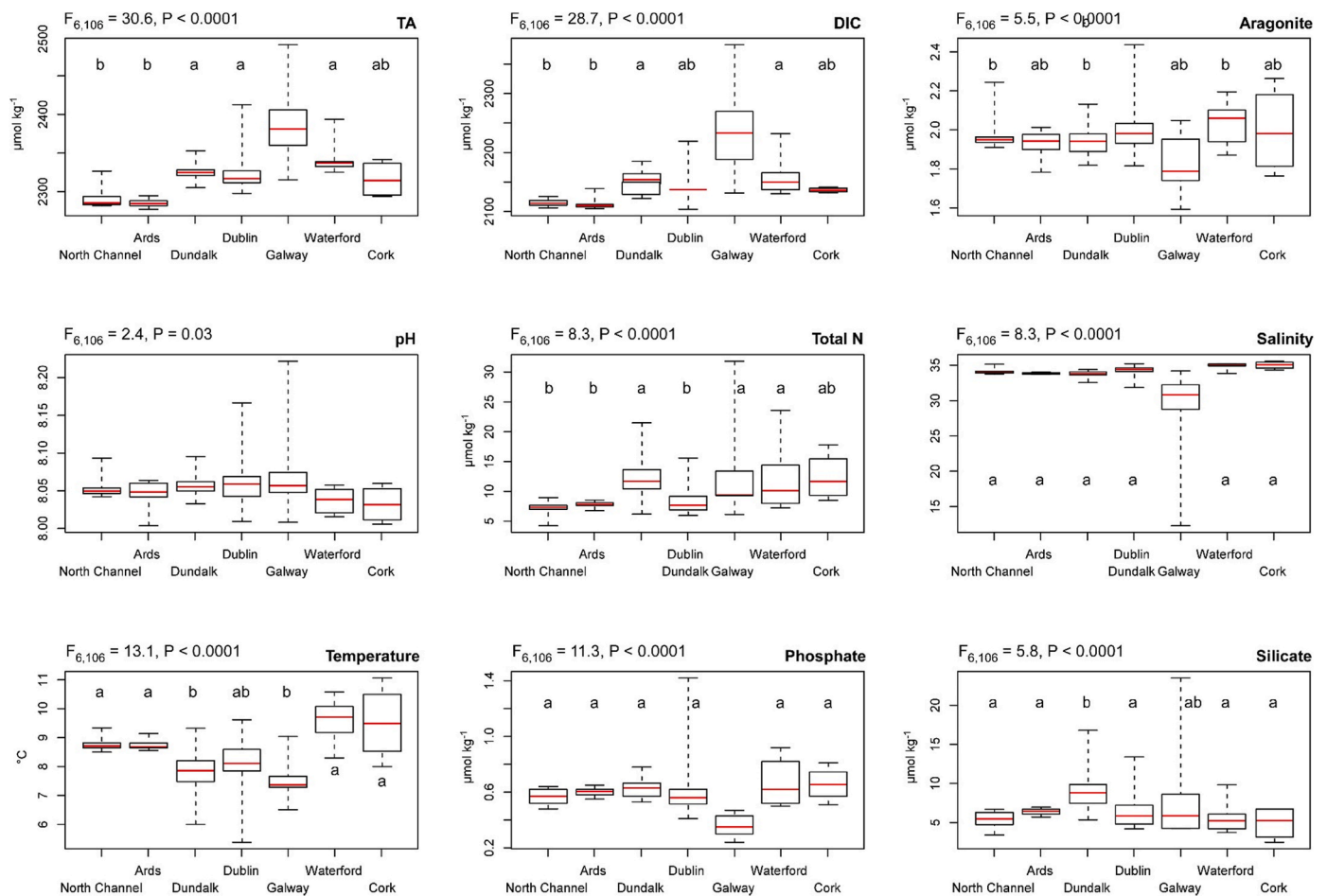
coastal areas, conversely, the carbonate chemistry of water masses is more complex to be modelled and predicted, and an in-depth understanding of the contribution of watershed inputs and other sources of land-derived freshwater is required (St-Laurent et al., 2020; Hao et al., 2023).

Enrichments of inorganic carbon associated with freshwater inputs have been commonly observed in coastal areas, reflecting in a reduction in pH over shorter time scale compared to the open ocean (De Weys et al., 2011; Cyronak et al., 2013; McMahon et al., 2013; Santos et al., 2014). Furthermore, a number of investigations have indicated that the contribution of rivers to the alkalinity of coastal waters may also depend on the catchment area geology: loadings are generally high when watersheds are located in calcareous areas, while decrease remarkably when siliceous areas are drained (Hannigan and Kelly-Quinn, 2013; Kelly-Quinn et al., 2022). Noticeably, at a global scale, rivers are responsible for 40% of the content in Dissolved Inorganic Carbon (DIC) of coastal waters (Ludwig et al., 1996). The dissolution of carbonate rocks along river basins, or biogenic CO<sub>2</sub> resulting from bacterial respiration of marine terrestrial organic matter, can all contribute to coastal DIC pools (Brunet et al., 2009; Vargas et al., 2016). Increases in the delivery of inorganic carbon by freshwater inputs can alter coastal biogeochemical cycles, an effect intensified by human activities on land (Borges and Gypens, 2010; Campeau et al., 2017). Indeed, land use and other human-related activities can contribute nutrients originally accumulated in soils that are exported by rivers or by Submarine Groundwater Discharges (SGD) (Valiela et al., 1990; Cole et al., 2007; Deng et al., 2021; Li et al., 2022). Watershed inputs represent a source of organic and inorganic carbon as well as of nutrients to coastal waters; their nature and magnitude can vary remarkably from large surface

inputs by rivers or streams to small and localized contributions by SGD. Land-derived nutrients discharge can intensify eutrophication processes (Cai et al., 2011; O'Boyle et al., 2019). In estuarine areas, in particular, during eutrophication events a variation in the relationship between TA and DIC has been observed, paralleled by a drastic reduction in DIC (Dai et al., 2008).

The overarching aim of the present study was to increase our understanding of the role of coastal zones in the global carbon cycle by exploring the contribution of land-related factors to variations in the carbonate chemistry of Irish coastal areas. To this end, emphasis was given to land geology and river chemistry. In Ireland the central part of the island is mainly characterized by limestone (Sanders, 2008): therefore, in coastal areas freshwater discharge by rivers might represent a considerable source of carbonates. On the western coasts, conversely, SGD constitutes the main source of discharge (Rocha et al., 2015; Schubert et al., 2015). In addition, in the south and southeast of the island, agriculture is particularly developed; the widespread use of fertilizers ultimately determines a considerable load of nutrients to watercourses and, ultimately, to coastal areas; land-derived nitrogen and sulphate, in particular, are anomalously high as compared to the rest of the country's coastal waters (O'Boyle and Silke, 2010; O'Boyle et al., 2015, 2016, 2019).

On a global scale, a number of studies have demonstrated a decline in growth of different shellfish species due to ocean acidification (e.g., Talmage and Gobler, 2010; Barton et al., 2012; Stewart-Sinclair et al., 2020). In Ireland an important economic contribution is provided by the shellfish aquaculture industry (Callaway et al., 2012; Fernandes-Salvador et al., 2021); future activities can be potentially at risk from acidification phenomena, and therefore an advanced resolution of the



**Fig. 2.** MIFNM dataset: average concentration of TA, DIC,  $\Omega$  Aragonite, pH, total N, salinity, temperature, phosphate, and silicate across the seven marine sectors included in this study. The red line indicates median values, boxes the 25th and 75th percentiles, while the whiskers minimum and maximum values. Numbers in blue refer to data from the SGD database of EPA (<https://epawebapp.epa.ie/hydronet/#Groundwater> measuring date: April 2015) referring to Kinvarra Spring and are included for the sake of comparison. The results of 1-way ANOVA tests and post-hoc bivariate comparisons (Tukey HSD tests) are included; sectors showing identical letters do not differ at  $P < 0.05$ . (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

**Table 1**

Factor loadings, eigenvalues, and % contribution of the three principal component axes (PC1, PC2, and PC3) to variation in the MIFNM dataset.

	PC1	PC2	PC3
Eigenvalue	4.34	1.61	1.40
% Total	48.18	17.85	15.54
Cumulative	48.18	66.04	81.58
TA	-0.82	0.31	0.01
DIC	-0.91	0.19	-0.21
$\Omega$ Aragonite	0.63	0.27	0.61
pH	-0.30	0.49	0.80
Total N	-0.79	-0.40	0.07
Salinity	0.81	-0.38	0.01
Temperature	0.69	0.13	-0.29
Phosphate	0.07	-0.79	0.48
Silicate	-0.77	-0.46	0.16

carbonate system of the Irish coastal zone is required. McGrath et al., in 2016 provided a first assessment of TA and DIC variations in Irish waters by focusing on data collected from a number of oceanographic cruises performed between 2009 and 2013. They indicated that the heterogeneity in the carbonate system in Irish outer estuaries and coastal waters is primarily due to differences in catchment geology and land use of river inputs, the latter exerting a strong influence on coastal water TA and DIC. Here we built on these results, verifying their generality using a set of biogeochemical data collected by the Marine Institute Foras Na Mara

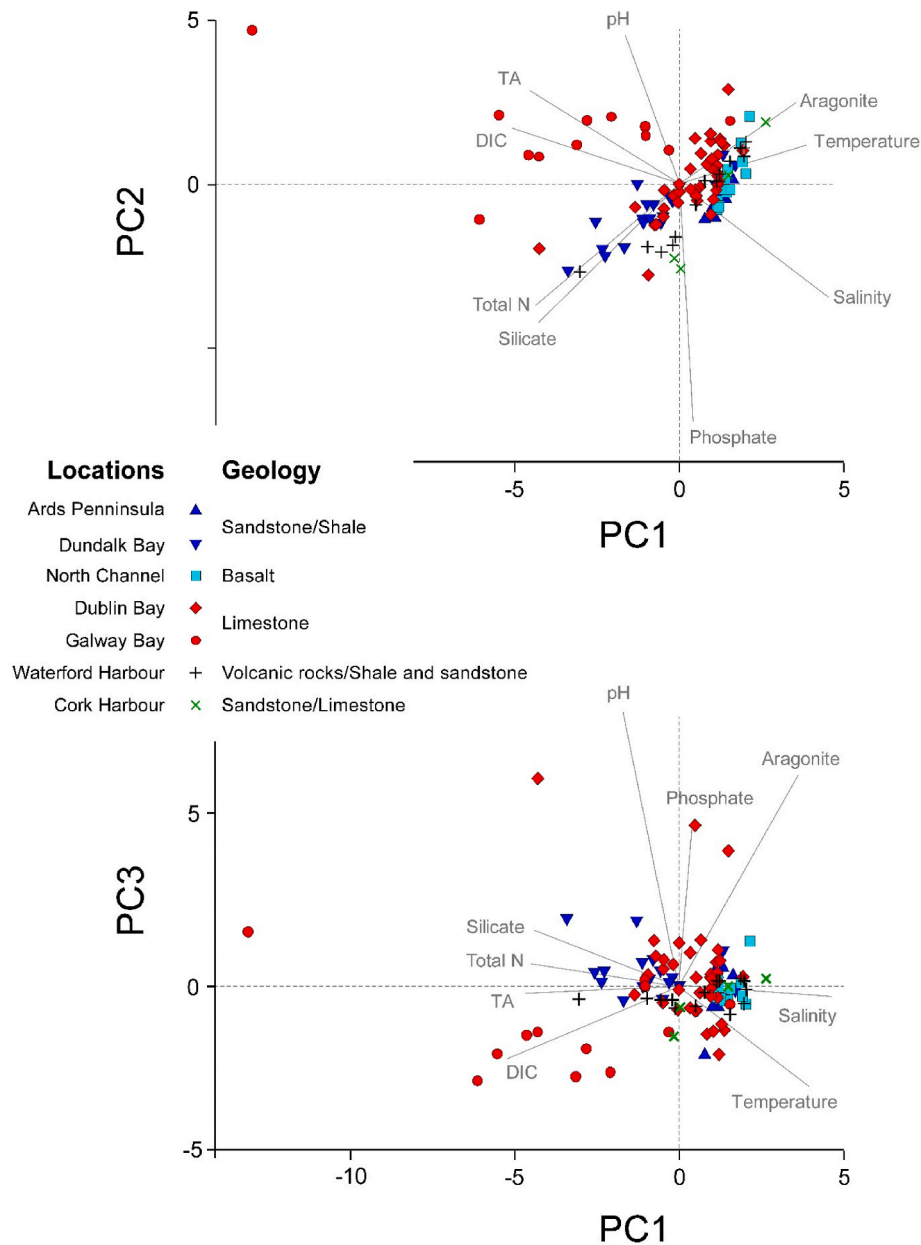
(MIFNM) between 2012 and 2016 for several Irish coastal locations. A comparison of multiple surveys performed in different periods of the year might help to understand the SGD impact on the carbonate chemistry in the adjacent coastal area (Cyronak et al., 2013; Webb et al., 2019) (Fig. 1A). To this end, we focused on the Galway Bay sector, known to be remarkably affected by SGD (Rocha et al., 2015; Schuler et al., 2018, 2020; Savatier et al., 2021) (Fig. 1C). The potential inter-annual variability in the bay was assessed by comparing MIFNM data, collected in February 2016, with those obtained during an oceanographic cruise performed in October 2017.

## 2. Materials and methods

### 2.1. The Marine Institute Foras Na Mara dataset

Chemical data collected between 2000 and 2018 from coastal and open ocean locations in Ireland were obtained from The Marine Institute Foras Na Mara (<https://www.marine.ie/>; MIFNM; Fig. 1A). Methodological information on the procedures used for the measurements are fully described in McGrath (2012).

Most of the MIFNM surveys were performed during wintertime; therefore, only temporally consistent data were selected and included in further analyses (Table S1); in addition, only samples collected in the first 10 m of the water column were selected. When multiple surveys



**Fig. 3.** MIFNM dataset: Principal components analysis (PCA) plots of PC1 vs. PC2 (top) and PC1 vs. PC3 (bottom). Information on the geological characteristics of the catchments related with the seven marine sectors included in the study are reported.

were available for the same sectors, data were averaged across surveys. The final dataset included seven sectors for a total of 113 sampling stations distributed across seven marine sectors (Fig. 1B). The selected dataset included temperature, salinity, total alkalinity (TA), dissolved inorganic carbon (DIC),  $\text{NO}_3^-$ ,  $\text{NO}_2^-$ ,  $\text{PO}_4^{3-}$  and  $\text{SiO}_4^-$ . Data were used to derive pH and  $\Omega$  Aragonite saturation state ( $\Omega_{Ar}$ ) using the CO<sub>2</sub>SYS excel software (v. 2.1; [https://cdiac.ess-dive.lbl.gov/ftp/co2sys/CO2SYS\\_calc\\_XLS\\_v2.1](https://cdiac.ess-dive.lbl.gov/ftp/co2sys/CO2SYS_calc_XLS_v2.1); Pierrot et al., 2006). For each location,  $\text{NO}_3^-$  and  $\text{NO}_2^-$  contents were cumulated (referred as “total N”). In addition, TA and DIC values were analysed “as-is” or, for the sake of comparison with the available literature, normalized to open ocean salinity (NTA and NDIC) using the equation (Chen and Pytkowicz, 1979; Chen and Millero, 1979)

$$NX = \frac{X_{obs}}{S_{obs}} \times S_{ref}$$

where  $NX$  is the normalized TA or DIC value,  $X_{obs}$  is the measured value,  $S_{obs}$  is the observed salinity value, and  $S_{ref}$  is the average salinity of the

ocean (35‰).

## 2.2. Catchment geology and river water chemistry

Geological information on the catchments of rivers feeding the selected study areas were obtained from the Geological Survey of Ireland (<https://www.gsi.ie/en-ie/data-and-maps/Pages/default.aspx>). Five different geological settings of the catchments were identified and assigned to the seven marine sectors included in the MIFNM database: “Shale/Sandstone” (Ards Peninsula and Dundalk Bay), “Basalt” (North Channel), “Limestone” (Galway Bay and Dublin Bay), “volcanic rocks” interconnected with shale and Sandstone (Waterford Harbour), and “Sandstone and Limestone” (Cork Harbour) (Sanders, 2008).

Water chemistry data for rivers were downloaded from the Catchment.ie website of the Environmental Protection Agency of Ireland (<https://www.catchments.ie/catchments-ie-changes-chemistry-data-downloads/>) and from the Department of Agriculture, Environment,



**Table 2**

MIFNM dataset: PERMANOVA post-hoc bivariate comparisons. Non-significant results at  $P(\text{MC}) > 0.05$  are reported in bold.

Comparison	t	P(MC)
Ards Peninsula vs. Dundalk	3.83	<0.001
Ards Peninsula vs. North Channel	1.70	0.04
Ards Peninsula vs. Dublin	2.05	0.01
Ards Peninsula vs. Galway	3.62	<0.001
Ards Peninsula vs. Waterford	3.57	<0.001
Ards Peninsula vs. Cork	2.13	0.01
Dundalk vs. North Channel	4.59	<0.001
Dundalk vs. Dublin	2.65	<0.001
Dundalk vs. Galway	3.34	<0.001
Dundalk vs. Waterford	3.69	<0.001
Dundalk vs. Cork	2.38	0.01
North Channel vs. Dublin	2.03	0.01
North Channel vs. Galway	4.03	<0.001
North Channel vs. Waterford	3.64	<0.001
North Channel vs. Cork	2.10	0.02
Dublin vs. Galway	4.42	<0.001
Dublin vs. Waterford	2.93	<0.001
Dublin vs. Cork	1.69	0.04
Galway vs. Waterford	3.58	<0.001
Galway vs. Cork	2.14	0.02
Waterford vs. Cork	0.79	<b>0.49</b>

**Table 3**

Factor loadings, eigenvalues, and % contribution of the two principal component axes (PC1, and PC2) to variation in the river chemistry dataset.

	PC1	PC2
Eigenvalue	2.36	1.06
% Total	47.26	21.14
Cumulative	47.26	68.41
TA	0.90	-0.01
Salinity	0.76	0.21
Phosphate	0.33	-0.59
pH	0.92	-0.08
Total N	0.15	0.81

and Rural Affairs of Northern Ireland (DAERA, <https://www.daera-ni.gov.uk/articles/river-water-quality-monitoring>). After identifying the main catchments feeding each of the seven sectors included in the study, we collated chemistry data only for river stretches located in sub-catchments directly feeding the sea. For the sake of consistency with the MIFNM dataset (Table S1), only measurements carried out in rivers in January and February between 2012 and 2016 were selected and averaged over months and years. Chemical data included TA (expressed as  $\text{mg CaCO}_3 \text{ L}^{-1}$ ), total nitrogen (calculated as  $\text{NO}_3^- + \text{NO}_2^-$ ),  $\text{PO}_4^{3-}$ ,  $\text{Cl}^-$  (expressed in  $\text{mg L}^{-1}$ ), pH, and salinity. Total nitrogen and phosphate data were converted to molalities (i.e.,  $\mu\text{mol kg}^{-1}$ );  $\text{Cl}^-$  concentrations were converted to salinity considering a ratio chlorinity/salinity of 1.80655.

### 2.3. Oceanographic cruise

In October 2017, an oceanographic cruise of the MIFNM's Celtic Voyager vessel CV17038 was performed in the Galway Bay area (Fig. 1C). The sampling strategy was based on a transect approach and aimed at highlighting the impact of freshwater inputs and SGD on local carbonate system parameters. Accordingly, the stations identified in the bay (Fig. 1C) covered the area from the mouth of local watercourses (i.e., River Corrib) to offshore. The measurements of carbonate system parameters were performed at a 3-m depth with the aim to focus the survey on the surface layer in the water-atmosphere interface and the effects driven by the freshwater discharge. During the survey, samples for TA-DIC and pH analyses were collected with 500 ml borosilicate glass bottles and immediately poisoned with 0.05% of  $\text{HgCl}_2$ , as suggested in Dickson et al. (2007). The Conductivity Temperature Depth

meter (CTD) rosette of the Celtic Voyager vessel recorded the parameters at each station. Water samples were analysed by closed cell potentiometric titration at the marine laboratory station SNAPOCO2-LOCEAN in Sorbonne University in Paris, France. Detailed information on the methodological procedures can be found in Text S1, the dataset is available on <http://www.tara.tcd.ie/handle/2262/97899>. In brief, the automated system used for the simultaneous determination of TA and DIC in seawater was based on the potentiometric method introduced by Edmond (1970) (i.e., dosage of sea water by a strong acid in a variable volume air-tight cell during dosing). The measurement system was calibrated using Certified Reference Materials (CRMs). The precision of the system, evaluated from the analysis of CRMs, was  $\pm 3 \mu\text{mol kg}^{-1}$  for both TA and DIC. The reproducibility of measurements, based on the analysis of replicate samples, was in the range of  $5 \mu\text{mol kg}^{-1}$  or lower for both TA and DIC.

### 2.4. Statistical analyses

All statistical procedures were implemented in the R package (R Development Core Team, 2023). For univariate statistical tests all data were preliminary checked for normality (Shapiro-Wilks test) and homoscedasticity (Levene's test) and log-transformed when required. Univariate comparisons were carried out using Pearson product-moment correlation analyses, parallelism F-tests, and parametric ANOVAs followed by post-hoc Tukey HSD tests. Statistical significance was evaluated at  $\alpha = 0.05$ .

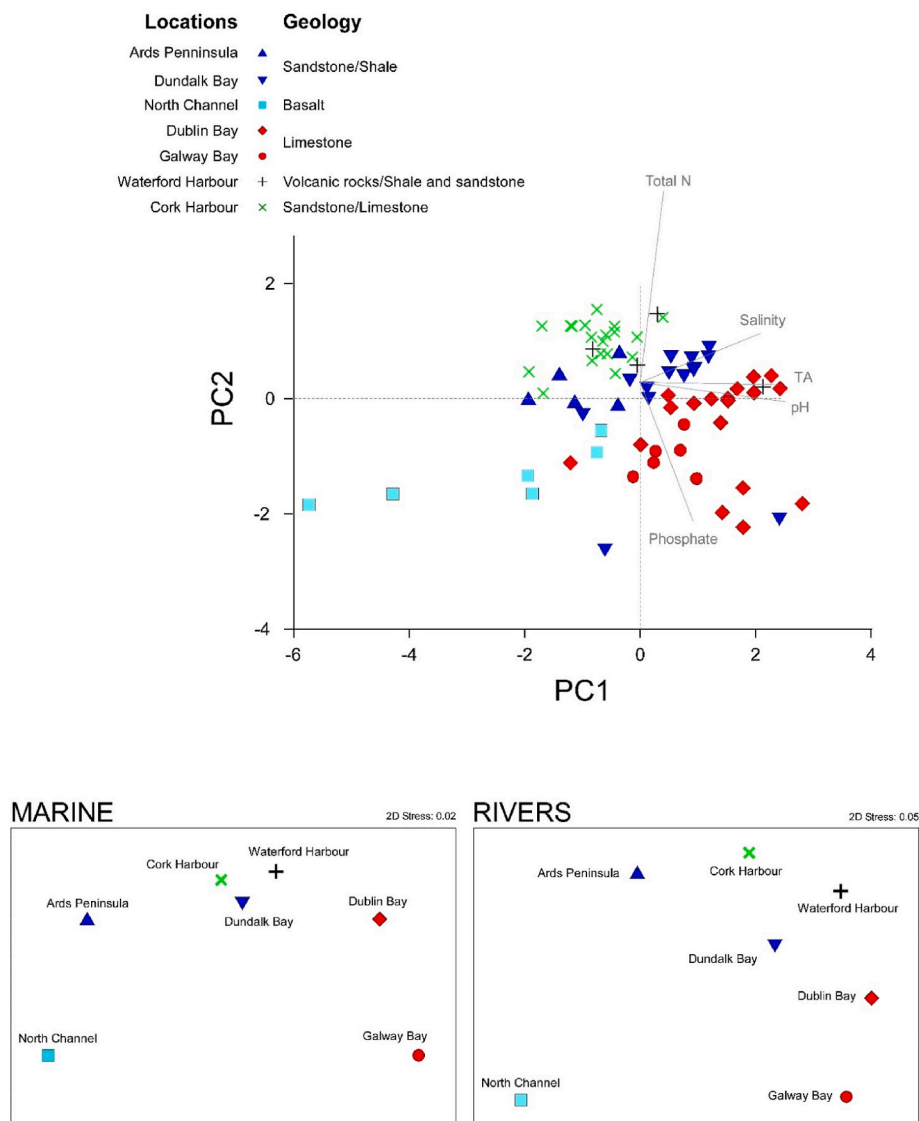
Exploratory Principal Component Analysis (PCA) was performed with (log+1)-transformed and Z-scaled MIFNM and river chemistry data to visualize multivariate differences among the seven sectors included in the study as affected by each chemical variable comprised in the dataset itself. For the PCA, we considered only eigenvalues  $>1$  for extraction of the principal components. Subsequently, Euclidean distance similarity matrices were constructed and Type III (partial sum of squares) 1-way permutational multivariate analyses of variance (PERMANOVA; Anderson, 2017) followed by post-hoc bivariate comparisons were performed to verify the effect of either the factor "sector" (fixed factors with seven and five levels, respectively) on water chemistry multivariate patterns (McArdle and Anderson, 2001; Zhang et al., 2014). A Canonical Analysis of Principal Components (CAP; Anderson and Willis, 2003), i.e., a constrained ordination procedure based on any distance or dissimilarity measure (Anderson and Willis, 2003) was further performed to emphasize changes in water chemistry across the different sectors or geological types. In general,  $P$  values for PERMANOVA tests were calculated using Monte Carlo permutations  $[P(\text{MC})]$ .

To verify the congruence between the river chemistry and MIFNM data (after the number of variables included in the latter were reduced to meet that of the river chemistry dataset), the centroids of sectors were calculated on the Euclidean distance similarity matrices of both datasets, represented in a non-metric multidimensional context, and the strength of their concordance was assessed using the Spearman coefficient Rho via Mantel tests with 9999 permutation.

## 3. Results

### 3.1. General features of the MIFNM dataset

Fig. 2 illustrates the average concentration of TA, DIC, nutrients and salinity across the seven coastal sectors included in the MIFNM dataset (see also Fig. S1). Mean TA and DIC concentration determined at Galway Bay were  $2384.8$  and  $2232.9 \mu\text{mol kg}^{-1}$  significantly higher than those determined in the remaining sectors (Fig. 2), where TA and DIC ranged respectively between minima of  $2285.1$  and  $2112.5 \mu\text{mol kg}^{-1}$  (Ards Peninsula) and maxima of  $2340.3$  and  $2157.7 \mu\text{mol kg}^{-1}$  (Waterford). In addition, Galway Bay showed salinity and phosphate concentrations of  $29.4$  and  $0.36 \mu\text{mol kg}^{-1}$ , significantly lower than those observed in the other sectors, where salinity varied between  $33.7$  and  $34.9$  (Dundalk and



**Fig. 4.** River chemistry dataset: (top) principal components analysis (PCA) plots of PC1 vs. PC2; information on the geological characteristics of the catchments related with the seven marine sectors included in the study are reported; (bottom) non-metric multidimensional scaling (nMDS) representation of the centroids calculated over the Euclidean distance matrix of the MIFNM dataset (after reduction of the number of variables; see text for details) and the river chemistry dataset.

Waterford, respectively) while phosphate concentrations ranged between  $0.56 \mu\text{mol kg}^{-1}$  (North Channel) and  $0.67 \mu\text{mol kg}^{-1}$  (Waterford). Noticeably, after normalizing TA and DIC values by open ocean salinity, Galway Bay waters still showed the highest alkalinity and inorganic carbon content (Fig. S2). Other parameters determined at Galway Bay were in the range observed in the remaining sectors (Fig. 2). Indeed,  $\Omega$  aragonite ranged from 1.59 to 2.04, pH from 8.00 to 8.23, temperature from  $6.50^\circ\text{C}$  to  $9.04^\circ\text{C}$ , and silicate from  $4.23 \mu\text{mol kg}^{-1}$  to  $23.50 \mu\text{mol kg}^{-1}$ . Normalized TA and DIC values showed negligible differences among sectors, with the exception of Galway Bay (Fig. S2). Ards Peninsula and North Channel were also characterized by the lowest contents in total N (Fig. 2).

### 3.2. Influence of geology on marine water chemistry

The PCA analysis performed on MIFNM data identified three components with eigenvalues  $>1$ , respectively explaining 48.2, 17.9, and 15.5% of the total variance (Table 1). PC1 was affected mainly by variations in DIC, TA, salinity, total N and silicate, while phosphate and pH where the variables primarily associated with PC2 and PC3 (Table 1; see also Fig. 3). Noticeably, in both the PC1 vs. PC2 and PC1 vs. PC3 plots

(Fig. 3) TA and DIC were strictly associated and showed an opposite pattern to that of salinity. In addition, phosphate did not co-varied with total N, the latter in turn resulting strongly associated with silicate, while showing an opposite pattern as compared with  $\Omega$  aragonite and temperature in the PC1 vs. PC2 plot (Fig. 3).

Galway clearly differentiated from the other sectors, showing a high variability in water chemistry across the different sampling sites; furthermore, Waterford and Cork grouped in a distinct cluster (Fig. 3). Even though the segregation of the remaining sectors was less evident, a PERMANOVA indicated significant differences (Pseudo- $F_{6,112} = 10.3$ ,  $P_{MC} = 0.0001$ ). Additionally, post-hoc comparisons showed that independently from the geology of the catchment, significant bivariate dissimilarities occurred among all the sectors with the exclusion of Waterford and Cork (Table 2), being characterized by different geological units in their respective catchments (i.e., volcanic rocks/shale and sandstone for the former, sandstone/limestone for the latter). Further discriminant analyses ultimately confirmed the limited contribution of geology to the water chemistry of the sectors included in the study. Indeed, a CAP analysis (Fig. S3), indicated for the factor “sector” a higher discrimination power (29% misclassification error ratio) compared with the factor “geology”, for which a misclassification error

**Table 4**

River chemistry dataset: PERMANOVA post-hoc bivariate comparisons. Non-significant results at  $P(\text{MC}) > 0.05$  are reported in bold.

	t	P(MC)
Ards Peninsula vs. Dundalk	2.31	0.01
Ards Peninsula vs. North Channel	2.45	0.01
Ards Peninsula vs. Dublin	3.45	<0.001
Ards Peninsula vs. Galway	5.01	<0.001
Ards Peninsula vs. Waterford	2.37	0.01
Ards Peninsula vs. Cork	4.36	<0.001
Dundalk vs. North Channel	3.69	<0.001
Dundalk vs. Dublin	1.84	0.03
Dundalk vs. Galway	2.69	<0.001
Dundalk vs. Waterford	1.25	<b>0.21</b>
Dundalk vs. Cork	3.69	<0.001
North Channel vs. Dublin	4.39	<0.001
North Channel vs. Galway	2.95	0.01
North Channel vs. Waterford	2.75	0.01
North Channel vs. Cork	4.83	<0.001
Dublin vs. Galway	2.02	0.01
Dublin vs. Waterford	1.85	0.02
Dublin vs. Cork	5.74	<0.001
Galway vs. Waterford	3.22	<0.001
Galway vs. Cork	6.91	<0.001
Waterford vs. Cork	2.53	0.01

ratio of 38% was observed.

### 3.3. Influence of river inputs

The water chemistry data collated for watercourses (Table S2) comprised only a subset of the parameters included in the MIFNM dataset. For the sake of comparison, the latter was reduced accordingly. It is worth noting that after eliminating DIC,  $\Omega$  aragonite, temperature, and silicate the structure of MIFNM data in the multivariate space remained highly consistent with that of the original, complete dataset, as testified by a Mantel test performed on the respective Euclidean resemblance matrices (Spearman Rho = 0.88,  $P < 0.0001$ , 9999 permutations).

A PCA analysis performed on rivers chemistry data identified two components with eigenvalues  $>1$ , respectively explaining 47.3, and 21.1% of the total variance (Table 3). PC1 expressed the variation in TA, pH, and to a minor extent salinity, while PC2 related with total N and phosphate (Table 3; Fig. 4). A PERMANOVA indicated significant differences among the different sectors (Pseudo- $F_{6,71} = 12.1$ ,  $P_{\text{MC}} = 0.0001$ ); as observed for marine waters, bivariate comparisons indicated a negligible effect of geology, as significant inter-sector differences were generally observed with the exception of Dundalk and Waterford, the first characterized by a river catchment lying on Sandstone/Shale, the second on volcanic rocks (Table 4).

Noticeably, the centroids of sectors calculated on Euclidean distance matrices for both the MIFNM, and river chemistry datasets (Fig. 4) indicated a significant congruence between the multivariate pattern of variation of river water chemistry data and that of marine waters (Mantel test, Rho = 0.65,  $P = 0.035$ , 9999 permutations).

### 3.4. Relationships between salinity and TA and DIC

Depending on the sector considered, TA and DIC showed different patterns of co-variation with salinity (Fig. 5). TA and DIC at Galway showed negative, significant relationships; similarly, negative trends were observed for Dundalk, Waterford, and Dublin. Noticeably, the negative relationships with salinity observed for both TA and DIC in the Dublin sector were determined by a single sampling site (Fig. 5); after eliminating it, no significant relations were further observed ( $P < 0.05$  for both parameters). Conversely, TA varied positively with salinity in the Ards Peninsula and North Channels sectors; a positive, yet not significant co-variation was observed at Cork (Fig. 5). DIC varied with

salinity reproducing in general the patterns determined for TA; an exception was represented by the Ards Peninsula, for which a negligible relationship was determined, and by the Cork sector, where the positive co-variation with salinity observed for TA was not confirmed (Fig. 5).

The comparison performed for Galway Bay of the MIFNM data collected in February 2016 and those collected in the oceanographic cruise performed in October 2017 provided evidence of the effect of seasonality on TA and DIC relationships with salinity. Indeed, in both sampling dates significant relationships were observed between salinity and both TA and DIC; however, a significant increase in the slope of the regression model occurred from October to February (Fig. 6; parallelism test:  $F_{2,24} = 14.1$ ,  $P < 0.0001$  for TA;  $F_{2,24} = 22.9$ ,  $P = 0.0001$ ). This in turn reflected in a significant decrease in the slopes of TA-DIC relationships between October 2017 and February 2016 (Fig. 6;  $F_{2,24} = 13.1$ ,  $P < 0.0001$ ). TA and DIC normalisation by open ocean salinity had no effects on the observed differences (Fig. S4).

## 4. Discussion

In the present study we showed the general features of coastal marine chemistry along the Irish coastal sea, focusing on carbonate system parameters (TA and DIC), nutrients ( $\text{PO}_4^{3-}$ ,  $\text{SiO}_4$ ,  $\text{NO}_3^- + \text{NO}_2^-$ ) and salinity. From a first analysis it was possible to identify the study areas variabilities, among them Galway Bay showed higher concentration of TA, DIC and nutrients. It is worth mentioning some studies related to the open ocean carbonate chemistry to have a comparative result. In the open ocean the range of DIC and NDIC observed ranged from approximately 1980 to 2150  $\mu\text{mol kg}^{-1}$  (Bates et al., 2014). In our study, the range for DIC and NDIC was approximately from 2100 to 2350  $\mu\text{mol kg}^{-1}$ . These findings indicate a distinct variance not solely attributable to the increase in anthropogenic  $\text{CO}_2$  in the atmosphere, but likely influenced by an additional carbonate source absent in the open ocean. Moreover, in open ocean studies where TA values are unavailable, these have been approximated from salinity (Leseurre et al., 2020) using empirical relationships (Friis et al., 2003). This approach is not applicable in coastal areas, as our results have demonstrated an absence of a consistent linear relationship between salinity and alkalinity. This has been also shown in previous literature studies, where in Irish coastal estuarine waters alkalinity ranged from approximately 1900 to 3300  $\mu\text{mol kg}^{-1}$  and the higher values were associated with limestone areas (McGrath et al., 2019). In open ocean studies, the primary driver of inorganic carbonate chemistry is the uptake of  $\text{CO}_2$  from the atmosphere. Furthermore, pH variabilities in open ocean studies were often associated with temperature changes (García-Ibañez et al., 2016). In coastal ecosystems climate change contributes to increased rainfall events and intensified weathering processes, significantly influencing coastal chemistry (McGrath et al., 2019). Previous literature studies have suggested that geological factors exercises a greater influence on coastal chemistry when compared to human activities occurring on land (Zeng et al., 2011; McGrath et al., 2019). In the present study both geology and rivers were considered; PCA and PERMANOVA have been carried out also on rivers chemistry data (Fig. 4), showing the relevance of sectors over the geology. Based on these findings, the observed variations across the study areas can be attributed to differences in freshwater composition, which are influenced by human activities taking place on land (Li et al., 2019).

### 4.1. Differences in inorganic carbonate chemistry among the selected study areas

The high TA values observed in the south of the country might be explainable with the increase of organic matter originated by the use of fertilizers (Oh et al., 2003; Laurent et al., 2020) besides, the national population in Ireland increased by a quarter of a million since 2013, leading to more wastewater (O'Boyle et al., 2015). River Lee which feeds Cork Harbour is characterized by high dissolved organic materials and

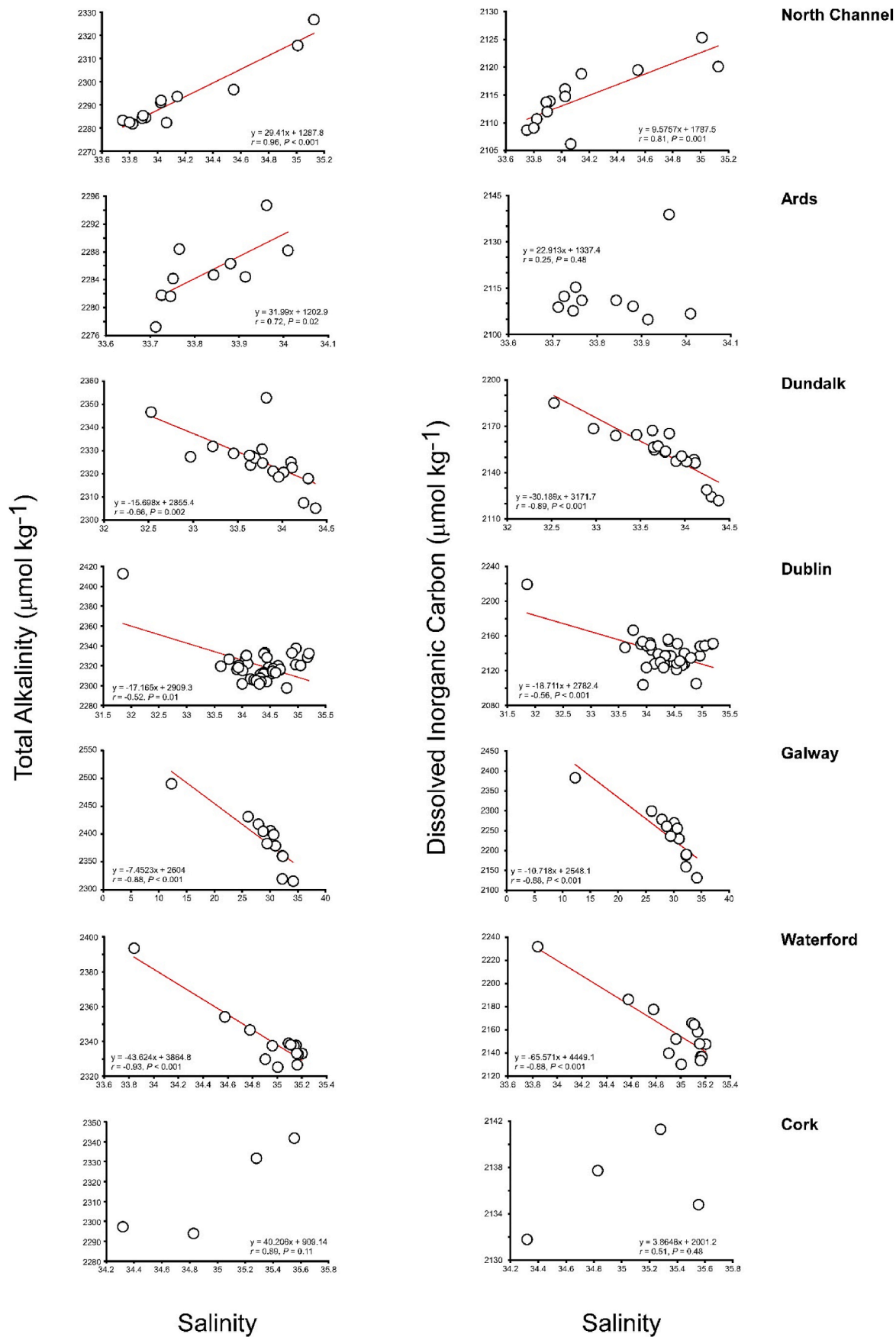
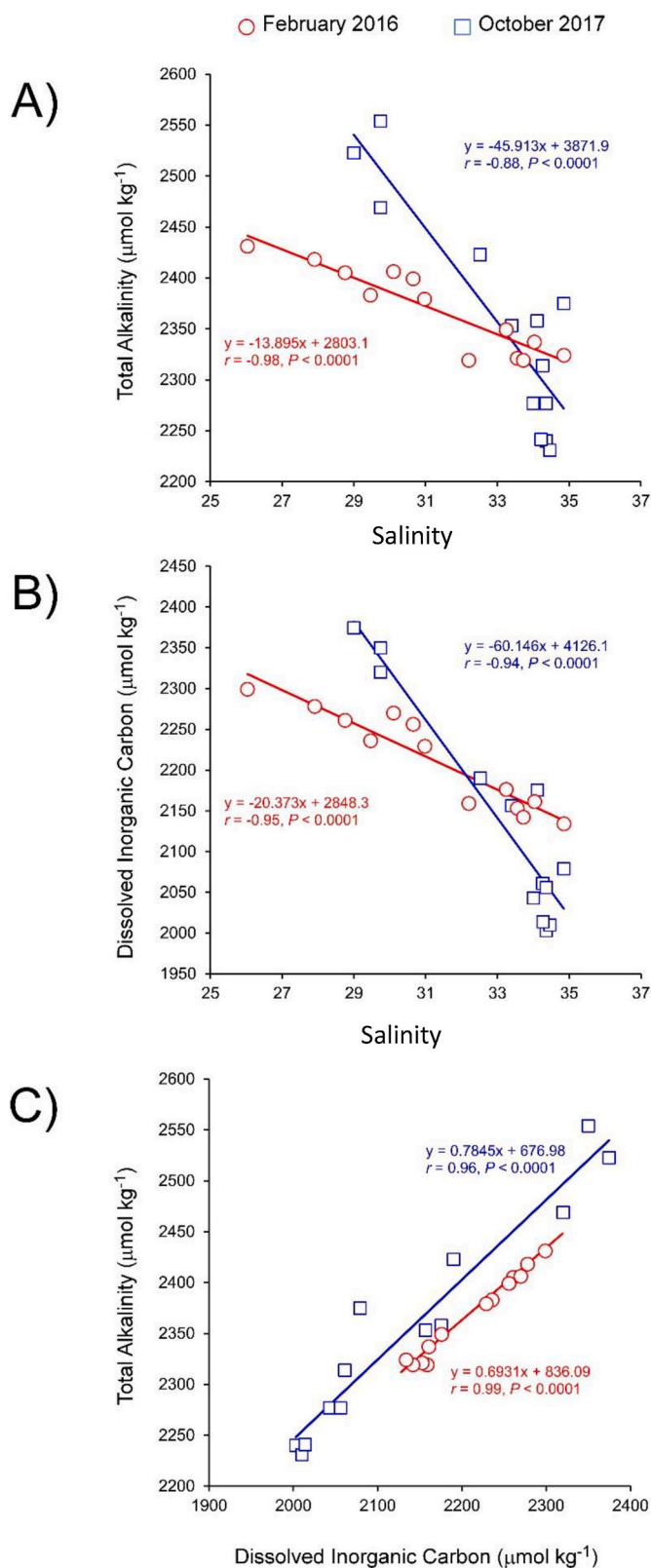


Fig. 5. MIFNM dataset: relationships between salinity and TA and DIC values across the seven marine sectors included in the study. The equations of the regression models fitted to the data are included; the respective Pearson coefficients  $r$  and the level of significant  $P$  are also reported.





**Fig. 6.** Galway Bay: seasonal comparison of the relationships between salinity and TA (A), DIC (B), and TA vs. DIC (C) determined using data collected in February 2016 (MIFNM dataset) and in the oceanographic cruise carried out in October 2017. The equations of the regression models fitted to the data are included; the respective Pearson coefficients  $r$  and the level of significant  $P$  are also reported.

less than 50% of oxygen saturation (O'Boyle et al., 2019), which suggest that respiration enhances DIC in the neighbouring coastal system. Waterford Harbour is the area that showed higher nitrogen value at the time of the selected survey, probably due to the intense agriculture and use of fertilizers (O'Boyle et al., 2016, 2019). However, it is noteworthy to highlight that among the studied areas, Waterford harbour and Cork Harbour were the only two regions where PERMANOVA analysis demonstrated significant outcomes for the geology factor. Indeed, in Waterford Harbour a large input of  $\text{pCO}_2$  comes from Suir Estuary and the river Barrow, both inserted into karstic catchment areas. As previously said, the intense rainfall enhanced by climate change will increase flooding events and bicarbonate weathering (McGrath et al., 2019). In addition, the high TA and DIC values recorded in this area might also derive from SGD sources and not only from the rivers. Satellite imagery study showed temperature anomalies along the west and south of Ireland which are linked with SGD plumes (Wilson and Rocha, 2012). Further studies to localized freshwater springs to quantify their TA and DIC contribution to the coast are necessary (Wilson and Rocha, 2012).

For what concerns the other areas analysed in this work, geology cannot be identified as the driver of the coastal chemical composition. Similar results come out from the PCA performed on river chemistry data. In this work we focused on the effects of rivers but particularly in karstic areas there might be further inputs coming from SGD. We are acknowledging from previous literature studies the presence of springs that might affect the coastal areas (EPA, 2011; Kelly, 2018), indeed, the water coming from groundwater systems can accumulate  $\text{CO}_2$  since no interaction with the atmosphere occurs, differently rivers  $\text{CO}_2$  equilibrates with the atmosphere. For the sake of comparison, we added the value recorded in Kinvarra Castle spring, one of the main SGD spring feeding Galway Bay (Schubert et al., 2015) (see Fig. S5). TA and DIC relationship with salinity was explored in the different study areas, showing different patterns of co-variation. North Channel and Ards Peninsula clearly showed lower TA and DIC values at the same salinity level compared to the other coastal locations, the loading of these elements from rivers is lower compared to the other study areas. Negative correlations with salinity were observed in Galway Bay, Dublin Bay, Waterford Harbour, Dundalk Bay. This result indicates that catchment areas are acting as significant sources of carbonates versus the coast. Recent literature studies have demonstrated that significant sources of TA discharge into Dublin Bay, with values well over the average oceanic water TA (Cyronak et al., 2018; Gregor and Gruber, 2021), ranging from 2264 to 4675  $\mu\text{mol kg}^{-1}$  (Kerr et al., 2023). Even though the Dublin Bay area has a similar catchment geology to Galway Bay (west of Ireland), TA and DIC showed lower values. This might be explained with the different typology of freshwater sources. Indeed, in Dublin Bay the main freshwater input is in the form of river discharge, where the Liffey River is the main source of nutrients (O'Higgins and Wilson, 2005) and alkalinity (McGrath et al., 2016; Kerr et al., 2023). Differently, in Galway Bay, even if a few rivers are draining into in the north site (characterized by granite and Ordovician igneous volcanic rocks) e.g., Corrib River; most of TA and DIC sources come from the numerous small bays feeding the area, e.g. Kinvarra Bay, Aughinish Bay, Bell Harbour which are in turn fed by SGD (Drew, 2008).

#### 4.2. The Galway Bay case

Two transects were compared in Galway Bay area; TA and DIC show linear relations with salinity in both surveys, however, TA-salinity and DIC-salinity slope is steeper in the survey of October 2017. The difference in the slopes might be related with the loading of TA and DIC coming from the freshwater inputs that vary seasonally. Kinvarra Castle Spring reached an average value of 4700  $\mu\text{mol kg}^{-1}$  and 4500  $\mu\text{mol kg}^{-1}$  in summer period (Kelly, 2018).

The estimated water flux from SGD in Kinvarra Castle spring was 8.7  $\text{m}^3 \text{s}^{-1}$  by McCormack et al. (2014), and, using radon, a value of  $10.4 \pm 6.3 \times 10^4 \text{ m}^3 \text{ d}^{-1}$  (Rocha et al., 2015) was found in summer time.

Moreover, a value of approximately  $20 \times 10^5 \text{ m}^3 \text{ d}^{-1}$  was measured in winter time (Savatier and Rocha, 2021). Seasonal variations are associated with groundwater floods, leading to different loadings of carbonates and nutrients to the coast (McCormack et al., 2014; Schuler et al., 2018, 2020). The results obtained from the comparison of the TA and DIC in two different seasons in Galway Bay, legitimate the hypothesis that SGD can change TA:DIC ratio, the same hypothesis that also arose from previous studies (Hall and Tank, 2005; Johnson and Wiegner, 2014).

## 5. Conclusions

The analysis carried out in this work considered only the marine samples collected in the first 10 m depth to focus on the freshwater effects in the upper layer. The chemical data were not always available for the selected surveys on both surface and deep water. Considering the importance of vertical mixing, future investigations should consider spatial and temporal variabilities and stratification in the different seasons. Additionally, groundwaters have an important role in the chemistry of coastal seas; even if the groundwater systems are monitored in Ireland, it has not yet quantified the influence of those waters to the coast through the groundwater springs. This work showed that in coastal areas different factors contribute to carbonate system variabilities that might contribute to accelerate coastal acidification. Therefore, a deeper comprehension of the land-oceans interactions is necessary, as well as to coordinate freshwater monitoring programs and coastal surveys.

## CRedit authorship contribution statement

**Maria Teresa Guerra:** Writing – review & editing, Writing – original draft, Methodology, Formal analysis, Data curation, Conceptualization. **Giorgio Mancinelli:** Writing – review & editing, Supervision, Methodology, Data curation.

## Declaration of competing interest

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

## Data availability

Data from Marine Institute were used after a signed agreement, therefore, can be available on request.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.ecss.2024.108623>.

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