

SPATIOTEMPORAL DYNAMICS OF CARBONATE CHEMISTRY IN RIVER
AND GROUNDWATER INPUTS TO THE NORTHEASTERN
MEDITERRANEAN COAST

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**SPATIOTEMPORAL DYNAMICS OF CARBONATE CHEMISTRY IN
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MEDITERRANEAN COAST**

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ABSTRACT

SPATIOTEMPORAL DYNAMICS OF CARBONATE CHEMISTRY IN RIVER AND GROUNDWATER INPUTS TO THE NORTHEASTERN MEDITERRANEAN COAST

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Freshwater inputs onto coastal regions play a critical role in shaping marine carbonate chemistry, nevertheless their influence remains undefined in many semi-enclosed seas. This study presents the first comprehensive assessment of spatiotemporal carbonate dynamics in both riverine and groundwater discharges along the Northeastern Mediterranean coast, with a particular focus on the Cilician Basin. A total of 301 samples were collected from nine rivers and ten groundwater wells, including a one-year high-frequency monitoring program at METU-IMS coastal wells (5m, 10m, 20m, 50m) and the Lamas River, as well as seasonal spatial surveys in the entire Basin during wet (April) and dry (September) periods.

Total alkalinity (TA) and pH were directly measured, while dissolved inorganic carbon (DIC) and pCO_2 were calculated using CO2SYS program. The results revealed consistently higher and more stable TA and DIC values in groundwater, often exceeding 6000 $\mu\text{mol/kg}$, driven by prolonged water–rock interaction in carbonate-rich rocks. In contrast, rivers exhibited greater seasonal variability and lower carbonate concentrations, especially during the wet season due to dilution.

Statistically significant seasonal increases in TA were observed in river systems during the dry season ($p=0.007$), while groundwater pH showed a significant seasonal decline ($p=0.023$).

Meteorological variables further influenced carbonate variability: wind speed showed a significant correlation on riverine TA ($\beta=-246.01$, $p=0.029$), and precipitation effects were delayed by up to 9 weeks in both systems. Annual TA and DIC fluxes from rivers were quantified for the first time in this region, with the Ceyhan and Asi Rivers contributing disproportionately larger amounts to the coastal carbonate budget (>24 Gmol/year each). While riverine carbon inputs accounted for only $\sim 0.04\%$ of the total coastal inventory, their localized and seasonal impacts may be considerable, especially under restricted exchange or stratification.

This thesis emphasizes the complementary roles of rivers and groundwater in regulating coastal carbonate chemistry and buffering capacity. The findings underscore the importance of integrating both surface and subsurface freshwater sources into regional acidification assessments and marine carbon budgets, particularly in data-scarce regions such as the Eastern Mediterranean basin.

Keywords: Carbonate Chemistry, River Discharge, Groundwater Discharge, Northeast Mediterranean Basin.

ÖZ

KUZEYDOĞU AKDENİZ KIYISINA ULASAN NEHİR VE YERALTI SUYU GİRDİLERİNDEKİ KARBONAT KİMYASININ ZAMANSAL VE MEKÂNSAL DİNAMİĞİ

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Kıyı bölgelerine ulaşan tatlı su girdileri, deniz karbonat kimyasının şekillenmesinde kritik bir rol oynamaktadır; ancak yarı kapalı denizlerin çoğunda bu etkiler hâlen net bir şekilde tanımlanamamıştır. Bu çalışma, Kuzeydoğu Akdeniz kıyılarında, özellikle Kilikya Havzası'na odaklanarak, hem nehir hem de yeraltı suyu deşarjlarındaki mekânsal ve zamansal karbonat dinamiklerinin ilk kapsamlı değerlendirmesini sunmaktadır. Toplamda 9 nehir ve 10 yeraltı suyu kuyusundan 301 örnek toplanmıştır. Bu kapsamda METU-IMS kıyı kuyularında (5 m, 10 m, 20 m, 50 m) ve Lamas Nehri'nde bir yıllık yüksek frekanslı izleme programı ile birlikte, yağışlı (Nisan) ve kurak (Eylül) dönemlerde mevsimsel mekânsal gözlemler yürütülmüştür.

Toplam alkalinite (TA) ve pH doğrudan ölçülmüş, çözünmüş inorganik karbon (DIC) ve pCO_2 ise CO2SYS programı kullanılarak hesaplanmıştır. Sonuçlar, karbonatça zengin kayalarla uzun süreli su–kaya etkileşimi nedeniyle, yeraltı suyunda genellikle $6000 \mu\text{mol/kg}$ 'ı aşan, sürekli olarak daha yüksek ve daha stabil TA ve DIC değerleri ortaya koymuştur. Buna karşılık, nehirler özellikle yağışlı

dönemde seyreltme etkisi nedeniyle daha düşük karbonat konsantrasyonları ve daha yüksek mevsimsel değişkenlik göstermiştir. Kurak dönemde nehir sistemlerinde TA'da istatistiksel olarak anlamlı mevsimsel artışlar ($p=0.007$), yeraltı suyu pH'ında ise anlamlı mevsimsel düşüşler ($p=0.023$) gözlenmiştir.

Meteorolojik değişkenler de karbonat değişkenliğini etkilemiştir: rüzgâr hızı, nehir TA'sı üzerinde anlamlı bir negatif etki göstermiştir ($\beta=-246.01$, $p=0.029$) ve yağışın etkileri her iki sistemde de 9 haftaya kadar gecikmeli olarak gözlemlenmiştir. Bölgede ilk kez nehirlerden yıllık TA ve DIC yükleri hesaplanmış ve Ceyhan ile Asi Nehirlerinin kıyı karbonat bütçesine yüksek katkılar sağladığı belirlenmiştir (her biri >24 Gmol/yıl). Nehir kaynaklı karbon girdileri kıyı envanterinin yalnızca yaklaşık %0.04'ünü oluştursa da, kısıtlı değişim veya tabakalaşma koşullarında lokal ve mevsimsel etkileri önemli olabilmektedir.

Bu tez, kıyı karbonat kimyasının ve tamponlama kapasitesinin düzenlenmesinde nehirlerin ve yeraltı sularının tamamlayıcı rollerini vurgulamaktadır. Bulgular, yüzey ve yeraltı tatlı su kaynaklarının bölgesel asitleşme değerlendirmeleri ve deniz karbon bütçelerine dâhil edilmesinin önemini özellikle veri yetersizliği olan Doğu Akdeniz gibi bölgelerde ortaya koymaktadır.

Anahtar Kelimeler: Karbonat Kimyası, Nehir Desarjı, Yeraltı Suyu Deşarjı, Kuzeydoğu Akdeniz Havzası.

To unconditional love and everything that makes me who I am today –
to my family.

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LIST OF ABBREVIATIONS

ANOVA: Analysis of Variance

aq: aquatic

CaCO₃: calcium carbonate

CO₂: carbon dioxide

CO₃⁻²: carbonate ion

DEKOSIM: Marine Ecosystem and Climate Research Center

DIC: dissolved inorganic carbon

Eq: equation

Gmol: gigamole (1 Gmole = 10⁹ mole)

H₂CO₃: carbonic acid

IPCC: Intergovernmental Panel on Climate Change

kg: kilogram

K_{sp}: solubility product

L: liter

m: meter

METU: Middle East Technical University

P: pressure

pCO₂: partial pressure of carbon dioxide

RF: Revelle Factor

SGD: submarine groundwater discharge

SK: water well

T: temperature

TA: total alkalinity

Tmol: teramole ($1 \text{ Tmol} = 10^{12} \text{ mole}$)

μmol : micromole

Ω : saturation state



1. INTRODUCTION

Water is an essential and irreplaceable resource for all life on Earth. Freshwater reserves, especially rivers and groundwater, are vital for human survival and ecological balance. Despite comprising only a small fraction of the global water budget, glaciers and groundwater constitute the most accessible sources of freshwater. In recent years, the significance of rivers and groundwater has become increasingly apparent; not only for their ecological and social importance, but also for their influence on key marine processes, particularly the carbonate system and ocean acidification (Zeebe, 2012). Additionally, water plays a key role in the global carbon cycle, directly linking terrestrial, atmospheric, and oceanic carbon fluxes and connecting to the broader challenges of climate change (Gattuso et al., 2011; Sabine and Feely, 2004). While the global carbon cycle has been extensively studied, understanding of how these processes operate within the semi-enclosed Mediterranean, and particularly its northeastern part, remains incomplete.

Coastal water chemistry is shaped by a complex interplay between oceanic and terrestrial processes. This dynamic system supports critical ecological functions such as primary productivity, nutrient cycling, and the delivery of ecosystem services like fisheries, carbon sequestration, and shoreline protection (Zeebe, 2012). Changes in coastal chemical conditions, including shifts in pH and alkalinity, can directly impact marine organisms, particularly calcifiers, and can alter food webs and biodiversity (Moore, 2010). Land–sea interactions, especially inputs of riverine nutrients, organic matter, and pollutants, play a pivotal role in modulating coastal chemistry. While such inputs can create zones of high productivity, they also increase the vulnerability of coastal areas to eutrophication, hypoxia, and acidification (Zeebe, 2012). Understanding these biogeochemical interconnections is crucial for predicting ecosystem responses to environmental change and for guiding sustainable coastal management.

1.1 Land-Sea Interactions

Coastal zones are influenced by both surface water and groundwater transport, making that essential to understand their interactions to interpret coastal dynamics (Crossland et al., 2005; Liu et al., 2014). Surface water inputs, primarily from rivers, are highly variable and depend on seasonal and climatic conditions; while groundwater contributions are often continuous and less visibly apparent (Moore, 2010; Burnett et al., 2006). Both pathways deliver essential materials, including nutrients, sediments, trace elements, and contaminants, that affect water chemistry, biological productivity, and sediment processes (Syvitski et al., 2005). Effective coastal management requires a comprehensive understanding of these combined influences, particularly in vulnerable and rapidly changing regions like the Northeastern Mediterranean Basin.

The interactions between water and terrestrial systems drive a range of dynamic processes, shaping landscapes, supporting ecosystems, and influencing geological formations such as karst systems. Rivers and groundwaters act as major transport pathways, transferring nutrients, organic matter, trace metals, and pollutants from land to sea. River discharge typically supplies large, seasonally driven pulses of freshwater, sediments, and dissolved materials; while groundwater discharge provides more continuous, yet often underestimated, inputs of dissolved and particulate substances into coastal environments (Moore, 2010; Burnett et al., 2006). Together, these land–sea exchanges regulate primary productivity, control sediment deposition and erosion, and influence nearshore ecological dynamics (Alongi, 1998; Valiela, 2006).

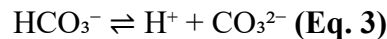
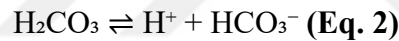
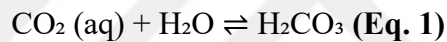
Human activities, including urbanization, deforestation, agriculture, and climate change; have significantly altered natural land–sea interactions, often increasing nutrient and sediment loading and changing hydrological regimes (Seitzinger et al., 2010). These changes have contributed to widespread coastal impacts, such as eutrophication, hypoxia or in extreme cases anoxia, harmful algal blooms, and biodiversity declines (Diaz and Rosenberg, 2008). To mitigate these impacts, it is

essential to understand how terrestrial inputs affect key biogeochemical cycles, including the carbonate system in coastal waters.

1.2 Carbonate System

The carbonate system is one of the most important chemical buffering systems in seawater. It regulates pH, total alkalinity (TA), partial pressure of carbon dioxide ($p\text{CO}_2$), and the balance among dissolved inorganic carbon (DIC) species. This system maintains the chemical conditions necessary for marine life, particularly for calcifying organisms such as corals, mollusks, echinoderms, and planktonic calcifiers (Feely et al., 2004; Orr et al., 2005).

When atmospheric CO_2 dissolves in seawater, it participates in a series of reversible reactions:



These reactions are strongly pH dependent. At low pH, CO_2 and H_2CO_3 dominate; at intermediate pH (approximately 6.5–8.5), bicarbonate (HCO_3^-) is the dominant species; and at the high pH, carbonate (CO_3^{2-}) becomes increasingly important (Zeebe & Wolf-Gladrow, 2001; Dickson et al., 2007). This distribution provides the water body with its exceptional buffering capacity, stabilizing pH even under variable CO_2 inputs. Figure 1 illustrates how the relative proportions of CO_2 , HCO_3^- , and CO_3^{2-} changes with pH. This dynamic distribution has important implications for ocean acidification.

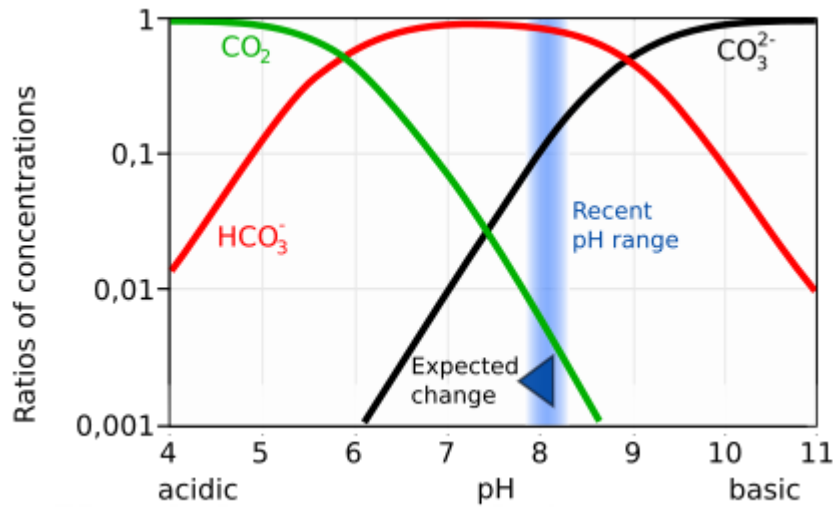


Figure 1. A Bjerrum plot of distribution of carbon dioxide (CO_2), bicarbonate ion (HCO_3^-), and carbonate ion (CO_3^{2-}) as a function of seawater pH (from Zeebe and Wolf-Gladrow 2001) (*CO_2 in this figure corresponds to carbonic acid (H_2CO_3)).

The carbonate system depends on four main parameters, each with its own role and needing separate explanation. Total alkalinity (TA) refers to the seawater's capacity to neutralize acids, and contains major bases such as bicarbonate, carbonate, and borate ions (Millero, 1979; Dickson, 1981). It is defined as the sum of all titratable bases (mainly HCO_3^- , CO_3^{2-} , and borate).

In seawater, total alkalinity is defined as:

$$\text{TA} = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{B(OH)}_4^-] + [\text{OH}^-] - [\text{H}^+] + \{\text{minor bases (e.g. PO}_4^{3-}, \text{SiO(OH)}_3^-, \text{H}_3\text{AsO}_4, \text{H}_3\text{BO}_3, \text{HS}^-, \text{organic acids)}\} \quad (\text{Eq. 4})$$

This formula accounts for the major bases that can accept protons, including the borate system $[\text{B(OH)}_4^-]$, which is important in seawater but usually negligible in freshwater (Millero, 1979). Minor contributions from phosphate and silicate species may also be included when they are significant.

For freshwater, the definition of alkalinity typically focuses on:

$$\text{Alkalinity} = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-] - [\text{H}^+] \quad (\text{Eq. 5})$$

In this context, it is often called carbonate alkalinity, as the contribution from borate and other seawater specific ions is usually ignored.

Typical oceanic TA values range between 2300–2400 $\mu\text{mol kg}^{-1}$ (Lee et al., 2006), though in high-evaporation basins such as the Mediterranean, values can exceed 2700 $\mu\text{mol kg}^{-1}$ (Alvarez et al., 2023; Millero et al., 2008). Notably, the Black Sea exhibits higher alkalinity, often surpassing 3000 $\mu\text{mol kg}^{-1}$, due to its unique freshwater inflow and biogeochemical characteristics (Murray et al., 1991; Stanev et al., 2004; Konovalov et al., 2006).

DIC represents the total CO_2 related species in seawater, which includes $\text{CO}_2(\text{aq})$, H_2CO_3 , HCO_3^- , and CO_3^{2-} , and typically ranges from 1900 to 2150 $\mu\text{mol kg}^{-1}$ in the open ocean (Millero, 2007; Sabine et al., 2004). DIC changes through gas exchange with the atmosphere, photosynthesis (which decreases DIC), respiration (which increases DIC), and CaCO_3 cycling. For example, in the Mediterranean, DIC concentrations can reach $\sim 2200 \mu\text{mol kg}^{-1}$ in deep waters due to restricted exchange and intense remineralization (Sisma-Ventura et al., 2016).

$p\text{CO}_2$ represents the equilibrium pressure of CO_2 gas over seawater and it is a key driver of air–sea CO_2 exchange. Surface seawater $p\text{CO}_2$ typically ranges from ~ 350 to $420 \mu\text{atm}$; however it varies seasonally, spatially, and with biological productivity (Takahashi et al., 2009). When seawater $p\text{CO}_2$ is lower than atmospheric $p\text{CO}_2$ (which is $\sim 420 \mu\text{atm}$ today), CO_2 enters the ocean; when it is higher, CO_2 outgasses. Coastal and estuarine zones often show extreme $p\text{CO}_2$ variability, from $<200 \mu\text{atm}$ in highly productive zones to $>1000 \mu\text{atm}$ in eutrophic or upwelling regions (Cai et al., 2008). Over the past century, atmospheric CO_2 has increased by about 40% (Solomon et al., 2009), and the global ocean has absorbed roughly one-third of this anthropogenic carbon through air–sea exchange (Le Quéré et al., 2009; Sabine et al., 2004). This enhanced CO_2 uptake leads to increased DIC and $p\text{CO}_2$ in seawater while simultaneously lowering pH, a process widely known as ocean acidification, which also speeds up calcium carbonate (CaCO_3) dissolution (Doney et al., 2009; Feely et al., 2004).

pH is the negative logarithm of hydrogen ion concentration; which reflects seawater acidity, and is typically around 8.1 in surface waters (Dickson et al., 2007). It is defined mathematically as $\text{pH} = -\log[\text{H}^+]$, meaning that a decrease of 1 pH unit corresponds to a 10-times increase in hydrogen ion concentration because of logarithmic correlation. pH variability in the ocean is closely linked to variations in DIC and TA, influenced by key processes such as photosynthesis, respiration, air–sea CO_2 exchange, and calcium carbonate precipitation or dissolution (Gattuso and Hansson, 2011; Zeebe and Wolf-Gladrow, 2001). Photosynthesis increases pH by consuming CO_2 , while respiration and organic matter degradation lower pH by producing CO_2 . In coastal areas, pH variability can be much larger due to freshwater inputs, eutrophication, and benthic metabolism (Santos et al., 2021). After the beginning of the industrial era, surface ocean pH has already decreased by 0.1 units, dropping from 8.2 to 8.1, largely due to anthropogenic CO_2 emissions. This trend, commonly referred to as ocean acidification, is projected to continue, with several studies estimating a potential decline of up to 0.7 pH units by the 24th century (Zeebe et al., 2008; IPCC, 2007).

Integrating pH measurements with DIC and TA facilitates a comprehensive characterization of carbonate system dynamics. If any two of the 4 unknown parameters (DIC, pH, TA, pCO_2) are known (in conjunction with temperature, salinity, and pressure), the other two unknown carbonate system variables can be calculated. (Zeebe, 2012).

1.2.1 Calcium Carbonate Dynamics and Saturation State

Calcium carbonate precipitation and dissolution are tightly linked to the carbonate system. The key reaction is:



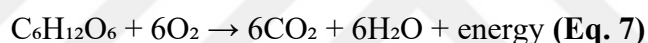
The balance between these processes is governed by the saturation state (Ω), calculated as the product of calcium and carbonate ion concentrations divided by the

solubility product (K_{sp}) of the relevant mineral phase (e.g., calcite or aragonite). When $\Omega > 1$, seawater is supersaturated and CaCO_3 precipitation is favored; when $\Omega < 1$, dissolution occurs (Millero, 2007). Many marine organisms require supersaturated conditions to be able to form shells or skeletons, making Ω a critical metric in ocean acidification research.

1.2.2 Biological and Physical Controls on Carbonate Chemistry

In coastal and open-ocean systems, several biological and physical processes have effect on DIC, alkalinity, pH, and pCO_2 .

- a) Photosynthesis and respiration: Respiration refers to the process of breaking down organic matter by using oxygen in order to produce energy, CO_2 , and water:



Photosynthesis removes CO_2 , lowers DIC, reduces pCO_2 , and raises pH; respiration releases CO_2 , increases DIC and pCO_2 , and lowers pH (Cai et al., 2008). This daily and seasonal cycling strongly influences surface water chemistry.

- b) CO_2 air–sea exchange: CO_2 flux across the ocean–atmosphere interface is controlled by the pCO_2 gradient between seawater and air and modulated by temperature, wind speed, and surface turbulence (Wanninkhof, 1992). When seawater pCO_2 is lower than atmospheric pCO_2 , the ocean absorbs CO_2 (invasion); when it's higher, the ocean releases CO_2 .
- c) Calcium carbonate precipitation/dissolution: Calcifying organisms remove Ca^{2+} and CO_3^{2-} from seawater, lowering alkalinity and releasing CO_2 , which can slightly decrease pH. Dissolution of CaCO_3 in sediments or the water column increases both DIC and alkalinity, buffering acidification and raising pH (Andersson et al., 2007).
- d) Freshwater inputs from rivers and groundwater: Rivers and submarine groundwater discharge can alter carbonate chemistry by adding DIC, Ca^{2+} , or

alkalinity, depending on geology of watershed. In some regions, they dilute seawater buffering capacity, while in others they supply alkalinity and mitigate acidification (Groves and Meiman, 2005; Burnett et al., 2006).

Figure 2 summarizes the effects of major physical and biological processes on carbonate system parameters. Photosynthesis lowers DIC and $p\text{CO}_2$ while increasing pH, by having minimal influence on alkalinity. In contrast, respiration raises DIC and $p\text{CO}_2$ and decreases pH, again with little effect on alkalinity. Calcium carbonate precipitation simultaneously decreases both DIC and alkalinity, increases $p\text{CO}_2$, and reduces pH, whereas CaCO_3 dissolution increases both DIC and alkalinity, decreases $p\text{CO}_2$, and increases pH. The invasion of CO_2 into the water body increases DIC and decreases pH with negligible changes in alkalinity, while the outgassing of CO_2 reduces DIC and raises pH, also with minimal impact on alkalinity.

These processes, acting alone or in combination, explain the complex patterns observed in coastal biogeochemical cycles.

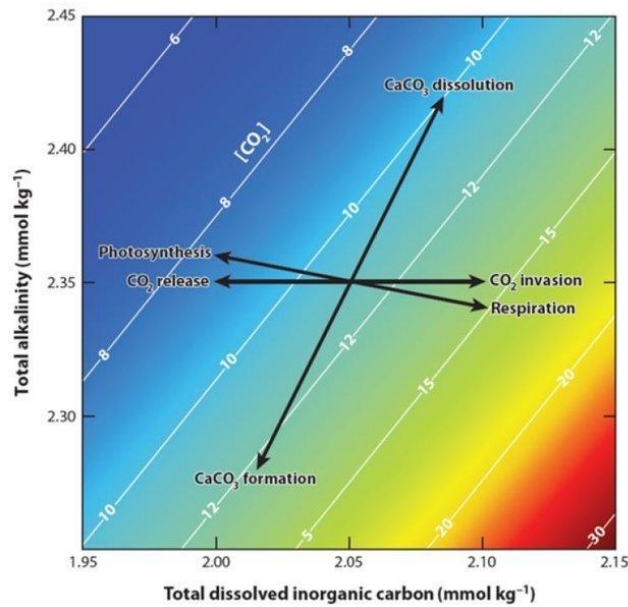


Figure 2. Effect of key biological and physical processes on dissolved inorganic carbon (DIC), total alkalinity (TA), partial pressure of carbon dioxide ($p\text{CO}_2$), and pH (from Zeebe and Wolf-Gladrow, 2001).

1.3 Rivers

Rivers serve as one of the primary links between terrestrial and marine environments, transporting water, sediments, nutrients, organic matter, and chemical constituents to coastal ecosystems. They play a crucial role in the hydrological and biogeochemical cycles that regulate coastal and oceanic chemistry. Rivers originate from precipitation, groundwater discharge, and glacier or snowmelt in catchment areas. As they flow toward the sea, they collect materials from weathering and erosion of rocks, soils, and anthropogenic discharges within their drainage basins (Viers et al., 2007). The discharge of rivers into the coastal ocean affects salinity, temperature, nutrient concentrations, and sediment dynamics, making river-influenced coastal zones among the most productive and dynamic regions on the Earth.

The chemical composition of river water is shaped by local lithology, climate, hydrology, and land use. Weathering of carbonate and silicate rocks delivers

dissolved ions such as calcium (Ca^{2+}), magnesium (Mg^{2+}), bicarbonate (HCO_3^-), and silica (Si) to rivers. Rivers draining carbonate-rich catchments supply substantial bicarbonate and calcium, raising alkalinity and contributing the global carbon cycle (Viers et al., 2007; Groves & Meiman, 2005). Typical bicarbonate concentrations in rivers range from approximately 1 to 5 mmol L^{-1} , depending on geology and climate, and can reach even higher levels in carbonate terrains. Dissolved organic carbon (DOC) concentrations generally range from 1 to 20 mg L^{-1} , while nutrient levels (nitrate, phosphate, silicate) vary widely depending on land use, often showing elevated values in agricultural and urbanized basins.

When river waters mix with seawater, they alter carbonate system parameters by changing salinity, DIC, alkalinity, pH, and pCO_2 . Rivers can function as either sources or sinks of alkalinity, depending on their chemical characteristics. For instance, rivers flowing on carbonate-rich terrains contribute alkalinity, in this way it enhances the buffering capacity of seawater. In contrast, rivers originating from silicate-dominated or organic-rich watersheds often exhibit lower alkalinity, which can potentially reduce coastal pH (Cai et al., 2008; Viers et al., 2007). Additionally, riverine inputs affect coastal CO_2 dynamics. Elevated organic matter inputs near river mouths can increase respiration and enhance CO_2 production, leading to increased pCO_2 and promoting CO_2 outgassing to the atmosphere. On the contrary, high primary production driven by nutrient enrichment can decrease pCO_2 , leading to promoting CO_2 uptake from the atmosphere (Cai et al., 2008).

River flow and water chemistry change a lot with the seasons, mostly because of rain, melting snow, or monsoon cycles. When rivers have high flow, they bring large amounts of freshwater and dissolved materials to coastal areas, which can change the physical and chemical conditions there. For example, Mediterranean rivers have clear seasonal patterns, with the most water in winter and early spring and the least in summer. This influences both the timing and magnitude of DIC and alkalinity inputs to the marine environment (Sisma-Ventura et al., 2016).

Human activities potentially have significantly altered river systems. Changes in land use, dam construction, water extraction, and pollution have impacted flow patterns, sediment transport, and water chemistry. Increased nutrient and organic matter inputs from agriculture and urbanization can lead to eutrophication, hypoxia, and acidification in estuarine and coastal environments. River damming also reduces sediment and particulate organic carbon transport to the ocean, disrupting natural biogeochemical fluxes (Viers et al., 2007).

1.4 Groundwater

Groundwater transport is a crucial but often underestimated pathway that connects land and sea. Submarine groundwater discharge (SGD), which is a hydrological process that cycling of water on seabed as well as submarine inflow of groundwater from land to the sea; delivers freshwater, dissolved ions, nutrients, trace metals, and sometimes pollutants to coastal ecosystems (Burnett et al., 2006; Moore, 2010). Although it is less visually obvious than rivers, SGD can locally or regionally exceed riverine inputs in terms of water and solute fluxes, particularly in regions with permeable coastal geology.

Groundwater comes from rainwater that soaks into the ground, passing through soil and rocks, and collects in underground layers which are called aquifers. Near the coast, groundwater flows toward the sea due to pressure differences and goes out through beaches, coastal springs, estuaries, lagoons, and underwater vents. The magnitude and composition of SGD are strongly influenced by geological settings, including the presence of karstic systems, rock formation, or permeable sediments, as well as by local hydrological conditions, tidal forcing, and human use (Burnett et al., 2006; Groves and Meiman, 2005).

Karst systems, formed by the dissolution of carbonate rocks such as limestone, gypsum, and dolomite, are particularly important for groundwater seepage. Rainwater is naturally acidic due to dissolved CO₂ (pH is approximately 5.0–5.8), infiltrates into the subsurface and over extended periods, dissolves carbonate

minerals leads to the formation of caves, sinkholes, and underground conduits (Dreybrodt, 1988; Groves and Meiman, 2005). These systems deliver groundwater enriched in calcium and bicarbonate, making them major contributors to coastal alkalinity and carbonate cycling.

Groundwater composition varies widely depending on geology, land use, and residence time. In carbonate-rich areas, groundwater often contains high Ca^{2+} and HCO_3^- concentrations. Calcium concentrations in groundwater range from 1 to 5 mmol L^{-1} , and HCO_3^- concentrations can reach $\sim 10 \text{ mmol L}^{-1}$ or more in karst systems. (Liao et al., 2025). Such groundwater inputs can significantly alter coastal alkalinity, DIC, and pCO_2 (Moore, 2010; Liu et al., 2014). In certain coastal systems, groundwater decreases pCO_2 and elevates alkalinity, thereby contributing to the buffering of acidification. However, in other areas, especially where groundwater contains high concentrations of dissolved CO_2 or nutrients, submarine groundwater discharge (SGD) can raise pCO_2 and reduce pH, therefore raise acidification risks (Santos et al., 2021).

Measuring submarine groundwater discharge is difficult because of its spatially heterogeneous nature. A combination of techniques, including direct measurements, seepage meters, natural tracers (e.g., radon, radium isotopes), hydrological models, and remote sensing, are often used to estimate SGD fluxes and their chemical impacts (Burnett et al., 2006; Cable et al., 1996; Taniguchi et al., 2003, Rodellas 2015, Lino et al., 2023). Human activities can significantly alter groundwater quantity and quality. Over-extraction of water lowers underground water levels and can reduce groundwater flowing into the sea. At the same time, agricultural runoff, urban waste, and factory pollution can add pollutants such as nitrates, phosphates, heavy metals, and organic chemicals into coastal groundwater, which are causing problems like eutrophication, hypoxia, and increased acidity (Santos et al., 2021).

Riverine inputs and submarine groundwater discharge collectively influence the carbonate chemistry of coastal waters by affecting key parameters such as alkalinity, dissolved inorganic carbon, pCO_2 , and pH. Understanding these combined effects is

critical for predicting how coastal ecosystems respond to natural variability and anthropogenic pressures.

1.5 Combined Effects of Rivers and Groundwaters to Carbonate Chemistry Parameters

Rivers and groundwater flows are among the most important sources of material fluxes into marine ecosystems, affecting a range of chemical, physical, and biological processes. These inputs significantly impact carbonate chemistry parameters, particularly TA, DIC, $p\text{CO}_2$, and pH. The magnitude and direction of these effects depend on the volume, composition, and variability of freshwater inflows.

Rivers and groundwater transport large amounts of calcium and bicarbonate ions (Ca^{2+} and HCO_3^-), which increase the alkalinity of receiving waters. In carbonate-rich regions, weathering of limestone and dolomite produces Ca^{2+} and HCO_3^- , contributing substantially to riverine and groundwater alkalinity (Viers et al., 2007; Groves and Meiman, 2005). Typical TA values in seawater range from 2300 to 2400 $\mu\text{mol kg}^{-1}$, while river waters influenced by carbonate weathering may have TA values between 500 and 2000 $\mu\text{mol kg}^{-1}$ depending on geology and flow regime (Roche & Millero, 1998). Groundwater from karstic aquifers can carry even higher alkalinity, sometimes exceeding 3000 $\mu\text{mol kg}^{-1}$. These inputs help regulate the buffering capacity of seawater, mitigating pH fluctuations and ocean acidification in some cases.

The Mediterranean Sea has higher TA concentrations (Mean = 2588 $\mu\text{mol kg}^{-1}$), with even higher concentrations in the Eastern Mediterranean Basin (Max TA = 2666 $\mu\text{mol kg}^{-1}$) compared to the mean global total alkalinity average (Mean = 2200 $\mu\text{mol kg}^{-1}$) (Hassoun et al., 2015). TA values of the surface waters could exceed 2700 $\mu\text{mol/kg}$ locally, depending on the freshwater inputs such as the Adriatic Sea, which

is influenced by the Po River; and the Aegean Sea, which is influenced by the Black Sea (Álvarez et al., 2023). TA values of the water masses at Atlantic and Pacific Oceans are generally less than 2300 $\mu\text{mol/kg}$ (Millero et al., 1998).

DIC includes CO_2 , bicarbonate (HCO_3^-), and carbonate (CO_3^{2-}), and it is an important part of the carbon cycle. Rivers carry DIC derived from the weathering of rocks and the organic matter decay. Groundwater DIC concentrations are often higher than in rivers because of longer residence times and enhanced CO_2 from soil respiration and mineral dissolution (Liu et al., 2014). For example, river DIC concentrations typically range from ~ 1000 to $2000 \mu\text{mol kg}^{-1}$, while groundwater in carbonate aquifers may reach $\sim 2500 \mu\text{mol kg}^{-1}$ or higher. The delivery of DIC from rivers and groundwater directly affects the carbon balance of coastal ecosystems, influencing primary production, respiration, and CO_2 air-sea exchange (Cai et al., 2008).

DIC varies between $2095 \mu\text{mol kg}^{-1}$ at the West Mediterranean Basin and $2359 \mu\text{mol kg}^{-1}$ at the East Mediterranean Basin, with a mean of $2308 \mu\text{mol kg}^{-1}$ (Hassoun et al., 2015). DIC values of the surface waters could exceed $2400 \mu\text{mol/kg}$ locally, depending on the freshwater inputs such as the Adriatic Sea, which is influenced by the Po River; and the Aegean Sea, which is influenced by the Black Sea (Álvarez et al., 2023). Atlantic waters generally have lower DIC values, with less than $2250 \mu\text{mol/kg}$.

The pCO_2 of seawater is a critical parameter determining the direction and magnitude of CO_2 exchange between ocean and atmosphere. Rivers and groundwater can act as sources or sinks of CO_2 , depending on their CO_2 content. Groundwater typically contains elevated CO_2 concentrations from soil and rock interactions, which can increase pCO_2 and enhance CO_2 loss upon discharge to the sea (Santos et al., 2021). In contrast, rivers with high photosynthetic activity may deliver CO_2 -depleted water, lowering seawater pCO_2 and enhancing atmospheric CO_2 uptake. Reported pCO_2 values in coastal areas influenced by freshwater inputs can vary widely, from ~ 200

μatm in highly productive areas to over 1000 μatm in nutrient-rich, eutrophic, and/or groundwater influenced zones.

Over the previous century, there has been a 40% increase in atmospheric CO_2 (Solomon et al., 2009). In the meantime, the ocean has absorbed approximately one-third of the anthropogenic carbon through the air-sea exchange (Le Quéré et al., 2009; Sabine et al., 2004). Increased CO_2 concentrations in the seawater environment result in the decline of pH, known as ocean acidification, and potentially enhance CaCO_3 dissolution (Doney et al., 2009).

The pH of seawater is regulated by the balance of DIC and TA. Freshwater inputs affect this balance by altering both components. River water, depending on its alkalinity, can dilute or enhance seawater buffering capacity. Groundwater in carbonate regions typically has pH values between 6.5 and 7.5; reflecting high DIC and CO_2 levels. When groundwater mixes with seawater, it may lower the pH first, but over time it can increase buffering capacity and stabilize pH by adding alkalinity (Moore, 2010; Viers et al., 2007). In contrast, low-alkalinity rivers or polluted groundwater can lower coastal pH and increase vulnerability the water body to acidification.

The combined effect of rivers and groundwater on coastal carbonate chemistry is complex and site-specific. While some freshwater inputs enhance alkalinity and buffering capacity, and reducing acidification risks; others could introduce CO_2 rich water or pollutants that increase acidification and ecosystem stress. Quantifying these fluxes is essential for understanding the coastal carbon budget, evaluating acidification trends, and developing effective management strategies (Santos et al., 2021; Cai et al., 2008).

Although carbonate chemistry has been extensively investigated in open-ocean and estuarine environments, the northeastern Mediterranean coast remains one of the least explored regions in terms of freshwater-driven carbonate dynamics. This coastal zone is characterized by complex karstic formations, semi-enclosed circulation patterns, and strong anthropogenic influence along the Cilician Basin, all

of which likely contribute to pronounced local variability in TA and DIC. Yet, most Mediterranean studies have focused on the western or central sub-basins, such as the Gulf of Lions (Cossarini et al., 2015), the Adriatic Sea (Giani et al., 2023, Cantoni et al., 2012), or the Aegean coastal systems (González-Dávila et al., 2016), leaving a significant knowledge gap for the eastern basin. In particular, the contribution of rivers and SGD to regional alkalinity and carbon fluxes has not been quantified in this coastal stretch. Earlier studies conducted in other Mediterranean regions, including the karstic groundwater systems of southern Italy (Polemio, 2016; Xanke et al., 2024), the Levantine Basin (Hassoun et al., 2015; 2019), and the Adriatic karst systems (Cantoni et al., 2012), have emphasized the dominant role of SGD and karstic rivers as sources of alkalinity to the coastal ocean. However, comparable data are missing for the Turkish sector of the Eastern Mediterranean. This thesis addresses this gap by providing the first integrated assessment of both riverine and groundwater carbonate fluxes along the northeastern Mediterranean coast, quantifying their spatiotemporal variability and evaluating their influence on coastal buffering capacity and acidification resilience.

1.6 Scope of the Study

The primary aim of this study is to investigate how riverine and coastal groundwater inputs affect carbonate chemistry in the Northeastern Mediterranean Sea, with a specific focus on the Cilician Basin. This work represents one of the first regional efforts to simultaneously assess the spatiotemporal variability of carbonate system parameters, particularly TA and pH, in both surface and groundwater environments along the southeastern coast of Turkey.

To achieve this, the study conducted: (1) high-frequency sampling over one year in the Lamas River and nearby coastal groundwater wells at multiple depths, and (2) spatial surveys across nine major rivers and ten wells spanning from Anamur to Samandağ during wet and dry seasons. In total, 301 samples were analyzed to determine pH and TA, while DIC and $p\text{CO}_2$ were calculated using CO2SYS

program. These data were used to evaluate the influence of freshwater inputs on coastal carbonate dynamics.

The specific objectives of this study were to:

1. Characterize seasonal and spatial variability in TA and pH in major rivers and groundwater systems discharging to the Cilician Basin;
2. Estimate the annual alkalinity loads from key rivers, providing the first regional flux-based assessment for the Eastern Mediterranean coast;
3. Investigate the relationships between meteorological drivers (precipitation, wind speed, wind direction) and carbonate system variability in both surface and groundwater systems;

This study provides new empirical data on the carbonate chemistry of two distinct freshwater sources and their role in shaping coastal seawater buffering capacity. The results demonstrate that while groundwater TA is relatively stable throughout in a year, rivers show significant seasonal variation, particularly during the dry season, when alkalinity is more concentrated. Moreover, the total annual input of carbon from studied rivers, as TA and DIC fluxes, into the Cilician Basin have been estimated for the first time. Furthermore, wind speed and rainfall affected TA levels, with delayed but clear impacts, showing that short-term weather changes influence coastal carbon inputs. These findings improve the understanding of coastal acidification risks and inform future monitoring and management strategies in the Eastern Mediterranean.

2. MATERIALS AND METHODS

2.1 Study Area

This study was conducted along the northeastern coast of the Eastern Mediterranean Sea, focusing on the Cilician Basin, including Mersin Bay and Iskenderun Bay. The area has high anthropogenic activities due to high agricultural and industrial activities. Mersin Province, covering 1,585,300 hectares and home to over 1.95 million people as of 2023, dedicates approximately 21% of its land to agriculture according to Mersin Governorship; and cement, fertilizer, glass, and plastic industries are dominant. Hatay Province covers 552,400 hectares and had a population of over 1.54 million in 2023, with nearly 50% of its area allocated to agriculture according to Hatay Governorship; and the cement and iron-steel industry is important, as well as mining activities such as iron, chrome, asbestos, marble, and dolomite.

Although the Cilician Basin is generally considered oligotrophic, with low nutrient concentrations and primary productivity (Yilmaz and Tugrul, 1998), elevated nutrient levels have been reported in the coastal waters of Mersin and Iskenderun Bays. These increases are primarily attributed to riverine discharge and domestic and industrial wastewater inputs from the surrounding catchments (Yucel, 2018). The catchment is primarily dominated by karstic geology, mainly composed of limestone, dolomite, calcite, and marl, which are all kinds of different CaCO_3 composed minerals (Figure 3& Figure 4).

A dual sampling strategy was applied to examine spatial and temporal changes in freshwater carbonate chemistry. Spatial surveys were carried out in April (wet season) and September (dry season) at 19 locations, including 9 rivers and 10 groundwater wells. The rivers; Anamur, Göksu, Lamas, Berdan, Seyhan, Ceyhan, Asi, and two branches of Deliçay (Mersin and Hatay); together contribute over 95% of the total river discharge into the Cilician Basin according to General Directorate

of State Hydraulic Works (DSİ, 2018). Groundwater samples were collected from wells in Anamur, Gilindre, Boğsak, two sites in the Göksu basin, Tarsus, Dörtöyl, and Samandağ, as well as from four depths (5m, 10m, 20m, and 50m) at the METU Institute of Marine Sciences (IMS) campus.

Temporal variability was examined through one year long high frequency monitoring program, which is conducted between 22 December 2023 and 25 December 2024. Weekly samples were collected from the Lamas River (36.5580° N, 34.2470° E) and from wells that have 4 different depths, located approximately 35m inland at the METU-IMS campus (36.5688° N, 34.2575° E). These wells were sampled at depths of 5m, 10m, 20m, and 50m. Using this high-frequency dataset, seasonal and sub-seasonal variations in total alkalinity, pH, and related carbonate system components were thoroughly analyzed.

This combined spatial and temporal approach enables a strong evaluation of how river and groundwater inputs shape coastal carbonate chemistry in this significant and vulnerable Eastern Mediterranean region.

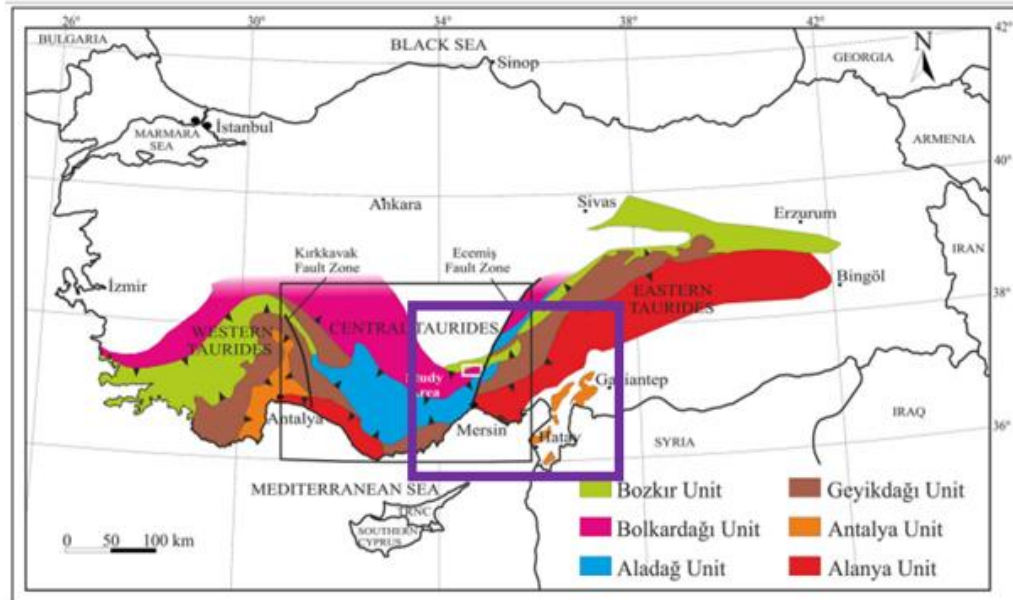


Figure 3. The lithology map of the Taurides region (retrieved from Esirtgen, Tolga and Isik, Veysel (2021)). “Geological characteristics of the boundary between

Bolkardagi-Bozkir Units and the Ulukisla Basin and the structural evolution of the region, Central Taurides, Turkey”).

At Figure 3, purple rectangle indicates the sampling area. Alanya unit is mainly composed of crystallized limestone, cherty dolomite, amphibolite, and mica; the first three of which contain CaCO_3 . Aladag unit mainly consists of carbonates, and Geyikdagi unit mainly consists of metamorphic rocks.

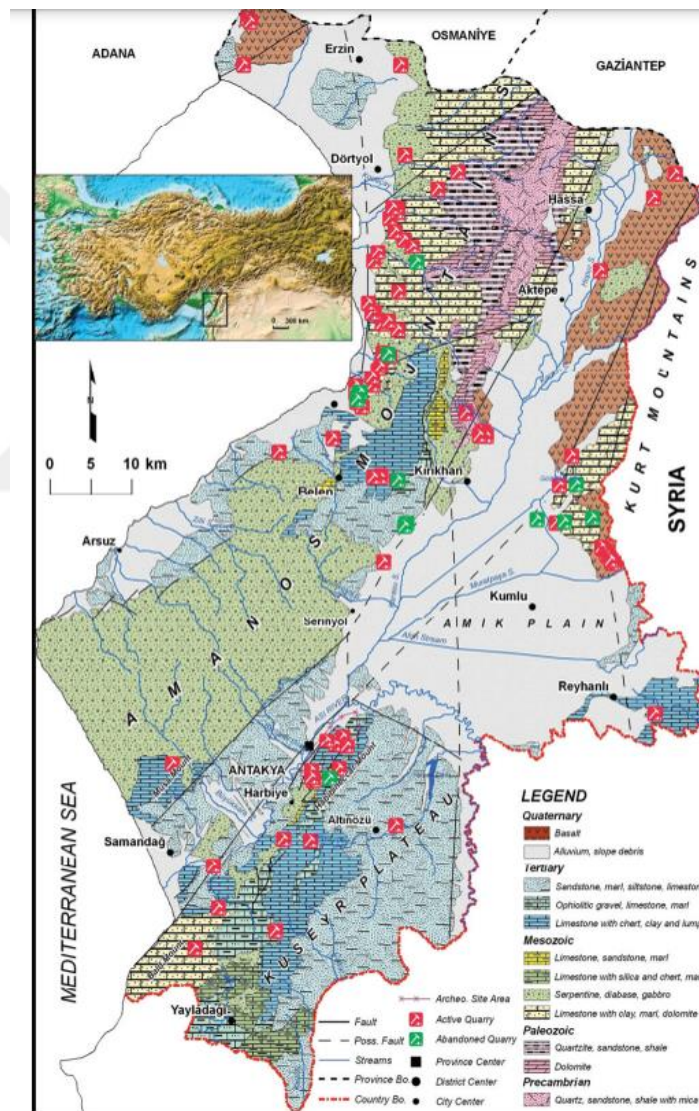


Figure 4. The lithology map of Hatay region. (retrieved from: Ozdemir, Adil and Sahinoglu Alperen (2018) "Prospective Areas For Petroleum Exploration And Oil & Gas Potential Of The Onshore Hatay (Southern Turkey)", 18th International Multidisciplinary Scientific GeoConference SGEM 2018.)

The lithology of Hatay is named by the geological age of unit (Quaternary is the youngest, and Precambrian is the oldest unit) since it was the simplest classification to comprehend the general geology of the area. The rock formation of the Hatay region mainly consists of basalt and alluvium for the Quaternary unit; limestone for the Tertiary unit; limestone and marl for the Mesozoic unit; dolomite for the Paleozoic unit; quartz and mica for the Precambrian unit (Figure 4).

37 samples for spatial monitoring, and 270 samples for high-frequency monitoring; a total of 301 samples were analyzed. Deliçay (Hatay) station was dried during the dry season, therefore the sample cannot be taken. Also six samples (SK5, SK50 and Lamas samples taken at 24/04/2023; SK5 and SK50 samples taken at 05/09/2023; and Lamas sample taken at 12/09/2023) were used for both spatial and temporal analysis.

2.1.1 Study Area - Spatial Monitoring

In the northeastern Mediterranean, the Cilician Basin forms an active interface between land and sea, where natural and anthropogenic processes intersect. The spatial monitoring in this study aimed to assess the chemical variability of riverine and groundwater inputs entering this semi-enclosed area. The aim was to characterize the spatial heterogeneity of carbonate chemistry parameters, particularly TA, DIC, pCO₂, and pH, across different locations and water types.

The Cilicia Sea Basin is adjacent to four main hydrological basins with high flow and discharge in Anatolia. These basins are the Eastern Mediterranean, Ceyhan, Seyhan, and Asi Basins from west to east. The 9 rivers with the highest flow in the basin were selected as sampling points for monitoring. The annual total flow discharges of the selected rivers according to DSI are as follows from largest to smallest; Ceyhan, Seyhan, Asi, Göksu, Anamur, Berdan, Deliçay (Hatay), Lamas, Deliçay (Mersin). They correspond to a total flow of 14 km³ (Table 3).

Nineteen sampling sites were selected across a broad coastal stretch between Anamur and Samandağ, encompassing a range of hydrogeological, land-use, and

anthropogenic conditions. These included nine rivers (Anamur, Göksu, Lamas, Berdan, Deliçay-Mersin, Seyhan, Ceyhan, Deliçay-Hatay, and Asi) and ten coastal groundwater wells (Anamur, Gilindire, Boğsak, Göksu-1, Göksu-2, Tarsus, METU-IMS wells at four depths, Dört Yol, and Samandağ. Their geographical distribution and the surrounding environmental features are illustrated in **Error! Reference source not found.**, which provides a spatial overview of the basin and station layout.

Those sampling points are selected because the five largest rivers in the catchment are Ceyhan, Seyhan, Asi, Göksu, and Anamur Rivers according to their total discharge accounts for more than 95% of total riverine discharge into the basin (General Directorate of State Hydraulic Works, Türkiye, 2018).



Figure 5. Spatial sampling areas, orange R's represents rivers, and red W's represents the wells.

Each sampling station was described by its distance from the coast, lithology and upstream land use. A summary of sampled rivers, coordinates, and altitudes is provided in Table 1; while Table 2 details sampled wells, coordinates, altitudes, the depth of the wells and lithological information about the sampling area. Table 3

summarizes annual average flows of DSI stations that are selected to calculate the total flow of rivers, station code, and available observation interval.

Table 1. Locations, latitudes, longitudes and altitudes (in meter) of the sampled rivers.

Sampling Area	Latitude	Longitude	Altitude (m)
Anamur	36.0772	32.8734	4
Göksu	36.3456	34.0207	2
Lamas	36.558	34.247	1
Berdan	36.7659	34.9151	2
Deliçay (Mersin)	36.8148	34.7073	1
Seyhan	36.7847	35.0632	3
Ceyhan	36.6223	35.583	2
Deliçay (Hatay)	36.8339	36.1777	2
Asi	36.0474	35.9684	1

Table 2. Locations, karstic properties, latitudes, altitudes (in meter), and depths (in meter) of the sampled wells.

Sampling Area	Geological Feature	Latitude	Longitude	Altitude (m)	Depth (m)
Anamur	limestone, alluvium	36.1011	33.0186	14	18
Gilindire Cave	calcite, limestone	36.1308	33.4026	4	47
Boğsak	limestone, calcite	36.2702	33.8128	5	2
Göksu-1	alluvium	36.3427	34.0104	5	9
Göksu-2	alluvium	36.3414	34.0101	4	40
METU	limestone, calcite	36.5688	34.2575	3	5, 10, 20, 50
Tarsus	alluvium	36.8949	34.9604	12	40
Dörtyol	alluvium	36.8859	36.1429	18	32
Samandağ	limestone, marl, dolomite	36.0684	35.9976	18	28

Table 3. Annual average flows of General Directorate of State Hydraulic Works (DSI) stations selected to calculate the total flow on rivers, flow observation station code (AGI), and observation interval available in DSI records.

Selected Rivers and Their Belonging City	Average Flow (m³/s)	Station Code (AGI)	Observation Interval
Anamur (Mersin)	23.304	E17A021	31.10.1967 - 30.09.2015
Göksu (Mersin)	34.130	E17A014	01.06.1961 - 30.09.2015
Lamas (Mersin)	2.749	D17A049	01.10.1999 - 30.09.2015
Deliçay (Mersin)	1.448	D17A006	03.11.1959 - 30.09.2015
Berdan (Mersin)	5.011	E17A033	29.03.1994 - 30.09.2015
Seyhan (Adana)	80.029	D18A045	23.12.1997 - 30.09.2015
Ceyhan (Adana)	190.176	E20A004	28.08.1970 - 30.09.2015
Deliçay (Hatay)	3.935	D19A014	01.11.1976 - 30.09.2015
Asi (Hatay)	63.983	D19A009	01.08.1968 - 30.09.2015

Figure 6 presents all DSI flow observation stations along the rivers where samples were collected. Figure 7 shows which stations were selected for flow calculations, and Table 3 represents sample points for rivers along the basin.

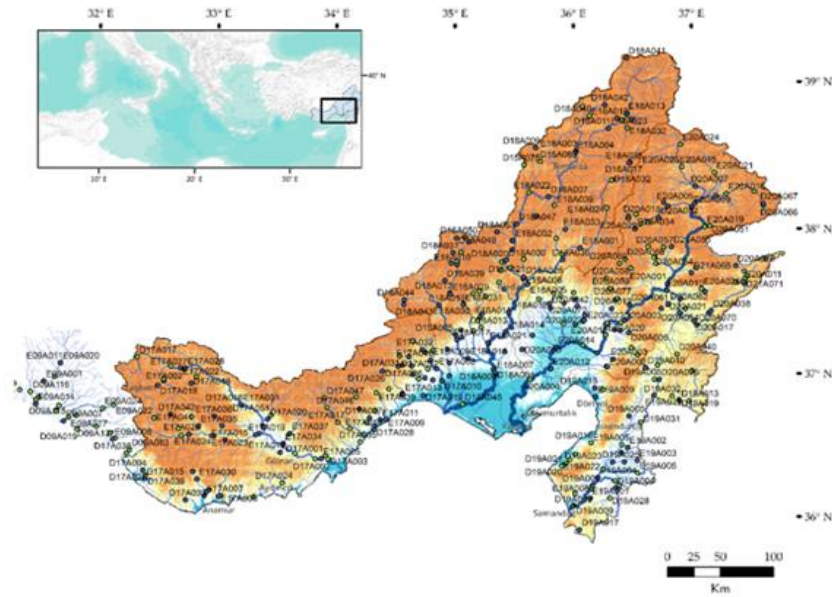


Figure 6. Map showing all General Directorate of State Hydraulic Works (DSI) flow observation stations located on the rivers sampled (Ertugrul, 2025, unpublished doctoral dissertation).

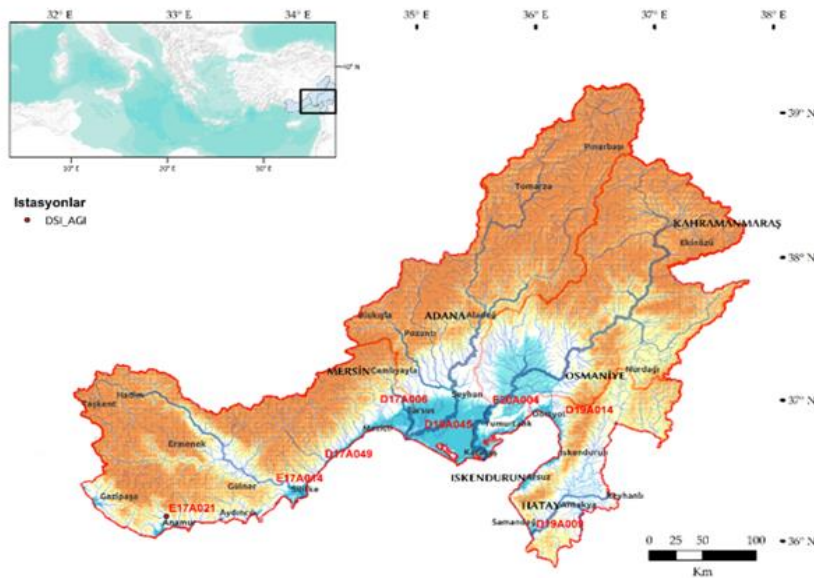


Figure 7. Map showing General Directorate of State Hydraulic Works (DSI) flow observation stations that are selected for flow calculations (Ertugrul, 2025, unpublished doctoral dissertation).

2.1.2 Study Site - High Frequency Monitoring

High-frequency temporal monitoring was conducted within the Lamas River catchment, located on the southern coast of Turkey (Figure 8). This study aimed to understand short-term changes in freshwater carbonate chemistry caused by both rivers and groundwater inputs. The monitoring was supported by the Marine Ecosystem and Climate Research Center (DEKOSİM) at the Middle East Technical University's Institute of Marine Sciences (METU-IMS), located in Erdemli.

To achieve this, four coastal groundwater observation wells were established in August 2019 on the METU-IMS campus (36.5688° N, 34.2575° E), located about 35 meters inland from the shoreline. These wells allow different sampling at four depths: 5m, 10m, 20m, and 50m. Surface water samples were also collected from the Lamas River (36.5580° N, 34.2470° E), located approximately 1.5 km east of the campus, which serves as a key freshwater source flowing into the basin.

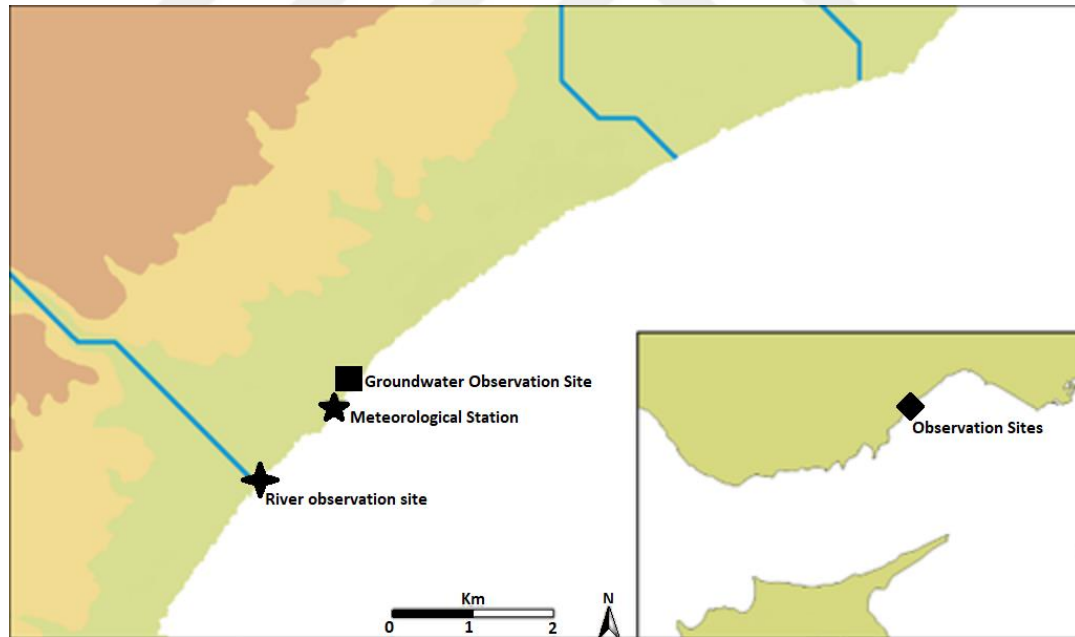


Figure 8. General representation of groundwater and surface water where high-frequency monitoring studies are carried out (Ertugrul, 2025, unpublished doctoral dissertation).

The Lamas River originates from the Taurus Mountains and has an average discharge of approximately 2.75 m³/s. Its drainage basin extends over 1356 km², reaching a maximum altitude of 2745 m and extends from the sea to 70 km inland. Detailed hydrological and geological characteristics of the basin are summarized in Table 1 and Table 3, while a spatial representation of the Lamas catchment is provided in Figure 9.

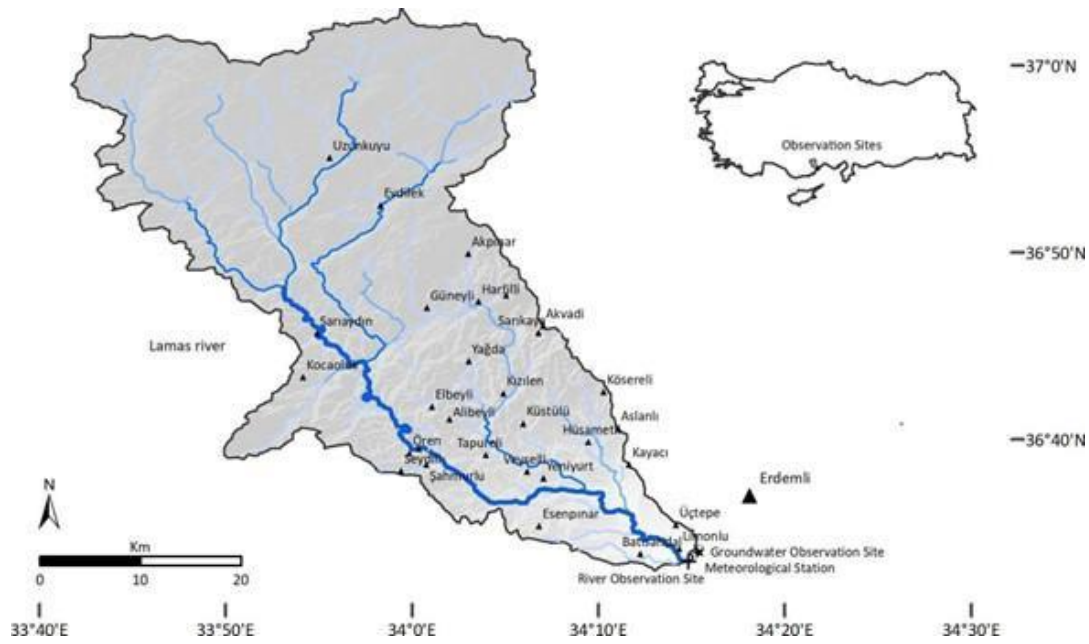


Figure 9. Lamas River catchment (Ertugrul, 2025, unpublished doctoral dissertation).

The high-frequency sampling was conducted weekly over one year, from 22 December 2023 to 25 December 2024. This high temporal resolution enabled detailed observation of seasonal and short-term changes in carbonate chemistry in both surface and groundwater of the Lamas catchment.

To evaluate the influence of meteorological factors, one year of data on wind direction, wind speed, temperature and precipitation was obtained from the Turkish State Meteorological Service (Türkiye - MGM). Data from stations 17958 (Erdemli)

and 17490 (Erdemli Marine Sciences), were used to ensure the consistency of the results, which are located near the sampling site.

2.2 Sampling and Analysis

During spatial sampling, in-situ measurements of electrical conductivity ($\mu\text{S}/\text{cm}$) were performed using a Lovibond SensoDirect Con 110, and water temperature ($^{\circ}\text{C}$) was recorded using a mercury thermometer at all river and well stations. For high-frequency temporal sampling, WTW LF-330 conductivity meters were used to measure both temperature and conductivity in-situ. The reported precision for both instruments is $\pm 0.5\%$ of the measured value. Salinity was calculated from conductivity data using the Practical Salinity Scale, suitable for low-salinity environments (Hill et al., 1986).

Water samples were collected in 250 mL PET bottles by devoid of any bubbles, and the bottles were filled entirely with no empty space to avoid air entrapment and potential gas exchange. In rivers with direct access, samples were taken by hand at mid-depth near the riverbank. In locations where shoreline access was limited, an extended pole sampler was used. Groundwater samples were obtained using submersible pumps. Prior to sampling from each well, a volume of water equivalent to at least four times the well-pipe volume was drained to remove stagnant water and ensure representative samples.

To arrest biological activity, 50 μL of saturated HgCl_2 solution was added to each sample. Bottles were sealed immediately and stored in the dark at ambient temperature until laboratory analysis.

Measurements of pH and TA were carried out using a Metrohm automatic titrator. pH was determined with two decimal points precision using a calibrated combined electrode. TA was measured following the open-cell potentiometric titration method according to the Standard Operating Procedure (SOP) 3b by Dickson et al. (2007), with a modification of extra addition of initial HCl to drop to pH below 3.5.

Carbonate system parameters, $[H^+]$ (nmol/kg), pCO_2 (μatm), fCO_2 (μatm), HCO_3^- ($\mu mol/kg$), CO_3^{2-} ($\mu mol/kg$), CO_2 ($\mu mol/kg$), OH^- ($\mu mol/kg$), Revelle Factor (RF), and xCO_2 dry at 1 atm (ppm), were calculated using the CO2SYS v2.5 Excel interface (Lewis & Wallace). Inputs included in-situ temperature, pressure, conductivity-derived salinity, measured TA, and pH values. The following constants were used in the calculations: carbonic acid dissociation constants (K_1 and K_2) from Millero (1979), sulfate constants from Dickson (1990), fluoride constants from Perez and Fraga (1987), and borate constants from Lee et al. (2010). The NBS pH scale (mol/kg- H_2O) was selected for all calculations. All carbonate system variables were computed under in-situ conditions matching the original sampling environment.

2.3 Statistical Analysis

A range of statistical approaches, both parametric and non-parametric were applied to evaluate the influence of environmental and temporal factors on carbonate system parameters. All statistical analyses were performed using the R programming language (version 4.4.2) within the RStudio environment.

To assess the distributional characteristics of the data, the Shapiro-Wilk normality test was applied to continuous variables, including pH, total alkalinity, and wind speed. Variables with p-values > 0.05 were considered normally distributed and subjected to parametric statistical tests.

Paired t-tests were used to evaluate seasonal differences in pH and TA between the wet season (April) and the dry season (September). These tests were applied both collectively across all sites and separately for rivers and wells. Statistically significant differences were pointed out when $p < 0.05$.

To evaluate whether pH and TA values differ significantly between wind direction categories (e.g., N, NE, E), one-way Analysis of Variance (ANOVA) was conducted. When the ANOVA results indicated significant results ($p < 0.05$), Tukey's Honest Significant Difference (HSD) test was applied as a post-hoc method to identify which

specific wind direction pairs differed. However, most wind direction comparisons were not statistically significant.

Correlation analyses were employed to explore relationships between meteorological variables (e.g., wind speed, precipitation) and carbonate chemistry parameters (e.g., TA, pH). Pearson's correlation was used for normally distributed variables, while Spearman's rank correlation was applied when normality assumptions were not met. Most variables followed normal distributions, favoring the use of Pearson's method.

To explore potential lagged effects of precipitation on total alkalinity, a lagged correlation analysis was conducted using weekly data from the one year high frequency time series. This method helped identify potential time-shifted responses of TA to meteorological changes, indicating whether TA was more strongly influenced by conditions from previous weeks.

Finally, multiple linear regression models were constructed to evaluate the combined influence of wind speed and wind direction on pH and TA. Wind speed was found to have a statistically significant effect on both variables. However, wind direction categories did not individually demonstrate significant effects.

Throughout these statistical analyses, the study examined how time and meteorology influences the carbonate chemistry parameters, with a focus on pH and TA in surface waters and groundwaters.

3. RESULTS

3.1 Overview of Physical and Hydrochemical Conditions

Meteorological records from the study region show distinct seasonal variability in temperature, wind speed, and precipitation over the course of the year (Figure 10). Air temperature displayed a typical Mediterranean trend, ranging from around 5 °C in winter to over 30 °C in summer, with peaks in July and August. Wind speed remained relatively stable, ranging mostly between 0.5 and 2.5 m/s, with no pronounced seasonal pattern, although slight increases were observed in late spring and early autumn. Precipitation was clearly seasonal, concentrated between January and April, with frequent high-rainfall events in February and March. The dry season, extending from June through October, showed minimal rainfall, with September characterized by almost completely dry conditions. This contrast in hydroclimatic conditions between April's wet season and September's dry season underpins the interpretation of river flow patterns and their influence on carbonate chemistry variability in the region.

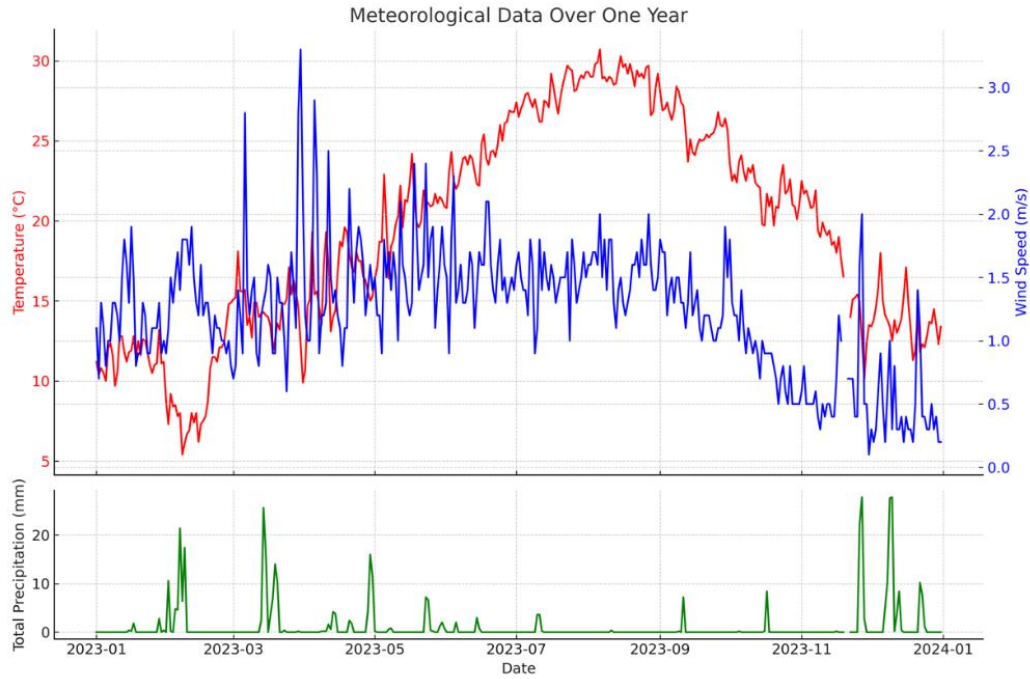


Figure 10. Daily meteorological conditions recorded in the study region from January 2023 to January 2024. The top panel shows air temperature ($^{\circ}\text{C}$, red line) and wind speed (m/s , blue line), while the bottom panel displays total daily precipitation (mm , green line).

The high-frequency monitoring data show clear hydrographic differences between groundwater wells and the adjacent river (Figure 11). The river consistently had lower salinity than the wells, highlighting its mainly freshwater nature and seasonal changes. Minimum salinity values were observed during the spring and early summer months, likely driven by increased river discharge from snowmelt and rainfall. Unlike the river, well salinity was stable throughout the year, exhibiting only small increases during the dry period, potentially indicating longer residence time and stable subsurface flow paths.

Temperature trends further emphasize the differences between surface and subsurface systems. River temperatures exhibited strong seasonal dynamics, increasing steadily from winter lows around 13°C to summer highs exceeding 27°C , before cooling in autumn. These fluctuations closely follow atmospheric conditions

and suggest a direct connection between the surface and atmosphere. Meanwhile, well temperatures remained nearly constant (20–22 °C) on the year around, suggesting that the groundwater system is thermally buffered and largely decoupled from short-term meteorological variability. Together, these hydrographic contrasts provide critical context for interpreting seasonal carbonate chemistry variability in the coastal zone.

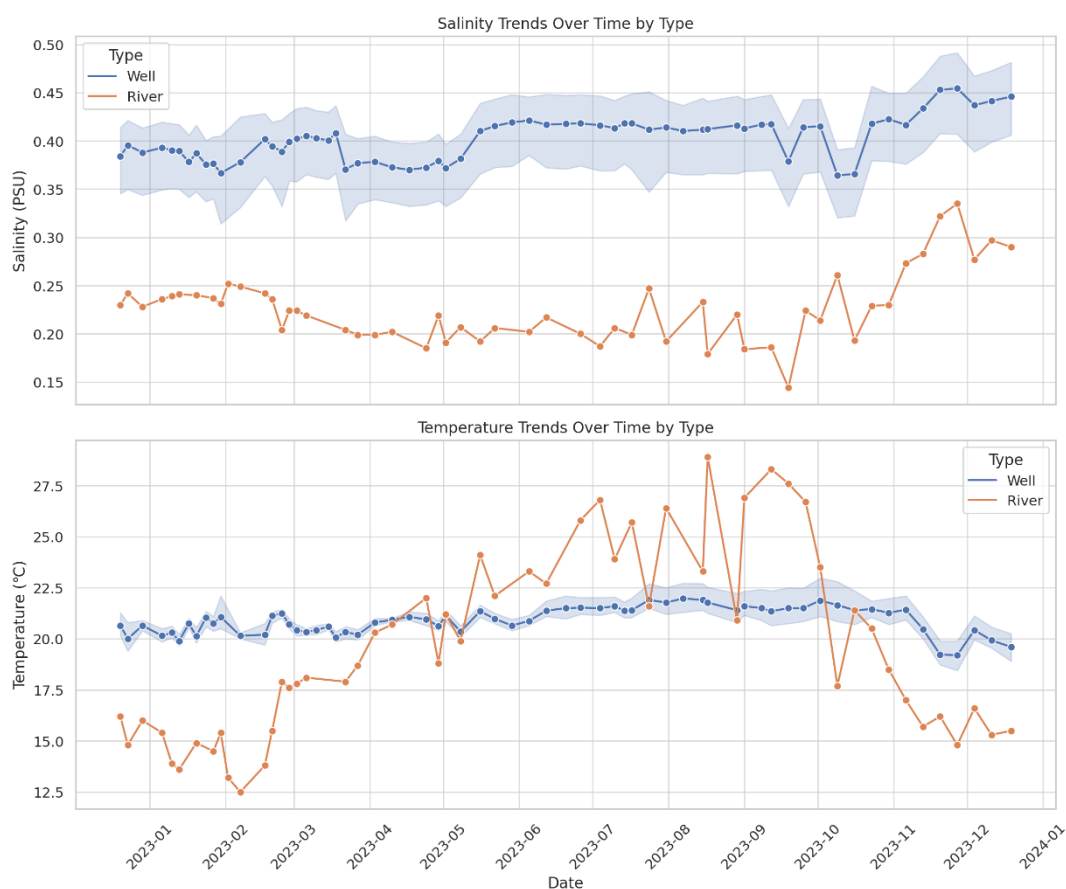


Figure 11. High-frequency time series of salinity (top panel) and temperature (bottom panel) from river (orange) and well (blue) stations between January and December 2023. Shaded areas represent ± 1 standard deviation around the 7-day rolling mean.

Vertical profiles of salinity and temperature in the wells showed a highly stable hydrographic structure throughout the year, with slight but consistent variations depending on depth (Figure 12). Salinity values across all depths remained relatively constant, generally ranging from 0.38 to 0.44, suggesting a well-mixed and mineral-rich subsurface source. Minor seasonal increases in salinity were most apparent in the deeper wells (20m&50 m), possibly reflecting reduced recharge during the dry season or upward diffusion from deeper geologic layers.

Temperature profiles exhibit a clear stratification with depth. The shallowest well (5m) displayed minor seasonal variation, with a slight warming trend during the summer months. However, wells at 10 m, 20 m, and 50 m showed increasingly stable temperature regimes, fluctuating between 20 and 21 °C until December 2023.

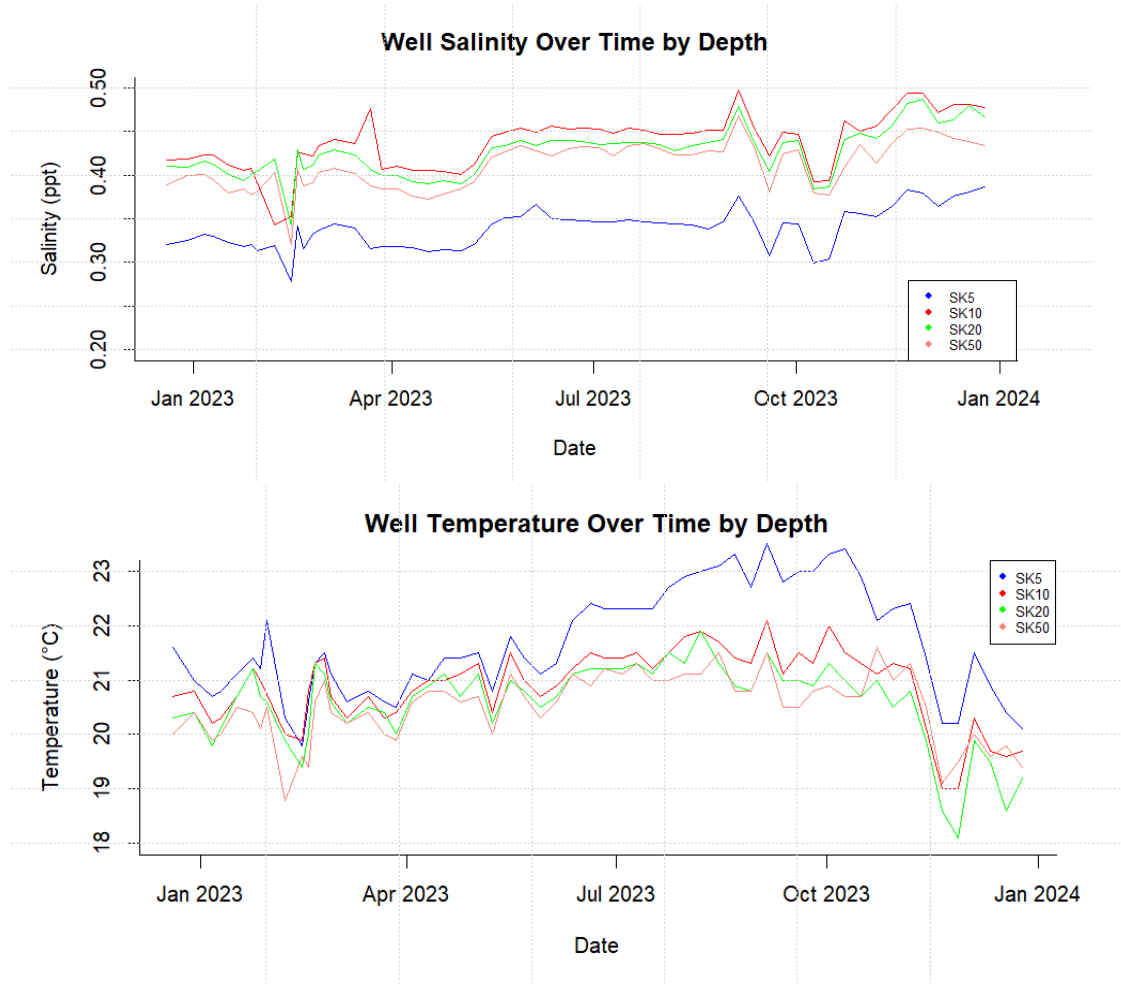


Figure 12. Time series of salinity (top panel) and temperature (bottom panel) in the Middle East Technical University (METU) groundwater well at four depths (5m, 10m, 20m, 50m) from January 2023 to January 2024.

3.2 Seasonal Variability of Carbonate Chemistry

3.2.1 Spatial and Seasonal (April vs. September) Differences Across Stations

To assess spatial variability between groundwater and river systems, samples were collected from 9 rivers and 10 wells, a total of 37 samples, during both in the wet season (April) and in the dry season (September). The Deliçay River (Hatay) was dry in September; therefore, no sample could be collected from this site.

Seasonal patterns in TA, pH, and DIC were compared between river and well stations (Figure 13). TA values in rivers were generally lower than those in wells, typically ranging from 2500 to 5000 $\mu\text{mol/kg}$. River inputs have higher total carbonate alkalinity at dry season. In wells, TA values were much higher, often above 7000 $\mu\text{mol/kg}$. Seasonal variability had no significant effect on alkalinity levels in groundwater.

pH values were higher and more stable in wells. River pH showed more variation between seasons, with slightly lower values in September at several stations.

DIC values followed a similar pattern to TA. Rivers showed lower and more variable concentrations, while wells had consistently higher DIC values, with no meaningful seasonal changes. Overall, the data show that carbonate chemistry is more variable in river waters and more stable in wells, but these seasonal differences were not statistically significant.



Figure 13. Seasonal variation of key carbonate system parameters; total alkalinity (TA), pH (in-situ), partial pressure of carbon dioxide ($p\text{CO}_2$), and dissolved inorganic carbon (DIC); across river (left) and well (right) stations in April and September. Each panel shows April (green) and September (orange) mean values at individual stations, with a vertical dashed line marking the boundary between surface (river) and subsurface (well) waters.

3.2.2 Statistical Analysis of Grouped Data (Rivers vs. Wells, Seasonality)

Grouped comparisons of TA, DIC, and pH were conducted to evaluate differences between water types and seasons (Figure 14). Boxplots show that both TA and DIC

values are generally higher in well samples than in rivers, with less variation across seasons. In contrast, pH values are more variable and slightly lower in rivers compared to wells.

Statistical analysis using the Mann–Whitney U test supports these observations. A significant difference was found between rivers and wells for both TA ($p = 0.0003$) and DIC ($p = 0.0002$), indicating clear compositional differences between surface and groundwater sources. For pH, a significant seasonal difference was observed between April and September ($p = 0.0276$), while no significant seasonal effect was found for TA or DIC.

These results confirm that water type has a strong influence on TA and DIC, while seasonal difference is only evident for pH. Rivers tend to have lower alkalinity and carbon content but are more sensitive to seasonal pH shifts, whereas wells are chemically more stable in the year.

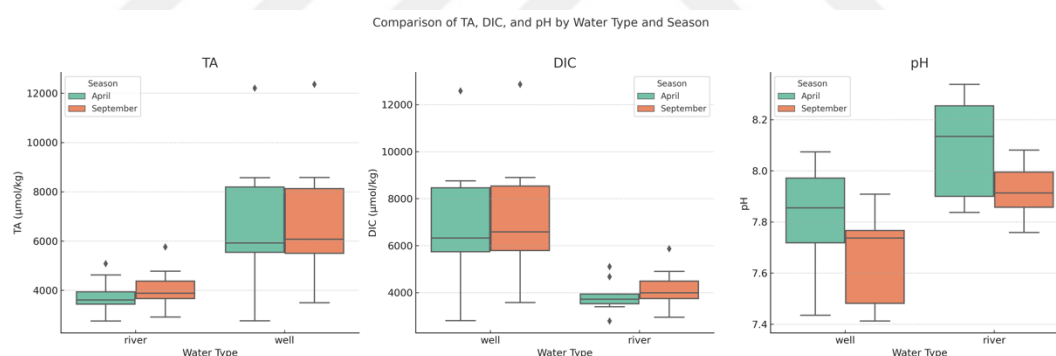


Figure 14. Boxplots of total alkalinity (TA), dissolved inorganic carbon (DIC), and pH (in-situ) for river and well stations during April and September. Each parameter is shown by water type (river vs. well) and season (April in green, September in orange).

3.3 Temporal Dynamics of Carbonate Chemistry in Groundwater and Surface Water Systems

In the METU wells, TA and DIC remained relatively stable throughout the year across all depths (5, 10, 20, and 50m), except for an unexplained decrease in February (Figure 15). No clear seasonal pattern was observed, and differences between depths were small. TA values generally ranged between 5500 and 6400 $\mu\text{mol/kg}$, while DIC concentrations were close to or above 6000 $\mu\text{mol/kg}$ in one year. pH values also showed little variability at depth, although the 5m well displayed minor fluctuations during the warmer months. These results suggest that the groundwater system is chemically stable over time and not strongly affected by seasonal changes.



Figure 15. Time series of total alkalinity (TA), pH (in-situ), and dissolved inorganic carbon (DIC) from Middle East Technical University (METU) wells at 5m, 10m, 20m, and 50m depths, recorded throughout 2023.

Average values of carbonate system parameters show distinct differences between groundwater and surface water (Table 4). METU well samples have higher salinity, TA, and DIC than the Lamas River; with concentrations of TA and DIC increasing slightly with depth, suggesting extended residence times and enhanced water–rock interaction in the karstic aquifer. In contrast, the Lamas River has lower TA and DIC but a higher average pH, reflecting surface-atmosphere exchange and photosynthetic influence. Groundwater shows more CO₂-rich but buffered conditions, while the river appears more seasonally dynamic.

Table 4. Average physicochemical and carbonate chemistry parameters of METU wells and Lamas River.

Properties	SK5	SK10	SK20	SK50	Lamas River
Salinity	0.34	0.44	0.43	0.40	0.23
Temperature	21.6	20.9	20.6	20.5	19.6
TA	5504.3	6005.3	6209.3	5901.1	3940.6
pH	7.62	7.61	7.60	7.45	7.92
DIC	5827.4	6362.1	6592.7	6436.5	4045.8

Figure 16 compares carbonate system parameters between the METU well system (averaged across 5m, 10m, 20m, and 50m depths) and the Lamas River over the course of 2023, with average values summarized in Table 4. In the METU wells, TA and DIC remained highly stable throughout the year, with depth-averaged values ranging from approximately 5500 to 6200 $\mu\text{mol/kg}$ for TA, and 5900 to 7000 $\mu\text{mol/kg}$ for DIC. pH values in the wells were also relatively stable, yet they decreased slightly with depth (from 7.62 at 5m to 7.45 at 50m). These

patterns reflect a well-buffered subsurface system, with minimal short-term variation and strong chemical stability.

In contrast, the Lamas River showed more seasonal variability, especially in pH, which gradually declined during the summer and early autumn months. Despite the clear pH trend, TA and DIC in the river remained relatively stable, with average values of 3940 $\mu\text{mol/kg}$ and 4046 $\mu\text{mol/kg}$, respectively. The higher pH and lower carbon content of the river water reflect its surface exposure, biological activity, and hydrological sensitivity.

Combined, the figure and table illustrate a major contrast between the systems; showing that groundwater maintains high, stable carbonate concentrations, whereas surface water responds more strongly to seasonal changes, especially in pH.

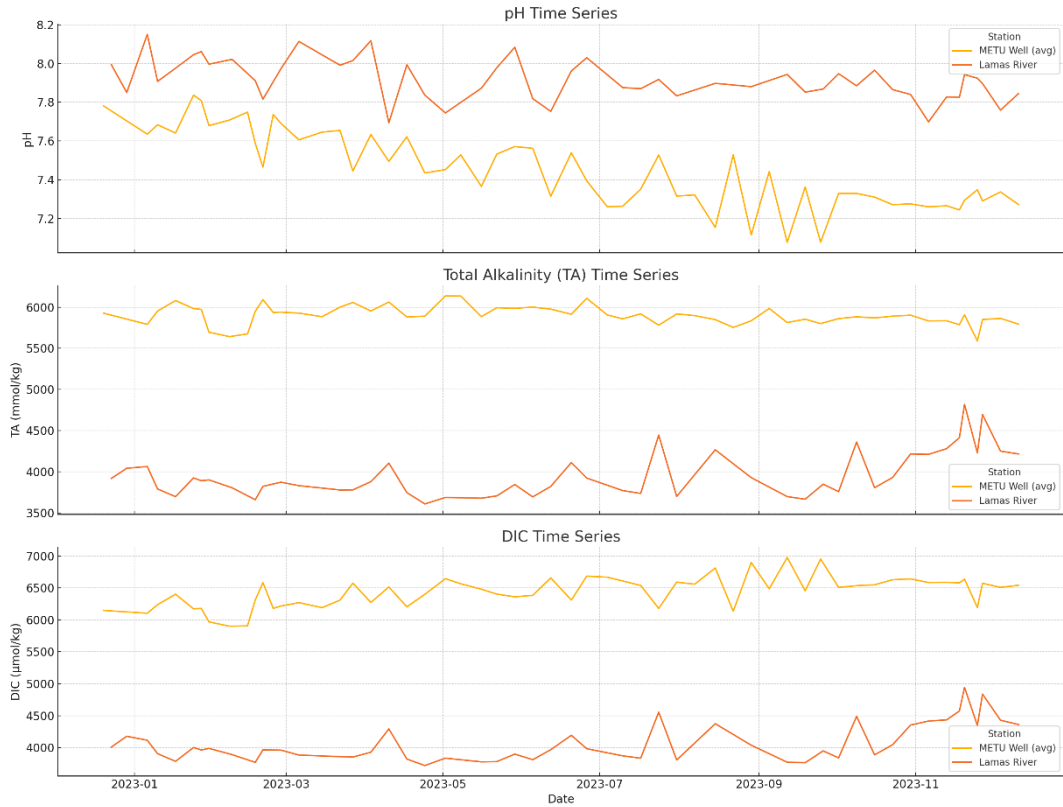


Figure 16. Time series of pH (in-situ), total alkalinity (TA), and dissolved inorganic carbon (DIC) in the METU well (average of all depths) and the Lamas River throughout 2023.

3.4 TA and DIC Fluxes

River discharge data were obtained from the Directorate General for State Hydraulic Works of Turkey (DSI). Due to data accessibility limitations, discharge values represent multi-year averages from the period 2012–2015, while 2015 is the most recent year available. River contributions of TA and DIC to the northeastern Mediterranean during the wet season (April) were determined by using average discharge rates and flow-weighted concentration data to reduce bias, and intervals with missing data were not included in the calculation. (Table 5).

Among the rivers, Ceyhan and Asi stood out as the dominant contributors, delivering over 24 Gmol/year and 10 Gmol/year, respectively, for both TA and DIC (Figure 17). Göksu and Seyhan followed with intermediate fluxes ranging between 8–10 Gmol/year, while smaller rivers such as Lamas, Berdan, and both Deliçay branches exhibited much lower fluxes (<1 Gmol/year).

Despite having lower average TA and DIC concentrations, the Ceyhan River's high discharge volume drives TA and DIC fluxes that are almost 2.5 times higher than those of the other rivers. On the other hand, although the Asi River has less flow than the Seyhan and Göksu Rivers, its much higher TA and DIC concentrations place it second in total TA and DIC flux (Table 5). It emphasize that both water chemistry and flow volume play key roles in carbon fluxes.

These river inputs supply significant alkalinity and inorganic carbon to the coastal system and can strongly affect local carbonate chemistry, especially during high flow periods.

Table 5. Average discharge of rivers and their corresponding TA and DIC flux. Calculated from $\text{Flux} = \text{Concentration} \times \text{Flow} \times \text{Time}$ formula.

River	Average Discharge (m³/s)	TA Flux (Gmol/year)	DIC Flux (Gmol/year)
Ceyhan	167.3	24.37	24.67
Göksu	84.9	9.67	9.83
Seyhan	76.3	8.79	9.04
Asi	62.7	10.05	10.10
Anamur	23.8	2.06	2.09
Berdan	5.4	0.59	0.60
Deliçay (Hatay)	4.7	0.50	0.50
Lamas	3.1	0.35	0.36
Deliçay (Mersin)	1.6	0.20	0.20

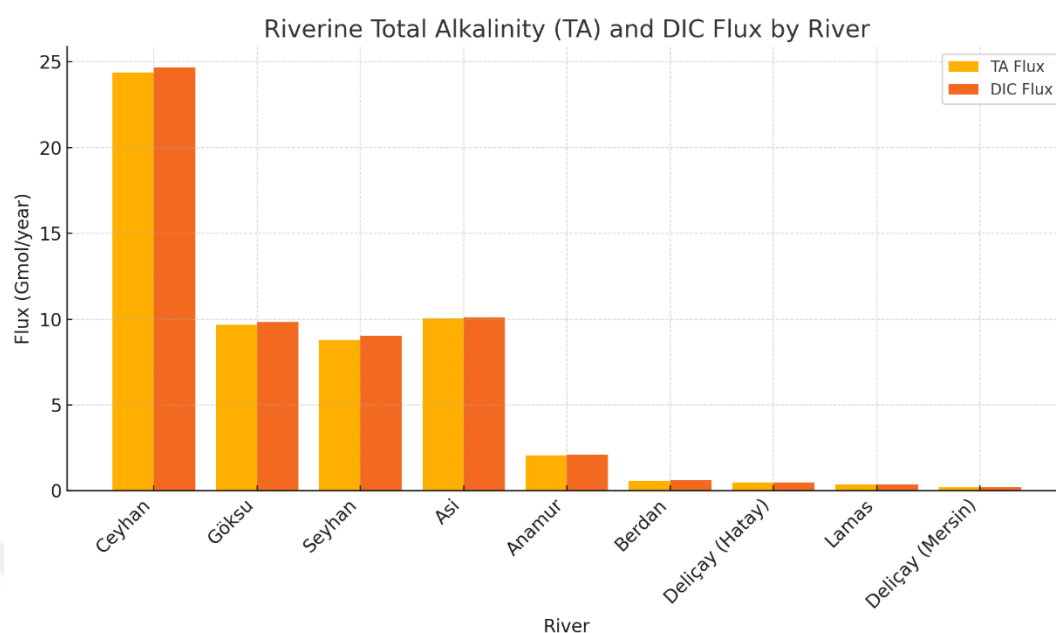


Figure 17. Annual riverine fluxes of total alkalinity (TA) and dissolved inorganic carbon (DIC) from major rivers discharging into the Cilician Basin, expressed in Gmol/year. Fluxes were calculated using average discharge rates (m^3/s) and measured concentrations of TA and DIC ($\mu\text{mol}/\text{kg}$).

According to Cossarini et al. (2015); among the Mediterranean basins, the Aegean and Adriatic Seas exhibit the highest total alkalinity inputs (1265 and 319 Gmol/yr, respectively), while the Ionian and Alboran basins contribute the lowest. Notably, the Levantine sub-basin, which is representing the easternmost Mediterranean region, receives relatively modest alkalinity inputs (79 Gmol/yr), primarily from the Nile River (32 Gmol/yr) with an average concentration of 2200 mmol m^{-3} ($\sim 2146 \mu\text{mol}/\text{kg}$).

3.5 Important Trends

River inputs have higher total carbonate alkalinity at dry season; whereas groundwater inputs significantly enhanced alkalinity, due to the total carbonate alkalinity is nearly 2-fold higher at well samples compared to river samples. This suggests groundwater is the dominant source of carbonate alkalinity. Higher alkalinity from groundwaters enhances buffering capacity, potentially mitigating acidification stress. Also seasonal variability had no significant effect on alkalinity levels in groundwater. Wells at all depths showed a similar trend for total carbonate alkalinity throughout the year, except for an unexplained decrease in February.

Generally, pH is higher at wet season. pH change throughout the year is statistically significant for both Lamas and METU wells, however relation is stronger and more significant at wells. The reason for the pH fluctuation in September is unknown, but the fact that the same trend occurs at all depths weakens the possibility of an error during the analysis.

The total annual carbon input from rivers to the Cilician Basin, expressed as TA and DIC fluxes, exceeded 50 gigamoles per year for both parameters. This finding underscores the potential impact of riverine TA and DIC inputs on carbonate chemistry at site-specific spatial scales.

4. DISCUSSION

4.1 High-Frequency Observations

Monitoring rivers and groundwater at high temporal resolution provides important information on variability in key physical and chemical parameters, such as salinity and temperature, which directly impact carbonate system processes. In this study, weekly measurements from the METU groundwater wells and the Lamas River over a full annual cycle reveal clear contrasts between the two freshwater sources, with groundwater exhibiting greater stability and river water showing pronounced seasonal fluctuations.

4.1.1 Salinity and Temperature Dynamics in Groundwater vs. River Water

Salinity in the METU wells remained within a relatively narrow range (0.278–0.428), reflecting the stability of subsurface hydrological systems (Figure 11). The slight vertical gradient in salinity, with lower values observed at the 5m depth, suggests limited vertical mixing and a potential influence of meteoric recharge at shallower levels. In contrast, deeper wells exhibited slightly elevated salinity, possibly due to longer residence times and increased water–rock interaction with carbonate-rich formations.

In the Lamas River, salinity ranged from 0.144 to 0.352, exhibiting far greater variability over time. Seasonal shifts, especially in the dry months, caused higher salinity levels, likely driven by reduced freshwater flow and greater evaporation. This greater salinity variability in the river highlights its dependence on surface hydrological and meteorological conditions, unlike the stable, buffered conditions observed in the wells.

Temperature patterns similarly reveal distinct behaviors between river and groundwater sources (Figure 11). In the wells, temperature ranged from 18.1 °C to 23.5 °C throughout the year, with very limited fluctuations below 10m depth. The

5m well consistently exhibited higher temperatures than deeper wells, likely due to its closeness to the surface and direct influence from air temperature and solar radiation. Its shallow depth makes it more sensitive to seasonal temperature changes in the atmosphere, yet the overall well system retains thermally buffered.

Conversely, the Lamas River showed large seasonal fluctuations in temperature, with values dropping as low as 12.5 °C in winter and exceeding 28 °C in summer. These shifts correspond directly with atmospheric conditions and are characteristic of shallow, open surface waters. This high degree of variability reflects the strong coupling between river water and external meteorological conditions, particularly solar radiation and air temperature.

4.1.2 Implications for Carbonate Chemistry Monitoring

The stability of salinity and temperature in the groundwater wells implies a highly buffered environment with minimal short-term changes, making them reliable end-members for evaluating carbonate system baseline conditions. In contrast, the river experiences short-term fluctuations that can significantly impact carbonate chemistry parameters, including pH, DIC, and TA. This variability is influenced by processes such as dilution, evaporation, biological activity, and interactions with other water masses.

Understanding the physical context provided by these salinity and temperature dynamics is essential for interpreting carbonate chemistry trends. The observations underscore the importance to differentiate between surface and subsurface sources when evaluating risks of coastal acidification and carbon flux dynamics.

4.1.3 Controls on TA and DIC Variability

TA levels were consistently higher in wells than in river waters, with average TA values in groundwater nearly 2 times higher than those observed in the Lamas River. In addition to being elevated, TA values in the wells were notably stable throughout the year, while riverine TA exhibited greater fluctuations.

This contrast can be primarily attributed to hydrogeological and geochemical differences between subsurface and surface systems. Groundwater in this region flows through carbonate-rich formations, such as limestone and dolomite, which promote the dissolution of carbonate minerals (Figure 3 and Figure 4). This process increases concentrations of bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) ions, which are the key contributors to TA. The dominance of carbonate rocks in the study region establishes a geochemical environment that is supportive of continuous mineral weathering. Furthermore, groundwater typically has a longer residence time ranging from years to decades compared to river water, which may only remain in the system for hours or days (Gleeson et al., 2015; Jones et al., 2017). This extended contact time enables more extensive water–rock interaction and mineral dissolution, contributing to the elevated TA and DIC levels observed in groundwater samples.

The role of dilution must also be considered. Groundwater, being less influenced by short-term precipitation events and surface runoff, exhibits reduced dilution and therefore maintains more concentrated levels of carbonate species. River water masses, on the other hand, are frequently diluted during wet seasons and are influenced by inputs from lower alkalinity sources such as direct rainfall, snowmelt, and runoff.

In addition to geological and hydrological controls, external environmental factors such as wind speed and direction can influence TA and DIC in coastal systems. Wind affects water exchange, mixing, and air–sea CO_2 fluxes. In coastal aquifers, onshore winds can promote seawater intrusion and increase groundwater salinity, while offshore winds may enhance the discharge of fresher groundwater. Wind-driven sea

level changes can also modulate SGD, altering the flux of alkalinity and carbon-rich waters to the coast.

At SK5, a Pearson correlation analysis revealed a moderate and statistically significant positive correlation between wind speed and TA ($r = 0.317$, $p = 0.0207$), suggesting that wind induced effects may contribute to variability. A one-way ANOVA revealed a marginally non-significant variation in TA among different wind direction categories ($p = 0.0806$), suggesting that wind-driven processes might influence surface-subsurface exchange or evaporation. Conversely, at the Lamas River, a statistically significant negative correlation was found between wind speed and TA ($r = -0.329$, $p = 0.0222$). This relationship may reflect enhanced outgassing of CO₂ or dilution effects caused by wind driven mixing with lower alkalinity waters. A multiple linear regression model for the Lamas River confirmed that wind speed had a significant negative effect on TA ($\beta = -246.01$, $p = 0.029$), while wind direction categories were not statistically significant contributors. The model explained approximately 29% of the variance in TA ($R^2 = 0.2909$).

Precipitation also emerged as a key driver of TA variability. As a component of the hydrological cycle, precipitation enhances groundwater recharge, affects river discharge volumes, and alters chemical composition through dilution, leaching, and sediment transport. In rivers, heavy rainfall can reduce TA concentrations through dilution or enhance them by mobilizing soil carbonates and organic matter.

To explore these effects, lagged correlation analyses were conducted. In the Lamas River, a significant positive correlation was observed between TA and precipitation with a lag of approximately 5 weeks (Lag -5 , $r \approx 0.45$), indicating that prior precipitation had a delayed impact on river alkalinity (Figure 18).

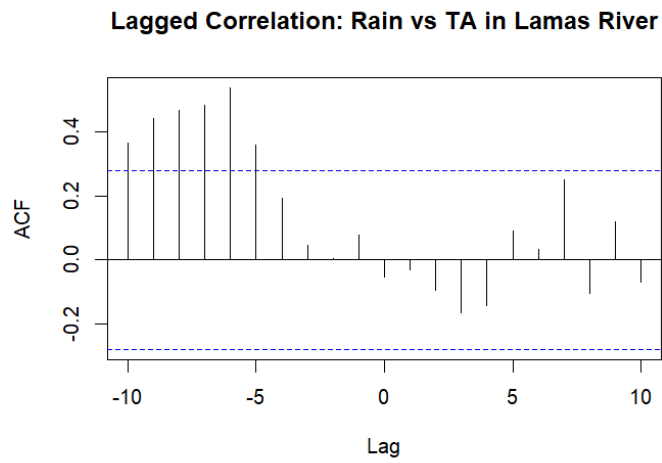


Figure 18. Cross-correlation between rainfall and total alkalinity (TA) in Lamas River.

At station SK5, a positive correlation was found with a 9-week lag ($r \approx 0.30$), suggesting delayed recharge or flow through the unsaturated zone (Figure 19).

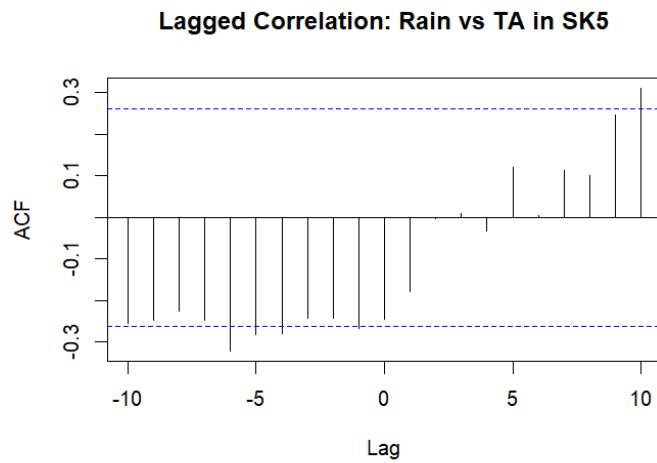


Figure 19. Cross-correlation between rainfall and total alkalinity (TA) in SK5 (5m METU well).

Similar patterns were observed at SK10 (7–10 weeks, $r \approx 0.25$) and SK20 (6–10 weeks, $r \approx 0.22$), although these trends were not statistically significant (Figure 20 and Figure 21)

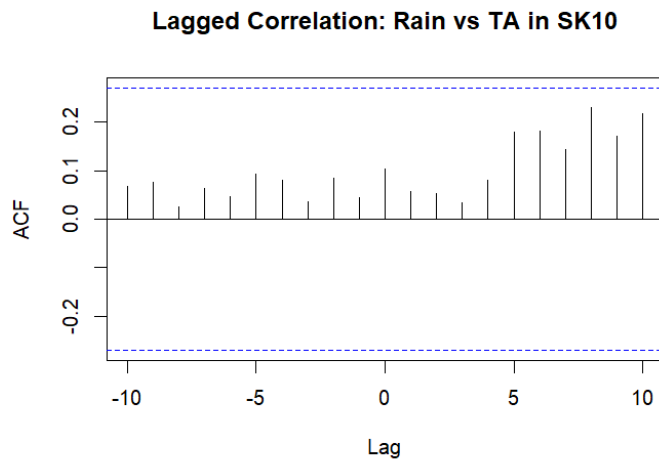


Figure 20. Cross-correlation between rainfall and total alkalinity (TA) in SK10 (10m METU well).

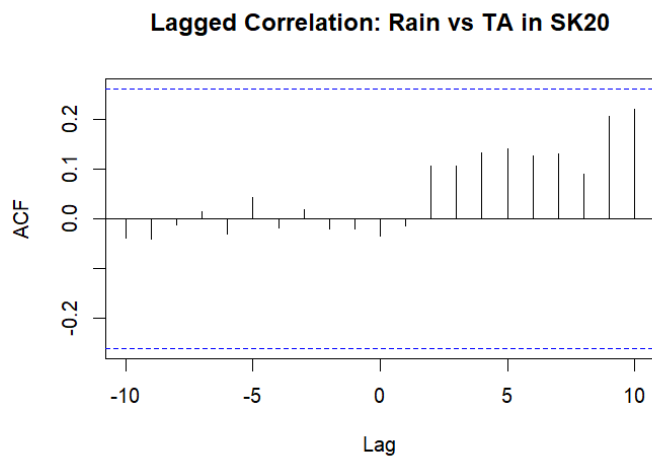


Figure 21. Cross-correlation between rainfall and total alkalinity (TA) in SK20 (20m METU well).

At SK50, a slightly stronger delayed correlation (8–10 weeks, $r \approx 0.30$) was observed, likely reflecting solute transport times through deeper pathways (Figure 22).

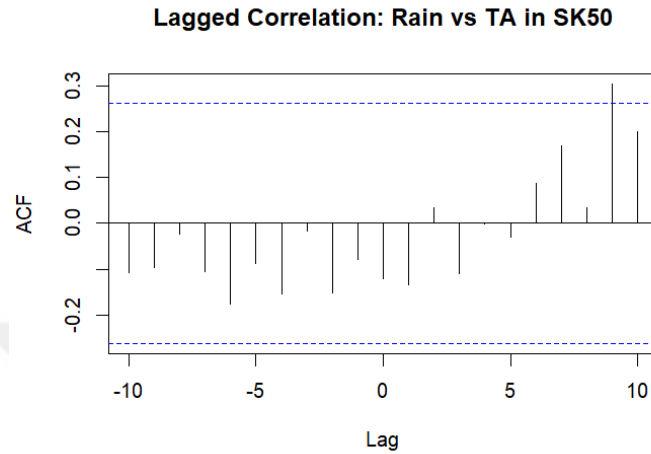


Figure 22. Cross-correlation between rainfall and total alkalinity (TA) in SK50 (50m METU well).

These delayed correlations suggest that precipitation influences TA through both rapid surface runoff and slower subsurface infiltration pathways, depending on the depth and hydraulic connectivity of each well. According to Chen et al. (2002), the response of groundwater to precipitation is produced with a time delay; and Lorenzo-Lacruz et al. (2017) reported that the rain effect appears within 1-3 months in Mediterranean, although it varies by sub-region. A summary of the lag analyses can be found at Table 6. Lagged correlation between rainfall and total alkalinity (TA) at temporal observation stations.

Table 6. Lagged correlation between rainfall and total alkalinity (TA) at temporal observation stations.

Station	Maximum Correlation (r)	Lag (weeks)	p-value	Interpretation
Lamas River	0.45	-5	< 0.01	TA is affected approximately 5 weeks before rainfall, indicating an indirect effect.
SK5	0.30	+9	≈ 0.02	TA increases approximately 9 weeks after rainfall.
SK10	0.25	+9	> 0.05	A delayed positive trend is observed, but the correlation is not statistically significant.
SK20	0.22	+8	> 0.05	A delayed TA increase is observed, but the correlation is not statistically significant.
SK50	0.30	+9	≈ 0.02	A delayed effect of rainfall on TA is observed after 8–10 weeks.

To further understand the drivers of total alkalinity variability, a regression analysis was conducted to assess the relationship between TA and salinity for both river and groundwater samples (Figure 23). The results revealed a strong positive relationship in both systems, with the following linear models:

Wells: $TA = 5399.89 \times \text{Salinity} + 3763.80$ ($R^2 \approx 0.58$)

Rivers: $TA = 9440.18 \times \text{Salinity} + 1917.20$ ($R^2 \approx 0.58$)

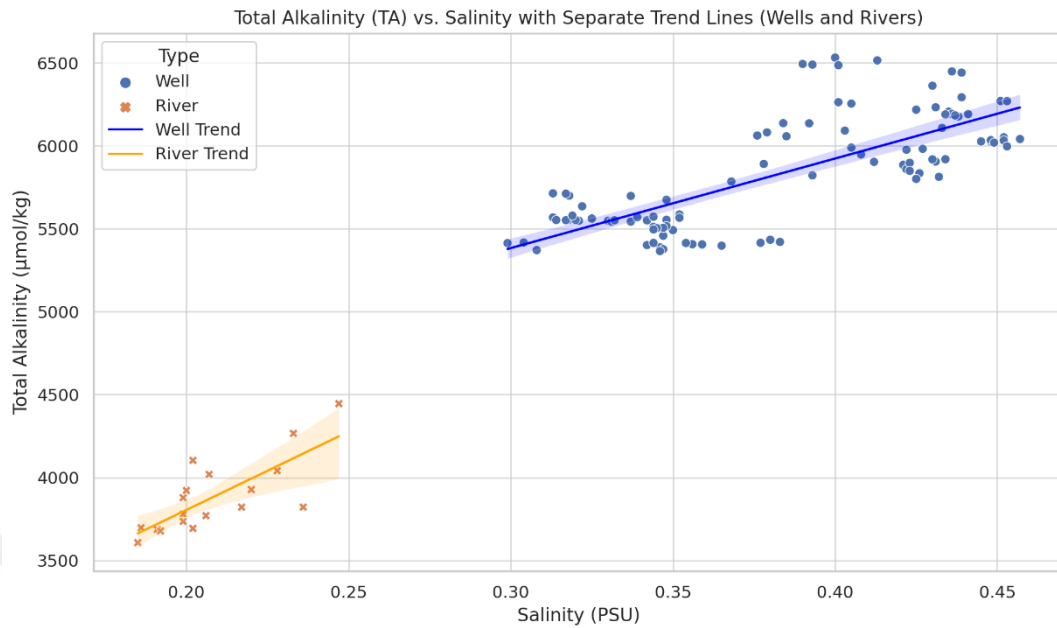


Figure 23. Relationship between total alkalinity (TA in $\mu\text{mol/kg}$) and salinity (PSU) in river and well samples. Separate linear regression lines are shown for each source type.

According to Schneider et al. (2007), freshwater inputs tend to increase the slope of the TA–S relationship. Despite having similar R^2 values, indicating moderate explanatory power, the slopes differ markedly. The sharper slope in rivers points to a quicker TA increase with salinity, likely driven by stronger mixing processes, variable upstream geochemistry, and cumulative evaporative effects (Hassoun et al., 2015). In contrast, the gentler slope in well samples reflects more consistent groundwater–rock interactions and a consistent buffering capacity. For comparison, Hassoun et al. (2015) reported that in the Eastern Mediterranean Basin, the surface TA–S relationship follows the equation $AT = 89 \times S - 846$ ($R = 0.86$); however, no significant relationship was identified for the Levantine sub-basin.

To explore potential depth-dependent differences in the well data, regression analyses were also performed separately for each depth. However, these depth-specific models exhibited weaker relationships (R^2 ranging from 0.06 to 0.37), likely due to limited sample size and localized geochemical influences. As a result,

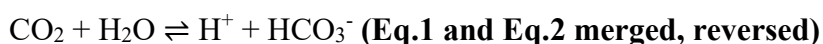
combining data from all well depths gives a stronger base for understanding. These findings highlight that while salinity is a useful proxy for TA, its predictive strength can vary with hydrogeologic context and sampling resolution.

In addition to TA, patterns in DIC closely followed those of alkalinity, as both parameters are controlled by similar sources and processes. In wells, DIC levels were consistently high and stable, further indicating carbonate mineral dissolution and long residence times. In contrast, riverine DIC was more variable and occasionally elevated during wet seasons, potentially due to inputs from soil respiration, organic matter degradation, or rapid flushing of CO₂-rich shallow soils.

Overall, TA and DIC variability across river and groundwater systems is governed by a combination of geological, hydrological, and meteorological factors. Groundwater systems maintain buffered, high-alkalinity conditions as a result of extended water–rock interactions, whereas riverine systems exhibit greater variability, responding rapidly to meteorological events, biological processes, and catchment-scale dynamics. Understanding these controlling mechanisms is vital for accurately simulating and managing carbonate chemistry in coastal regions receiving mixed freshwater inputs.

4.1.4 pH Variability and Controlling Factors

pH values are higher at the Lamas River compared to groundwater (Figure 14). This is consistent with expectations, as surface waters are more directly influenced by atmospheric CO₂ exchange and biological activity, both of the processes that potentially increase pH. River waters are in constant contact with the atmosphere, facilitating CO₂ degassing. Additionally, photosynthetic activity by primary producers reduces CO₂ levels during daylight hours, decreasing carbonic acid concentration and increasing pH. This can be represented by the equilibrium:



The removal of CO₂ leads to shifting the left side of equation, causing a decrease of H⁺ ions, thus raising the pH. In contrast, groundwater typically exhibits lower pH values due to its prolonged contact with organic-rich soils, where humic and fulvic acids are released. These weak acids contribute to the slight acidification of subsurface waters.

A Pearson correlation analysis was conducted to evaluate the relationship between wind speed and in-situ pH at station SK5. The analysis indicated a positive but statistically non-significant correlation ($r = 0.245$, $p = 0.0772$). Also, at SK5, one-way ANOVA showed no significant difference in in-situ pH across different wind direction categories ($F(5,42) = 0.36$, $p = 0.875$), indicating that wind had a limited impact on groundwater pH.

In contrast, at the Lamas River, wind speed showed a statistically significant positive correlation with pH ($p = 0.04609$), indicating that increased wind may enhance gas exchange processes and promote CO₂ degassing. However, wind direction did not significantly influence pH ($F(5,42) = 0.36$, $p = 0.875$). A multiple linear regression model further confirmed that wind speed had a significant positive effect on pH ($\beta = +0.119$, $p = 0.018$), although the overall model explained only 16.4% of the variance (Adjusted $R^2 = 0.0416$).

Although no seasonal trend was observed for pH levels across the year, a gradual decreasing trend was observed from the beginning to the end of the sampling on an annual basis, more explicitly in the 5m well at METU than in the Lamas River. This long-term trend could reflect cumulative biogeochemical changes or shifts in CO₂ inputs over time, but further investigation would be needed to confirm the mechanisms.

4.2 Spatial Observations

Carbonate chemistry parameters were determined of 9 rivers and 10 wells selected from all basins adjacent to the Cilician Basin (Figure 5). Two catchment expeditions were carried out for this purpose, one in the wet (April) and one in the dry (September) season. The spatial comparison aimed to differentiate the hydrochemical influences of surface and subsurface freshwater inputs on coastal carbonate dynamics.

4.2.1 Salinity and Temperature

Salinity and temperature showed clear spatial differences. Rivers typically exhibited lower salinity and greater seasonal variability compared to wells. Salinity values observed in wells are generally higher at dry season (except Samandağ sample). In this study, two samples cannot be considered as freshwater due to their salinity values which are more than 2ppt. One of the samples is from Gilindire, in the dry season. Gilindire has been determined that the first 10 meters of lake water has the characteristics of mixed water, and as going down from this depth, it becomes completely sea water. The lake water is largely sea water, and the groundwater that reaches the lake by leaking from precipitation is largely mixed with sea water at the upper elevations of the lake (Nazik et al., 2000). Another sample that has more than 2ppt salinity is the Boğsak sample during the dry season. Boğsak is the closest groundwater sampling point to the sea among spatial samples. Note that this sample also has the highest temperature value among the groundwater samples; due to its shallowness. While the well is the shallowest one, it can be affected more easily by temperature.

In both wells and rivers, the temperature is higher during the dry season, September. The temperature of the Lamas River has the highest value among the rivers in the dry season, followed by the Anamur River. This may be due to the low flow rates at the point where the samples were taken. Boğsak well has the highest temperature

difference among groundwater samples, possibly due to Boğsak station being the only well that has the opening. Likewise high frequency observations, the difference between seasons are higher at rivers compared to groundwater samples.

4.2.2 Spatial Total Carbonate Alkalinity (TA) Variations

Spatial patterns in TA revealed significantly higher values in wells compared to rivers. Among wells, values ranged broadly (often exceeding 6000 $\mu\text{mol/kg}$), while riverine TA values were lower and more seasonally dynamic (between 2753 $\mu\text{mol/kg}$ at Anamur, wet season; and 5762 $\mu\text{mol/kg}$ at Asi, dry season). This aligns with the prolonged residence time and carbonate-rich geology influencing groundwater. Coastal rivers with low discharge (e.g., Deliçay (Mersin), Lamas) tended to show greater variability and lower TA values, likely reflecting dilution and reduced mineral contact. Statistically, no significant seasonal difference was observed in well TA, while rivers exhibited significantly higher TA during the dry season ($p = 0.0070$), potentially due to reduced dilution and evaporative concentration.

Temperature can significantly impact the determination of TA, as it affects the solubility and dissociation of bicarbonates, carbonates, and hydroxides in water. As temperature rises, the dissociation of bicarbonate (HCO_3^-) into carbonate (CO_3^{2-}) (Eq.3) becomes more favored. This results in higher alkalinity at higher temperatures, as the increased carbonate ions contribute to the overall alkalinity. All the sampled rivers follow this trend, as having higher TA in dry season where temperature values are higher.

In well samples, the mean TA during the wet season was 6613 $\mu\text{mol/kg}$ ($\text{SD} = 2700 \mu\text{mol/kg}$), while during the dry season it was 6730 $\mu\text{mol/kg}$ ($\text{SD} = 2616 \mu\text{mol/kg}$). A paired t-test indicated that the seasonal difference was not statistically significant ($p = 0.1684$), suggesting that seasonal variability had no significant effect on TA levels in groundwater. Also, according to information received from well owners, fertilization activities are intensive between January and May in the region, while

fertilization is not carried out in the summer months of July and August. Fertilization is carried out before rainfall, and generally not carried out during the dry season. While fertilizer usage can result in leaching into groundwater, and affecting pH and alkalinity; land use and agricultural practices may affect the seasonal difference among well samples.

In river samples, the mean TA during the wet season was 3837 $\mu\text{mol/kg}$ (SD = 722 $\mu\text{mol/kg}$), while during the dry season it was 4089 $\mu\text{mol/kg}$ (SD = 862 $\mu\text{mol/kg}$). A paired t-test revealed a statistically significant seasonal difference ($p = 0.0070$), indicating that TA levels in river water were significantly higher during the dry season compared to the wet season.

Although well concentrations are generally high, the exact magnitude of SGD remains uncertain, preventing a precise determination of whether groundwater helps or worsens the ocean acidification. Nevertheless, given that all contributions exceed the Mediterranean's average TA, groundwaters likely contribute to enhancing resilience against ocean acidification.

Table 7. Comparison of total alkalinity (TA) between seasons.

Type	Season	Mean TA ($\mu\text{mol/kg}$)	SD	Paired t-test p-value	Significant Difference	Interpretation
Well	April	6613.21	2700.63	0.1684	No	No significant seasonal effect on groundwater TA
Well	September	6730.10	2616.02	0.1684	No	No significant seasonal effect on groundwater TA
River	April	3837.49	721.95	0.0070	Yes	TA is significantly higher in dry season for rivers

River	September	4089.15	862.19	0.0070	Yes	TA is significantly higher in dry season for rivers
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4.2.3 Spatial pH Variations

Spatially, pH was higher in river systems compared to wells, consistent with atmospheric CO₂ exchange and photosynthetic activity. River pH also showed greater seasonal variation and site specific anomalies such as Deliçay (Mersin), possibly due to localized anthropogenic influences. Conversely, groundwaters maintained a more stable but reduced pH, reflecting contributions from soil CO₂ and respiration occurring within subsurface. Both rivers and wells showed a statistically significant seasonal decrease in pH, although this trend was more pronounced in groundwater. Except Anamur and Lamas Rivers, all other sampled rivers follow this trend. This could be attributed to other factors affecting pH, such as photosynthesis rate and the dissolution of CaCO₃. The solubility of CaCO₃ decreases with increasing water temperature, therefore dissolution of CaCO₃ could not lead to this discordance of the pH values. Due to the absence of photosynthesis data, the underlying cause of this inconsistency cannot be determined with certainty. Still, this result may be due to the flow rates of rivers. The Lamas River, with an average discharge, is the second lowest among the nine rivers, while the Anamur River ranks fifth for having the lowest average discharge. Since rivers with higher discharges are more likely to mix, the discharge rate may have influenced this result. To obtain more precise results, it is necessary to determine the distances traveled by the rivers and how deviate or change the river direction.

The pH of Deliçay (Mersin) site has the highest difference between seasons. The industrialization in the area dates back to the early 1950s with the establishment of ATAS petroleum refinery in Karaduvar, near to the Deliçay River in Mersin (Guler, 2009). Also, pH can be affected by autumnal leaf fall by increasing the organic

matter in rivers. Decomposition process of the leaves result the producing organic acids that lowers pH values. Especially Deliçay (Mersin), Berdan and Asi Rivers had high organic matter during September.

Groundwater samples typically have lower pH than river samples because they are often enriched in dissolved CO₂ from soil respiration and microbial activity in the subsurface, which forms carbonic acid and lowers pH.

In well samples, the mean in-situ pH during the wet season was 7.83 (SD = 0.20), while during the dry season it was 7.66 (SD = 0.18). A paired t-test indicated that this difference was statistically significant ($p = 0.0228$), suggesting a seasonal decline in groundwater pH levels. In river samples, the mean in-situ pH during the wet season was 8.06 (SD = 0.18), compared to 7.92 (SD = 0.11) during the dry season. A paired t-test revealed a statistically significant difference ($p = 0.0426$), indicating a slight seasonal decrease in river pH.

During the 2013 MedSeA cruise, the average pH of the Mediterranean Sea was 8.074 ± 0.034 , ranging from a minimum of 7.962 to a maximum of 8.148 (Hassoun et al., 2015). Based on these values, it can be interpreted as groundwater consistently lowers pH throughout the year, whereas riverine inputs also reduce pH during the dry (September) period, but their effect during the wet (April) period exhibits local variability.

Such spatial patterns highlight the contrasting biogeochemical roles of river and groundwater contributions to the Cilician Basin. While groundwater represents a stable, alkalinity-rich endmember, riverine inputs are comparatively dynamic and strongly influenced by surface processes. This distinction is crucial for understanding buffering capacity and acidification risks in nearshore waters, where the relative contribution of each source may shift seasonally and spatially. Future monitoring and modeling efforts should consider these spatial heterogeneities to improve predictions of coastal carbonate chemistry and ecosystem response.

Table 8. Comparison of in-situ pH between seasons.

Type	Season	Mean in-situ pH	SD	Paired t-test p-value	Significant Difference	Interpretation
Well	April	7.83	0.20	0.0228	Yes	pH significantly lower in dry season for groundwater
Well	September	7.66	0.18	0.0228	Yes	pH significantly lower in dry season for groundwater
River	April	8.06	0.18	0.0426	Yes	pH significantly lower in dry season for river water
River	September	7.92	0.11	0.0426	Yes	pH significantly lower in dry season for river water

4.3 Riverine Contributions to the Coastal Carbonate Budget

The annual fluxes of TA and DIC from the 9 sampled rivers highlight the dominant role of high discharge systems such as the Ceyhan, Göksu, Seyhan, and Asi Rivers in shaping the coastal carbonate budget of the Cilician Basin (Table 5). Among these, the Ceyhan River alone accounts for over 40% of the total TA and DIC flux, delivering approximately 24.4 Gmol/year of alkalinity and 24.7 Gmol/year of DIC. This is more than double the combined contribution of the next two largest rivers, Göksu and Seyhan.

To assess the relative significance of these fluxes, it is crucial to be compared with the estimated standing stocks of TA and DIC in the Cilician coastal zone. Assuming a coastal water body of 200 km length, 50 km width, and 50m average depth, the

total volume amounts to approximately $5 \times 10^{11} \text{ m}^3$. Using typical regional concentrations of $\sim 2600 \text{ } \mu\text{mol/kg}$ for TA and $\sim 2300 \text{ } \mu\text{mol/kg}$ for DIC, and assuming a seawater density of 1000 kg/m^3 , the standing stocks correspond to approximately 130 Tmol of TA and 115 Tmol of DIC.

In this context, the total annual riverine flux ($\sim 56.5 \text{ Gmol}$ of TA and $\sim 57.3 \text{ Gmol}$ of DIC) represents only about 0.04% of the total TA and DIC inventories in the defined coastal volume. While this proportion may seem negligible at first glance, it becomes more significant when considered on shorter time scales, during high-discharge periods or events, or when evaluating localized buffering capacity in river plumes and estuarine zones. Even though these flux values are minor compared to open-ocean budgets, they play an important role at the local scale. Riverine inputs are thus likely to shape nearshore carbonate dynamics, especially under conditions of seasonal stratification or restricted water exchange.

For comparison, Schneider et al. (2007) estimated the mean riverine total TA flux for the Mediterranean region as $2080 \text{ } \mu\text{mol/L}$. However, this value is considered outdated and does not fully represent the current understanding of TA dynamics in Mediterranean catchments. In the present study area, the geological structure exhibits distinctly karstic characteristics. The widespread presence of carbonate-rich rocks, particularly limestone and dolomite, provides a significant source of carbonate ions through weathering processes. This geological setting likely explains the relatively high TA values observed in the study area. Supporting this interpretation, other karst-dominated systems also show similar patterns; for instance, the James River at Lamoure (North Dakota, USA) has reported TA concentrations of up to $4400 \text{ } \mu\text{mol/L}$ (Kaushal et al., 2013).

The main limitation of calculating the carbonate budget lies in the load estimations, which rely heavily on accurate river discharge data. However, discharge measurements are not always taken at the river mouths, introducing uncertainty into the calculated fluxes. This limitation is particularly evident for the Ceyhan River, where upstream monitoring stations may not accurately represent the actual

discharge reaching the coast. Furthermore, part of the river water may be diverted for agricultural or other purposes before reaching the sampling point. Therefore, the estimated loads should be considered potential maximum values and interpreted with caution.

While riverine inputs can be quantified with some degree of certainty, the contribution of SGD remains largely unknown in the study region. Groundwater samples exhibited substantially higher TA and DIC concentrations than rivers, often nearly double, suggesting that even modest SGD rates could deliver large carbon fluxes to the coastal zone. However, the lack of SGD flow rate measurements currently prevent the calculation of total fluxes from these sources.

Numerous studies have shown that SGD can be a dominant pathway for land to ocean carbon transfer in karst dominated or fractured coastal systems; particularly those with carbonate geology, such as the study site, Cilician Basin coast. Therefore, while rivers currently appear to be the major quantified source of land derived TA and DIC to the basin, the true magnitude and importance of SGD remains an open question. Addressing this will require future studies that combine hydrological tracers (e.g., ^{222}Rn , ^{223}Ra), hydrogeological modeling, and in-situ SGD measurements.

These results collectively highlight several broader implications for coastal carbon dynamics in the northeastern Mediterranean and beyond. The observed variability in TA and DIC across northeastern Mediterranean rivers and groundwater systems demonstrates that even relatively small coastal catchments could have disproportionate control on nearshore carbonate chemistry. In semi-enclosed and oligotrophic basins such as the Cilician Basin, these inputs can locally offset acidification by enhancing buffering capacity, particularly during periods of intense runoff or groundwater discharge. Comparable mechanisms have been reported for the Adriatic (Cantoni et al., 2012) and Levantine coasts (Hassoun et al., 2015; 2019), suggesting that karstic terrains act as overlooked natural regulators of coastal pH stability. Therefore, understanding these fluxes is not only relevant for regional water

quality management, but also for refining basin-scale carbon budgets across the Mediterranean Sea.

The temporal variability identified in this study highlights how hydrological forcing and biogeochemical processing collectively shape coastal carbonate chemistry. Elevated TA concentrations following rainfall and enhanced groundwater discharge indicate that seasonal reactivation of karstic aquifers can temporarily increase the buffering potential of surface waters. This implies that changes in precipitation regimes or groundwater extraction under future climate scenarios could directly modify the alkalinity balance at the land–sea interface. These dynamics emphasize the need to integrate coastal carbonate fluxes into predictive models assessing acidification trajectories and resilience in nearshore ecosystems.

Beyond their local relevance, these findings contribute to the broader understanding of how terrestrial carbon fluxes modulate ocean acidification processes in semi-enclosed seas. The northeast Mediterranean, with its dense population centers and rapid coastal development, represents a critical testing ground for evaluating how anthropogenic alterations in hydrology interact with natural buffering mechanisms. Continued monitoring that integrate carbonate system parameters with hydrological and isotopic tracers would allow for a clearer distinction between natural processes and human-induced contributions to total alkalinity. Such interdisciplinary and data-driven approaches are crucial for developing effective mitigation strategies, particularly in the contexts of watershed management, groundwater protection, and carbon budgeting across Mediterranean coastal systems.

5. CONCLUSION

This thesis provides the first integrated and high-resolution assessment of carbonate system parameters in rivers and groundwater discharging into the northeastern Mediterranean Sea. By combining spatial and high-frequency temporal observations of TA, DIC, and pH, it establishes a valuable regional baseline for future biogeochemical and hydrological assessments. This study filled the gap in the literature that had overlooked the groundwater and riverine contribution to carbonate parameters at the Northeast Mediterranean coasts. By including both weekly monitoring and seasonal surveys in wet and dry periods, the study captures important contrasts in the carbonate chemistry of different freshwater sources.

The results reveal distinct but complementary behaviors of riverine and groundwater systems. Groundwater samples consistently exhibited higher and more stable TA and DIC concentrations (often exceeding $6000 \mu\text{mol kg}^{-1}$) reflecting prolonged water–rock interaction and strong buffering capacity. In contrast, rivers displayed greater temporal and seasonal variability, especially in pH, driven by hydrological and meteorological factors such as rainfall and evaporation. The significant increase in riverine TA during the dry season (peaked at $4400 \mu\text{mol kg}^{-1}$) highlights the role of dilution and evaporation in shaping carbonate balance under variable flow regimes.

Although no distinct seasonal cycle was detected in pH values, a gradual decreasing trend was observed throughout the year in both rivers and groundwater wells. Wind speed and precipitation emerged as potential drivers of variability in TA, with their effects varying by location and often appearing after a delay of up to 9 weeks. However, wind direction showed only limited influence on any of the measured parameters. Quantitative flux analysis indicates that total annual riverine TA and DIC inputs to the Cilician Basin may exceed 50 Gmol yr^{-1} , with the Ceyhan River alone may be contributing nearly half of this amount, emphasizing its dominant role in the basin's carbon and alkalinity dynamics. Although this flux represents only a small fraction

of the basin's overall carbon inventory, it can exert strong local influence on nearshore buffering capacity, particularly during stratified or low-exchange periods. The study also identifies the likely importance of SGD as an unquantified but potentially significant contributor to coastal carbon budgets.

Collectively, these findings demonstrate the critical importance of combining spatial and high-frequency temporal monitoring to effectively characterize freshwater influences on coastal carbonate chemistry, both surface and subsurface. They also emphasize the need to integrate such land–sea carbon fluxes into broader Mediterranean carbon budgets and acidification models, which currently overlook these pathways.

Looking forward, these findings highlight the importance of establishing long-term and integrated monitoring programs to better capture the spatial and temporal variability of carbonate chemistry in coastal systems. Continuous observations of TA, DIC, and pH in both riverine and groundwater inputs are essential for accurately quantifying their contributions to coastal carbon budgets. Coupled observations of hydrology, meteorology, and isotopic tracers will be essential for distinguishing natural versus anthropogenic sources of alkalinity and for improving predictions under changing climate conditions.

Such interdisciplinary approaches will strengthen our understanding of coastal carbon cycling in the northeastern Mediterranean and inform effective management strategies for vulnerable coastal ecosystems in the northeastern Mediterranean. Future interdisciplinary researches that integrates hydrological, biogeochemical, and modeling approaches will be key to understanding how changing climatic and anthropogenic pressures reshape the coastal carbon cycle.

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APPENDICES

A. Physicochemical and carbonate chemistry parameters from 5m well in METU

Date	Salinity (ppt)	Temperature (°C)	pH (in-situ)	TA (umol/kg)	DIC (umol/kg)	pCO2 (ppm)	Revelle Factor
20/12/2022	0.321	21.6	7.91	5548.9	5687.1	4249.9	31.87
29/12/2022	0.325	21.0	8.01	5562.2	5666.6	3406.0	36.91
06/01/2023	0.332	20.7	7.80	5550.1	5744.3	5476.6	25.57
10/01/2023	0.330	20.8	7.96	5548.5	5671.8	3806.4	34.00
17/01/2023	0.322	21.1	7.81	5635.5	5825.4	5446.0	26.26
24/01/2023	0.318	21.4	7.94	5554.5	5681.8	3970.8	33.40
27/01/2023	0.320	21.2	7.90	5553.5	5697.3	4333.4	31.17
30/01/2023	0.314	22.1	7.84	5554.0	5723.0	5069.2	28.12
07/02/2023	0.320	20.3	7.81	5543.9	5733.8	5306.8	25.98
14/02/2023	0.278	19.8	7.98	5391.8	5504.0	3424.5	35.22
17/02/2023	0.342	20.6	7.79	5550.8	5749.3	5563.9	25.18
20/02/2023	0.316	21.3	7.67	5698.3	5972.0	7596.1	20.08
24/02/2023	0.332	21.5	7.74	5551.2	5771.8	6268.4	23.27
27/02/2023	0.337	21.1	7.78	5543.1	5742.9	5677.4	25.02
06/03/2023	0.344	20.6	7.75	5572.9	5792.1	6073.9	23.47
15/03/2023	0.339	20.8	7.72	5569.4	5807.4	6576.8	22.03
22/03/2023	0.316	20.6	7.80	5551.9	5743.5	5399.1	25.82
27/03/2023	0.318	20.5	7.69	5699.9	5963.5	7170.3	20.71
03/04/2023	0.319	21.1	7.76	5579.5	5793.8	6042.6	23.88
10/04/2023	0.317	21.0	7.62	5711.7	6028.8	8634.5	17.85
17/04/2023	0.313	21.4	7.72	5568.6	5802.3	6583.3	22.32
24/04/2023	0.314	21.4	7.64	5552.9	5844.0	8050.8	18.70
02/05/2023	0.313	21.5	7.69	5713.6	5977.8	7398.6	20.69
16/05/2023	0.344	21.8	7.59	5511.7	5833.9	8949.9	17.09
22/05/2023	0.352	21.4	7.69	5586.5	5839.6	7080.5	21.03
29/05/2023	0.352	21.1	7.70	5566.7	5819.6	7010.9	20.99
05/06/2023	0.367	21.3	7.68	5785.6	6059.4	7606.0	20.32
12/06/2023	0.350	22.1	7.53	5492.2	5864.6	10357.6	15.07
20/06/2023	0.348	22.4	7.70	5554.0	5795.6	6979.5	21.69
26/06/2023	0.348	22.3	7.63	5674.8	5969.4	8363.4	18.84
04/07/2023	0.347	22.3	7.44	5463.8	5915.8	12553.5	12.70
10/07/2023	0.347	22.3	7.52	5458.3	5832.0	10448.1	14.95
17/07/2023	0.348	22.3	7.56	5516.4	5856.7	9559.8	16.33
24/07/2023	0.347	22.7	7.57	5505.9	5839.0	9472.5	16.60
31/07/2023	0.345	22.9	7.55	5504.3	5853.0	9950.6	15.96
07/08/2023	0.344	23.0	7.52	5496.2	5868.9	10630.2	15.06
15/08/2023	0.342	23.1	7.44	5402.1	5843.8	12546.5	12.83
22/08/2023	0.340	23.3	7.76	5292.6	5496.9	5708.4	23.79
29/08/2023	0.346	22.7	7.36	5388.5	5928.6	15095.2	10.75
05/09/2023	0.376	23.5	7.60	5426.2	5726.7	8783.1	17.86
12/09/2023	0.347	22.8	7.32	5376.9	5959.3	16300.3	10.05

19/09/2023	0.308	23.0	7.29	5371.4	5997.1	17588.4	9.44
25/09/2023	0.346	23.0	7.36	5365.7	5894.7	14914.3	10.91
02/10/2023	0.344	23.3	7.43	5414.8	5869.2	12971.0	12.54
09/10/2023	0.299	23.4	7.43	5413.7	5862.6	12855.0	12.67
16/10/2023	0.304	22.9	7.42	5417.3	5889.5	13316.9	12.13
23/10/2023	0.359	22.1	7.45	5406.0	5851.1	12294.2	12.75
30/10/2023	0.355	22.3	7.37	5407.2	5937.7	14671.0	10.95
06/11/2023	0.353	22.4	7.38	5414.3	5929.5	14296.0	11.25
13/11/2023	0.365	21.4	7.50	5404.2	5797.1	10683.9	14.20
20/11/2023	0.382	20.2	7.47	5420.9	5858.8	11461.6	12.97
27/11/2023	0.379	20.2	7.40	5433.9	5943.6	13289.6	11.39
04/12/2023	0.364	21.5	7.37	5398.3	5934.3	14486.1	10.84
11/12/2023	0.376	20.9	7.39	5415.7	5933.4	13767.5	11.20
18/12/2023	0.380	20.4	7.46	5368.5	5805.3	11496.2	12.89
25/12/2023	0.387	20.1	7.59	5280.3	5600.5	8452.5	16.58

B. Physico-chemical and carbonate chemistry parameters from 10m well in METU

Date	Salinity (ppt)	Temperature (°C)	pH (in-situ)	TA (umol/kg)	DIC (umol/kg)	pCO ₂ (ppm)	Revelle Factor
20/12/2022	0.418	20.7	7.66	5456.8	5732.4	7488.3	19.29
06/01/2023	0.423	20.2	7.77	5857.3	6078.2	6079.1	24.23
10/01/2023	0.423	20.3	7.68	5655.7	5925.4	7273.0	20.21
17/01/2023	0.412	20.7	7.63	5903.7	6223.4	8645.1	18.22
27/01/2023	0.408	21.0	7.64	5550.5	5842.3	7973.8	18.66
07/02/2023	0.343	20.0	7.58	5702.8	6050.3	9144.7	16.51
14/02/2023	0.352	19.9	7.73	5508.7	5745.3	6365.3	21.96
17/02/2023	0.427	20.8	7.62	5982.4	6311.2	8908.7	17.99
20/02/2023	0.424	21.3	7.71	6218.1	6490.8	7625.3	21.59
24/02/2023	0.422	21.4	7.86	6067.9	6243.4	5204.4	29.10
27/02/2023	0.434	20.7	7.73	5798.7	6039.6	6655.6	22.52
06/03/2023	0.441	20.3	7.82	6063.7	6266.4	5684.3	26.44
15/03/2023	0.436	20.7	7.73	5887.2	6131.8	6757.2	22.52
22/03/2023	0.476	20.3	7.69	5706.3	5974.2	7236.6	20.46
27/03/2023	0.406	20.4	7.75	5912.4	6148.6	6496.5	23.20
03/04/2023	0.410	20.8	7.72	5882.9	6132.4	6899.0	22.16
10/04/2023	0.405	21.0	7.63	6254.9	6592.8	9217.9	18.25
17/04/2023	0.405	21.0	7.84	6108.3	6296.3	5450.6	27.95
24/04/2023	0.405	21.1	7.62	5989.8	6321.5	9060.1	17.88
02/05/2023	0.401	21.3	7.66	6263.1	6575.6	8644.8	19.48
16/05/2023	0.445	21.5	7.63	6033.2	6354.4	8895.3	18.47
22/05/2023	0.449	21.0	7.76	6124.1	6361.3	6659.8	23.75
29/05/2023	0.453	20.7	7.77	6125.0	6359.0	6526.5	23.99
05/06/2023	0.367	20.9	7.65	6270.4	6589.5	8715.7	19.17
12/06/2023	0.457	21.2	7.56	6041.3	6420.4	10312.9	16.10
20/06/2023	0.453	21.5	7.72	6128.0	6385.9	7282.7	22.28

26/06/2023	0.453	21.4	7.57	6269.7	6657.4	10615.9	16.30
04/07/2023	0.452	21.4	7.48	6051.5	6513.2	12530.1	13.63
10/07/2023	0.448	21.5	7.50	6025.1	6467.4	12056.7	14.08
17/07/2023	0.454	21.2	7.66	6119.9	6421.4	8325.7	19.68
24/07/2023	0.451	21.5	7.68	6114.1	6403.4	8084.3	20.32
31/07/2023	0.446	21.8	7.69	6060.9	6333.6	7716.9	21.15
07/08/2023	0.446	21.9	7.66	6110.0	6405.8	8344.1	19.95
15/08/2023	0.448	21.7	7.40	6034.7	6585.0	14986.8	11.67
22/08/2023	0.437	20.9	7.72	5933.9	6186.2	6995.4	22.12
05/09/2023	0.497	22.1	7.66	6088.9	6388.9	8499.5	19.67
12/09/2023	0.453	21.1	7.33	5996.9	6648.0	17369.1	10.03
19/09/2023	0.422	21.5	7.56	6079.5	6460.0	10443.3	16.13
25/09/2023	0.449	21.3	7.32	6019.5	6687.0	17902.4	9.85
02/10/2023	0.447	22.0	7.57	6086.9	6456.0	10291.6	16.57
09/10/2023	0.393	21.5	7.52	6096.6	6522.1	11621.6	14.71
16/10/2023	0.394	21.3	7.53	6079.3	6491.6	11207.3	15.08
23/10/2023	0.461	21.1	7.49	6083.1	6537.2	12230.7	13.88
30/10/2023	0.450	21.3	7.52	6072.9	6493.8	11431.0	14.80
06/11/2023	0.456	21.2	7.47	6096.8	6576.6	12934.9	13.27
13/11/2023	0.475	20.1	7.49	6064.9	6525.3	12040.1	13.69
20/11/2023	0.493	19.0	7.50	6085.6	6553.2	11833.2	13.55
27/11/2023	0.494	19.0	7.50	6088.8	6547.8	11622.3	13.78
04/12/2023	0.472	20.3	7.56	6072.7	6459.4	10241.7	15.91
11/12/2023	0.480	19.7	7.44	6072.3	6593.0	13406.0	12.32
18/12/2023	0.480	19.6	7.50	6046.8	6498.3	11640.1	13.89
25/12/2023	0.477	19.7	7.58	5902.6	6271.2	9602.1	16.18

C. Physico-chemical and carbonate chemistry parameters from 20m well in METU

Date	Salinity (ppt)	Temperature (°C)	pH (in-situ)	TA (umol/kg)	DIC (umol/kg)	pCO2 (ppm)	Revelle Factor
20/12/2022	0.410	20.3	7.85	6339.6	6533.1	5503.1	28.14
29/12/2022	0.409	20.4	7.64	5654.7	5954.9	8057.7	18.52
06/01/2023	0.416	19.8	7.88	6394.7	6575.5	5134.9	29.60
10/01/2023	0.413	20.1	7.72	6084.8	6350.3	7172.3	21.69
17/01/2023	0.400	20.7	7.83	6532.0	6744.6	6053.5	26.94
24/01/2023	0.394	21.2	7.69	5926.7	6197.3	7520.9	20.90
27/01/2023	0.401	20.7	7.61	5741.4	6069.7	8847.0	17.41
30/01/2023	0.405	20.6	7.55	5547.0	5915.0	9815.3	15.36
07/02/2023	0.393	19.9	7.64	5553.0	5850.8	7870.5	18.37
14/02/2023	0.343	19.4	7.94	6181.7	6328.9	4281.6	32.85
17/02/2023	0.429	20.0	7.71	6362.7	6648.2	7671.4	21.22
20/02/2023	0.407	21.3	7.64	6515.1	6850.1	9246.3	19.01
24/02/2023	0.412	21.1	7.78	6285.4	6512.0	6438.2	25.03
27/02/2023	0.423	20.6	7.72	6152.3	6413.9	7189.8	22.12
06/03/2023	0.429	20.2	7.80	6132.7	6350.9	6047.4	25.30
15/03/2023	0.424	20.5	7.72	6257.1	6523.8	7308.0	22.08
22/03/2023	0.407	20.4	7.74	6117.7	6369.3	6896.3	22.70

27/03/2023	0.399	20.0	7.70	6178.3	6461.3	7588.7	20.88
03/04/2023	0.400	20.7	7.80	6352.1	6572.7	6224.9	25.73
10/04/2023	0.393	20.9	7.58	6489.8	6883.4	10633.3	16.58
17/04/2023	0.390	21.1	7.75	6345.0	6593.9	7001.1	23.51
24/04/2023	0.393	20.7	7.37	5822.1	6402.9	15340.7	10.80
02/05/2023	0.390	21.1	7.68	6494.1	6799.1	8429.8	20.45
08/05/2023	0.401	20.2	7.72	6486.4	6766.5	7597.4	21.87
16/05/2023	0.431	21.0	7.52	6232.7	6671.0	11793.9	14.62
22/05/2023	0.434	20.8	7.72	6310.7	6580.4	7452.6	22.03
29/05/2023	0.439	20.5	7.75	6312.6	6565.5	6973.0	23.16
05/06/2023	0.434	20.7	7.57	6449.0	6848.8	10726.7	16.27
12/06/2023	0.439	21.1	7.59	6293.0	6660.9	10016.4	17.09
20/06/2023	0.440	21.2	7.70	6312.2	6595.4	7881.2	21.20
26/06/2023	0.439	21.2	7.62	6441.5	6791.3	9592.3	18.18
04/07/2023	0.435	21.2	7.46	6206.5	6705.6	13444.5	13.02
10/07/2023	0.436	21.3	7.43	6192.6	6732.5	14552.3	12.14
17/07/2023	0.437	21.1	7.64	6386.9	6716.0	9033.1	18.97
24/07/2023	0.437	21.5	7.64	6286.9	6610.1	8973.6	19.01
31/07/2023	0.435	21.3	7.66	6282.0	6593.9	8630.8	19.56
07/08/2023	0.428	21.9	7.64	6272.3	6598.0	9140.0	18.85
15/08/2023	0.434	21.3	7.33	6189.7	6874.5	18366.2	9.87
22/08/2023	0.451	21.4	7.73	6057.0	6308.0	7078.3	22.55
29/08/2023	0.441	20.8	7.33	6191.6	6875.0	18069.3	9.89
05/09/2023	0.479	21.5	7.57	6236.6	6618.5	10492.5	16.44
12/09/2023	0.438	21.0	7.30	6176.9	6899.8	19206.8	9.40
19/09/2023	0.404	21.0	7.49	6251.7	6722.9	12650.3	13.77
25/09/2023	0.437	20.9	7.25	6184.0	7001.3	21618.5	8.46
02/10/2023	0.439	21.3	7.49	6258.9	6727.3	12685.9	13.85
09/10/2023	0.384	21.0	7.47	6240.6	6729.4	13103.7	13.32
16/10/2023	0.387	20.7	7.44	6246.1	6780.3	14163.3	12.34
23/10/2023	0.440	21.0	7.48	6219.5	6704.3	12999.1	13.38
30/10/2023	0.447	20.5	7.44	6229.5	6762.4	14044.5	12.34
06/11/2023	0.442	20.8	7.44	6228.9	6754.2	13970.1	12.50
13/11/2023	0.456	19.9	7.44	6195.7	6726.9	13758.7	12.32
20/11/2023	0.481	18.6	7.49	6226.5	6718.8	12300.8	13.22
27/11/2023	0.486	18.1	7.45	6203.5	6741.8	13212.9	12.20
04/12/2023	0.459	19.9	7.55	6187.1	6598.6	10752.4	15.33
11/12/2023	0.463	19.5	7.47	6214.9	6713.4	12785.6	13.05
18/11/2023	0.480	18.6	7.44	6212.4	6755.3	13524.7	12.12
25/11/2023	0.467	19.2	7.58	6054.0	6435.7	9794.6	16.05

D. Physico-chemical and carbonate chemistry parameters from 50m well in METU

Date	Salinity (ppt)	Temperature (°C)	pH (in-situ)	TA (umol/kg)	DIC (umol/kg)	pCO2 (ppm)	Revelle Factor
20/12/2022	0.388	20.0	7.78	5927.7	6147.8	6031.3	24.53
06/01/2023	0.401	19.9	7.64	5791.4	6103.5	8246.7	18.30
10/01/2023	0.395	20.0	7.68	5953.3	6237.2	7588.9	20.22
17/01/2023	0.379	20.5	7.64	6081.4	6401.1	8611.0	18.67
24/01/2023	0.384	20.4	7.84	5982.9	6172.8	5381.4	27.40
27/01/2023	0.377	20.1	7.81	5973.7	6179.5	5711.3	25.89
30/01/2023	0.381	20.5	7.68	5695.7	5967.9	7384.4	20.17
07/02/2023	0.429	18.8	7.71	5642.5	5900.8	6687.7	20.90
14/02/2023	0.320	19.6	7.75	5675.3	5906.2	6190.4	22.90
17/02/2023	0.407	19.4	7.59	5948.3	6310.8	9371.8	16.52
20/02/2023	0.388	20.6	7.46	6091.9	6581.7	12970.6	13.02
24/02/2023	0.392	21.0	7.74	5937.0	6179.8	6779.0	22.78
27/02/2023	0.403	20.4	7.69	5940.3	6216.5	7485.8	20.62
06/03/2023	0.407	20.2	7.61	5928.0	6269.4	9065.5	17.31
15/03/2023	0.252	20.4	7.65	5884.6	6190.9	8231.4	18.83
22/03/2023	0.388	20.0	7.65	6001.3	6309.0	8182.4	19.06
27/03/2023	0.385	19.9	7.44	6057.9	6574.9	13390.6	12.37
03/04/2023	0.384	20.6	7.63	5954.1	6272.6	8593.6	18.41
10/04/2023	0.376	20.8	7.49	6062.3	6514.9	12084.4	13.88
17/04/2023	0.372	20.8	7.62	5881.5	6204.0	8738.3	18.03
24/04/2023	0.378	20.6	7.43	5891.0	6399.7	13443.4	12.24
02/05/2023	0.384	20.7	7.45	6136.8	6644.5	13472.5	12.70
08/05/2023	0.392	20.0	7.53	6135.9	6564.2	11201.2	14.71
16/05/2023	0.421	21.1	7.37	5885.5	6479.6	15868.9	10.69
22/05/2023	0.427	20.7	7.53	5993.6	6403.0	10936.0	14.99
29/05/2023	0.433	20.3	7.57	5986.4	6361.1	9933.7	16.14
05/06/2023	0.197	20.6	7.56	6000.9	6383.0	10209.1	15.91
12/06/2023	0.422	21.1	7.31	5976.7	6656.8	18128.4	9.63
20/06/2023	0.430	20.9	7.54	5914.2	6310.4	10654.5	15.23
26/06/2023	0.433	21.2	7.39	6108.3	6684.0	15446.8	11.34
04/07/2023	0.431	21.1	7.26	5905.5	6668.0	20289.8	8.64
10/07/2023	0.422	21.3	7.26	5859.0	6608.4	20059.1	8.71
17/07/2023	0.434	21.0	7.35	5919.3	6538.3	16475.4	10.37
24/07/2023	0.436	21.0	7.53	5781.8	6179.5	10715.0	14.89
31/07/2023	0.430	21.1	7.32	5918.6	6590.6	17911.0	9.65
07/08/2023	0.423	21.1	7.32	5897.9	6558.1	17602.7	9.77
15/08/2023	0.423	21.5	7.15	5849.3	6811.6	25837.8	7.02
22/08/2023	0.430	20.8	7.53	5754.3	6135.1	10966.1	15.38
29/08/2023	0.426	20.8	7.11	5834.7	6897.9	27962.1	6.45
05/09/2023	0.467	21.5	7.44	5984.9	6485.9	13599.6	12.57
12/09/2023	0.432	20.5	7.08	5813.3	6975.6	30289.1	5.97
19/09/2023	0.381	20.5	7.36	5854.1	6454.8	15767.1	10.54
25/09/2023	0.425	20.8	7.08	5800.7	6952.4	30275.0	6.00
02/10/2023	0.429	20.9	7.33	5861.3	6508.2	17154.3	9.89
09/10/2023	0.380	20.7	7.33	5884.0	6535.0	17161.7	9.87
16/10/2023	0.377	20.7	7.31	5869.7	6548.7	17887.5	9.50
23/10/2023	0.409	21.6	7.27	5891.4	6627.6	19878.6	8.88

30/10/2023	0.435	21.0	7.28	5903.3	6641.0	19581.4	8.88
06/11/2023	0.414	21.3	7.26	5833.0	6584.4	20108.8	8.65
13/11/2023	0.436	20.5	7.27	5835.1	6586.8	19660.2	8.65
20/11/2023	0.452	19.1	7.29	5908.4	6636.5	18290.7	8.99
27/11/2023	0.454	19.5	7.29	5849.8	6572.3	18365.8	8.97
04/12/2023	0.449	20.0	7.34	5864.4	6508.6	16645.9	9.93
11/12/2023	0.442	19.6	7.27	5794.6	6541.0	19019.8	8.65
18/12/2023	0.439	19.8	7.24	5787.6	6579.9	20289.9	8.21
25/12/2023	0.433	19.4	7.35	5588.4	6192.3	15336.7	10.08

E. Physico-chemical and carbonate chemistry parameters from Lamas River

Date	Salinity (ppt)	Temperature (°C)	pH (in-situ)	TA (umol/kg)	DIC (umol/kg)	pCO2 (ppm)	Revelle Factor
23/12/2022	0.242	14.8	7.99	3918.3	4007.6	2275.0	33.85
29/12/2022	0.228	16.0	7.85	4042.0	4177.2	3328.9	26.50
06/01/2023	0.236	15.4	8.15	4062.6	4114.7	1653.9	42.99
10/01/2023	0.239	13.9	7.91	3790.5	3904.3	2662.2	28.63
17/01/2023	0.216	15.3	7.98	3696.5	3784.5	2254.5	33.00
24/01/2023	0.234	14.6	8.05	3924.9	4001.4	2019.8	36.71
27/01/2023	0.237	14.5	8.06	3889.8	3961.8	1925.0	37.61
30/01/2023	0.231	15.4	8.00	3900.5	3987.4	2271.2	34.22
08/02/2023	0.352	12.5	8.02	3804.7	3889.7	2017.5	34.35
14/02/2023	0.339	13.0	8.03	3585.5	3662.3	1874.1	35.09
17/02/2023	0.241	13.8	7.91	3659.3	3768.3	2543.4	28.79
20/02/2023	0.204	15.5	7.82	3822.0	3963.7	3386.3	24.62
27/02/2023	0.224	17.6	7.97	3872.6	3960.3	2447.2	33.78
06/03/2023	0.219	18.1	8.11	3830.3	3882.3	1756.0	41.90
22/03/2023	0.204	17.9	7.99	3778.0	3858.2	2298.6	34.92
27/03/2023	0.199	18.7	8.02	3779.1	3851.7	2196.2	36.59
03/04/2023	0.199	20.3	8.12	3878.9	3926.9	1813.5	42.73
10/04/2023	0.202	20.7	7.69	4104.2	4292.4	5156.1	20.82
17/04/2023	0.189	20.5	7.99	3746.2	3820.2	2344.5	35.97
24/04/2023	0.185	22.0	7.84	3607.8	3718.6	3312.9	27.87
02/05/2023	0.191	21.2	7.74	3687.3	3834.4	4145.9	23.17
16/05/2023	0.192	24.1	7.87	3678.0	3776.2	3200.2	30.35
22/05/2023	0.205	22.1	7.98	3705.9	3780.0	2455.8	35.59
29/05/2023	0.171	21.0	8.08	3844.2	3897.9	1962.3	41.14
05/06/2023	0.202	23.3	7.82	3693.9	3810.6	3603.7	27.31
12/06/2023	0.217	22.7	7.75	3821.6	3967.1	4302.3	23.96
20/06/2023	0.197	25.3	7.96	4111.2	4192.4	2961.1	35.54
26/06/2023	0.200	25.8	8.03	3922.4	3982.1	2424.7	39.37
10/07/2023	0.206	23.9	7.88	3770.6	3870.6	3247.2	30.48
17/07/2023	0.198	25.7	7.87	3736.1	3833.8	3344.7	30.63
24/07/2023	0.247	21.6	7.92	4445.8	4554.7	3364.8	32.12
31/07/2023	0.192	26.4	7.83	3699.3	3805.7	3643.8	28.85
15/08/2023	0.233	23.3	7.90	4266.4	4373.7	3464.0	31.51
22/08/2023	0.228	22.0	7.91	3571.4	3661.4	2798.6	31.51
29/08/2023	0.220	20.9	7.88	3928.0	4036.8	3211.8	29.84

12/09/2023	0.186	28.3	7.94	3697.5	3770.5	2894.2	35.20
19/09/2023	0.144	27.6	7.85	3665.9	3763.7	3512.6	30.13
26/09/2023	0.224	26.7	7.87	3848.6	3948.0	3508.6	30.78
02/10/2023	0.214	23.5	7.95	3757.8	3838.4	2724.7	34.30
09/10/2023	0.261	17.7	7.88	4360.7	4488.5	3384.7	28.97
16/10/2023	0.193	21.4	7.97	3805.6	3886.2	2570.5	34.70
23/10/2023	0.229	20.5	7.87	3929.6	4044.3	3311.6	28.89
30/10/2023	0.230	18.5	7.84	4215.3	4352.6	3664.7	26.94
06/11/2023	0.272	17.0	7.70	4211.1	4415.4	4984.1	19.97
13/11/2023	0.282	15.7	7.83	4279.8	4433.1	3702.4	25.26
20/11/2023	0.321	16.2	7.94	4818.1	4942.0	3210.7	31.53
27/11/2023	0.334	14.8	7.90	4694.8	4837.1	3420.8	28.44
04/12/2023	0.276	16.6	7.76	4250.1	4428.4	4350.9	22.41
11/12/2023	0.297	15.3	7.84	4215.7	4361.1	3484.6	25.97
18/12/2023	0.289	15.5	7.83	4413.1	4572.5	3820.5	25.12
25/12/2023	0.273	15.5	7.92	4228.7	4345.3	2915.1	30.21

F. Physico-chemical and carbonate chemistry parameters of spatial sampling points

Station	Type	Period	Salinity (ppt)	Temperature (°C)	pH (in-situ)	TA (umol/kg)	DIC (umol/kg)	pCO ₂ (ppm)	Revelle Factor (RF)
Anamur	well	April	0.39	19.0	7.70	5958.2	6238.0	7271.5	20.48
Anamur	river	April	0.14	16.0	8.14	2753.4	2789.6	1162.5	42.38
Asi	river	April	0.44	21.3	8.25	5083.0	5108.7	1752.4	48.69
Berdan	river	April	0.23	19.9	7.90	3437.0	3528.9	2651.7	30.53
Boğsak	well	April	1.24	18.0	8.07	7510.4	7630.6	3773.6	39.82
Ceyhan	river	April	0.29	18.6	8.13	4620.8	4677.4	2034.5	43.18
Deliçay (Hatay)	river	April	0.26	17.7	8.34	3392.3	3400.9	922.7	50.38
Deliçay (Mersin)	river	April	0.53	21.4	8.34	3935.3	3939.0	1115.5	50.12
Dört Yol	well	April	0.53	19.9	7.97	8570.9	8755.8	5593.4	34.68
Gilindire	well	April	1.78	21.6	8.03	2759.2	2805.2	1600.8	38.36

Göksu	river	April	1.11	19.5	8.04	3611.4	3672.6	1980.4	38.52
Göksu-1	well	April	0.44	20.7	7.78	8425.6	8732.0	8591.4	24.90
Göksu-2	well	April	0.24	20.4	7.97	3720.9	3800.6	2461.9	34.55
Lamas	river	April	0.18	22.0	7.84	3607.8	3718.6	3312.9	27.87
Samandağ	well	April	1.29	19.7	7.85	12205.0	12583.4	10533.8	27.92
Seyhan	river	April	0.27	21.0	7.87	3651.2	3754.2	3036.3	29.50
SK5	well	April	0.31	21.4	7.64	5552.9	5844.0	8050.8	18.70
SK50	well	April	0.38	20.6	7.43	5891.0	6399.7	13443.4	12.24
Tarsus	well	April	1.11	19.6	7.86	5538.1	5705.7	4730.9	28.30
Anamur	well	September	0.43	25.4	7.42	6167.6	6682.8	15570.1	12.58
Anamur	river	September	0.26	27.6	8.08	2914.8	2948.2	1640.7	41.98
Asi	river	September	0.55	24.0	8.00	5762.0	5863.6	3695.3	37.65
Berdan	river	September	0.64	22.0	7.79	3558.4	3682.7	3645.1	25.51
Boğsak	well	September	3.59	25.9	7.41	7530.3	8166.8	19488.3	12.46
Ceyhan	river	September	0.36	24.0	7.88	4777.6	4901.9	4059.9	30.89
Deliçay (Hatay)	river	September	dried out						
Deliçay (Mersin)	river	September	0.42	24.1	7.88	4239.5	4350.4	3629.5	30.75
Dört Yol	well	September	0.64	22.0	7.77	8581.2	8894.1	9106.7	24.82
Gilindire	well	September	2.21	23.2	7.91	3494.1	3579.3	2763.3	32.03
Göksu	river	September	0.15	24.5	7.99	3817.4	3886.5	2535.7	36.98
Göksu-1	well	September	0.50	22.5	7.74	8326.2	8656.5	9653.8	23.31
Göksu-2	well	September	0.25	22.0	7.87	3690.7	3794.5	3153.0	29.51
Lamas	river	September	0.19	28.3	7.94	3697.5	3770.5	2894.2	35.20
Samandağ	well	September	1.12	22.0	7.73	12361.5	12862.4	14396.0	22.96

Seyhan	river	September	0.35	24.0	7.76	3946.0	4090.8	4460.7	24.58
SK5	well	September	0.38	23.5	7.60	5426.2	5726.7	8783.1	17.86
SK50	well	September	0.47	21.5	7.44	5984.9	6485.9	13599.6	12.57
Tarsus	well	September	1.18	21.0	7.74	5738.3	5970.0	6476.4	23.01

G. Photos from sampling



Photo 1. Anamur Well (left- wet season)



Photo 2. Anamur River



Photo 3. Gilindire Cave



Photo 4. Boğsak Well



Photo 5. Göksu-2 Well



Photo 6. Göksu-1 Well



Photo 7. Göksu River



Photo 8. Deliçay (Mersin) River



Photo 9. Tarsus Well



Photo 10. Berdan River (left-wet season)



Photo 11. Seyhan River



Photo 12. Ceyhan River



Photo 13. Deliçay (Hatay) River. (left-wet season. Note that in the right-dry season the river dried out)



Photo 14. Asi River (left- wet season)



Photo 15. Samandağ Well



Photo 16. Lamas River



Photo 17. METU- 50m Well (SK50)