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Geochemical characterization of coastal sediments: a preliminary study of seasonal variations at Lido degli Estensi (Ferrara, Italy)

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SUPPLEMENTARY MATERIALS

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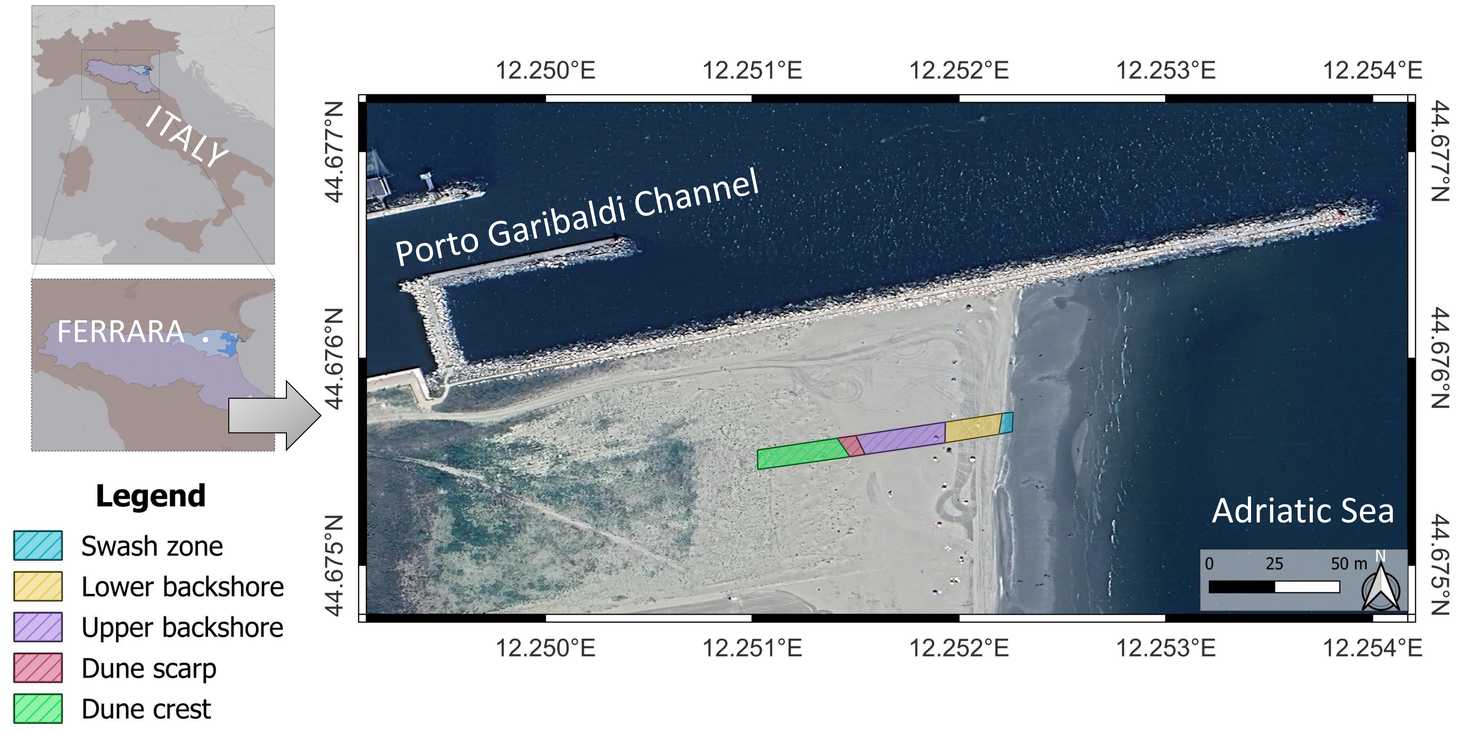
1. INTRODUCTION

- This preliminary study focuses on the seasonal and cross-shore characterization of sediments at Lido degli Estensi (Ferrara, Italy). The aim is to identify potential vulnerabilities and/or critical aspects related to environmental pollution that require further investigation
- The selected site is one of the few area on the Ferrara coastline not subject to coastal erosion; instead, it experiences accretion due to the construction of jetties at the mouth of the Porto Garibaldi navigable channel (Comacchio, Ferrara). These jetties trap sediments transported from the south as a result of longshore drift
- A cross-shore beach profile was seasonally assessed over a one-year monitoring period and was divided into five zones based on local geomorphological conditions and slope gradients (Marshak, 2015): swash zone (**SZ**), lower backshore (**LB**), upper backshore (**UB**), dune scarp (**DS**), and dune crest (**DC**)
- The characterization includes the evaluation of carbonate content, the composition of major oxides, and heavy metal concentrations across the different seasons, utilizing eight sampling points per season



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2. MATERIALS AND METHODS

- Sampling activities were carried out between Summer 2023 and Spring 2024
- Depending on the cross-shore extension of each beach zone, the following number of samples were collected: **SZ** - 1 sample; **LB** - 2 samples; **UB** - 2 samples; **DS** - 1 sample; **DC** - 2 samples. Where two samples per zone were collected, the results represent their average values
- Surface sediment collection was performed concurrently with sampling for microplastic extraction. For this purpose, 500 ml of sediment were collected using a metal scoop and stored in appropriately labeled glass jars
- In the laboratory, each sample was quartered and further subdivided into subsamples allocated for geochemical analysis, microplastic extraction, and textural analyses
- Based on the methodology outlined by Aquilano et al. (2023), the subsamples intended for geochemical analysis were dried and ground to a fine, homogeneous powder. This preparation enabled the determination of:
  - Carbonate content, through **calcimetric analysis** using an electronic calcimeter
  - The composition of major oxides and heavy metal (**HM**), using Wavelength Dispersive X-ray Fluorescence (**WD-XRF**) spectrometry
- To assess the quality of the collected sediments, our data were compared with background (**BG**) data (Migani, 2012) and the following indices were applied:
  - Enrichment Factor (**EF -** Reimann and De Caritat, 2005)
  - Geoaccumulation Index (**Igeo -** Buccolieri et al., 2006)
  - Contamination Factor (**CF -** Loska et al., 2004)
  - Pollution Load Index (**PLI -** Ferreira et al., 2022)

$$EF = \frac{\left(\frac{C_i}{C_{ie}}\right)_s}{\left(\frac{C_i}{C_{ie}}\right)_{rs}}$$

$$Igeo = log_2\left[\frac{C_i}{(1.5\ C_{ri})}\right]$$

$$CF = \frac{C_i}{C_{ri}}$$

$$PLI = (CF_1 \times CF_2 \times CF_3)^{1/n}$$

- Finally, HM concentrations detected in the samples were compared with the limits established by current Italian legislation - DL 152/06

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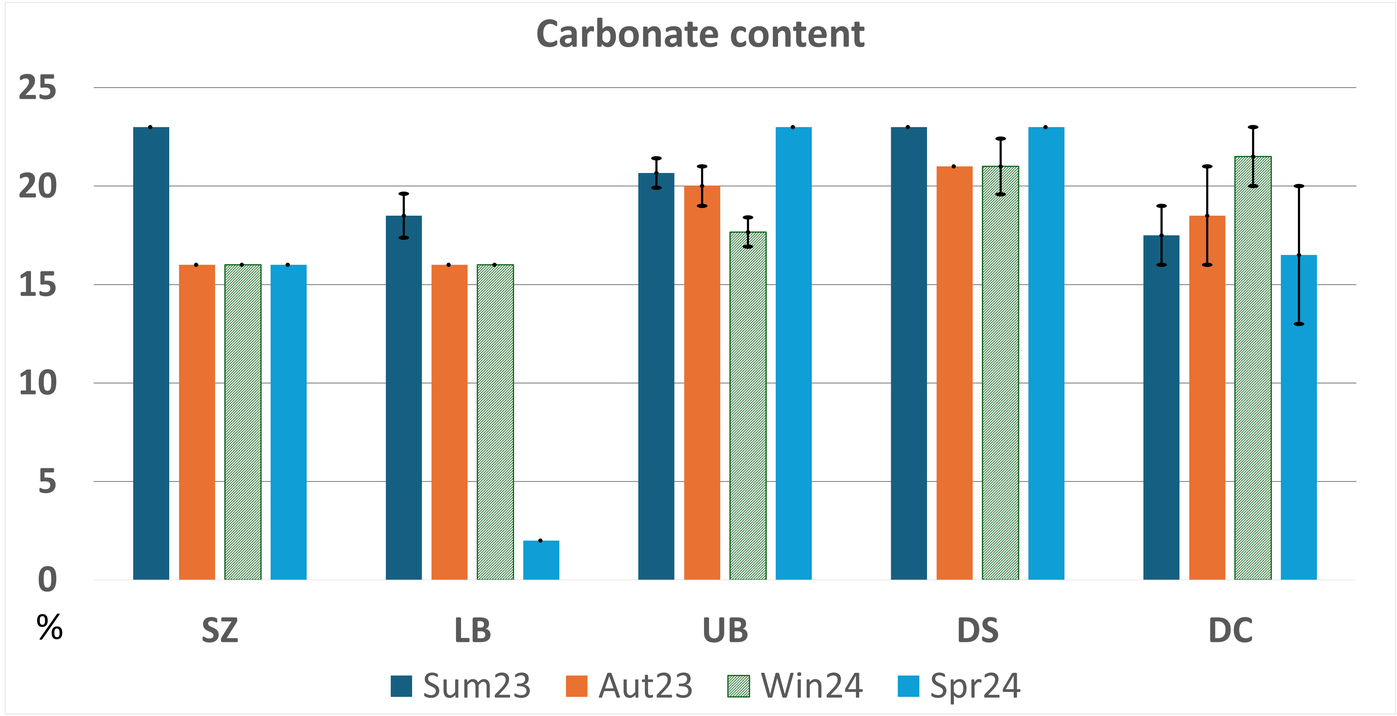
3.A RESULTS - Carbonate content

- Carbonate content in sediments is consistently below 25% across all seasons and geomorphological zones
- Calcite was the dominant carbonate phase, with no dolomite detected
- The swash zone (**SZ**) and lower backshore (**LB**), characterized by higher hydrodynamic energy, exhibit specific carbonate trends:
  - The carbonate peak observed in the **SZ** during summer 2023 (Sum23) is likely attributed to the deposition of calcareous shells, leading to carbonate precipitation in this area
  - The reduced carbonate content in the **LB** during spring 2024 (Spr24) coincides with beach cleaning activities involving heavy machinery, indicating a disturbed environment
- The upper backshore (**UB**), dune scarp (**DS**), and dune crest (**DC**), primarily influenced by wind dynamics, show seasonal variations in carbonate content that align with expected sediment transport and mobilization patterns



SZ - swash zone | LB - lower backshore | UB - upper backshore | DS - dune scarp | DC - dune crest

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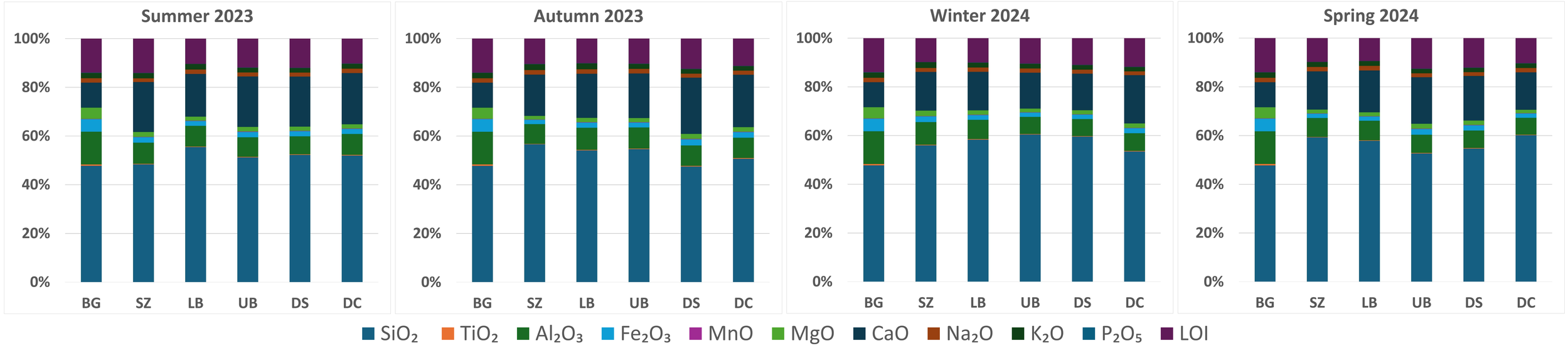
3.B RESULTS - Major oxides composition

- Compared to background (BG) values, the percentage composition of major oxides exhibits variable proportions, yet maintains a similar trend across all geomorphological zones throughout the different seasons
- The analyzed sediments are primarily composed of SiO_2 (54.8 ± 3.7 wt%), CaO (18.3 ± 2.4 wt%), and Al_2O_3 (8.0 ± 0.7 wt%)
- Minor oxides include Fe_2O_3 and K_2O (totaling 4.0 ± 0.4 wt%), MgO and Na_2O (totaling 3.5 ± 0.3 wt%), and TiO_2, MnO, and P_2O_5 (totaling 0.4 ± 0.0 wt%)
- The percentage content of volatile compounds, determined by Loss on Ignition (LOI) analysis, is 11.0 ± 1.2 wt%



BG – background level | SZ - swash zone | LB - lower backshore | UB - upper backshore | DS - dune scarp | DC - dune crest

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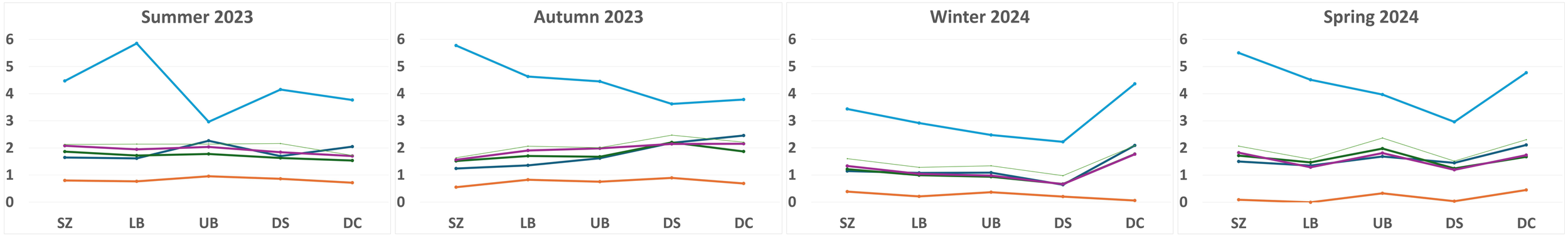
3.C RESULTS - Pollution indexes - Enrichment Factor (EF)

- For this preliminary study, the analyzed heavy metals (HMs) included Cr, Cu, Ni, Pb, V, and Zn, which were normalized against Sc as immobile element in the reference sample; as background values (Migani, 2012) the same elements were used for comparison



SZ - swash zone | LB - lower backshore | UB - upper backshore | DS - dune scarp | DC - dune crest

- Mean EF values for Cr, Cu, Ni, V, and Zn are generally < 2, indicating "**depletion to mineral enrichment**"; exceptions where sediments fall into the "**moderate enrichment**" category [EF values from 2 to 5] include:
  - Cr: UB (summer), DS (autumn), DC (all seasons) [EF from 2.05 to 2.46]
  - Ni: DS (autumn) [EF= 2.20]
  - V: SZ and UB (summer), DS and DC (autumn) [EF from 2.04 to 2.15]
  - Zn: Exhibits the most seasonal variation, with "moderate enrichment" in SZ, LB, UB, and DS during the summer [EF from 2.13 to 2.16]; LB, UB, DS, and DC during the autumn [EF from 2.01 to 2.47]; DC during the winter [EF= 2.08]; SZ, UB, DC during the spring [EF from 2.07 to 2.37]
- Pb shows the highest EF values, generally indicating "moderate enrichment" [EF from 2.22 to 4.47] across all zones, with rare "significant enrichment" in LB during the summer [EF=5.86] and SZ during autumn and spring [EF= 5.77 and 5.50, respectively]

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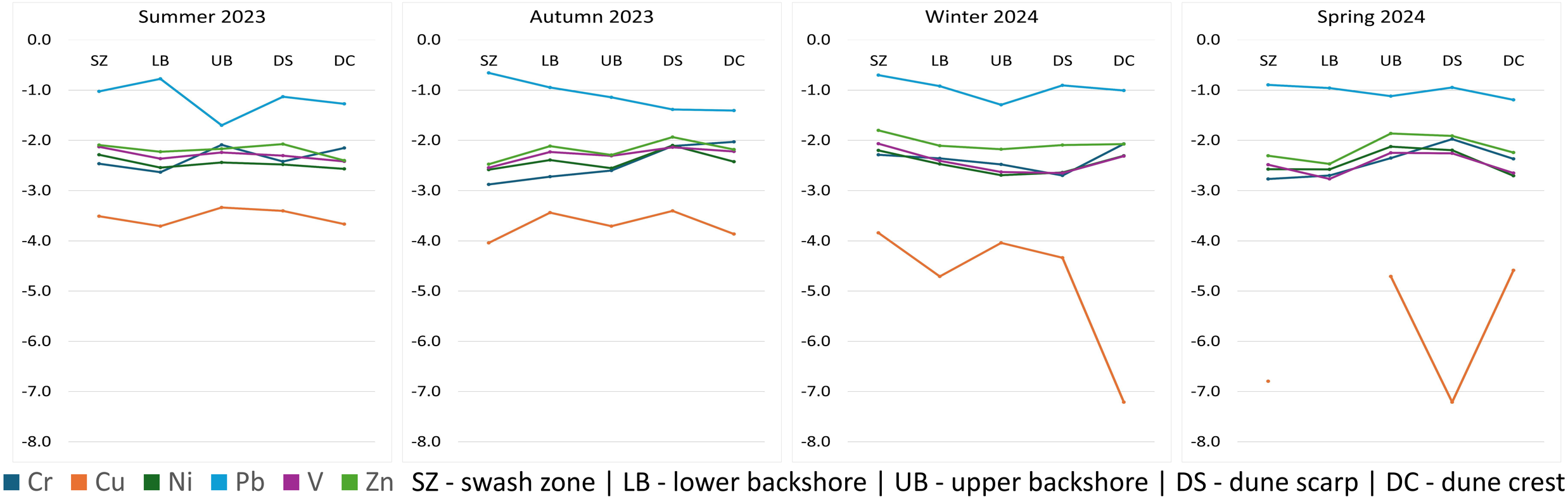
3.D RESULTS - Pollution indexes - Geoaccumulation Index (Igeo)

- For this preliminary study, the analyzed heavy metals (HMs) included Cr, Cu, Ni, Pb, V, and Zn; as background values (Migani, 2012) the same elements were used for comparison



- Regarding the geoaccumulation index, all sediments investigated in each seasons and zones fall into the "**unpolluted**" category [Igeo value ≤0] for all investigated elements

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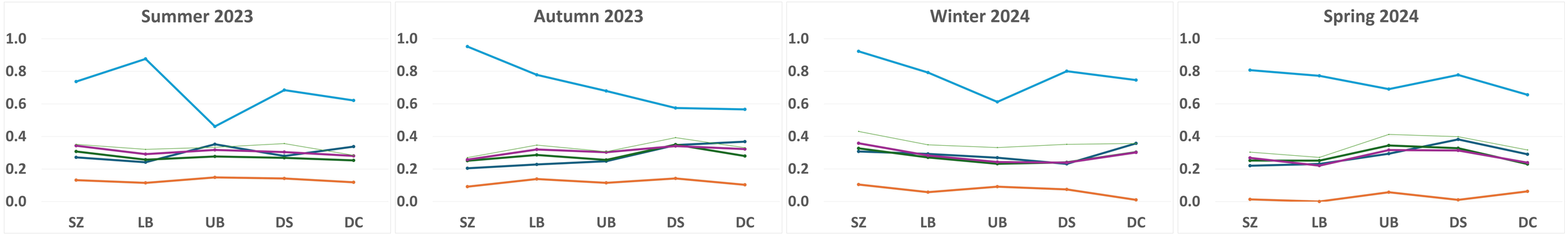
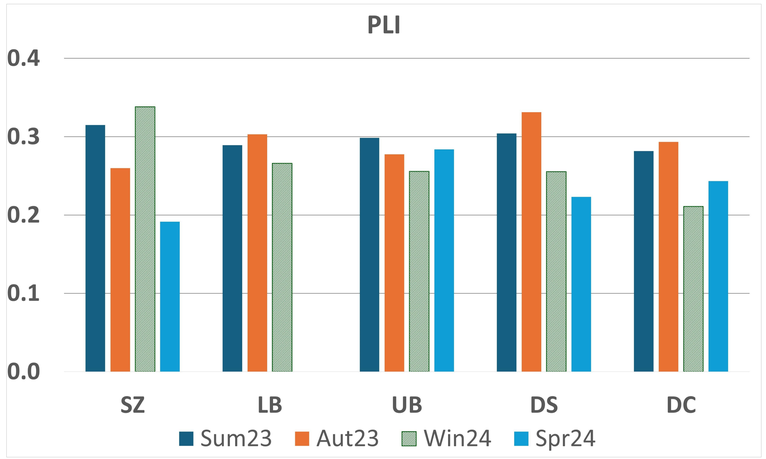
3.E RESULTS - Pollution indexes - Contamination Factor (CF) and Pollution Load Index (PLI)



SZ - swash zone | LB - lower backshore | UB - upper backshore | DS - dune scarp | DC - dune crest



- Regarding the contamination factor, all sediments investigated in each seasons and zones fall into the "**low contamination**" category [CF value <1] for all investigated elements
- Similarly, in terms of pollution load index, all sediments investigated for each zone and season can be classified as "**not polluted**" [PLI value <1]

3.F RESULTS - Limit values comparison (DL 152/06)

- HM concentrations in the examined coastal sediments were compared to the threshold contamination levels for sediments in public, private, and residential green areas, as defined by the Italian DL 152/06. This comparison revealed that HM concentrations were significantly **below the legal limits**, indicating good sediment quality at the time of sampling

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4. CONCLUSION

- This preliminary study of Lido degli Estensi sediments, a significant tourist area, reveals generally good sediment quality across the investigated cross-shore profile at the sampling time
- Carbonate content remained consistently low (<25%) across all zones and seasons, dominated by calcite
- The major oxide composition was relatively stable, with SiO_2, CaO, and Al_2O_3 as the dominant constituents, showing similar trends across the geomorphological zones
- While Enrichment Factor analysis indicates some seasonal and localized moderate enrichment for specific metals (Cr, Ni, V, Zn), the distinct enrichment pattern of Pb, particularly during summer, suggests a need for continued monitoring and source identification, potentially linked to specific cross-shore dynamics
- Overall sediment quality, as assessed by Igeo, CF, and PLI, consistently suggests an unpolluted status
- Importantly, heavy metal concentrations remain significantly below Italian legal limits (DL 152/06), confirming the good quality of sediments in this area
- Future research should focus on the identified localized enrichments, their potential sources in relation to sediment composition and transport processes, as well as the ongoing monitoring of this dynamic coastal environment.

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6. ACKNOWLEDGMENTS

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