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Seasonal changes of chemical contamination in coastal waters during sediment resuspension

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Abstract

The potential of remobilization of pollutants is a major problem for anthropogenic ecosystems, because even when the anthropogenic source of pollution is identified and removed, pollutants stored in sediments can be released into the water column and impact pelagic communities during sediment resuspension provoked by dredging, storms or bottom trawling. The objectives of the present study were to assess the changes observed in the chemical composition of the water column following resuspension of a polluted marine sediment and the consequences for the chemical composition of adjacent marine waters according to season. For that purpose, an experimental sediment resuspension protocol was performed on four distinct occasions, spring, summer, fall and winter, and the changes in nutrients, organic contaminants and inorganic contaminants were measured after mixing sediment elutriate with lagoon waters and offshore waters sampled nearby. Significant seasonal variations in the chemical composition of the contaminated sediments were observed, with a strong accumulation of PAHs in fall, whereas minimum PAH concentrations were observed during winter. In all seasons, sediment resuspension provoked a significant enrichment in nutrients, dissolved organic carbon, and trace metal elements like Ni, Cu, and Zn in offshore waters and lagoon waters, with enrichment factors that were season and site dependent. The most pronounced changes were observed for offshore waters, especially in spring and winter, whereas the chemical composition of lagoon waters was weakly impacted by the compounds supplied by sediment resuspension.

Keywords

Lagoon, offshore, trace metal elements, pesticides, PAHs, enrichment factor, elutriate

1 Introduction

It is now well recognized that the risk of environmental contamination by chemical pollutants is particularly high in coastal environments (Schwarzenbach et al., 2006;

Simonich and Hites, 1995), where past, present, and forecasted demographic increases (James, 2002; Small and Nicholls, 2003) are amplifying the pressures on these ecosystems. In coastal zones, organic contaminants (polycyclic aromatic hydrocarbons PAHs, pesticides, organic-metals) and inorganic (trace elements) accumulate in sediments (Baumard et al., 1999). The sediment becomes such an important place for storage of pollutants. However, this storage is not definitive: pollutants can be released into the water column during a resuspension of sediments. This potential of remobilization of pollutants is a major problem for anthropogenic ecosystems (Schafer et al., 2006), because even when the anthropogenic source of pollution is identified and removed, pollutants stored in sediments can be released into the water column and impact pelagic communities. The potential for remobilization of pollutants depends on sediment characteristics (granulometry, organic matter, pH, etc.), the type of contaminants, and the height of the water column (Eggleton and Thomas, 2004). In shallow environments, where the average depth does not exceed a few meters, conditions favor the resuspension of sediments with their trail of chemical pollutants and nutrients, especially during strong gales.

In coastal environments, sediment contamination can be impacted by the temporal variations of anthropogenic activities as well as by the seasonal fluctuations of riverine water discharges. Consequently, temporal variations of sediment contamination can be observed for organic contaminants in marine coastal ecosystems such as pesticides (Li et al., 2014; Tham et al., 2019) or PAHs (Gdara et al., 2017; Guigue et al., 2014) as well as for inorganic compounds such as metals (Khaled-Khodja et al., 2018; Najamuddin et al., 2016) or nutrients (Clavero et al., 2000; Yasui et al., 2016). In shallow environments, these temporal variations can have a significant impact on the composition of the overlying water during a sediment resuspension event following a storm or a strong wind gust event. Changes in the water composition upon sediment resuspension can severely impact the functioning of the ecosystem by impacting the primary productivity (Schallenberg and Burns, 2004) as well as the planktonic diversity (Garstecki et al., 2002). Most of the studies on the consequences of a sediment resuspension event have focused on the nutrient water composition after sediment resuspension. Nutrient fluxes in the water column strongly depend on the seasonal dependent vegetal cover (Hasegawa et al., 2008; Horppila and Nurminen, 2005)

and on the seasonal changes of nutrient sediment concentration (Cabrita and Brotas, 2000; Clavero et al., 2000; Smith et al., 2011). In contrast, although the water changes observed for organic or inorganic contaminants after sediment resuspension and their possible ecological effects are relatively well documented (Roberts, 2012), the seasonal variations observed in the sediment composition is rarely taken into account in ecotoxicology studies.

The objectives of the present study were to assess the possible seasonal changes observed in the water column chemical composition following resuspension of a polluted marine sediment and the consequences for the chemical composition of adjacent marine waters. For that purpose, an experimental sediment resuspension protocol was performed on four distinct occasions (spring, summer, fall and winter) and the changes in nutrients, organic contaminants, and inorganic contaminants were measured after mixing sediment elutriate with lagoon and offshore waters sampled nearby.

2 Materials and Methods

2.1 Study sites and sampling

The study was conducted in southwestern Mediterranean ecosystems, the lagoon and the bay of Bizerte (Fig. 1), during the four seasons, spring (April 2014), winter (February 2015), fall (November 2015) and summer (July 2016). Like most of the Mediterranean coastal lagoons, the Bizerte lagoon (Lagoon station) in the North of Tunisia is a polluted coastal ecosystem subject to intense agriculture, urbanization, and industrialization pressures, as well as pressures from naval and commercial shipping harbors. Consequently, sediments are strongly contaminated by a wide range of pollutants, including organic contaminants (PAHs, pesticides, and herbicides) and metals (Barhoumi et al., 2014a, 2014b; Yoshida et al., 2002). The Bizerte bay is less contaminated than the lagoon, although local PAHs contamination has been recorded in the effluent from the oil refinery located on the shore of the bay (Mhadhbi et al., 2019; Zrafi-Nouira et al., 2009, 2008). The sampling was carried out in an offshore station (station O, 37°16'46.46"N 9°53'50.98"E) and a lagoon station (station L 37°12'43.96"N 9°50'79.78"E) (Fig. 1). Water samples were collected from 2 m depth. More details of the sampling procedure can be found in Pringault et al. (2016).

Contaminated water was obtained from polluted sediment resuspension following the protocol described by Bonnet et al. (Bonnet et al., 2000). This protocol, recommended by the Environmental Protection Agency (US EPA), has been successfully used to characterize the contamination level and toxicity of sediments using non-adapted species (Bonnet et al., 2000; Carr and Chapman, 1995). Polluted sediment was sampled in front of a cement factory in the lagoon channel (station C, 37°15'40.22"N 9°51'30.49"E Fig. 1) using a Van Veen grab. On the same day of sediment sampling, channel water was also sampled in the same station following the sampling procedure used for the lagoon and offshore water sampling. This area is among the most polluted sites in the Bizerte lagoon (Ben Said et al., 2010; Yoshida et al., 2002), and according to the water circulation and the wind regime (Harzallah, 2003), contaminants released by sediment resuspension following strong gusts or stormy events can affect the pelagic communities both in the lagoon and offshore stations.

2.2 Sediment resuspension

Directly after sampling, sediment was sieved (2 mm mesh) to remove large particles (mainly solid wastes) and stored in a cool box until its return to the laboratory. In the laboratory, sediment was mixed with channel water (1:4 w/v ratio) and sediment was gently stirred for 8 h. After a 12 h settling period, the overlying solution, labeled thereafter as elutriate, was gently siphoned off and a part of it was stored in the dark at 4 °C until chemical analysis. Elutriate was then mixed with offshore and lagoon waters (1:4 v/v) and concentrations of nutrients, dissolved organic carbon (DOC), (organo-)metals, PAHs and pesticides were measured after mixing in order to calculate the enrichment factor (EF) according to the following equation:

$$"EF"=C_{\text{mix}}/C_{\text{(in situ)}}$$

where C_{mix} corresponds to the concentration after mixing and $C_{\text{(in situ)}}$ to the concentration measured in situ in the offshore or lagoon waters.

2.3 Organic compound and metallic compound analysis

2.3.1 Pesticides analysis

Water samples (2 L) were extracted using the solid phase extraction (SPE) procedure HLB cartridges. Prior to extraction, each sample was fortified with 50 ng of atrazine-d5 (50 µl of

atrazine-d5 at 1 mg.L⁻¹ in Acetonitrile). Analytes were recovered by eluting the cartridges with 8 mL of acetonitrile at a flow rate of 3 mL min⁻¹. The sample volume was reduced to 1.5 mL under a gentle stream of nitrogen. All sample extracts were spiked before analysis with 120 µL of the deuterated internal standard simazine-d10 (1.2 mg L⁻¹) and analyzed by high performance liquid chromatography – tandem mass spectrometry (HPLC-MS/MS) in triplicate.

Air-dried sediments were homogenized and passed through a 200 µm stainless steel sieve following the procedure of Nesor et al. (2012), then extracted with an accelerated solvent extractor (ASE 350 Dionex, France). The internal standard (50 µl of atrazine-d5 at 1 mg.L⁻¹ in Acetonitrile) is added to sediment sample. The ASE extraction was carried out for 15 min with a solvent mixture (hexane/acetone, 50/50) at 120 °C and 1500 psi of nitrogen. After extraction, the extract was cleaned on a Strata SAX (8B-S008-JCH). All sample extracts were spiked before analysis with 120 µL of the deuterated internal standard simazine-d10 (1.2 mg L⁻¹) and analyzed by HPLC-MS/MS.

Pesticide analyses were performed by HPLC-MS/MS using an Alliance HPLC system (Waters Series 2695). Analytic separation was achieved with a Kinetex C18 analytical column (100 mm*4.6 I.D*260Å, Phenomenex). A triple quadrupole mass spectrometer (Micromass Quatro micro™, Waters) equipped with an electrospray ionization source (ESI) was used as the detector. The spectrometer was operated in positive ESI mode. Acquisition for each compound was performed in the multiple reaction-monitoring mode (MRM). Two transitions were retained; one was used for quantization and the other one was used for the confirmation.

2.3.2 PAHs analysis

PAHs analysis was adapted from the analytical protocol described by Barhoumi et al. (2014a). An accelerated solvent extractor (ASE 350 Dionex, France) with 22 mL extraction cells was used to perform the extraction of samples. ASE was carried out for 15 min with a solvent mixture (hexane/acetone, 50/50) at 120 °C and 1500 psi of nitrogen. After extraction, the extract was cleaned on a Strata Florisil (FL-PR, 32138). Purified extracts were analyzed on a GC-MS (Varian 450-GC and Varian 240 MS) working in the electron impact mode at 70 eV. A DB-5ms (Agilent) chromatographic column (30m, 0.25mm ID and 0.25µm of film

thickness) was used. Acquisition was carried out in the single ion monitoring (SIM) using characteristic ions for each target analyte. Internal standard calibration was performed with Acenaphthylene-D8, Acenaphthene-D10, Naphthalene-D8, Fluoranthene-D10, and Phenanthrene-D10. The whole procedure (extraction, clean up, and GC/MS analysis) was validated using a certified sediment RTC-CRM104-050 (LGC).

2.3.3 Metals and organotin analysis

Samples for trace element analyses were filtered through 0.22 µm acetate cellulose filters and preserved by acidification to 1‰ with nitric acid (Merck Suprapur). Trace element concentrations were measured using inductively coupled plasma mass spectrometry (ICP-MS-Q, iCAP-Q, Thermo Fisher Scientific®) equipped with a high matrix interface. In and Bi were used as internal standards to correct for changes in peak intensities due to instrumental drift. The accuracy and the precision of the methods have been tested using a seawater standard CASS-5 and NASS-6 certified by the Canadian National Research Council (CNRC). Measured concentrations for certified elements (Co, Ni, Cu, Zn, and Cd) agreed with recommended values, ±10%.

For analysis of organotin compounds, the butyl- and methyltin species (monobutyltin (MBT), dibutyltin (DBT) and tributyltin (TBT), monomethyltin (MMT), dimethyltin (DMT), and trimethyltin (TMT)) concentrations were measured using a gas chromatograph (Focus GC Thermo Fisher Scientific®) coupled with an inductively coupled plasma mass spectrometer (ICP-MS X Series II-Thermo Fisher Scientific®).

Previously, sediments were gently extracted using glacial acetic acid under agitation for one night and alkylation of water samples or acidic extracts of sediment samples was then performed. Quantification was done by standard additions. The accuracy of this methodology was evaluated by analysis of the sediment standard reference material, PACS-2 (National Research Council, Canada).

Based on trace metal elements and PAH concentrations, the potential toxicity of the Bizerte channel sediment was assessed according to sediment quality guidelines (Buhman, 2008; Long et al., 1995). The threshold effect level (TEL) represents the concentration below which adverse biological effects are expected to occur rarely. The probable effect level (PEL) defines the level above which adverse effects are expected to occur frequently (Buhman,

2008). The effects range-low (ERL), indicates the concentration below which adverse effects rarely occur, while the effects range-median (ERM) represents the concentration above which effects frequently occur (Long et al., 1995).

2.3.4 Nutrient and dissolved organic carbon

Samples for nutrient analyses were collected using 100 mL polyethylene flasks, filtered (0.2 μ m), and stored at -20 °C until treatment. Ammonium concentrations were measured using the method of Holmes et al. (Holmes et al., 1999) with a detection limit of 5 nM. NO₃⁻ + NO₂⁻, PO₄³⁻, and Si(OH)₄ concentrations were determined on a Bran Luebbe Autoanalyzer III according to Raimbault et al. (Raimbault et al., 1990) and Grasshoff et al. (Grasshoff et al., 1983). Dissolved organic carbon concentration (DOC) was determined from 30 mL filtered (Whatman GF/F) samples collected in pre-combusted (450 °C, overnight) amber glass tubes, sealed with a Teflon lined cap, and preserved with 36 μ L of 85% phosphoric acid (H₃PO₄). Samples were stored at ambient temperature in the dark until measurement. DOC concentration was measured using a Shimadzu TOC VCPH analyzer.

2.4 Statistical analysis

Differences in the chemical environment between stations were estimated by principal component analysis (PCA) with MVSP v3.12d software (Kovach Computing Service, Anglesey Wales). One-way analysis of variance (ANOVA) was performed to test the null hypothesis that there was no significant difference between concentrations measured in situ and those measured after mixing with elutriate. When these conditions were not met, differences between concentrations were tested using the non-parametric Kruskal-Wallis ANOVA test. Posteriori paired multiple-comparisons were then performed using the Tukey HSD test. ANOVA tests and Tukey's HSD tests were carried out with the level of significance set at $p < 0.05$

3 Results and discussion

3.1 In situ conditions according to seasons

Physico-chemical conditions in lagoon and offshore waters strongly varied according to season and stations. The lagoon exhibited the highest concentrations in nutrients with

maximum values observed during spring for ammonium ($15.3 \mu\text{M} \pm 2.4$) and fall for silicates ($11.20 \mu\text{M} \pm 0.6$). Nutrient concentrations and temporal dynamics were comparable to what have been observed previously in the Bizerte lagoon (Pringault et al., 2016; Salhi et al., 2018) and in similar Mediterranean ecosystems (Bec et al., 2005; Solidoro et al., 2004). Pesticide concentrations were, as a general rule, more important in the lagoon rather than in the offshore waters. However, there were strong variations observed depending on the seasons and the herbicide type. Simazine, alachlor, and diuron were detected in the four seasons with maximal concentrations during spring, especially for lagoon waters; while some herbicides were only detected during specific seasons (e.g., oxadixyl in winter or imidachlopride in fall). Pesticide concentration in surface waters is strongly related to the cultural practices in the watershed (Mhadhbi et al., 2019; Zalidis et al., 2002) as well as the occurrence of rainy periods that favor water runoff. In Southwest Mediterranean ecosystems, rainfall mostly occurs during fall and winter, while long periods of dryness are common during spring and summer. Previous studies have shown a low use of pesticides by farmers in this low-income region (0.2 kg of active ingredient per hectare) compared to 3-4 kg in France or USA (Ben Salem et al., 2016). Consequently, pesticide concentration in sediments (Ben Salem et al., 2017) as well as in surface waters (Table 1) did not exhibit important concentrations, although recent monitoring performed with POCIS (Polar Organic Chemical Integrative Samplers) have shown that strong variations can be observed in surface waters following a rainy period (Mhadhbi et al., 2019). No PAHs in the dissolved phase were detected in lagoon and offshore waters either in the channel or elutriate waters, while a strong accumulation of these compounds was observed in channel sediment (Table 2) as well as in lagoon and offshore stations (Barhoumi et al., 2014a; Zrafi-Nouira et al., 2008). PAH compounds are strongly hydrophobic, thus favoring their sorption on organic matter particles (Tremblay et al., 2005) and their subsequent accumulation in the sediment. Overall, concentrations of trace metal elements in the dissolved phase were low in offshore and lagoon waters (table 1) compared to similar coastal ecosystems (Censi et al., 2006; Drira et al., 2018; Morabito et al., 2018), although some potentially toxic metals (Ni, Zn, and Cu) could exhibit concentrations above $1 \mu\text{g L}^{-1}$, especially in lagoon waters during the winter season.

Principal component analysis (PCA) performed with the physicochemical matrix of the lagoon and offshore waters (Fig. 2, Table S1 Supplementary Materials) showed a clear separation of the station along the main axis (axis 1), whereas seasons were separated along the vertical axis (axis 2). Both axes explained more than 60% of the total variance, and lagoon waters were structured mostly by pesticides (during winter), DOC, and dissolved metals like Ni, Cu, Co Mn, and Fe. Offshore waters were positively structured by Cr and As concentrations, especially during fall season, while physical parameters (T °C, pH) and oxygen appear as neutral variables for both ecosystems. PCA performed with chemical data of the channel sediment clearly showed a seasonal structuration with dry seasons (summer and spring) in a same cluster and a net separation of wet seasons, winter and fall. Dry seasons were explained by TBT, MBT, Pb, Al, and Sn concentrations, while fall was mostly explained by PAHs Ni, Cd, and Ba concentrations.

Characterization of contamination levels in coastal ecosystems is mostly performed with sediment analyses, considering the important role of the latter in contaminant accumulation. In contrast, data for dissolved contaminants in surface waters are relatively scarce, because the low concentrations observed require using high performance analytical tools. The present study has shown that lagoon waters and offshore waters were characterized by distinct chemical compositions that varied according to season. The spatial separation between lagoon and offshore waters might be explained by the difference in hydrodynamic conditions. The lagoon ecosystem is mostly influenced by water runoff from the watershed and from several rivers, mainly from lake Ichkeul, as well as a local hydrology that favors accumulation of chemical compounds due to a long water residence time (Bejaoui et al., 2017). In contrast, offshore waters are mostly influenced by oceanic currents which result in short water residence times favoring the dilution of chemical compounds that can be supplied by the lagoon channel or water runoff (Bejaoui et al., 2017). Similar seasonal and spatial patterns were also observed for plankton (bacterioplankton, phytoplankton and zooplankton) (Meddeb et al., 2018; Salhi et al., 2018) as well as in comparable coastal ecosystems (Aubry and Acri, 2004) suggesting close interactions between the planktonic communities and the chemical composition of the marine water (Goni et al., 2018; Pringault et al., 2016).

As observed for the water column in lagoon and offshore waters, sediment contamination in the channel station exhibited clear seasonal variations, especially for PAH concentrations (Table 2). Among the 21 different pesticides measured in the water column, only three of them (metalaxyl, acetochlore, and alachlore) were detected in the channel sediment. Minimum concentrations of PAHs were observed during winter ($1648 \pm 297 \mu\text{g Kg}^{-1}$) whereas maximum concentrations were measured during fall, with values representing up to five times what was observed in winter (191 vs $1048 \mu\text{g Kg}^{-1}$ for benzo(b) fluoranthene, respectively). The sum of PAHs ranged from 1650 and $5950 \mu\text{g Kg}^{-1}$. According to Baumard et al. (1998), channel sediments are highly contaminated with possible toxic effects on biota according to the classification of Long et al. (1995) with PAH values above ERL thresholds (Table 2). For trace metal elements as well as for organotin compounds the seasonal variations were less marked, concentrations were roughly similar between seasons. Principal component analysis, performed with the chemical sediment matrix, clearly separated the four seasons (Fig. 3, Table S2 Supplementary Materials). Fall was characterized by maximum concentration of PAHs, Ni, Cu, and Cd; summer and spring were explained by concentration peaks for Pb, TBT, and Sn; whereas, the winter period was characterized by minimum concentrations for Ag and maximum concentrations for Co, Cs, and DBT. The seasonal variation of marine sediment contamination is rarely explored. Nevertheless, a few studies have documented significant changes according to season for organic contamination in marine sediments (Baniemam et al., 2017). The source of PAHs (petrogenic/pyrogenic) can impact PAH contamination according to season, with a dominance of pyrogenic during winter (Janadeleh et al., 2018), whereas rainy seasons in South Mediterranean regions can strongly increase organic contamination in sediment due to water runoff, especially for hydrophobic organic molecules that are bound on particles (Guigue et al., 2014).

3.2 Impact of the sediment elutriate on water composition

Sediment elutriate was prepared with channel sediment mixed with seawater sampled at the same station as the sediment. As a rule, the concentration of dissolved compounds in elutriate was higher than those measured in channel, lagoon, or offshore waters (Table 1).

This was particularly true for DOC and nutrients (silicates and NH_4^+). Interestingly, no PAH compounds were detected in the dissolved phase neither in elutriate nor in in situ waters (channel, offshore and lagoon). Although the sediment used for resuspension was highly contaminated by PAHs, the absence of dissolved PAHs might be explained by the hydrophobic properties of PAHs which favor their binding to particles, thus decreasing their concentration in the dissolved phase (Guigue et al., 2017) in favor of the particulate phase as previously observed in a simulated sediment resuspension strongly contaminated by PAHs (Latimer et al., 1999). The enrichment factor (EF), which measured impact of elutriate on in situ waters, was strongly dependent on stations as well as on seasons (Fig. 4). Irrespective of station and season, the greatest EFs were measured for ammonium with values up to 64.5 ± 9.67 for offshore waters in winter. In offshore waters, EF was, as a rule, always significantly ($p < 0.05$) above 1, indicating that elutriate enriches *in situ* offshore waters for most of the dissolved chemical compounds measured. For lagoon waters, the impact of elutriate was less pronounced with values close to 1 except for particular compounds such as Mo, Ni and U and Fe. Principal component analysis (PCA) performed with EF values measured for the three stations and the four seasons, clearly separated the offshore station from the other stations, the lagoon, and the channel (Fig. 5, Table S3 Supplementary Materials). EF strongly varied with seasons with the highest concentrations for pesticides, DOC, NO_2 , PO_4 , and Mn and NH_4^+ observed during spring and winter; whereas summer and fall were characterized by significant enrichment in Zn, Ni, Cu, Rb, and Mo. Interestingly, the impact of elutriate on in situ waters, especially for offshore waters, strongly depends on seasons (Figs 4 and 5). Dry seasons were mostly characterized by an enrichment in trace elements, whereas wet seasons were mostly enriched by pesticides and nutrients. These seasonal variations can be partly explained by the seasonal changes observed in the channel water composition (data not shown) as well as by the seasonal changes in the channel sediment composition (Fig. 3). As explained above, the South Mediterranean region is characterized by two distinct periods, a dry period with a low amount of rain and a wet season with strong storms and raining events. Consequently, the strong water runoff observed during the wet season can severely enrich the lagoon waters which represent a receptacle for the surrounding watershed (Jemai et al., 2018). The wet

period is also characterized by strong winds and storms that can strongly mix waters and provoke important sediment resuspension (Roberts, 2012). In contrast, the dry period is characterized by long periods of low winds and high temperatures, which favors water stratification (Bejaoui et al., 2017) and strongly reduces sediment resuspension. Consequently, according to our experimental approach, a storm event that is likely to occur during the wet season would strongly enrich marine waters in pesticides as well as in nutrients. This enrichment in pesticides and nutrients can strongly impact the planktonic community with significant effects on ecosystem functioning (Goni-Urriza et al., 2018). Nevertheless, the concomitant release of nutrients and dissolved organic matter with toxic compounds (pesticides and trace metal elements) upon sediment resuspension can alleviate the potential toxicity of the toxic elements (Pringault et al., 2016), nutrients and organic matter are known to decrease the toxicity of trace metal elements (Anu et al., 2018; Huang et al., 2016) or pesticides for phytoplankton (Chia et al., 2016; Coquillé et al., 2018). The structure and diversity of phytoplankton (Lafabrie et al., 2013) and bacterioplankton (Pringault et al., 2016) can be strongly impacted by sediment resuspension in shallow waters with significant consequences on the primary production as well on the microbial biomass (Ding et al., 2017; McSweeney et al., 2017; Pringault et al., 2016). Similarly, the interactions between the primary producers and the heterotrophic compartment can be significantly altered with consequences on the carbon transfer within the trophic web (Goni-Urriza et al., 2018).

It is worth noticing that the consequences of elutriate mixing with *in situ* waters were more pronounced for offshore waters than for lagoon waters, irrespective of the season. The difference observed can be explained by the water composition of each ecosystem. Due to their localization, the lagoon ecosystems represent the receptacle for the surrounding watershed, therefore lagoon waters are often considered as a buffer system in coastal ecosystems (de Wit et al., 2001). Consequently, lagoon waters are characterized by concentrations in nutrients as well in contaminants that are often higher than those observed in the adjacent marine waters (Clark et al., 2006; Souchu et al., 1997). Therefore, sediment resuspension will have a more pronounced effect on marine offshore waters than for lagoon waters, because the enrichment in contaminants and/or nutrients will be lower for the latter.

4 Conclusion

Sediment resuspension can provoke strong modification of the chemical composition of the overlying water with the release of contaminants that might become available for planktonic species, impacting so the functioning and the diversity of the ecosystem (Roberts, 2012). This study shows that the resuspension of a sediment contaminated by organic and inorganic contaminants can strongly enrich the dissolved compartment of the coastal waters located nearby the contaminated sediment, especially for nutrients and trace metal elements. This enrichment can have important consequences on the functioning of the coastal ecosystem, with impact on phytoplankton and bacterioplankton diversity as well as impact on the productivity and the carbon transfer within the trophic web. In contrast, although the sediment was highly contaminated by PAHs, no PAH was detected in the dissolved phase, decreasing so their potential bioavailability and consequently their toxicity for pelagic organisms. Seasonal and spatial fluctuations were observed, with a stronger enrichment for marine waters relative to coastal (lagoon) ecosystem, and with a stronger enrichment in spring and winter for pesticides and NH_4^+ whereas summer and fall were characterized by strong accumulation in trace metal elements (Ni, Zn, and Cu). Ecological impacts of these changes in the water column composition consecutive to sediment resuspension have to be assessed in further studies by taking into account the seasonal variation observed.

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7 Figure legends

Figure 1: Map of the study site with the sampling stations, Channel (C), Lagoon (L) and Offshore (O)

Figure 2: Principal component analysis performed with the physicochemical composition of Lagoon and Offshore waters as a function of season.

Figure 3: Principal component analysis performed with the physicochemical composition of the Channel sediment as a function of season

Figure 4: Enrichment factor (EF) in Lagoon and Offshore waters for the different seasons. Enrichment factor (EF) was calculated considering the concentrations measured in situ and the concentrations measured after mixing in situ water with elutriate (75% and 25%, respectively)

Figure 5: Principal component analysis performed with the Enrichment Factor (EF) measured for Offshore and Lagoon waters as a function of season.

Table 1: Physicochemical composition of the different waters observed during the four sampling seasons (min and max). DCPMU 1-(3,4 dichlorophenyl)-3-methyl urea; DCPU 1-(3,4-dichlorophenyl)urea; DIA deisopropylatrazine. n.d.: below the detection limit.

| | OFFSHORE | | LAGOON | | CHANNEL | | ELUTRIATE | |
|---|---------------|---------|--------------|---------|---------------|---------|---------------|---------|
| | Min | Max | Min | Max | Min | Max | Min | Max |
| pH | 8.10 | - 8.25 | 8.11 | - 8.26 | 8.11 | - 8.26 | 7.86 | - 8.30 |
| T°C | 12.4 | - 25.1 | 11.8 | - 26.6 | 11.8 | - 25.6 | 10.6 | - 22.5 |
| Oxygen (mg L ⁻¹) | 8.24 | - 10.32 | 8.04 | - 11.64 | 8.04 | - 10.98 | 8.52 | - 10.74 |
| Conductivity(mS cm ⁻¹) | 53.67 | - 56.80 | 53.70 | - 54.20 | 53.70 | - 55.50 | 52.70 | - 55.60 |
| DOC (mg C L ⁻¹) | 1.08 | - 1.39 | 1.07 | - 2.52 | 1.07 | - 1.91 | 3.43 | - 5.18 |
| SiOH ₄ (μmoles L ⁻¹) | 0.82 | - 3.13 | 0.98 | - 9.28 | 0.98 | - 4.34 | 13.1 | - 26.8 |
| NH ₄ (μmoles L ⁻¹) | 0.22 | - 1.52 | 0.62 | - 2.00 | 0.62 | - 3.00 | 26.9 | - 122 |
| PO ₄ (μmoles L ⁻¹) | 0.05 | - 0.27 | 0.04 | - 0.33 | 0.04 | - 0.43 | 0.21 | - 0.55 |
| NO ₂ (μmoles L ⁻¹) | 0.04 | - 0.23 | 0.10 | - 0.27 | 0.10 | - 0.41 | 0.18 | - 0.94 |
| NO ₃ (μmoles L ⁻¹) | 0.62 | - 3.26 | 1.07 | - 3.26 | 1.07 | - 2.30 | 1.72 | - 2.67 |
| Pesticides (ng L⁻¹) | | | | | | | | |
| Acetochlore | 2.5 | - 6.6 | 1.4 | - 5.8 | 2.9 | - 8.5 | 2.9 | - 7.5 |
| Alachlor | 2.9 | - 7.8 | 2.8 | - 9.9 | 3.1 | - 8.4 | 4.6 | - 9.3 |
| Atrazine | 0.7 (Fall) | | 0.6 (Fall) | | 0.8 (Fall) | | 0.5 (Fall) | |
| Azoxystrobine | n.d. | | n.d. | | n.d. | | 5.19 (Winter) | |
| Chlortoluron | 3 | - 3.1 | 3.1 | - 3.9 | 2.4 | - 3.1 | 3.1 (Fall) | |
| DCPMU | 3.2 (Winter) | | 2.8 | - 5.3 | 3.4 (Winter) | | 8.5 (Winter) | |
| DCPU | 3.9 | - 4.8 | 3.8 | - 6.5 | 3.4 | - 16.8 | 3.9 | - 8.1 |
| DIA | n.d. | | 3.48 | - 5.44 | 4.92 | | 3.53 | - 5.03 |
| Diuron | 1.9 | - 3.3 | 0.4 | - 4.2 | 0.5 | - 6.3 | 0.9 | - 3.4 |
| Flazasulfuron | n.d. | | n.d. | | 5.79 (Winter) | | n.d. | |
| Imidaclopride | 1.16 (Fall) | | 1.6 | - | 1.0 (Fall) | | 1.3 | - 6.8 |
| Isoproturon | 0.8 | - 1.5 | 1.45 | - 1.51 | 0.8 | - 1.4 | 1.2 | - 1.5 |
| Linuron | 6.6 (Spring) | | 1.9 | - 3.4 | 4.9 (Spring) | | 3.5 | - 4.5 |
| Metalaxyl | n.d. | | 1.72 (Fall) | | n.d. | | n.d. | |
| Metolachlor | 3.7 (Spring) | | n.d. | | 4.8 (Spring) | | n.d. | |
| Oxadixyl | n.d. | | 5.1 (Winter) | | 1.5 (Spring) | | 12.6 (Winter) | |
| Propyzamide | 2.34 (Spring) | | n.d. | | 4.9 (Spring) | | n.d. | |
| Simazine | 2.9 | - 3.7 | 0.4 | - 15.2 | 0.6 | - 10.9 | 0.4 | - 6.4 |
| Sum of Pesticides | 4.81 | - 29.8 | 3.91 | - 54.7 | 3.91 | - 63.2 | 5.78 | - 62.4 |
| Trace elements (μg L⁻¹) | | | | | | | | |
| V | 1.41 | - 1.90 | 1.09 | - 1.31 | 1.09 | - 1.80 | 0.31 | - 2.77 |
| Cr | 0.11 | - 0.23 | 0.12 | - 0.30 | 0.12 | - 0.19 | 0.06 | - 0.06 |
| Mn | 0.24 | - 0.59 | 1.52 | - 6.32 | 1.52 | - 1.90 | 1.12 | - 7.97 |
| Fe | 0.42 | - 1.76 | 1.09 | - 2.21 | 1.09 | - 1.55 | 2.14 | - 6.20 |
| Co | 0.02 | - 0.02 | 0.03 | - 0.09 | 0.03 | - 0.07 | 0.05 | - 0.39 |
| Ni | 0.20 | - 0.51 | 0.23 | - 0.87 | 0.23 | - 0.74 | 1.47 | - 2.35 |
| Cu | 0.18 | - 0.73 | 0.24 | - 0.70 | 0.24 | - 0.94 | 0.24 | - 0.88 |
| Zn | 0.66 | - 1.16 | 0.43 | - 3.84 | 0.43 | - 7.47 | 0.81 | - 3.47 |
| As | 1.61 | - 1.73 | 1.51 | - 1.57 | 1.51 | - 1.72 | 0.97 | - 3.63 |
| Rb | 106 | - 120 | 104 | - 124 | 104 | - 123 | 122 | - 140 |
| Mo | 13.1 | - 13.8 | 12.9 | - 14.7 | 12.9 | - 14.5 | 71.1 | - 140 |
| Cd | 0.00 | - 0.01 | 0.01 | - 0.02 | 0.01 | - 0.02 | 0.01 | - 0.04 |
| Sn | 0.10 | - 0.10 | 0.17 | - 0.20 | 0.17 | - 0.79 | 0.12 | - 0.12 |
| Ba | 6.64 | - 7.44 | 9.09 | - 21.3 | 9.09 | - 14.95 | 22.6 | - 33.8 |
| Tl | 0.01 | - 0.01 | 0.01 | - 0.02 | 0.01 | - 0.02 | 0.00 | - 0.00 |
| Pb | 0.04 | - 1.08 | 0.04 | - 0.07 | 0.04 | - 0.35 | 0.02 | - 0.05 |
| U | 3.45 | - 4.07 | 3.62 | - 3.97 | 3.62 | - 4.04 | 7.41 | - 12.6 |
| Organotins (ngSn L⁻¹) | | | | | | | | |
| TMT | 0.17 | - 0.42 | 0.09 | - 0.41 | 0.09 | - 6.95 | 0.13 | - 1.83 |
| DMT | 5.28 | - 14.8 | 4.22 | - 4.35 | 4.22 | - 16.2 | 4.48 | - 48.2 |
| MMT | 0.95 | - 12.8 | 0.56 | - 7.10 | 0.56 | - 8.51 | 0.81 | - 45.2 |
| MBT | 1.30 | - 1.43 | 0.30 | - 3.13 | 0.30 | - 1.20 | 1.19 | - 2.40 |
| DBT | 0.20 | - 0.49 | 0.10 | - 0.26 | 0.10 | - 0.75 | 0.46 | - 0.51 |
| TBT | 0.09 | - 1.73 | 0.10 | - 0.59 | 0.10 | - 0.15 | 0.27 | - 0.27 |

Table 2: Average (\pm SD, n=3-5) concentrations of metals, organotin, herbicides and polycyclic aromatic compounds (PAH) observed in the Channel sediment during the four sampling seasons. n.d.: not detected, <d.l. : below the detection limit. TEL: Threshold Effect Level; ERL: Effect Range Low; PEL: Probable Effects Level; ERM: Effect Range Median; n.d.: below the detection limit.

| | SPRING | SUMMER | FALL | WINTER | TEL | ERL | PEL | ERM |
|--|---------------|---------------|---------------|---------------|-------|------|--------|------|
| Trace elements ($\mu\text{g}\cdot\text{g}^{-1}$) | | | | | | | | |
| As | 18.14 (2.27) | 16.88 (0.27) | 20.13 (2.09) | 19.37 (0.85) | 7.24 | 8.2 | 41.6 | 70 |
| Cd | 0.62 (0.09) | 0.51 (0.05) | 1.46 (1.69) | 0.59 (0.02) | 0.676 | 1.2 | 4.21 | 9.6 |
| Cr | 79.89 (8.10) | 65.85 (1.39) | 67.18 (20.21) | 91.03 (4.44) | 52.3 | 81 | 160.4 | 370 |
| Co | 7.06 (0.55) | 4.50 (0.10) | 6.82 (0.57) | 9.57 (7.08) | | | | |
| Cu | 33.64 (3.62) | 25.68 (1.07) | 38.39 (4.25) | 34.90 (1.28) | 18.7 | 34 | 108.2 | 270 |
| Ni | 28.80 (3.41) | 21.80 (0.36) | 33.83 (3.08) | 29.04 (0.60) | 15.9 | 20.9 | 42.8 | 51.6 |
| Pb | 83.78 (60.41) | 42.09 (1.38) | 56.86 (4.43) | 55.43 (0.91) | 30.24 | 46.7 | 112.18 | 218 |
| Zn | 270.2 (33.77) | 175.3 (7.37) | 237.3 (17.88) | 226.2 (7.06) | 124 | 150 | 271 | 410 |
| Ba | 174.1 (21.93) | 178.7 (5.06) | 186.5 (28.23) | 177.5 (15.75) | 7.24 | 8.2 | 41.6 | 70 |
| Mn | 164.3 (19.44) | 115.8 (3.75) | 115.8 (3.75) | 153.6 (3.54) | | | | |
| Mo | 3.39 (0.48) | 5.06 (0.14) | 5.06 (0.14) | 2.72 (0.07) | | | | |
| Rb | 44.39 (4.78) | 21.84 (6.77) | 49.16 (6.13) | 50.52 (1.19) | | | | |
| Sn | 4.19 (0.72) | 4.98 (3.74) | 3.61 (1.00) | n.d. | | | | |
| Th | n.d. | 2.44 (0.64) | 4.38 (1.26) | 4.83 (0.98) | | | | |
| V | 93.07 (12.2) | 79.13 (2.61) | 124.1 (12.65) | 102.3 (2.50) | | | | |
| Sr | 431.1 (51.63) | 605.4 (18.88) | 457.2 (91.73) | 486.8 (22.41) | | | | |
| Cs | 3.30 (0.30) | 2.56 (0.12) | 3.25 (0.70) | 4.04 (0.09) | | | | |
| Major elements (%) | | | | | | | | |
| Al | 3.31 (0.32) | 1.06 (0.28) | 1.23 (0.20) | 3.45 (0.80) | | | | |
| Fe | 2.01 (0.21) | 1.94 (0.04) | 1.97 (0.59) | 2.41 (0.33) | | | | |
| S | | 1.61 (0.31) | 1.43 (0.05) | 1.43 (0.05) | | | | |
| Ti | 0.27 (0.03) | 0.20 (0.00) | 0.29 (0.05) | 0.25 (0.01) | | | | |
| Organotins ($\text{ng}(\text{Sn})\text{g}^{-1}$) | | | | | | | | |
| MBT | 37.60 (2.37) | 51.26 (28.43) | 17.93 (3.65) | 42.22 (9.16) | | | | |
| DBT | 16.59 (1.26) | 5.55 (1.42) | 11.97 (10.2) | 17.58 (0.97) | | | | |
| TBT | 28.54 (5.21) | 19.14 (10.62) | 16.23 (4.67) | 14.53 (2.87) | | | | |
| PAH ($\mu\text{g}\text{kg}^{-1}$) | | | | | | | | |
| Naphtalene | n.d. | n.d. | 47.73 (11.92) | n.d. | 34.57 | 160 | 390.6 | 2100 |
| Acenaphthylene | n.d. | 10.43 (3.42) | 26.06 (5.51) | n.d. | 6.71 | 16 | 88.9 | 500 |
| Anthracene | 22.19 (12.24) | 60.50 (7.43) | 85.47 (14.45) | n.d. | 46.85 | 85.3 | 245 | 1100 |
| Fluorene | n.d. | 22.64 (3.84) | 32.43 (7.20) | n.d. | 21.17 | 19 | 144.3 | 540 |
| Phénanthrene | 336.9 (6.04) | 234.6 (29.36) | 342.7 (43.97) | n.d. | 86.68 | 240 | 543.5 | 1500 |
| Benzo(a) anthracene | 157.1 (7.75) | 278.5 (26.55) | 616.4 (59.70) | 151.2 (9.40) | 74.83 | 261 | 692.5 | 1600 |
| Chrysene | 163.9 (3.70) | 171.0 (11.42) | 619.5 (68.22) | 147.9 (9.36) | 107.7 | 384 | 845.9 | 2800 |
| Fluoranthene | 537.4 (15.85) | 202.1 (23.48) | 526.7 (55.68) | 168.5 (19.07) | 112.8 | 600 | 1493.5 | 5100 |
| Pyrene | 480.9 (2.87) | 192.8 (22.71) | 492.6 (43.34) | 141.1 (17.80) | 152.6 | 665 | 1397 | 2600 |
| Benzo(a) pyrene | 51.01 (0.89) | 299.6 (23.08) | 788.1 (250.6) | 225.9 (26.29) | 88.81 | 430 | 763.2 | 1600 |
| Benzo(b) fluoranthene | 324.1 (2.61) | 372.0 (23.48) | 1048 (200.9) | 191.3 (2.95) | | | | |
| Benzo(k) fluoranthene | 85.93 (12.15) | 108.2 (4.58) | 165.2 (7.20) | 33.16 (0.87) | | | | |
| Dibenz(ah) anthracene | 144.5 (55.44) | 121.8 (15.52) | n.d. | 191.0 (187.8) | 6.22 | 63.4 | 134.6 | 260 |
| Benzo(ghi) perylene | 435.5 (57.43) | 250.5 (32.26) | 598.8 (86.62) | 199.9 (12.82) | | | | |
| Indéno(1.2.3) pyrene | 336.9 (32.79) | 185.6 (24.63) | 558.7 (50.19) | 198.1 (10.49) | | | | |
| Herbicides ($\text{ng}\cdot\text{g}^{-1}$) | | | | | | | | |
| Metalaxyl | 0.2 (0.1) | n.d. | n.d. | n.d. | | | | |
| Acetochlore | 0.90 (0.73) | 3.53 (0.60) | 3.67 (1.40) | 1.79 (1.08) | | | | |
| Alachlor | 7.80 (1.92) | 4.12 (3.00) | 4.97 (3.10) | 5.21 (1.59) | | | | |

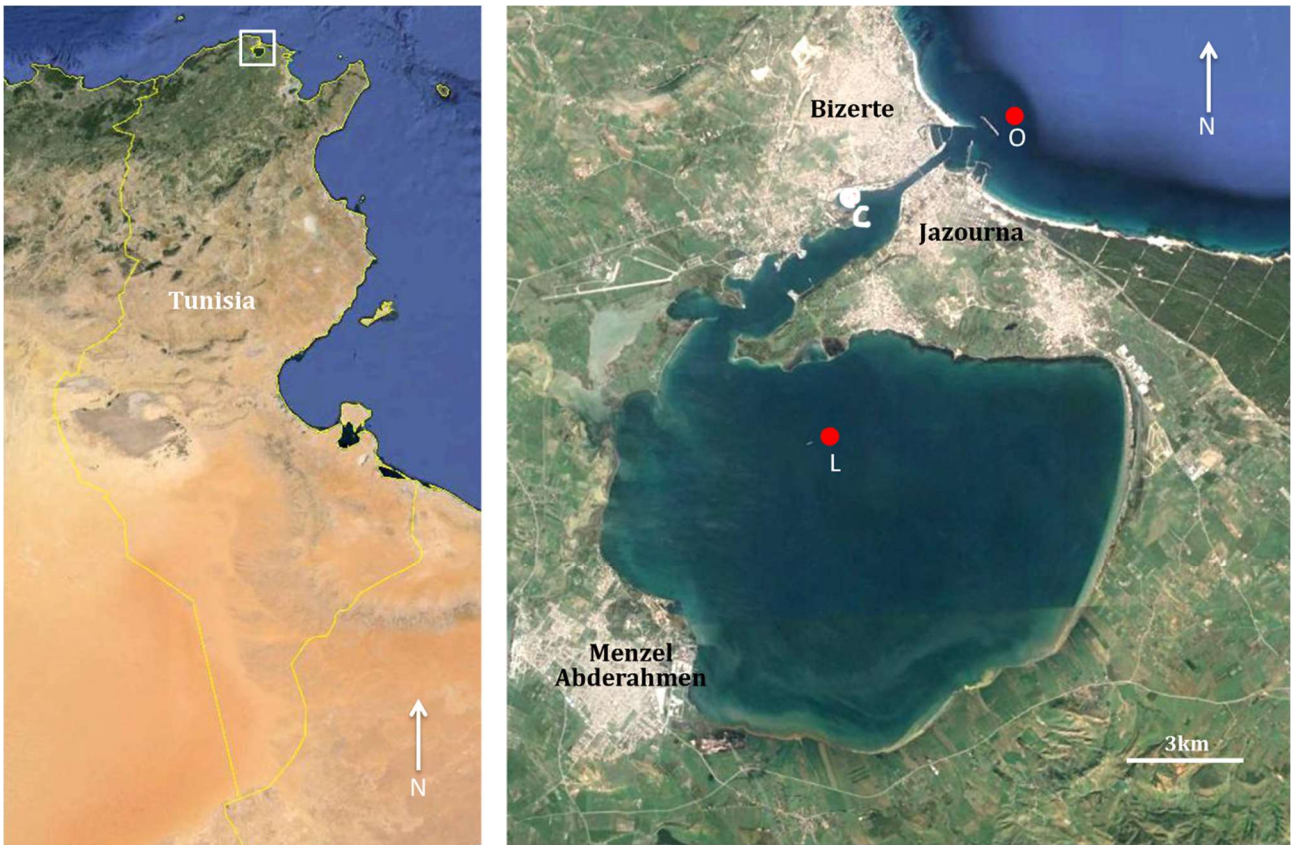


Figure 1

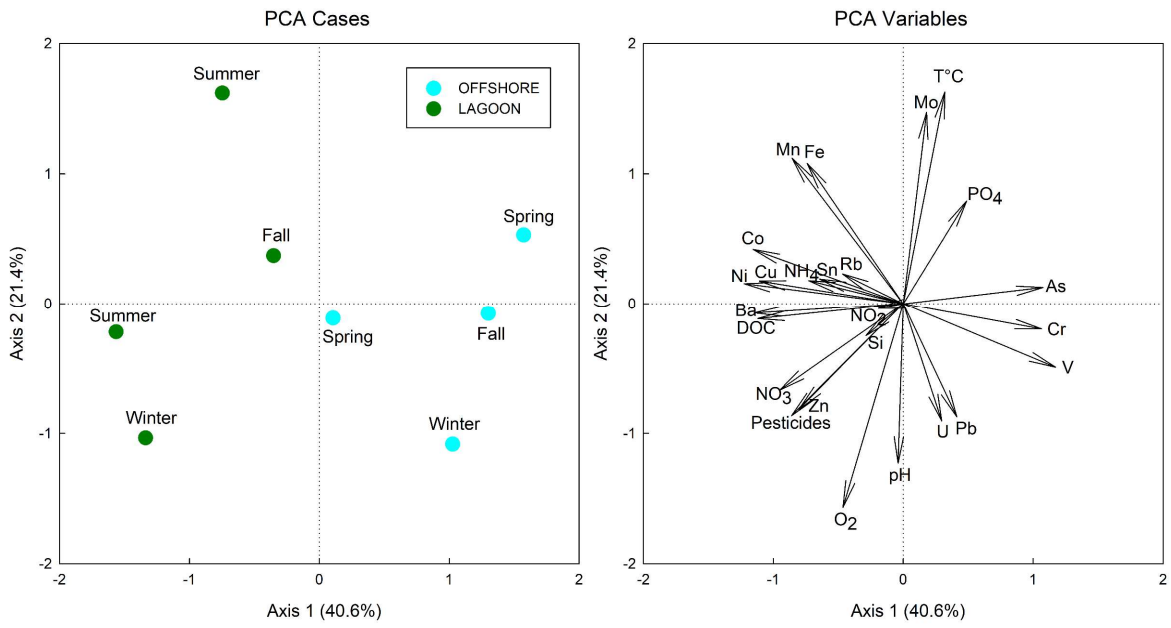


Figure 2

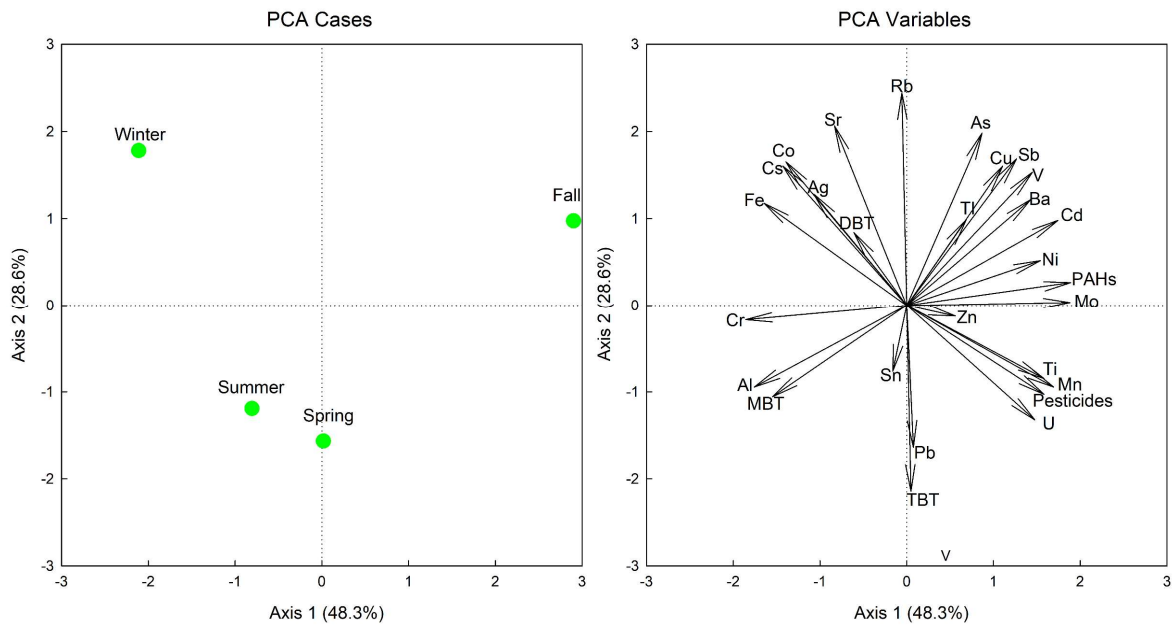


Figure 3

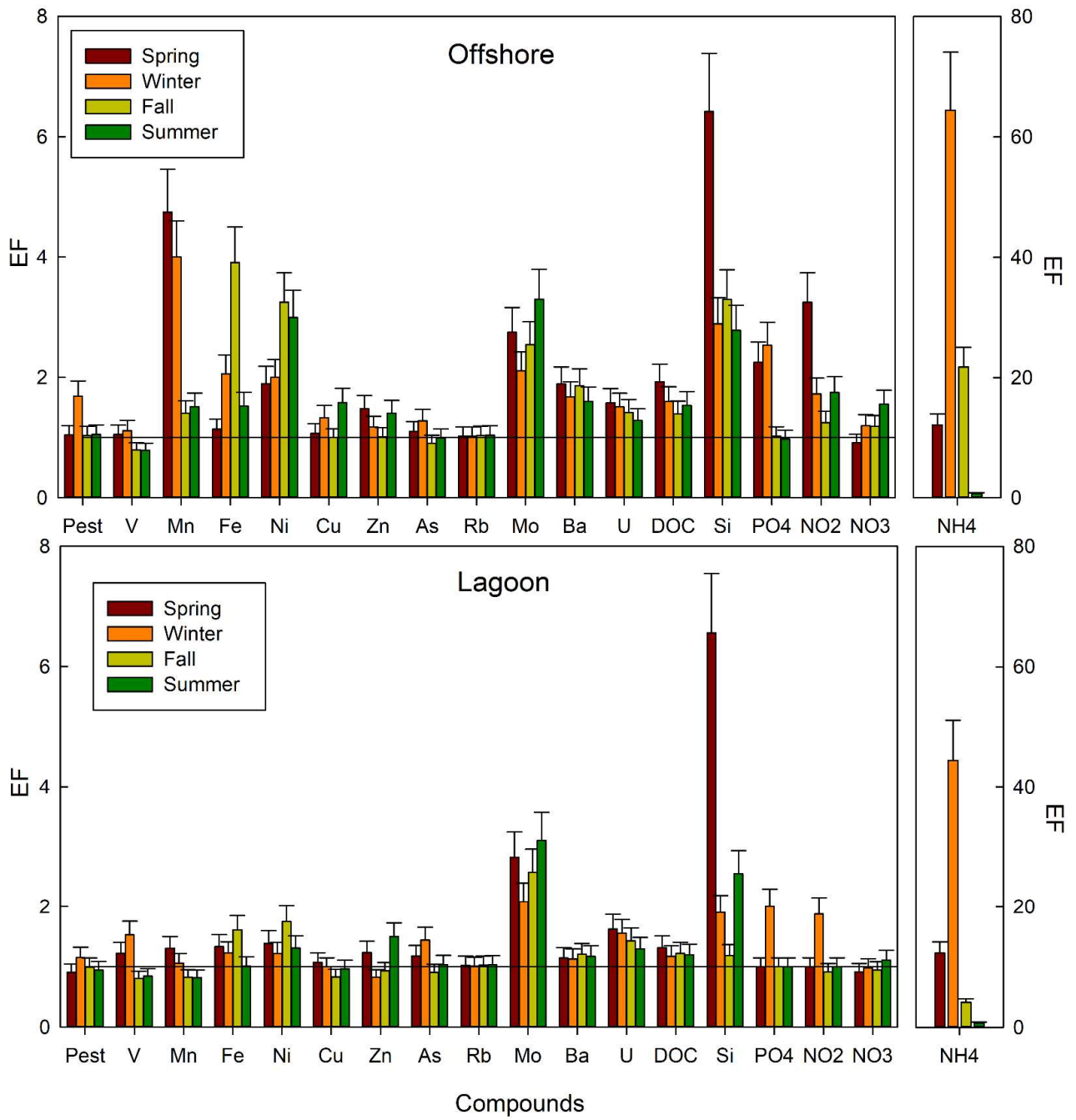


Figure 4

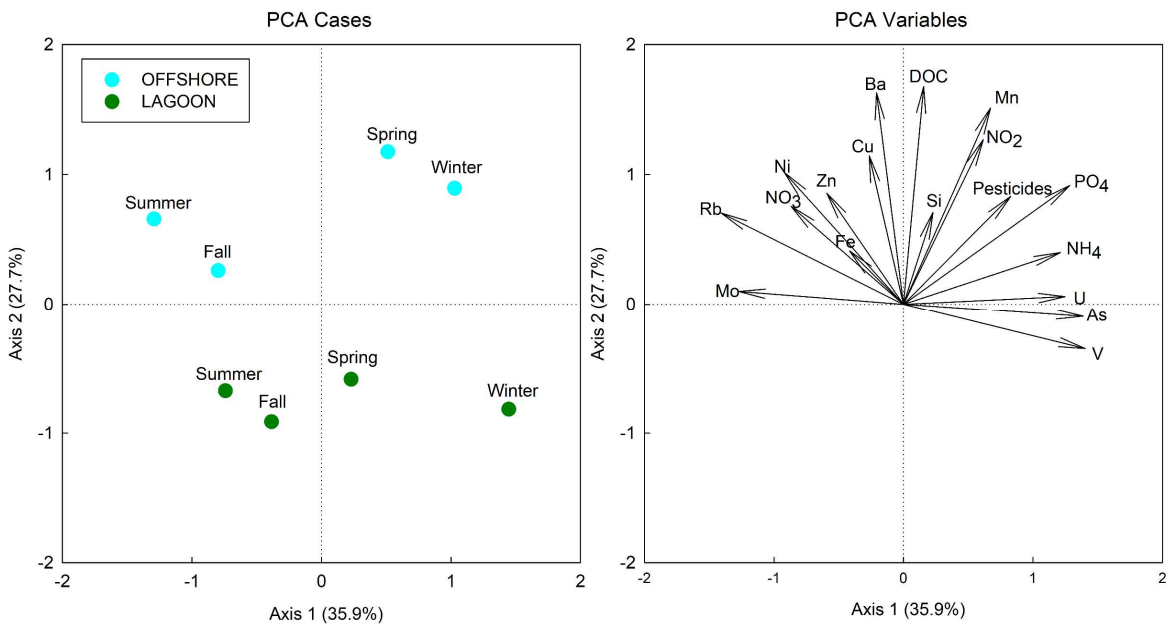


Figure 5