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Atmospheric Chemistry and Physics Discussions

Wet deposition in the remote western and central Mediterranean as a source of trace metals to surface seawater

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Abstract. This study reports the only recent characterisation of two contrasted wet deposition events collected during the PEACETIME cruise in the open Mediterranean Sea~~open seawater~~, and their

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impact on trace metal~~s~~ (TM~~s~~) marine stocks. Rain samples were analysed for Al, 12 ~~trace metals (~~TMs ~~hereafter~~, ~~including(~~ Co, Cd, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Ti, V and Zn) and nutrients (N, P, DOC) ~~concentrations~~. The first rain sample collected in the Ionian Sea (~~rain~~ Rain ION) was a ~~wet~~ typical regional background wet deposition event whereas the second rain sample, collected in the Algerian Basin (R~~r~~ain FAST), was a Saharan dust wet deposition event. The concentrations of TMs in the two rain samples were significantly lower compared to concentrations in rains collected at coastal sites reported in the literature, suggesting either less anthropogenic influence in the remote Mediterranean ~~environment~~Sea, or decreased anthropogenic emissions during the ~~last~~ preceding decades ~~in the Mediterranean Sea~~. The TM~~s~~ inventories in the surface microlayer and mixed layer (0-20 m) at ION and FAST stations before and after the events were~~,~~ compared to atmospheric fluxes which ~~,~~ showed that the atmospheric inputs were a significant source of particulate TMs for both layers. At the scale of the western and central Mediterranean, the atmospheric inputs were of the same order of magnitude as marine stocks within the ML for dissolved Fe, Co and Zn, ~~underlining~~ highlighting the role of the atmosphere in their biogeochemical cycles in the stratified Mediterranean Sea (state season) under background conditions (?). ~~In case of~~Our results suggest that ~~-~~intense dust-rich wet ~~dust~~ deposition events~~,~~ are an important source ~~the contribution of atmospheric inputs could be critical for~~ of dissolved ~~stocks of the majority of~~ TMs to the study region.

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1. Introduction

Atmospheric deposition of continental aerosol has long been recognized to influence trace element (TE) concentrations in remote oceanic surface waters (Buat-Ménard and Chesselet, 1979; Hardy, 1982; Buat-Ménard, 1983). In particular, the Mediterranean Sea (Med Sea) is an oligotrophic environment where marine biosphere growth is nutrient-limited during the long Mediterranean summer season, which is characterized by a strong thermal stratification of surface waters (The Mermex Group, 2011). The Mediterranean atmosphere is characterized by the permanent presence of anthropogenic aerosols from industrial and domestic activities around the basin (e.g., Sciare et al., 2003; Kanakidou et al., 2011). In addition to this anthropogenic background, the Mediterranean basin is also subject to seasonal contributions of particles from biomass fires in summer (Guieu et al., 2005) and to intense sporadic Saharan dust inputs (e.g., Loÿe-Pilot and Martin, 1996; Vincent et al., 2016). Several studies have emphasized that the atmospheric deposition of aerosols, notably through wet deposition, plays a significant role in the marine cycles of ~~both~~ nutrients, such as nitrogen (N) and phosphorus (P) (e.g. Pulido-Villena et al., 2010; Richon et al., 2018 a and b; Violaki et al., 2018) and micronutrients, such as iron (Fe) (Bonnet and Guieu, 2006). Recently, atmospheric dust inputs were identified to have a fertilizing effect on ~~the~~ planktonic stocks and fluxes, even in the presence of relatively high dissolved (/)~~nutrients~~ N, P and Fe ~~marine~~ concentrations (Ridame et al., 2011; reviewed in Guieu and Ridame, 2021). Mackey et al. (2012) showed that TMs provided by dust deposition could explain this fertilizing effect. Indeed, ~~some~~ many TMs, including Mn, Co, Ni (Mackey et al., 2012), Cu (Annett et al., 2008) and Zn (Morel et al., 1991), play physiological roles for phytoplanktonic organisms. These TMs are present in very low concentrations in oligotrophic systems such as the Med Sea, possibly limiting (or co-limiting) ~~the~~ phytoplankton growth (Pinedo-Gonzàles et al. 2015), ~~and implying the role~~pointing to the importantce of dust deposition as source of TMs for planktonic communities. On the other hand, atmospheric deposition of European aerosol ~~particless~~ was identified to have a negative effect on chlorophyll concentrations (Gallisai et al. 2014)~~,~~ by providing ~~trace metals, as~~ Cu~~,~~ at toxic levels (Jordi et al. 2012).

The atmospheric deposition of TMs in the Mediterranean is related to both dust and anthropogenic aerosol~~s~~ deposition (Desboeufs et al., 2018). The role of dust deposition as a source of TMs was observed from the correlation between the atmospheric deposition of mineral dust, and the enrichment of dissolved TMs (Cd, Co, Cu, Fe) in the Mediterranean Sea surface microlayer (Tovar Sánchez et al., 2014). For the water column, the adding of dissolved Fe and Mn was emphasized in mesocosm experiments after dust addition mimicking intense wet dust deposition (Wuttig et al., 2013). Yet, the direct impact of wet deposition ~~events~~ on TM~~s~~ concentrations in surface seawater has ~~never~~ not been studied and reported ~~*in situ*~~ where TM concentrations were determined in both rainwater and seawater samples collected from the same location before the present study, whether in the Mediterranean Sea

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or in other oceanic regions. Moreover, the two key criteria used to assess the potential impact of TM~~s~~ and nutrient~~s~~ wet deposition ~~are~~ and their respective concentrations (or fluxes) and solubility, i.e., the partitioning between dissolved and total concentrations in rainwaters. Indeed, it is considered that the dissolved fraction of nutrients and TMs can be directly assimilated by the phytoplankton (ref). A f~~F~~ew studies have ~~focussed on~~reported concentrations of TMs in rainwater samples ~~was~~ collected around the Mediterranean basin: Al-Momani et al., (1998), Kanellopoulou, (2001) and Özsoy and Örnektekin, (2009) in the eastern basin, and Losno (1989), Guieu et al. (1997), Frau et al., (1996), Chester et al., (1997) and Guerzoni et al. (1999b) in the western basin. These studies led to highly variable TM~~s~~ concentrations and solubility, illustrating ~~a more general~~the large variability of TM~~s~~ inputs during wet deposition events~~s~~ in the Mediterranean Sea (reviewed in Desboeufs, 2021). All these studies were performed at coastal sites. Offshore samples of rainwater have rarely been ~~studied~~ reported in the literature~~ so far~~. In the Mediterranean, to our knowledge, trace element concentrations from only three rain samples collected at sea in April 1981 have been reported in a PhD thesis (Dulac, 1986). However, due to the continental and local sources of pollution and the variety of anthropogenic aerosol sources (Amato et al., 2016), the TM~~s~~ rain composition of the coastal zone ~~could~~ may not be representative of atmospheric deposition ~~in~~ to the remote Mediterranean.

The PEACETIME cruise (ProcEss studies at the Air-sEa Interface after dust deposition in the MEditerranean Sea) performed in spring 2017 aimed ~~at~~ to study~~ing~~ the impacts of atmospheric deposition, in particular Saharan dust events, on the physical, chemical and biological processes in this marine oligotrophic environment (Guieu et al., 2020). We investigated ~~here~~ the concentration and solubility of TMs and nutrients ~~of~~ from two rain events~~waters~~ sampled in the open Mediterranean ~~open~~ S~~s~~ea during the cruise. We compare our results ~~on~~ of TM~~s~~ concentrations and solubility in rainwater with previous studies based on rainwater samples collected at coastal sites to investigate potential differences with the open sea. Additionally, to assess the impact of wet deposition on the surface TM~~s~~ concentrations, surface seawater, including the surface micro-layer, and rain water was concurrently collected. To the best of our knowledge, this is the first time TM data for these marine compartments have all been presented at the same time. ~~for the first time~~ with ~~rain samples~~.

2. Sampling and methods

2.1 Sampling and chemical analysis of rainwater

The PEACETIME oceanographic campaign (https://doi.org/10.17600/17000300) took place in the western and central Mediterranean Sea on-board the French research vessel ~~(~~R/V~~)~~ *Pourquoi Pas ?* between 11 May and 10 June 2017, i.e. at the beginning of the Mediterranean stratification season (Guieu et al., 2020). The rain collector was installed on the upper deck (22 m above sea level) where

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no on-board activities were taking place to avoid contamination. ~~A~~ The rain collector was equipped with an on-line filtration system to ~~directly~~ separate the dissolved and particulate fractions at the time of collection (details of the filtration system are available in Heimburger et al., 2012) allowing for the calculation of solubility of TMs in the rainwater ~~at the time of collection~~. The filtration device was equipped with a Nuclepore® polycarbonate membrane ~~(PC)~~ filter (porosity: 0.2 µm, diameter: 47 mm). T~~, and t~~he diameter of the funnel of the collector was 24 cm. The rain collector~~s~~ ~~were~~ was ~~installed~~ opened only when rain was expected and kept ~~closed within~~covered by an acid-washed, sealed plastic film ~~until the rainfall began~~when not in use. All the sampling materials were thoroughly acid-washed in the laboratory prior to the cruise departure (washing protocol described in Heimburger et al., 2012). No stabilizing ~~setup~~ device was used to keep the funnel level during the pitch and roll of the ship, preventing a precise assessment of the height of rainfall from the collected water volume. During the rain sampling, the ship was always facing the wind to avoid contamination by the ~~smoke~~ ship's exhaust ~~of the ship itself~~, as the chimney was situated on the lower deck and behind the collector.

Immediately after sampling, the collector was disassembled under ~~the~~ a laminar flow hood inside an on-board clean-room ~~on-board~~ laboratory. The dissolved fraction was separated into ~~4~~ four aliquots dedicated to i) dissolved organic carbon (DOC) determimation by high-temperature catalytic oxidation (HTCO) on a Shimadzu total organic carbon analyzer (as described in Van Wambeke et al 2021), ii) major ions by ion chromatography (IC), iii) ~~metals analysis~~TM determination by inductively coupled plasma coupled methods (ICP), and iv) pH measurement. For ICP measurements, the sample was acidified immediately to 1% by volume of ultra-pure nitric acid: 67-69%, Ultrapur, Normatom®, VWR. For DOC analysis… For IC analysis, the filtrate ~~sample~~ (dissolved fraction) was immediately frozen. The filter (particulate fraction) was dried under the laminar flow hood, and then put in a storage box and packed with a plastic bag to avoid contamination. After returning to the laboratory, filters were acid digested by using the ~~adapted~~ protocol adapted from Heimburger et al.
(2012) as follows: filters were placed in tightly capped Savillex™ PFA digestion vessels with 4 mL of a mixture of HNO_3 (67-69%, Ultrapur, Normatom®, VWR), H_2O and HF acids (40%, Ultrapur, Normatom®, VWR) in a proportion of ~~(~~3: 1: 0.5~~)~~, then heated in an oven at 130°C for 14 hours. After cooling, the acid solution was completely evaporated on a heater plate (ANALAB, 250, A4) at 140°C for about
2h, then 0.5 mL of H_2O_2 (30-32%, Romil-UpA™) and 1 mL of the acidified water (2% HNO_3) was added to the vessels and heated ~~during~~ for 30 min. to dissolve the dry residue in the bottom of the vessels; finally, 12 mL of acidified water (1% HNO_3) was added to obtain 13.5 mL of solution in a tube for ICP-MS analyses.

The dissolved fraction was analysed by IC (IC 850 Metrohm) for the inorganic and organic anions

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Commented [RS(-S14]: This should be number 1 as it is the focus of the paper. List = i) TMs, ii) DOC, iii) major seawater and atmospheric ions, iv) pH. Then a description of the methods used for each, in the order they are listed

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(NO_2^-, NO_3^-, PO_4^{3-}, SO_4^{2-}, F^-, Cl^-, Br^-, $HCOO^-$, CH_3COO^-, $C_2H_5COO^-$, MSA, $C_2O_4^{2-}$) and for the cation NH_4^+ (Mallet et al., 2017). ~~On the other hand,~~ the dissolved fraction and solution from the digestion of the particulate fraction of the rain samples ~~s~~ were analysed by ICP-AES (Inductively Coupled Plasma Atomic Emission Spectrometry, Spectro ARCOS Ametek®) for major elements (Al, Ca, K, Mg, Na, S) (Desboeufs et al., 2014) and by HR-ICP-MS (High Resolution Inductively Coupled Plasma Mass Spectrometry, Neptune Plus ™ at Thermo Scientific ™) for TMs: Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, P, Pb, Ti, V and Zn. The speciation of dissolved P was estimated by determining ~~the~~ dissolved inorganic phosphorus (DIP) from phosphate concentrations expressed as P and the dissolved organic phosphorus (DOP) from the difference between total dissolved phosphorus (TDP), obtained by ICP-MS, and DIP, obtained by IC.

In order to estimate the contamination of sampling and analytical protocols, ~~3~~ three blanks of rain samples (collected on-board during the cruise with the same protocol without rain events) were used and processed. The procedural limit of detections (LoD) were defined as 3 x standard deviation of blank samples both for dissolved and particulate fractions estimated after acid digestion. All ~~samples~~ dissolved and particulate sample concentrations were higher than LoD, except for NO_2^- in the two rain samples. The blank concentrations represented 10.2% o~~i~~n average for TMs and were typically lower than 20% of the sample concentrations, except for Cd (52%) and Mo (43%) in the dissolved fraction. ~~For the sample concentration computations, we subtracted these blanks values to elemental concentrations obtained in rain samples.~~ Blank concentrations were subtracted from all sample concentrations.

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2.2 Atmospheric ancillary measurements

The PEGASUS (PortablE Gas and Aerosol Sampling UnitS, www.pegasus.cnrs.fr) mobile platform of LISA is a self-contained facility based on two standard 20-feet containers, adapted with air conditioning, rectified power, air intake and exhausts for sampling and online measurements of atmospheric aerosols and gaseous compounds, and their analysis (Formenti et al., 2019). During the PEACETIME cruise, only the sampling module of the facility was deployed on the starboard side of deck 7 of the R/V. The PEGASUS instrumental payload of relevance to this paper included measurements of the major gases such as NOx, SO_2, O_3 and CO by online analysers (Horiba APNA, APSA, APOA and PICARRO respectively; 2-min resolution, detection limit for all analytes was 0.5 ppb and 1 ppb for CO). These gases~~, that~~ were used to estimate the origins of ~~collected air masses~~the sampled air.

From ~~the first of~~1st June 2017 (?) (not operational before), additional measurements by an ALS450® Rayleigh-

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Mie lidar (Leosphere ™; Royer et al., 2011) ~~was~~ were used to monitor the vertical distribution of aerosols over time and the associated integrated columns. The vertical lidar profiles were analysed to yield the apparent backscatter coefficient (ABC) corrected from the molecular transmission, as well as the volume depolarisation ratio (VDR). The inversion procedure (Chazette et al., 2016; 2019) to retrieve the aerosol extinction coefficient (unit km^{-1}) uses a vertical-dependent lidar ratio that takes into account two aerosol layers. The first layer corresponds to marine aerosols in the marine boundary layer (MBL), the second to a desert aerosol layer that can extend between ~1 and 6 km above mean sea level (amsl). In accordance with Chazette et al. (2016), for the same wavelength and region, the lidar ratios were set to 25 and 55 sr, respectively. The vertical profile of the aerosol extinction coefficient was retrieved from 0.2 km amsl ~~on~~ upwards with a vertical resolution of 15 m. Based on these profiles, the integrated column content of dust aerosols was estimated using a specific extinction cross-section of 1.1 m^2 g^{-1} as proposed by Raut and Chazette (2009).

In addition, detailed meteorological data such as air and sea temperature, atmospheric pressure, relative humidity, atmospheric pressure, heat flux and wind speed and direction were provided on a 30 second~~s~~ time step basis by the ship's permanent instrumentation.

2.3 Sampling and analysis of dissolved TMs in seawater

Before and after each rain, seawater samples were collected in the surface microlayer (SML: <1 mm) and subsurface seawater (SSW: <1 ~~-~~m depth) (Tovar-Sánchez et al., 2020, this ~~special~~ issue). SML and SSW samples were collected from a pneumatic boat 0.5-1 nautical miles away from the R/V in order to avoid any potential contamination. SML samples were collected using a silicate glass plate sampler (Stortini et al., 2012; Tovar-Sánchez et al., 2019) which had previously been acid-cleaned ~~with acid~~ overnight and rinsed thoroughly with ultrapure water (~~MQ water~~18 mΩ cm-1). The 39 x 25 cm ~~silicate~~ glass plate had an effective sampling surface area of 1950 cm^2 considering both sides. In order to check for procedural contamination, SML blanks were collected at some stations on board of the pneumatic boat by rinsing the glass plate with ultra-pure water and collecting 0.5 L of ultra-pure water using the glass plate system. The surface microlayer thickness was calculated following the formula of Wurl (2009). SSW was collected by using ~~an~~ acid-washed Teflon tubing connected to a peristaltic pump. The total fraction (i.e. T-SML) was directly collected from the glass plate system without filtration into ~~a~~ 0.5 L acid cleaned LDPE bottles, while the dissolved fraction in the SML (i.e. D-SML) and SSW (i.e. D-SSW) was filtered *in situ* through an acid-cleaned polypropylene cartridge filter (0.22 µm; MSI, Calyx®).

TM~~s~~ samples were also collected in the water column using ~~the~~ a titanium trace metal~~s~~ clean (TMC) rosette (mounted with 24 teflon-coated Go-Flo bottles) before and after the rain events~~s~~ (Bressac et al., 2021). Although rosette deployments were performed over the whole water column, we focus here

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on the 0-20 m ~~marine~~ mixed-layer (ML). ~~The water column was sampled using the TMC titanium rosette mounted with 24 teflon-coated Go-Flo bottles~~.

Immediately after recovery, the Go-Flo bottles were transferred inside a class-100 clean laboratory container. Seawater samples were directly filtered from the bottles through acid-cleaned 0.2 ~~-~~µm capsule filters (Sartorius Sartobran-P-capsule 0.45/0.2-µm). All samples were acidified on board to pH < 2 with Ultrapure-grade HCl under a class-100 HEPA laminar flow hood. Metals (namely Cd, Co, Cu, Ni, Mo, V, Zn and Pb) were pre-concentrated using an organic extraction method (Bruland et al., 1979) and quantified by ICP-MS (Perkin Elmer ELAN DRC-e) in the home laboratory. In order to breakdown metal-organic complexes and remove organic matter (Achterberg et al., 2001; Milne et al., 2010), the total fraction samples (i.e. T-SML) were ~~digested~~ UV-treated prior to the pre-concentration step using a UV system consisting of one UV (80 W) mercury lamp that irradiated the samples (contained in quartz bottles) ~~during~~ for 30 min. The accuracy of the pre-concentration method and analysis for TMs was established using Seawater Reference Material (CASS 6, NRC-CNRC) with recoveries ranging from 89% for Mo to 108% for Pb. Due to the complexity of the analytical method, all the TMC samplings were not analysed for these metals. Overall, 1 or 2 depths were obtained in the mixed layer (0-20 m). Dissolved Fe and Al concentrations were also measured on board. Dissolved Fe concentrations were measured using an automated Flow Injection Analysis (FIA) with online preconcentration and chemiluminescence detection (Bonnet and Guieu, 2006), and dissolved Al concentrations using the fluorometric method described by Hydes and Liss (1976). Sampling and analysis for dissolved Fe and Al concentrations are fully described in Bressac et al. (2021), and covered at least ~~4~~ four depths in the 0-20 m mixed layer.

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2.4 Enrichment factor and solubility

In order to better constrain the origin of TMs in the rain samples, their enrichment factor s(EF; Rahn 1976) relative to the Earth's crust ~~was~~ were calculated based on their total concentrations (dissolved + particulate fractions) as:

$$EF = \frac{([X]/[Al])sample}{([X]/[Al])crust} \quad (1)$$

where $[X]/[Al]$ is the ratio between an element X and Al concentrations in rainwater samples (at the numerator), and in the Earth's crust (denominator) from Rudnick and Gao (2003). Aluminium is currently used as a reference element as it only has a crustal origin. For a given TM, EF >1 indicates an enrichment with respect to the average composition of the Earth's crust. To account for the soil composition variability of mineral dust ~~atmospheric~~ sources, TMs with an EF value >10 are considered significantly enriched, which points to a ~~derived from~~ non-crustal source~~s~~ (Rahn, 1976).

Commented [RS(-S20]: Not exactly but the vast majority of Al is crustal. Therefore, it is currently accepted as one of the best proxy elements. It is predominantly crustal

The relative solubility of TMs in the two rainwater events was calculated as:

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$$S_X\% = \frac{[X]dissolved}{[X]total} \times 100 \qquad (2)$$

where $S_X\%$ is the relative solubility (in %) of an element X in the rainwater, $[X]_{dissolved}$ and $[X]_{total}$ are its soluble and total concentration, respectively.

2.5 Atmospheric deposition fluxes

Impacts on biogeochemical cycles and ecosystem functioning after a rain event occur on time scales of a few days (2-3), and space scales of tens of km (about 20-50 km within the radius of the ship's position). In the specific context of oceanographic cruising, the documentation of these impacts is restricted to the vertical dimension at the prescribed temporal scale. In this vertical dimension, the exchange of TMs ~~across~~ into the ML was controlled both by atmospheric inputs over the R/V position and by advection from surrounding water masses that may have been impacted by surrounding rainfall. Therefore, we had to consider this process in our estimation of the atmospheric flux~~es~~ contributions. For this purpose, the atmospheric fluxes have to be integrated to the extent of the rain area that can impact the marine surface layer~~s~~. We derived wet deposition fluxes by considering the total precipitation accumulated during the duration of the rain over the area around the R/V location. Thus, the wet deposition fluxes in our rain samples were calculated by multiplying the volume weighted mean rainfall concentration by the total precipitation (equation and explanation for using VWM rainfall here). The total precipitation of the rain events was issued from the hourly total precipitation accumulated during the rain events over the region from ERA5 ECMWF reanalysis (Herbasch et al., 2018) and from the rain rate composite radar products from the European OPERA database (Saltikoff et al., 2019), when it wa~~i~~s possible. Although subject to uncertainties (Morin et al., 2003), a surface-based weather radar is probably the best tool to estimate rainfall in the surroundings of the R/V because…. However, the OPERA database does not include Italian radars, which ~~anyway~~ did not cover the central area of the Ionian Sea during the cruise anyway. ERA5 data are available on regular latitude-longitude grids at 0.25° x 0.25° resolution. The accumulated precipitation was taken from the grid-points spanning the ship's location, ~~more or less~~approximately 0.25° around the central grid-point for integrating the regional variability. Surface rain rate radar composite images were available every 15 minutes with a spatial resolution of 2 km x 2 km. The accumulated precipitation was the sum of integrarated (?)~~l~~ rain rates during the rain duration averaged over the radar pixels spanning the ship's location within a radius of about 25 km around the ship location.

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2.6 Stocks in the surface seawater

For the surface microlayer (SML), stocks of TMs were estimated from the integration of TM~~s~~ concentration over the thickness of the ~~layer~~SML. The thickness ranged from 32 to 43 µm and from 26 to 43 µm at ION and FAST, respectively (Tovar-Sanchez et al., 2020).

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The trace metals stocks within the ML were calculated by trapezoidal integrations of marine concentrations from SSW and TMC rosette samplings. The upper water column was stratified along the cruise transect (Taillandier et al., 2020), with a ~~-~~ML depth ranging from 7 to 21 m (11 to 21 m at ION station and 11 to 19 m at FAST station (Van Wambeke et al., 2020). The ML depth (MLD) fluctuations, ~~for example~~ due to wind peaks associated with rain events for example, could create rapidly changing conditions of vertical advection from deeper waters. However, with no significant increase in TM~~s~~ concentrations being observed below the ML down to about 50 m (not shown), the enrichment observed in the ML after rainfalls could not be attributed to any mixing with deeper water due to high wind. In consequence, stocks in the ML have been integrated over a constant depth range of 0-20 m for comparison, ~~as~~ in accord with Bressac et al. (2021). For Cu, Fe, Ni and~~,~~ Zn, stocks were estimated both for the dissolved and particulate fractions in the SML and ML, for Co, Cd, Mo, Pb and V for the dissolved fraction only in the ML and for both fractions in the SML and for Mn and Ti only for the particulate fraction in the ML.

The partitioning coefficient between the particulate and dissolved phases (Kd =[particulate]/[dissolved]) was used to investigate exchange~~s~~ between the dissolved and particulate pools of TMs (ref).

3. Results

3.1 General conditions

The general meteorological conditions during the cruise indicated that the ION and FAST stations were highly affected by cloudy weather conditions. During these periods, ~~2~~ two significant rain events~~s~~ occurred over~~on~~ the R/V's position and ~~have been collected~~were sampled: The first rain sample (~~hereafter~~ Rain ION) was collected during the 4-day ION station occupation in the Ionian Sea in the early morning of 29/05 at 03:08 UTC.~~, and t~~The second rain event (~~hereafter~~ Rain FAST) occurred during the 5-day "Fast action" station, (~~hereafter '~~FAST~~'~~) in the Algerian Basin during the night of 05/06 at 00:36 UTC (Table 1). The two rain sample collections~~s~~ coincided with peaks in relative humidity and wind speed, and minima in air temperature (not shown).

Table 1: Information regarding the two rains collected during the PEACETIME cruise.

Sample	Sampling time	Station name (dates) and rain location	Estimated total precipitation
Rain ION	29 May 2017, 03:08-04:00 (UTC) 05:08–06:00 (local time)	ION (25–29 May) 35.36°N, 19.92°E	3.5 ±1.2 mm

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Rain FAST	05 June 2017, 00:36-01:04 (UTC) 02:36–03:04 (local time)	FAST (2–7 June) 37.94°N, 2.91°E	6.0 ±1.5 mm

3.1.1. Rain ION

The ERA 5 data reanalysis shows ~~2~~ two periods of precipitation in the ~~surrounding of~~vicinity of the ship's position, i.e. in the morning and evening of June 26 (not shown) and in the night between June 28 and 29, in agreement with on-board visual observations. The rain event collected at ION was the product of a large cloud system, covering an area of about 90 000 km^2 around the R/V position, spreading over the Ionian and Aegean Seas (Fig. 1). As n~~N~~o radar measurements ~~being~~ were available for this area, the accumulated rate (3.5 ±1.2 mm) was estimated from ERA 5 data reanalysis on the grid-point corresponding to the ION station ~~and was 3.5 ±1.2 mm~~(±0.25°) around the R/V position ~~(±0.25°).~~ The wash-out of the atmospheric particles was revealed by the decrease in aerosol number concentrations monitored onboard from about 1900 to 300 part.cm^{-3} (supplementary material Fig. S1). Air mass back-trajectories showed that the scavenged air masses came from Greece both in the marine boundary layer and in the free troposphere (Fig. S1). The satellite observations also showed low aerosol optical thickness during this period (not shown), meaning low amounts of aerosols in the atmospheric column. No significant European pollution influence was monitored by on-board measurements during this event, with major gas mixing ratios and aerosol concentrations ~~in~~ close to the average values of the cruise (Fig. S1) and typical of clean atmospheric concentrations, i.e. under detection limit for NOx, 1.2 ppb for SO_2, 51 ppb for O_3, 80 ppb for CO and 3000 part.cm^{-3}. On this basis, this wet event was representative of a Mediterranean background marine rain event (ref for these typical background concs).

Commented [RS(-S26]: Rate requires a time dimension

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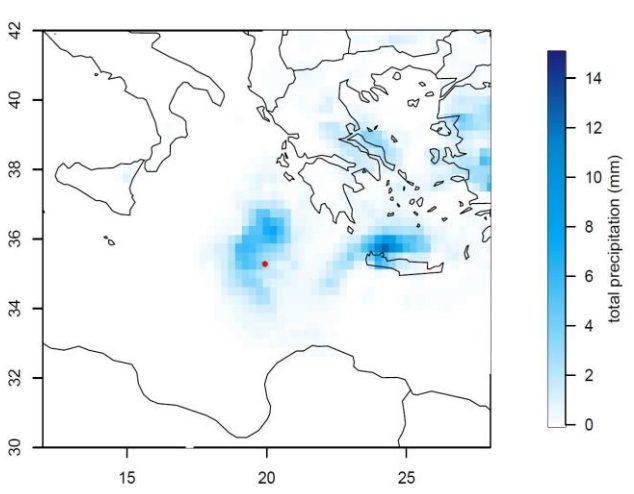

Figure 1: Total precipitation (mm) between 28 May 2017~~28~~ at 20:00 UTC and 29 May 2017 at 10:00 UTC from ERA5 ECMWF reanalysis. The red circle indicates the R/V position.

3.1.2. Rain FAST

As detailed in Guieu et al. (2020), the FAST station position was decided on the basis of regional model forecast runs and satellite observations, ~~in~~ for the purpose ~~to~~ of catching a wet dust deposition event. Significant dust emissions were observed from NASCube (http://nascube.univ-lille1.fr/, Gonzales and Briottet, 2017) over North Africa from the night of 30-31 May, then new dust emissions in the night from 3 to 4 June in Algeria and southern Morocco associated with a northward atmospheric flux. On 30 May, the SEVIRI AOD satellite product (https://www.icare.univ-lille.fr/dataaccess/browse-images/geostationary-satellites/, Thieuleux et al., 2005) confirmed the presence of atmospheric dust in a cloudy air mass over the western part of the Mediterranean, and from 2 June the export of a dust plume from North Africa south of the Balearic Islands with high AOD (>0.8) on the Alboran Sea was observed (Fig. S2). The dust plume was transported to the NE up to Sardinia on June 4, with AOD <0.5 ~~in all the area and c~~. Clear sky with low AOD was ~~left~~ observed west of 4°E on June
5.

On-board lidar measurements (Fig. 2 a,b,c) showed that the aerosol plume was present over the ship's position from 2 June at 21:00 UTC until the rain event, and corresponded to a dust aerosol layer ~~well~~ highlighted by the high depolarization. The dust plume was concentrated between 3 and 4 km at the beginning of the station occupation, then expanded down to the marine boundary layer (about 500 m

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amsl) by~~to~~ the end of the day on 3 June 2017~~3 down to the marine boundary layer (about 500 m amsl)~~. The mass integrated ~~contents~~ concentration of dust aerosols derived from the profiles of aerosol extinction ranged from a minimum of 0.18 ±0.005 g m^{-2} just before the rain to a maximum of 0.24 ±0.009 g m^{-2}, where standard deviations indicate the temporal variability (1 sigma).

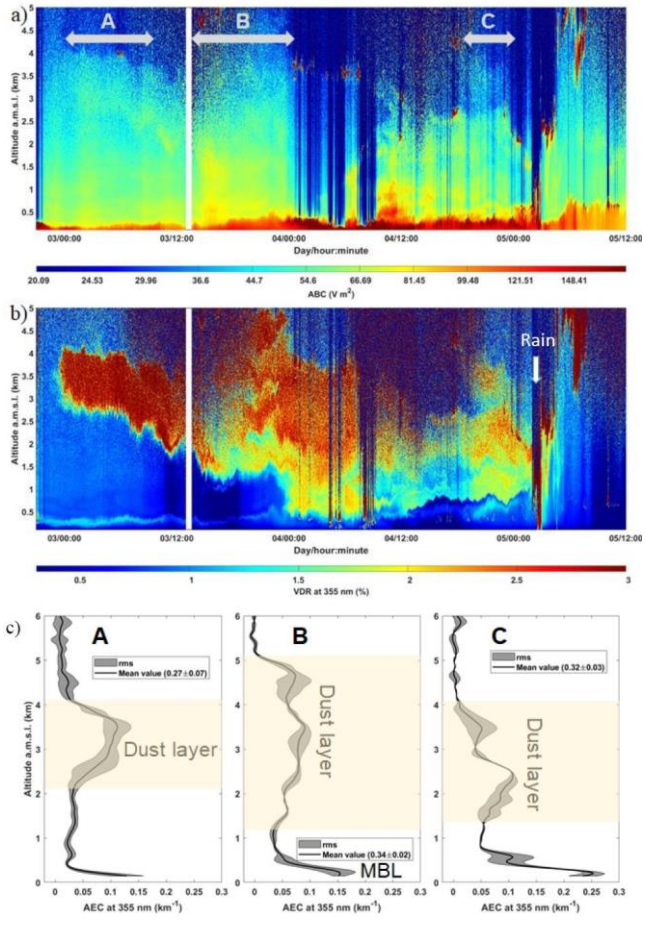

Figure 2: On-board lidar-derived a) Apparent backscatter coefficient (ABC), (b) Temporal evolution (in ~~Local~~ local ~~Time~~time) of the lidar-derived volume depolarization ratio (VDR) where the dust plume is highlighted for values higher than ~1.7 (yellow to red colours) and the rain by values higher than 3 (indicated by the arrow), and c) vertical profiles of the aerosol extinction coefficient (AEC) in cloud free condition, integrated over 3 periods along the dust plume event, noted A, B and C in

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panel~~figure~~ a (top). The grey shade represents the root mean square (rms) variability along the time of the measurement. The dust layer is highlighted on the profiles. The mean aerosol optical thickness is given in the boxed legend with its temporal variability (1 sigma). The location of the marine boundary layer (MBL) is also pointed.

Rain~~falls~~ ~~were~~ was observed by weather radar images in the ~~neighbouring~~ area ~~of~~ the R/V neighbouring from 3 June at 7:00 UTC. The rain~~falls~~ recorded around the FAST station ~~were~~ was associated with ~~2~~ two periods of rain: ~~the 03/06~~ from 07:00 to 14:00 UTC on 03/06, and from ~~the 04/06 at~~ 16:00 UTC on 04/06 to ~~05/06 at~~ 06:00 UTC on 05/06. For this latter case, a rain front (100 000 km^2), moving eastward from Spain and North Africa regions, reached the FAST station the night between the 4 and 5 June (Fig. 3). Wet deposition between the 4 and early 5 June in the FAST station area were confirmed by radar imagery, showing several other instances of rain ~~spots~~ around the R/V position before and after the rain sampling (Fig. 3). Continuous on-board lidar measurements confirmed the below-cloud deposition during the rain event of early 5 June (Fig. 2b). Rain FAST was a wet deposition event occurring at the end of an episode of transport of Saharan dust, whereas precipitation ~~of~~ on the 3 June occurred during the maximum of the dust plume (Fig. 2b and S2). The surface concentrations of gas and particles, measured on-board, suggest no clear dust or anthropogenic influence in the atmospheric boundary layer during ~~the~~ this period of wet deposition, in agreement with back trajectories of low altitude air masses (Fig S2.), presuming no local mixing between dust and anthropogenic particles into rain samples. The total precipitation estimated from radar rainfall ~~estimates~~ yield an accumulated precipitation of 6.0 ±1.5 mm (±25 km around the ship's position), in agreement with ECMWF reanalysis ERA5 (Fig. S2) for the wet deposition on the night of 4-5 June (5.7 ±1.4 mm in the grid-point spanning the R/V position, i.e. ±0.25° ~~around~~).

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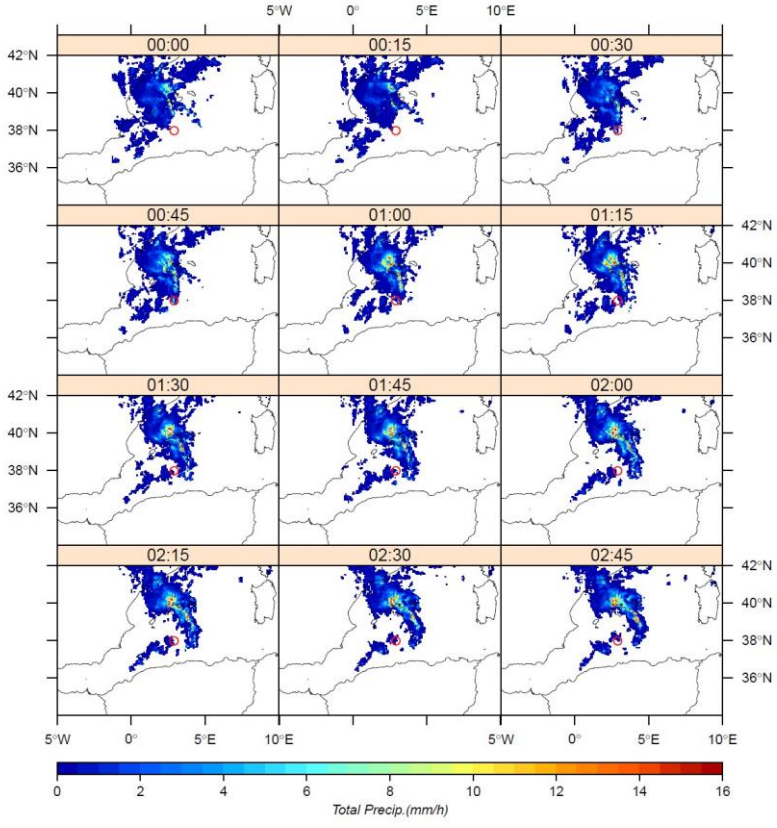

Figure 3: Rain rates (mm/h) during the night between the 4 and 5 June, when Rain ~~Fast~~ FAST w~~h~~as ~~been~~ collected on-board, issued from European rain radar composites (OPERA programme) of 5 June ~~5~~ between 00:00 and 02:45 UTC.

3.2. Chemical composition of rains

Dissolved and total concentrations of nutrients and TMs in the rain samples are presented in Table 2. Among all measured dissolved concentrations, NO_3^- was the most abundant nutrient, followed by ammonium (Table 2). The nitrite concentration was ~~under~~ below the limit of detection for the two rain samples. Regarding TMs in rain, Fe and Zn presented the highest concentrations in rain samples with the same order of magnitude (10 to 25 µg L^{-1}). Co, Cd and Mo had the lowest concentrations

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380 (<0.1 µg L-1 in both events), whereas the other TM~~s~~ concentrations ranged between 0.1 and 10 µg 381 L^{-1} in both rain samples~~s~~ (Table 2). Concentrations of nutrients and the majority of TMs were higher in the 382 dust-rich rain, except for Pb (similar concentrations in both rain samples~~s~~) and Cr (3 times higher concentration 383 in Rain ION relative to Rain FAST).

384 **Table 2: Dissolved and total concentrations of nutrients and TMs in the two rain samples~~s~~ collected during the** 385 **PEACETIME cruise in µg.L^{-1} or ng.L^{-1} and µmol.L^{-1} or nmol.L^{-1} in the parentheses (sd = standard deviation** 386 **from three replicates).**

			Rain ION				Rain FAST			
			Dissolved		Total		Dissolved		Total	
			concentrations	±sd	concentrations	±sd	concentrations	±sd	concentrations	±sd
Nutrients	NO_3^-	µg L^{-1} (µmol L^{-1})	1185 (19.1)	*71 (1.1)*			3694 (59.6	*222 (3.6*		
	NH_4^+	µg L^{-1} (µmol L^{-1})	366 (20.3)	*11 (0.6)*			654 (36.3	*19 (1.1*		
	DIN	µg L^{-1} (µmol L^{-1})	552 (39.4)	*82 (1.7)*			1343 (96)	*241 (17*		
	PO_4^{3-}	µg L^{-1} (nmol L^{-1})	18.1 (189)	*0.5 (6)*			19.0 (200)	*0.6 (6)*		
	DIP	µg L^{-1} (nmol L^{-1})	5.87 (189)	*0.18 (6)*			6.20 (200)	*0.19 (6)*		
	DOP	µg L^{-1} (nmol L^{-1})	8.63 (278)	*1.94 (75)*			4.91 (158)	*1.56 (57)*		
	TP	µg L^{-1} (nmol L^{-1})	14.51 (468)	*2.52 (81)*	16.6 (536)	*1.0 (33)*	11.11 (358)	*1.95 (63)*	58.7 (1894)	*3.5*
	DIN/DIP		(208)				(480)			
	DOC	(µmol L^{-1})	(105.7)	*(2.2)*			(95.5)	*(1.2)*		
Metals	Al	µg L^{-1} (nmol L^{-1})	13.0 (480)	*0.8 (30)*	14.6 (540)	*0.9 (32)*	23.4 (867)	*0.7 (24)*	440 (16308)	*7*
	Cu	µg L^{-1} (nmol L^{-1})	0.71 (11.1)	*0.02 (0.3)*	0.73 (11.5)	*0.02 (0.3)*	1.15 (18.0)	*0.04 (0.6)*	1.63 (25.7)	*0.06*
	Fe	µg L^{-1} (nmol L^{-1})	15.1 (270)	*0.4 (6)*	17.9 (321)	*0.6 (11)*	19.2 (344)	*0.1 (2)*	231 (4140)	*7*
	Mn	µg L^{-1} (nmol L^{-1})	0.55 (10.0)	*0.02 (0.3)*	0.60 (10.9)	*0.02 (0.4)*	3.17 (57.8)	*0.07 (1.2)*	5.26 (95.7)	*0.12*
	Ni	µg L^{-1} (nmol L^{-1})	0.52 (8.8)	*0.02 (0.3)*	0.67 (11.4)	*0.02 (0.4)*	0.59 (10.1)	*0.02 (0.4)*	0.84 (14.3)	*0.03*
	Ti	µg L^{-1} (nmol L^{-1})	0.48 (10.0)	*0.04 (0.8)*	0.65 (13.6)	*0.48 (3.2)*	0.22 (4.7)	*0.01 (0.1)*	33.36 (697)	*0.51*
	V	µg L^{-1} (nmol L^{-1})	0.37 (7.4)	*0.01 (0.2)*	0.38 (7.42)	*0.01 (0.25)*	1.37 (26.9)	*0.03 (0.5)*	2.02 (39.7)	*0.04*
	Zn	µg L^{-1} (nmol L^{-1})	24.8 (379)	*0.8 (12)*	25.3 (387)	*0.8 (12)*	22.7 (347)	*0.6 (8)*	26.3 (402)	*0.7*
	Cd	ng L^{-1} (pmol L^{-1})	12.9 (115)	*6.4 (57)*	13.1 (117)	*6.3 (56)*	20.2 (180)	*10.3 (92)*	23.7 (210)	*6.8*
	Co	ng L^{-1} (pmol L^{-1})	44 (749)	*13 (229)*	47.4 (804)	*14.5 (246)*	82 (1386)	*20 (347)*	157 (2661)	*28*
	Cr	ng L^{-1} (pmol L^{-1})	241 (4636)	*16 (300)*	628 (12079)	*5 (95)*	79 (1522)	*14 (260)*	443 (8514)	*43*
	Mo	ng L^{-1} (pmol L^{-1})	28 (288)	*10 (106)*	4.1 (43)	*1.4 (14)*	82 (855)	*11 (113)*	92.1 (960)	*16.2*
	Pb	ng L^{-1} (pmol L^{-1})	170 (822)	*11 (54)*	175.1 (845)	*1.4 (7)*	166 (801)	*9 (41)*	604 (2917)	*19*

387

388 **3.3. Marine concentrations and stocks**

389 All the TMs had significantly higher concentrations in the ML compared to deep water masses, in
390 agreement with a stratified profile associated with atmospheric input. The particulate and dissolved
391 trace metal concentrations within the ML (0-20 m) and the SML are displayed in Fig. 4.392
Concentrations were of the same order of magnitude ~~in~~ at ~~the two studied~~ stations ION and FAST, except for
the 393 particulate phase in the SML where the concentrations of Cu and Co were significantly lower (values)
at 394 ION station. The TMs were mainly in dissolved form~~s~~ in the ML (range of values), except for Fe,
whose dissolved 395 and particulate concentrations were o~~i~~n the same order of magnitude (values). On the
contrary, the particulate 396 phase ~~contribution~~ dominated for TMs in the SML, in particular at the ION
station. At both stations, 397 the highest TM~~s~~ concentrations in the surface seawater were found for Mo in
the dissolved fraction (values),

Commented [RS(-S32]: Are you really talking about deep water masses or just the water below the ML?

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in agreement with the abundance of dissolved Mo in seawater (~ 107 nM, Smedley and Kinniburgh, 2017), and Fe in the particulate fraction (value). All the particulate and dissolved TM~~s~~ concentrations measured during the cruise were ~~representative~~ within the range previously published for the Mediterranean Sea (Sherrell and Boyle, 1988; Saager et al., 1993; Morley et al., 1997; Yoon et al., 1999; Wuttig et al., 2013; Baconnais et al., 2019; Migon et al., 2020). Zn presented the largest range of concentrations within the ML both in the particulate and dissolved phases (values), due to some high concentrations. However, the concentrations stayed in the typical range of values ~~found~~ reported ~~in~~ for the Mediterranean Sea (Bethoux et al., 1990, Yoon et al., 1999). The concentrations ~~In~~ in the SML~~,~~ ~~the concentrations~~ were lower than in the ML and Pb dominated both in dissolved and particulate phases. Tovar-Sanchez et al. (2020) showed that the TM~~s~~ concentrations in the SML during the PEACETIME campaign were generally lower than those previously measured in the Mediterranean Sea, except ~~in~~ for the particulate phase ~~during~~ at the FAST station ~~after~~ following dust deposition.

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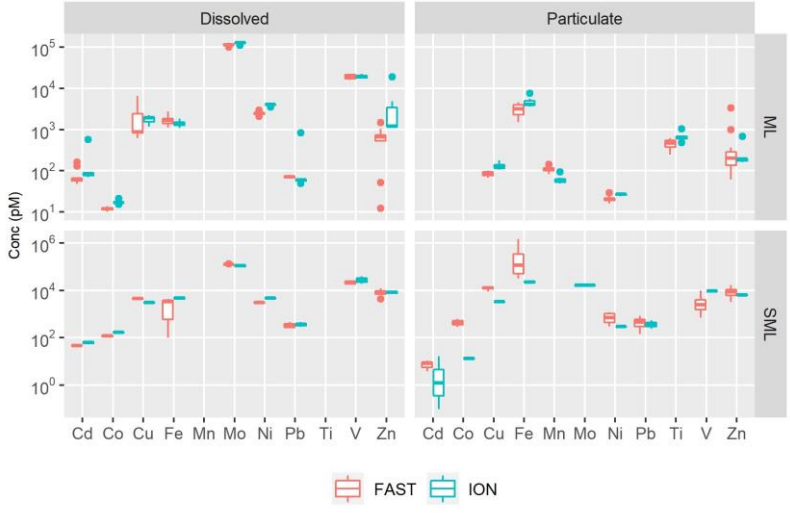

Figure 4: Box plots of dissolved (left panels) and particulate (right panels) marine concentrations (pM) for the different TMs within the ML (upper panels) and the SML (lower panels) at ION (green) and FAST (red) stations. In the box plots, the box indicates the interquartile range, i.e. the 25th and the 75-th percentile, and the line within the box marks the median. The whiskers indicate the quartiles

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±1.5 times the interquartile range. Points above and below the whiskers indicate outliers outside the 10-th and 90th percentile.

4. Discussion

4.1. Composition of rain collected over the remote Mediterranean Sea

4.1.1. Concentrations

Regarding nutrients, nitrogen species concentrations in rain samples were in good agreement with those reported in Mediterranean rain samples, ranging from 1130 to 5100 µg L^{-1} for NO_3^- and between 207 and 1200 µg L^{-1} for NH_4^+ (Loye-Pilot et al., 1990; Avila et al., 1997; Al Momani et al., 1998; Herut et al., 1999; Violaki et al., 2010; Izquieta-Rojano et al., 2016; Nehir and Koçak, 2018). The FAST rain concentrations were within the ~~average values~~published range, whereas the ION rain was in the low range, confirming a background signature at this station. The rainwater samples presented a large dominance of N in comparison to P, as observed from the N/P ratio derived from DIN/DIP (Table 2) ranging from 208 at ION to 480 at FAST. Previous observations showed a predominance of N relative to P in ~~the~~ atmospheric bulk deposition over the Mediterranean coast, with ratios higher than the Redfield ratio (Markaki et al., 2010, Desboeufs et al., 2018). The highest ratio observed reached 1200 (in the case of DIN/TDP), but ~~were on~~ averaged ~~around~~ about 100 in bulk deposition (unfiltered rain). The highest ratio could be linked to a washout effect of ~~the~~ gaseous N species (~~as~~ NOx and NH_3) by rain (Ochoa-Hueso et al., 2011). At the two stations, no high NOx concentrations were observed in the boundary layer before wet deposition (range). The presence of nitrate and ammonium in the background aerosols has been ~~emphasized~~ observed during recent campaigns in the remote Mediterranean atmosphere (e.g. Mallet et al., 2019). To our knowledge, no data are available on both P and N concentrations in Mediterranean aerosols. The lowest concentrations of P relative to N in aerosol particles in the Mediterranean ~~have been~~were observed during the cruise (value, Fu et al., in prep.). The TDP concentrations were consistent with the average value of 8.4 µg L^{-1} measured in African dust rain samples collected in Spain over the 1996-2008 period (Izquierdo et al., 2012). Inorganic phosphorus predominated in the dust-rich rain, whereas organic P was dominant in the background rain as the contribution of DOP to the TDP was 60% and 44% in Rain ION and Rain FAST, respectively. The DOP/TDP ratio presents a very large range in Mediterranean rains, spanning from 6% in Spanish dusty rain samples (Izquierdo et al., 2012) to 75-92% in rains from Crete ~~Islands~~ (Violaki et al., 2018). A reason for this wide range could be that Mediterranean European aerosols, as opposed to Saharan dust particles, are dominated by organic phosphorus compounds associated with bacteria (Longo et al., 2014).

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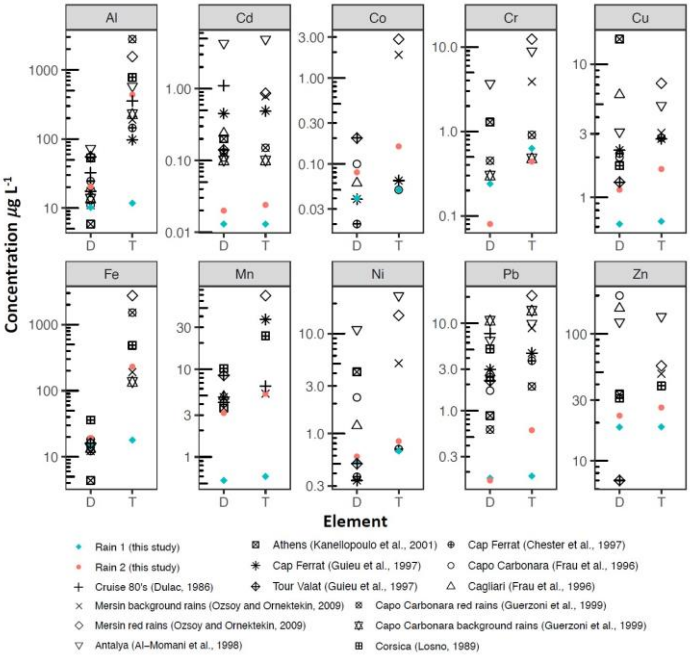

Figure 5: Comparison of dissolved (D) and total (T) TMs concentrations ~~along with data from 14 former studies carried out in~~ to previous studies in the eastern and western Mediterranean Sea.

The dissolved and total TM~~s~~ concentrations in the PEACETIME rains were lower than those reported in coastal areas (eastern Basin: Özsoy and Örnektekin, 2009; Al-Momani et al., 1998; Kanellopoulou et al, 2001 and western Basin: Guieu et al., 1997; Guerzoni et al., 1999b; Chester et al., 1997; Losno, 1989; Frau et al., 1996) (Fig. 5), ~~notably~~ especially for the background Rain ION. This suggests the probable effect of both local anthropogenic influence at coastal sites due to higher aerosol concentrations in comparison to the remote Mediterranean (Fu et al., in prep.) and due to the reduction of anthropogenic emission for some elements since most of the referenced works on coastal rainwaters date from the late 1990s. This is particularly true for ~~Cd and~~ Pb and Cd whose emissions have strongly decreased over the last decades, notably due to removal of lead in gasoline and reduction of coal combustion (Pacyna et al., 2007). This has resulted in a clear decrease in the particulate concentrations of these metals in the Mediterranean atmosphere (Migon et al., 2008), consistent with the fact that concentrations in the PEACETIME rains are one to two orders of magnitude lower than reported in

Commented [RS(-S38]: Are you comparing like with like here? You state that concentrations likely decrease offshore and, although emissions of TMs may have decreased, if the literature data is from coastal sites you don't have direct evidence for this decline over the open ocean. However, you could infer it from reductions in leaded fuel and coal combustion. Is the decreasing atmospheric input evident in the full depth water column samples? Perhaps this is what the Fu et al data shows but the reader can't check this as the reference is 'in prep'.
Later you mention the Dulac thesis as evidence. This paragraph needs rewriting and making more concise in order to strengthen your final, important statement.
As it stands, this section is too speculative.

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the literature. For these metals, the discrepancy is also observed between the concentrations in our open-sea rain samples and the concentrations (state which elements) measured in three rains collected at sea in April 1981 (Dulac, 1986), confirming that the large decrease of concentrations could be related ~~with~~ to the decrease ~~of~~ in anthropogenic emissions. Thus, our results show the ~~former literature~~data from before [year] ~~cannot~~ should not be used as a current reference ~~about~~ for coastal rain composition due to recent environmental mitigation ~~on~~ of ~~metals~~ TM emissions.

4.1.2. Enrichment factors

Enrichment Factors (EF) and solubility values of TMs and P observed during the two rain events were very contrasted (Fig. 6). In Rain ION, almost all elements were significantly enriched relative to the ~~earth~~upper continental crust (EF >10, and up to ~10^3 for Cd and Zn), whereas in Rain FAST, only Zn (73), Cd (48) and Mo (15) were ~~slightly~~ enriched. Only Ti, Fe, and Mn did not present a significant enrichment (EF < 10) in Rain ION, in agreement with previous studies in the Mediterranean environment showing that these metals are mainly associated with mineral dust in ~~-~~atmospheric deposition (e.g., Guieu et al., 2010; Desboeufs et al., 2018). For b~~B~~oth ~~rains~~rain samples, the EF of Zn was o~~i~~n average five times higher than the EF found in ~~the rains previously studied in~~rain samples from coastal sites (?) in the Mediterranean region (Özsoy and Örnektekin, 2009; Al-Momani et al., 1998; Losno, 1989). However, extremely high enrichments of Zn in rainwater have ~~also~~ been reported from island sites in the Mediterranean Sea, for example, ~~by~~ Frau et al. (1996) reported ~~with a~~ geometric mean EFs of ~~about~~~ 6500 in both crust-rich and crust-poor rains from two sites in southern Sardinia, and~~.~~ Fu et al. (2017) ~~also~~ reported EF ~~higher than~~> 1000 for Zn in atmospheric bulk deposition o~~i~~n Lampedusa Island. The Zn EF at station ION is the same order of magnitude as at these island sites which suggests – something about the anthro background signal being high in the open Med.

//The anthropogenic origin of particulate TM~~s~~ and P concentrations in seawater have been reported by several studies on atmospheric deposition in the western Mediterranean (e.g., Guieu et al., 2010; Sandroni and Migon, 2002; Desboeufs et al., 2018). For example, Desboeufs et al. (2018) showed that there is a large contribution of anthropogenic combustion sources to the ~~in~~ P, Cr, V and Zn background deposition fluxes. Aerosol composition monitoring over the Mediterranean coastal area showed the role of land-based sources and ship traffic sources on TM~~s~~ contents (Bove et al., 2016; Becagli et al., 2017). However, all these sampling sites were located in coastal areas, where it was difficult to discriminate the potential local influences. Here, even if the on-board atmospheric gas and particle measurements did not show a specific anthropogenic influence during the period of Rain ION, the particles scavenged by this rain ~~presented a clear~~suggest an anthropogenic signature for all TMs

Commented [RS(-S39]: Your rain was open ocean not coastal so doesn't really show that historical coastal TM concentrations are higher. The comparison is with the thesis. You could say that coastal values are not representative of open ocean values generally

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Commented [RS(-S41]: Change to dust-rich and dust-poor

Commented [RS(-S42]: Do you mean atmos bulk wet depo here? If so, for clarity best to just say rain. If bulk dry you need to state that too

Commented [RS(-S43]: What do you mean here? To resolve the contribution of various local industries and shipping or local inputs from long range transport

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except Ti, Fe and Mn.~~;~~ H~~h~~owever for Fe and Mn, ~~an~~ the influence of non-crustal sources in Rain ION is visible through a clear increase in the EF values compared to FAST (Fig. 6). This means that even over remote the Med Sea, the chemical composition of background aerosol particles is likely continuously impacted by anthropogenic sources.

Moreover, the EF values of TMs for Rain FAST were significantly lower than for Rain ION (Fig. 6) but similar to Saharan rains (Guerzoni et al., 1999b; Özsoy and Örnektekin, 2009). The comparison between dust-rich and background rains generally reveals a net difference of concentrations (at least higher by a factor 3 in dust-rich), notably for Al, Fe, Mn and Cr (Guerzoni et al., 1999b; Özsoy and Örnektekin, 2009). Such contrast was indeed observed for Al, Fe and Mn in the PEACETIME rains (Fig. 5), but also for Cu and Pb. The combination of higher concentrations and EF values <10 found in Rain FAST confirm that the dust contribution was important on deposition fluxes of many TMs.

4.1.3. Solubility

The solubility values were also ~~larger~~ higher in Rain ION than in the dusty Rain FAST, except for Mo for which the difference between both rain samples wa~~i~~s not significant (Fig. 6). For Rain ION, TMs and P presented solubility higher than 78%, except for Cr (38%). In Rain FAST, solubility values <10% were observed for Al and Fe, more than 10 times lower than in Rain ION. For the other TMs, the highest difference in solubility was observed for Pb whose solubility decreased from 97% in Rain ION to 27% in Rain FAST. In a review on TM~~s~~ solubility in Mediterranean rainwaters collected in coastal areas, Desboeufs (2021) emphasize the large range of solubility for all the TMs: Fe (0.8-41%), Cr (6-80%), Pb (5-90%), Ni (22-93%), Mn (16-95%), Cu (22-96%), Zn (14-99%), V (35-99%) and Cd (72-99%). The solubility ranges found in this study were generally consistent with those reviewed by Desboeufs (2021). In particular, the Mn solubility values in FAST (60%) and ION (92%) rains are close to those reported by Dulac (1986) from a dust-rich (57%) and an anthropogenic (83%) rain collected at sea in the Ligurian Sea and west of Sardinia in April 1981~~, respectively~~. Only Fe solubility (84%) found in Rain ION was higher than the average values previously reported. In the Rain FAST, Fe solubility was 8%, this is 10 times lower than the average Fe solubility in 10 dust-rich rains collected on the southeastern coast of Sardinia by Guerzoni et al. (1999b), but consistent with Saharan dust wet deposition collected in the Atlantic Ocean (Chance et al. 2015; Powell et al., 2015; Baker et al., 2017).

Commented [RS(-S44]: These two sentences disagree with each other. Need to be reworded.

Commented [RS(-S45]: How does this study compare to the factor of three increase in concs between background and dust influenced rains – use your values – and state how this would impact EFs – more Al drives down EFs, Al predominantly from dust, etc.

Commented [RS(-S46]: Vague, just say that concs were higher and EFs suggest the reason for this was the impact of the dust plume. The EFs don't really tell us this. This section needs tightening up.

Commented [RS(-S47]: Big target to hit!

Commented [RS(-S48]: Can you suggest a reason for the difference?

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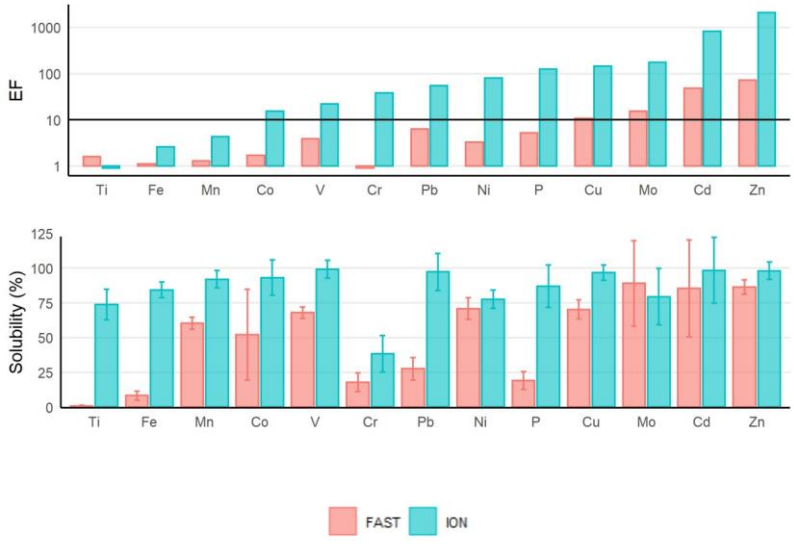

Figure 6: Enrichment Factors (EF, upper panel) and solubility (%, bottom panel) of phosphorus (P) and TMs ordered by increasing EF in the two rainwater samples.

Few studies have compared TM~~s~~ solubility between dust-rich and background rains in the Mediterranean. In Sardinia, Guerzoni et al. (1999b) observed an increase in solubility values from dust-rich to background rains for Al, Cr, Fe and Pb (~~and hardly~~but only a slight increase for Cd), and reported an inverse relationship between the particle concentration and solubility of Al, Fe, Pb and Cd. Similarly, Theodosi et al. (2010) showed a decrease in TM~~s~~ solubility with the increase in dust load in rains collected on Crete ~~Island~~. In those two studies, ~~this~~ the magnitude of the decrease was ~~dependent on the considered metal~~specific to the TM, with Pb presenting the highest decrease in solubility. The decrease in solubility from background to dust-rich rains was ~~also~~ observed for P in Spain (where?) by Izquierdo et al. (2012), with values of solubility decreasing from 25% to 7%, and for Mn in offshore rains as mentioned above (Dulac, 1986).

//Metal partitioning in rainwater can be influenced by a number of parameters, such as pH, presence of dissolved organic complexing ligands, in-cloud processinge~~s~~, particle origin and load (Desboeufs et al., 1999; Bonnet and Guieu, 2004; Paris and Desboeufs, 2013; Heimburger et al., 2013). However, the particulate ~~desert~~ mineral dust load, reflecting the dust ~~vs~~ versus anthropogenic signature, is the main control of TMs solubility in the Mediterranean rainwater (Özsoy and Örnektekin, 2009;

Commented [RS(-S49]: Could you make the two panels the same size and the bars the same width?

Commented [RS(-S50]: Could draw parallels with aero samples here, e.g. Jickells et al. (2016)

Commented [RS(-S51]: Dust loading is only one proposed control and may not be a direct control – provide explanation e.g. perhaps the CaCO3 concentration is or the reduced impact of acidic gases, low RH, etc is – ref Baker et al., 2021

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Theodosi et al., 2010). A much lower solubility of TMs in Rain FAST than in Rain ION (except for Mo) is consistent with the EFs in Rain FAST (Fig. 6), although no correlation between solubility and EF values could be observed. The case of Mo is unique, since its solubility was comparable in Rains ION and FAST despite a >20 times higher EF in Rain ION. As Mo solubility is seldom studied in the literature, we could not conclude ~~on the~~a reason for this particular outcome. It is interesting to note that despite the desert signature, the majority of metals have solubility greater than 50% in rain FAST.

4.2. Atmospheric wet deposition as a source of TMs to the surface seawater

4.2.1. Atmospheric fluxes

As mentioned before, the two collected rains were part of large rain systems, associated with patchy rainfalls that lasted several hours or days (section 3.1). This spatio-temporal variability led to heterogeneity in both rainwater concentrations and accumulated precipitation across the studied region. Such spatial variability has been observed by Chance et al. (2015) in the Atlantic Ocean. Moreover, even weak lateral advection can transfer surface water impacted by intense precipitation in the vicinity of the vessel. On this basis, the spatial extrapolation of wet deposition fluxes seems subject to ~~a~~ large uncertainties~~y~~ when the rain samples are not collected across the rain area (Chance et al., 2015). To best counteract this effect, spatial variability was taken into account to quantify the total precipitation i.e. 3.5 ±1.2 mm for rain ION and 6.0 ±1.5 mm for rain FAST (see 3.1) in order to quantify the wet deposition fluxes.

From the total (dissolved + particulate) Al concentration measured in the R~~r~~ain FAST sample, we estimated the wet mineral dust deposition flux at 65 ±18 mg m^{-2}, assuming 7.1% Al in dust (Guieu et al., 2002). The vertical distribution of dust particles (Fig. 2b) and the absence of high Al concentrations close to the sea surface (Fu et al., in prep.) indicate that dust dry deposition can be neglected. Based on the increase in total Al in the upper 20 m of the column water following the deposition events, Bressac et al. (2021) derived an average dust deposition flux of ~55 mg m^{-2} at FAST station which is~~,~~ comparable to our estimate. Although low compared to deposition fluxes reported in the western Mediterranean (Bergametti et al., 1989; Loÿe-Pilot and Martin, 1996; Ternon et al., 2010), ~~such~~ our flux ~~values~~ estimates are ~~among~~ similar to the most intense weekly dust deposition fluxes recorded ~~more recently in~~from Corsica between 2011 and 2013 (range) and ~~is~~ equivalent to the mean weekly flux (value) ~~observed in~~reported for Majorca ~~Island~~ during the same period (Vincent et al., 2016). The ~~aerosol~~ columnar aerosol concentration during the dust event at the FAST station ~~being~~ was estimated to be between 0.18 and 0.24 g m^{-2} (see Section 3.1.), the expected maximum values of atmospheric dust flux could be in this range. The comparison with the estimated

Commented [RS(-S52]: Therefore, your data does not support this argument. Disagreement within statement. The EFs close to crustal TMs in RainFAST combined with the higher concentrations point to the role of mineral dust in reducing the fractional solubility of TMs in rainwater – or the presence of mineral dust overwhelms the background signal resulting in a net decrease in fractional solubility – although the net effect is the same, I favour the latter explanation

Commented [RS(-S53]: Mo has a high conc in SW. If it has a predominantly marine source this could explain your uniform solubility. It would not explain your increase in EF necessarily but if there was an increase in seasalt aerosols it could do. You have the data to test this hypothesis

Commented [RS(-S54]: Marine source? How reliable were the solubility data? Close to LoD and blanks?

Commented [RS(-S55]: How large?

Commented [RS(-S56]: This is different than the Al proportion used in your EF calculations (Rudnick and Gao, 2003). Your EFs would be lower if you used concentrations based on 7.1% Al (Guieu et al., 2002) or your fluxes would be higher if you used the Rudnick and Gao(~ 8 %). It would be worth noting this variability. There is certainly an argument for using Saharan elemental ratios in your EF calcs (as discussed in Shelley et al. (2105)

Commented [RS(-S57]: Fluxes aren't measured directly so reported, calculated or estimated are better words

Commented [RS(-S58]: This is x3-4 higher than your flux estimates. A sentence to clarify why you support this view.

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flux indicates that the atmospheric column was probably not totally washed-out by the short rain event. Indeed, Fig. 2b shows that a significant depolarization was observed immediately after the rain ended on the ship, before atmospheric advection could have brought dusty air possibly not affected by rain. Satellite products (Fig. S2) confirm that on 5 June, the dusty air mass was transported farther to the north-east from the station where it was replaced by clear air.

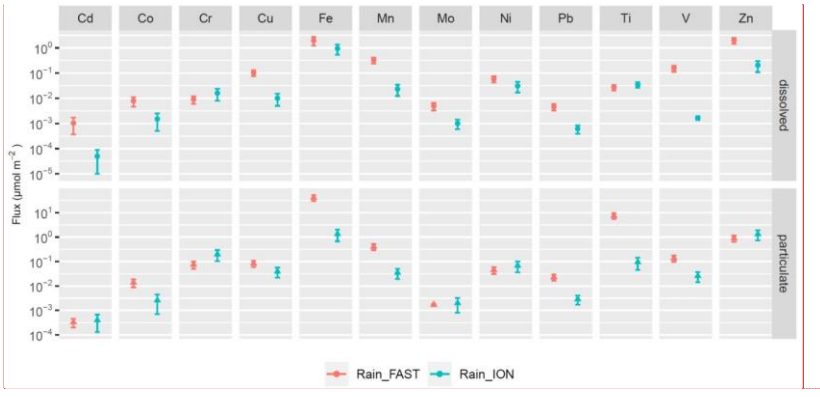

Figure 7: Dissolved (upper panels) and particulate (lower panels) wet deposition fluxes (µmol m^{-2}) for the different TMs estimated from the two rains sampled on board, considering the standard deviation on the TM~~s~~ concentrations and the spatial variability of total precipitation over the area of sampling (Rain ION in blue and Rain FAST in red). Note different scales on the y axes.

The atmospheric dissolved and particulate wet deposition fluxes of TMs, derived from the chemical composition of rain samples and total precipitation, are presented in Fig. 7. Co, Mo and Cd presented the lowest fluxes in the two rainfalls. Zn and Fe fluxes were o~~i~~n the same order of magnitude and were the highest dissolved fluxes compared to the other TMs in the two rains. The comparison showed that almost all the dissolved TM~~s~~ fluxes were higher in the dusty rain, except Cr and Ti. For the particulate phase, the fluxes were mainly increased by the presence of mineral dust ~~deposition~~ for Co, Fe, Mn, Pb, Ti and V. Our results ~~emphasized~~ support previous studies that report that the presence of mineral dust ~~deposition~~, even ~~here~~ in the case of ~~a~~ the moderate deposition input flux reported here, ~~enabled~~ resulted in higher atmospheric inputs of TMs than from ~~a~~ low perturbed, -anthropogenic background rain. We found this to most ~~This is~~ notably be the case for dissolved Cd, Cu, Mn, V and Zn and for particulate Fe and Ti with more than ~~one~~ an order of magnitude ~~fluxes~~ difference in input fluxes ~~between the~~estimated from the two rain events~~s~~. The orders of magnitude found in this study could be used as ~~"typical~~ a benchmark ~~atmospheric fluxes"~~ to estimate atmospheric inputs of TMs ~~by a rain~~

Commented [RS(-S59]: It would be useful to see the Al wet deposition flux as this is what you are using as the basis to estimate the bulk wet depo flux. It would also be nice to have a third panel showing the ratio or the Kd of dissolved to particulate TMs

Commented [RS(-S60]: Explain how these two parameters differ. Are they not the same thing here?

Commented [RS(-S61]: Explain why. They also have the greatest uncertainties – low concentrations and high blank contributions and >100% CRM recovery for Mo ?

Commented [RS(-S62]: Because these elements were primarily found in the particulate phase?

Commented [RS(-S63]: Emphasised is stretching it for data from just two samples

Commented [RS(-S64]: With the exception of Mn, these are predominantly considered pollution derived elements. It would be worth mentioning this.

Commented [RS(-S65]: Poorly soluble, lithogenic elements. Al should also be reported here. I'm assuming it showed the same behaviour as Fe and Ti?

Commented [RS(-S66]: Do you mean the range?

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~~event~~ from wet deposition to the western Med Sea. However, w~~W~~e must keep in mind~~, however,~~ that annual and long-term deposition fluxes of dust-related elements (e.g. Ternon et al., 2010), but also nitrogen species (e.g., Richon et al., 2018b), ~~in the Med Sea,~~ are dominated by a few atypical, intense deposition events in the Med Sea~~when they occurred~~, as is the case in many other oceanic regions (Duce et al., 1991)~~.~~

4.2.2. Comparison between TM~~s~~ wet deposition inputs and marine stocks at ION and FAST stations

Our sampling strategy of ~~Marine sampling sequences carried out~~collecting seawater before and after the rains were, to the best of our knowledge, the first direct observations intended to trace the fate of atmospheric ~~metals~~ TMs and nutrients in the water column after wet deposition events. The time chart of the sampling of rain and column water (surface microlayer, subsurface seawater and mixed layer) is presented in Fig. 8. The impact of the two wet deposition events on nutrient~~s~~ stocks in the Mediterranean surface waters is discussed in detail in van Wanbeke et al. (2020) and Pulido-Villena et al. (2021). To briefly summarise, b~~B~~oth nitrate and DIP increased in the ML following the rains. Although the closure of the N and P budgets had to necessarily take into account post-deposition processes such as new nutrient transfer through the microbial food web (uptake, remineralisation, and adsorption/desorption processes on sinking particles), it was shown that wet deposition was a significant source of nutrients for ML during the cruise (roughly what %?). We focus here on the role of ~~TMs~~wet deposition as a source of ~~metals~~ TMs to the column water. To do so, we estimated the potential enrichment of the SML and ML from the rain by calculating the difference (delta) in TM~~s~~ stocks before and after rain~~s~~.

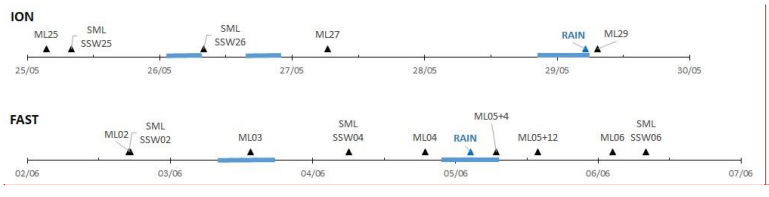

Figure 8: Sampling chronology during the ION and FAST stations for SML, SSW and ML. The blue periods correspond to rainfall in the station area (after ERA 5 reanalysis and radar imagery, see section 3.1). Sampling~~s~~ ~~were~~ was performed 4 days and 2 days before and 2 h after Rain ION, and at a higher frequency at the FAST station: 57, 37 and 7.5 hours before and 4.5, 12, 24 hours after Rain FAST. SML and SSW samples could not be collected immediately before and after the rains because of bad weather conditions, and were collected 3 and 4 days before Rain ION, and 57 and 20 h before and 30 h after Rain FAST.

Commented [RS(-S67]: What does this mean? All elements discussed or only lithogenic elements?

Commented [RS(-S68]: I'm wondering if concentrations or partitioning are a better choice of word than stocks (this applies throughout the paper)

Commented [RS(-S69]: … in an open ocean setting

Commented [RS(-S70]: Move to Methods

Commented [RS(-S71]: Move to methods

Commented [RS(-S72]: Given how quickly the SML TM concentrations respond to atmospheric inputs and their relatively short residence times in the SML (hours – Ebling and Landing, 2015), how can you be sure that your SML sampling resolution was capturing the impact of the wet deposition events of the SML, especially given that wind speed (and sea state) is a critical factor in determining the integrity of the SML?

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At ION, no SML sampling was done after rain, preventing the study of the rain effect. For the ML, the large variability in total and dissolved stocks between the two casts ML25 and ML27 before the rain makes the establishment of ~~a~~ background concentration levels before rain difficult. ML27 was used for the~~as~~ initial conditions ~~since~~ as it wa~~i~~s the closest sampling ~~from~~ point to the post-rain ~~measurements~~ sample collection (ML29). As mentioned previously, dusty rain deposition over the FAST station area started on 3 June. Bressac et al. (2021) showed that the dust signature, traced by changes in Al and Fe stocks in the ML, was already visible from the ML03 sampling. We defined the enrichment of seawater layers as the difference between the maximum stocks after rain~~s~~ (from SML 04 or 06 and ML05+4) and the initial seawater stocks (SML02 and ML02).

At ION, only particulate Cu (+27%) and Zn (+44%) stocks increased in the ML after the rain. Even if the dissolved forms of Cu and Zn predominated in the ML, this increase was accompanied by increasing Kd values, i.e. in the particulate/dissolved partitioning (0.07 vs 0.12 for Cu and 0.14 vs 0.2 for Zn). This was also the case for Fe (Kd increased from 2.6 to 4.3), although no significant difference (<5%) was observed on the particulate Fe stock. The Kd values in the ION rain sample being higher than in the marine stock before the rain, that suggests the wet deposition at ION is mainly an additional source of particulate TMs.

At FAST, the ML stocks increased in the particulate phase for Fe (+61%), Mn (+15%) and Zn (+9%) and in the dissolved phase for Cu (+9%), Fe (+46%), Pb (+8%) and Zn (+15%) (Fig. 9). In addition ~~of~~ to the marine inventories, the particulate TM~~s~~ inputs by rain was also observed on Kd values and total X/Al in the ML. For example, Kd(Fe) increased from 0.14 to 0.17 in ML and its Kd was 0.25 in the rain. Even for Ni, for which no change in stock could be evidenced, Kd(Ni) decreased from 0.1 to 0.07 and its Kd in the rain was 0.006. For Mn/Al, the Kd ~~which~~ fell from 0.27 before the rain to 0.008 after the rain (ML05+4), in accordance with the rain ratio (0.004). In the SML, the dissolved and particulate stocks increased following rains for all TMs, from a factor 1.5 (Mo) to 10 (Fe) for the dissolved phase and from a factor 1.6 (Ni) to 67 (Fe) for the particulate phase (Fig. 9).

Commented [RS(-S73]: As it reforms so quickly and rain disrupts it, how can you be sure that the SML sampled after the rain at FAST was in contact with the atmosphere and accumulating RW TMs?

Commented [RS(-S74]: Suggesting that there was a surface advective current?

Commented [RS(-S75]: Dissolved or particulate or both?

Commented [RS(-S76]: I wonder if this is because of the mismatch between SML sampling and rosette casts.

Commented [RS(-S77]: Additional to what?

Commented [RS(-S78]: Particles scavenging dissolved TMs?

Commented [RS(-S79]: Again, the SML samples may not have been representative of the wet depo inputs. In contrast, the ML likely was

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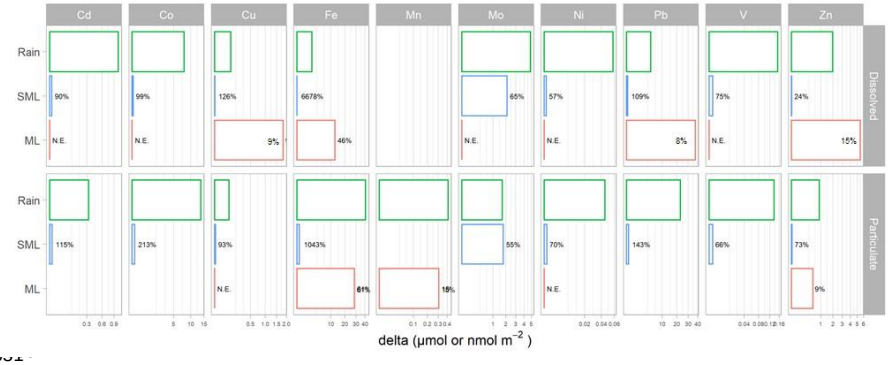

Figure 9: Comparison between TMs wet deposition fluxes (in green) and TMs marine stock deltas (before and after the rain) in the SML (in blue) and in the ML (in red) at FAST. Dissolved = upper panels and particulate = lower panels. Marine stocks increases are expressed in absolute values (Cd, Co and Pb stocks in nmol m^{-2}, and the other TMs in µmol m^{-2}) and in relative values (%). N.E.,: .= not enhanced (increase <5%).

The comparison between the observed enhancements in the SML stocks and the rain inputs at FAST (Fig. 9) indicates that the atmospheric fluxes inputs can explain support all observed deltas. Indeed, the atmospheric particulate and dissolved fluxes of TMs were 2 to 4 orders of magnitude higher than the mean stocks present in the SML, except Mo which was oin the same order of magnitude. In the ML, the magnitude of atmospheric particulate inputs was higher or similar to the particulate marine delta of Fe, Mn and Zn. For Cu, Fe, Pb and Zn, the increase in dissolved stocks within the ML was 2 to 10 times higher than what could be provided from the atmospheric inputs. As described in Guieu et al. (2020), marine dynamical conditions at FAST were favourable to observe any change in the water masses strictly attributed to external inputs coming from the atmosphere on a short time scale. However, a cumulative effect of previous and surrounding wet deposition events could explain this difference between atmospheric inputs from rain FAST and increase of marine dissolved stocks. We cannot exclude the possibility of lateral transport of metals TM from surrounding waters being enriched by the rain events of 3 June 3 for example, as revealed by the increase in the 0-20 m Fe and Al inventories (Bressac et al., 2021). Another hypothesis to explain that higher stock increases of metals in the ML than the one derived from atmospheric deposition is related to post-deposition processes. Indeed, once deposited, the atmospheric particulate fraction could still be partly solubilized in seawater, as the solubilisation of TMs (e.g. Fe) could occur over several hours or days (Wagener et al., 2008; Wuttig et al., 2013; Desboeufs et al., 2014). This could lead to an underestimate of the

Commented [RS(-S80]: If we assume that the SML samples were representative of this layer before and after rain (and even if we don't), the similarity in Mo concentrations suggests to me that this element is not primarily delivered by atmospheric inputs

Commented [RS(-S81]: From rain or total atmos depo?

Commented [RS(-S82]: Days?

Commented [RS(-S83]: Some ML residence time calculations could be of use here

Commented [RS(-S84]: Many people have shown a delayed response of the dissolved pool to atmospheric inputs

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dissolved TMs from atmospheric input~~s~~. Moreover, the time lag between the rain and the first SML sampling (1 day) does not allow us to conclude on the role played by SML as a "trap" of the added dissolved metals by rain. However, results showed clearly the increase of dissolved TMs in the SML even 24 h after the rain (Fig. 9). Even if this increase could be due to dissolution processes (Tovar-Sanchez et al., 2020), we cannot exclude that the residence time of dissolved atmospheric TMs in the SML was sufficient to mask the atmospheric inputs in the ML05+4 sample. It is also known that dissolved concentrations in the ML are subject to various biological processes such as phytoplankton uptake (Morel et al., 2003). The comparison between ML05+4 and ML05+12 samples performed after the rain shows that the dissolved and particulate stocks decreased quickly for all the TMs (not shown), in agreement with the predominance of removal processes (sedimentation, biological transfer, adsorption) on these stocks. However, the rate of decrease depended on the TMs, showing that some removal processes predominate over others depending on the metal. For example, the dissolved ~~metals~~ TM decreases could correspond to scavenging onto particles, which is a common physico~~al~~chemical process occurring in the ocean for Fe (Wagener et al., 2010; Bressac and Guieu., 2013) ~~or~~, -Co (Migon et al., 2020) and many other TMs.

Commented [RS(-S85]: It would be useful to see this – put in Supplementary Materials

//Finally, our results show that dusty wet deposition was a net source of all the studied trace metals for SML both in the dissolved and particulate fraction. For ML, atmospheric dust inputs were also a net source of particulate Fe, Mn, and Zn, and dissolved Cu, Fe, Pb and Zn. Due to various marine post-deposition processes, it ~~was~~ is more complicated to observe the effect of wet deposition on dissolved stocks, explaining why the SML and ML particulate stocks were more impacted by rain than the dissolved stocks. On a timescale of hours, the Fe inventory was the most impacted by the dusty rain input, both in dissolved and particulate phases, confirming that the dust-rich rains are a net source of Fe to the surface Mediterranean Sea (Bonnet and Guieu, 2006, Bressac et al., 2021).

Commented [RS(-S86]: I'm not completely convinced it does because of the resolution problem. It certainly suggests it might given Tovar-Sanchez's findings of increases 24 h after rain but the signal is likely to be (significantly) diminished after this time.

4.2.3. Comparison between TM~~s~~ wet atmospheric inputs and marine stocks ~~at the scale~~in the ~~Western~~ western and ~~Central~~ central Mediterranean Sea

As observed from dissolved TMs stocks measured before and after the rains, a large part of the uncertainties in the data analysis results from various removal processes of TMs after wet deposition, which could have time resolution shorter than the sampling step. In order to limit the effect ~~on~~ of these potential processes ~~in~~ on data analysis, here we further study the role of wet deposition by comparing atmospheric dissolved fluxes to marine dissolved stocks by using TM~~s~~ profiles in the ML at all 13 marine stations, i.e. 22 ML samplings, throughout the whole cruise (Fig. 10). Indeed, considering that the collected rains were originating from large rain systems covering more than 50 000 km^2 around the sampling zone and were typical of Mediterranean wet deposition, we hypothesized that they could

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have occurred in any of the explored areas during the cruise. Exceptional intense dust deposition events have been recorded in the Mediterranean, reaching 20 g m^{-2} (Bonnet et al., 2006). Sporadic and intense wet dust deposition higher than 1 g m^{-2} are regularly observed in the spring in the western Mediterranean basin (e.g., Vincent et al., 2016). At the beginning of the cruise, an intense wet dust deposition event (not collected) occurred over the South of Sardinia and over the Tyrrhenian Sea with fluxes reaching about 9 g m^{-2} (Bressac et al., 2021). In order to take into account the effect of such an event, we also estimated the atmospheric fluxes of dissolved ~~metals~~ TMs based on a 9 g m^{-2} wet dust deposition event ~~considering~~ using solubility values ~~found in the~~estimated from ~~rain~~ Rain FAST (Fig. 10). ~~The~~ As TM ~~metal~~ solubility ~~decreasing~~ decreases with increasing dust load (Theodosi et al., 2010), this estimation constitutes probably a maximum value of the dissolved inputs of trace metals by such a dust deposition event. In addition to removal processes, the impact of rain inputs on TM~~s~~ marine stocks is also controlled by MLD fluctuations ~~that~~ which we ignored in ~~the~~ this work ~~described above~~ by using a fixed ML depth for the FAST and ION stations. As ~~However,~~ s the variability of this MLD (7-21 m during the cruise, typical of Mediterranean thermal stratified period) could change the marine budgets by a factor of 3, ~~. So~~ we ~~considered~~ used the measured MLD (Van Wambeke et al., 2020) at each station for calculating the ~~marine budgets of~~ TM water budgets~~s at each station~~.

Commented [RS(-S87]: Which ones? Theodosi reports this for the TMs he studied but not your full suite. There are some that do, some that don't. See Jickells et al., 2016 and Baker et al., 2020. I appreciate these papers report data for the Atlantic rather than the Med but as they report data from Saharan and European air masses they are relevant.

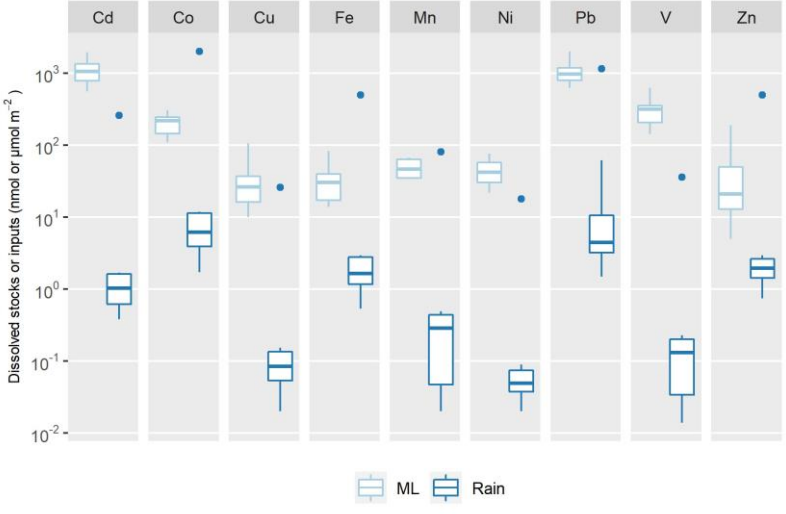

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Figure 10: Comparison of marine stocks in the ML at all the stations occupied during the PEACETIME cruise with atmospheric inputs estimated (1) from ION and FAST rains (~~Boxes~~boxes) and (2) from an intense wet dust deposition event of 9 g m^{-2} (blue dots). Cd, Co and Pb stocks are in nmol m^{2}, and the other TMs in µmol m^{-2}. For Mn, marine stocks are derived from surface concentrations close to Corsica coasts (Wuttig et al., 2013: samples OUT at 0, 5 and 10 m) and in the Ionian Sea (Saager et al., 1993: Bannock basin at 0, 10, and 15 m), as no measurement is available from the PEACETIME cruise. Boxes and whiskers as in Fig. 4.

Applying to the whole transect, the atmospheric inputs, obtained from our rain composition, were at least 100-fold smaller than the dissolved stocks in the mixed layer, except for Co, Fe and Zn. The atmospheric inputs represented more than 30% of the dissolved Zn stocks and 10 to 18% for Fe. This significant input of dissolved Fe is in agreement with our field observations in the ML. For Co, the maximum atmospheric fluxes estimated during the cruise represented >10% of stocks. Here the comparison is based only on dissolved TMs in rain water, yet as discussed previously, the solubilisation post-deposition of atmospheric particles in the water column could further enrich the marine dissolved stocks. In the case of the intense dust deposition event, the dissolved inputs are of the same order of magnitude as marine stocks for Co, Fe, Mn, Pb and Zn. The enrichment in dissolved Fe and Mn was previously observed by Wuttig et al. (2013) after artificial dust seeding in large mesocosms (simulating a wet deposition event of 10 g m^{-2}). The surface seawater could be significantly affected by the deposition of these dissolved elements in the case of wet dust deposition. As t~~T~~he marine TM~~s~~ concentrations measured during the cruise ~~being~~ were typical of Mediterranean surface seawater concentrations, we conclude from these comparisons that wet deposition events, notably wet dust deposition events, ~~prove to be~~were an external source of dissolved TMs for the Mediterranean Sea during the period of thermal stratification.

Commented [RS(-S88]: Only dissolved or dissolved and particulate?

5. Conclusions

This study provides both the dynamic~~al~~ properties and chemical characterization of two ~~rainwaters~~ rain events ~~collected~~ in the open Mediterranean Sea, concurrently with TM (list) ~~s~~ marine stocks in surface seawater. Our results are the only recent report of TM concentrations, EFs and fractional solubility values ~~for TMs~~ in rain samples collected in the remote Mediterranean Sea. By highlighting the discrepancy between TM~~s~~ concentrations with ~~the~~ previous offshore and coastal rain studies, this work demonstrates the need to provide a new and recent database on ~~metal~~ TM composition in Mediterranean rains in order to estimate the role of atmospheric TM~~s~~ deposition. We ~~showed~~ have shown the representativeness of ~~rain~~ Rain FAST as typical of Saharan dust wet deposition ~~as well~~ in its chemical composition as well as in its magnitude and extent, whereas Rain ION is ~~a~~ more typical

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of an ~~low-perturbed~~ anthropogenic background rain ~~of~~ for the remote Mediterranean Sea. On this basis, we suggest ~~to use~~using the chemical composition of PEACETIME rains as a new reference for ~~the~~ studies of TMs on wet deposition in the Mediterranean Sea.

Since atmospheric TMs have been identified as critical oligo-nutrients for the marine biosphere, it is important to study the response of the receiving waters to atmospheric inputs. ~~our~~ This study is the first to provide *in situ* evidence that atmospheric wet deposition constitutes a significant external source for some of these elements to surface stratified Mediterranean seawater. ~~Our results show~~ We recommend that the original approach developed here ~~is very relevant in this purpose and could be~~is used in other parts of the world where atmospheric wet deposition is ~~suspected~~ thought to impact the marine biosphere, such as in HNLC areas~~.~~

Commented [RS(-S89]: How about an extra statement suggesting additional dry depo sampling to directly compare the inputs of wet and dry depo in future? Dry depo seems to have been overlooked in this study. What is thought to be the relative contribution of wet-dry dust depo events in the Med. Is wet depo thought to have a disproportionally large impact on TM seawater concs during stratification?

Data availability. Guieu et al., Biogeochemical dataset collected during the PEACETIME cruise. SEANOE. https://doi.org/10.17882/75747 (2020). Atmospheric Data are accessible on http://www.obsvlfr.fr/proof/php/PEACETIME/peacetime.php.

Author contributions. KD and FF designed the study and wrote the manuscript; FF, ST, JFD, Ch.G made the on-board atmospheric measurements and sampling during the cruise; FF, ST and JD analysed the rain samples; MB, ATS, and ARR made the marine TMs sampling and analyses; PF was the reference scientist of PEGASUS, AF and FM managed all the technical preparation of atmospheric samplings, PC analysed the lidar data; KD, FD and Ce.G designed the cruise strategy; KD and Ce.G coordinated the PEACETIME project, FD coordinated the ChArMEx funding request, and near-real time and forecast survey of atmospheric conditions during the cruise; all the authors commented on the manuscript and contributed to its improvement.

Competing interests. The authors declare that they have no conflict of interest.

Special issue statement. This article is part of the special issue "Atmospheric deposition in the low-nutrient–low-chlorophyll (LNLC) ocean: effects on marine life today and in the future (ACP/BG inter- journal SI)". It is not associated with a conference.

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Figure Captions:

Figure 1: Total precipitation (mm) between May 28 at 20:00 UTC and 29 at 10:00 UTC from ERA5 ECMWF reanalysis. The red circle indicates the R/V position.

Figure 2: On-board lidar-derived a) Apparent backscatter coefficient (ABC), (b) Temporal evolution (in Local Time) of the lidar-derived volume depolarization ratio (VDR) where the dust plume is highlighted for values higher than ~1.7 (yellow to red colors) and the rain by values higher than 3 (indicated by the arrow), and c) vertical profiles of the aerosol extinction coefficient (AEC) in cloud free condition, integrated over 3 periods along the dust plume event, noted A, B and C in figure a. The grey shade represents the root mean square (rms) variability along the time of the measurement. The dust layer is highlighted on the profiles. The mean aerosol optical thickness is given in the boxed legend with its temporal variability (1 sigma). The location of the marine boundary layer (MBL) is also pointed.

Figure 3: Rain rates (mm/h) during the night between the 4 and 5 June, when Rain Fast was collected on board, issued from European rain radar composites (OPERA programme) of June 5 between 00:00 and 02:45 UTC.

Figure 4: Boxplots of dissolved (left panels) and particulate (right panels) marine concentrations (pM) for the different TMs within the ML (upper panels) and the SML (lower panels) at ION and FAST stations. In the box plots, the box indicates the interquartile range, i.e. the 25th and the 75th percentile, and the line within the box marks the median. The whiskers indicate the quartiles ±1.5 times the interquartile range. Points above and below the whiskers indicate outliers outside the 10th and 90th percentile.

Figure 5: Comparison of dissolved (D) and total (T) TMs concentrations along with data from 14 former studies carried out in the eastern and western Mediterranean Sea.

Figure 6: Enrichment Factors (EF, upper panel) and solubility (%, bottom panel) of phosphorus (P) and TMs ordered by increasing EF in the two rainwater samples.

Figure 7: Dissolved (upper panels) and particulate (lower panels) wet deposition fluxes (µmol m^{-2}) for the different TMs estimated from the two rains sampled on-board, considering the standard deviation on the TMs concentrations and the spatial variability of total precipitation over the area of sampling (Rain ION in blue and Rain FAST in red).

Figure 8: Sampling chronology during the ION and FAST stations for SML, SSW and ML. The blue periods correspond to rainfall in the station area (after ERA 5 reanalysis and radar imagery, see section 3.1). Samplings were performed 4 days and 2 days before and 2 h after Rain ION, and at a higher frequency at the

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FAST station: 57, 37 and 7.5 hours before and 4.5, 12, 24 hours after Rain FAST. SML and SSW samples could not be collected immediately before and after the rains because of bad weather conditions, and were collected 3 and 4 days before Rain ION, and 57 and 20 h before and 30 h after Rain FAST.

Figure 9: Comparison between TMs wet deposition fluxes (in green) and TMs marine stock delta (before and after the rain) in the SML (in blue) and in the ML (in red) at FAST. Dissolved = upper panels and particulate = lower panels. Marine stocks increase are expressed in absolute values (Cd, Co and Pb stocks in nmol m^{-2}, and the other TMs in µmol m^{-2}) and in relative values (%). N.E.: not enhanced (increase <5%).

Figure 10: Comparison of marine stocks in the ML at all the stations occupied during the PEACETIME cruise with atmospheric inputs estimated (1) from ION and FAST rains (Boxes) and (2) from an intense wet dust deposition event of 9 g m^{-2} (blue dots). Cd, Co and Pb stocks are in nmol m^{-2}, and the other TMs in µmol m^{-2}. For Mn, marine stocks are derived from surface concentrations close to Corsica coasts (Wuttig et al., 2013: samples OUT at 0, 5 and 10 m) and in the Ionian Sea (Saager et al., 1993: Bannock basin at 0, 10, and 15 m), as no measurement is available from the PEACETIME cruise. Boxes and whiskers as in Fig. 4.